

## Geology, geochemistry and evolution of the Esfordi Phosphate - Iron Deposit, Bafq Area, Central Iran

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# **Geology, Geochemistry and Evolution of the Esfordi Phosphate - Iron Deposit, Bafq Area, Central Iran**

by

**Morteza Jami**

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*Satellite image of the Bafq region.*

## ABSTRACT

Esfordi is a Kiruna-type Fe–P oxide deposit in the Bafq district of Iran. It formed within a predominantly rhyolitic volcanic sequence that formed in a continental margin tectonic regime and is of Cambrian age.

The gently dipping, stratabound ore body is lenticular and displays a well-developed mineralogical zonal pattern. The Fe-oxide rich core contains a central zone of massive magnetite and a more hematitic brecciated rim. The overlying P-rich ore body contains massive and brecciated, apatite-rich variants with accessory hematite and actinolite. A zone of apatite-bearing veins and disseminations envelopes the Fe-oxide and P-rich zones and extends into overlying volcanoclastics that contain detrital magnetite  $\pm$  apatite clasts. The main ore zones are surrounded by Ca-rich alteration, dominated by actinolite, extending  $\sim$ 100 m into the more permeable overlying volcanoclastics. Beyond this envelope is widespread development of secondary K-feldspar.

Mesoscopic and microscopic observations reveal a paragenetic sequence containing four generations of apatite. The early stage is a LREE-rich apatite 1 that occurs within the massive and brecciated magnetite core. The second generation is large and brecciated apatite 2, associated with hematite and actinolite. Both apatite 1 and 2 exhibit widespread dissolution and reprecipitation to form a LREE-poor granular apatite that is generally associated with quartz-carbonate $\pm$ REE minerals. The final stage involved an overprint of LREE-poor apatite 3-carbonate-quartz-actinolite-chlorite-epidote $\pm$ bastnaesite $\pm$ synchesite extending into the host rocks.

Fluid inclusions in apatite 1 have homogenisation temperatures of 375–425°C and indicate salinities of 14–18 wt. % NaCl. The magnetite displays low  $\delta^{18}\text{O}$  of  $-0.1$ – $1.7$  ‰, suggesting precipitation from fluids with  $\delta^{18}\text{O}$  of  $7.8$ – $9.6$  ‰ at  $\sim$ 400°C, consistent with a magmatic source. Fluid inclusions in apatite 2 homogenise between 195–295°C with indicated salinities of 13–19 wt. % NaCl. The associated hematite displays  $\delta^{18}\text{O}$  of  $-0.2$ – $2.3$  ‰ which would be in equilibrium with fluids having a  $\delta^{18}\text{O}$  of  $10.7$ – $13.0$  ‰ at  $\sim$ 250°C. Such enriched isotopic fluids suggest interaction of magmatic fluids with cooler saline fluids that were probably derived from the underlying carbonate-rich sequences. Fluid inclusions in apatite 3 and quartz homogenise at 145–155°C and, together with a quartz  $\delta^{18}\text{O}$  of  $16.0$ – $17.1$  ‰, suggests precipitation from a fluid with  $\delta^{18}\text{O}$  of  $-0.7$ – $2.1$  ‰ that is likely to have resulted from the introduction of a cooler, less saline and isotopically depleted fluid (such as sea water).

The results of this study clearly indicate a significant role for fluids in the evolution of the Esfordi deposit but do not preclude a role for immiscible Fe-oxide–P-rich melts in the initial stages of the mineralising process.

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## List of Minerals and Rocks Abbreviations

|         |                  |
|---------|------------------|
| Act     | Actinolite       |
| Alb     | Albite           |
| Allan   | Allanite         |
| Amp     | Amphibole        |
| Bar     | Barite           |
| Bas     | Bastnaesite      |
| Bio     | Biotite          |
| Bn      | Bornite          |
| Brt     | Britholite       |
| Cal     | Calcite          |
| Carb    | Carbonate        |
| Chl     | Chlorite         |
| Cpy     | Chalcopyrite     |
| Diop    | Diopside         |
| Epi     | Epidot           |
| Flu     | Fluorite         |
| Gal     | Galena           |
| Gar     | Garnet           |
| Gran Ap | Granular Apatite |
| Hed     | Hedenbergite     |
| Hm      | Hematite         |
| Hor     | Hornblend        |
| K-feld  | K-feldspar       |
| Lst     | Limestone        |
| Mol     | Molibdenite      |
| Mon     | Monazite         |
| Mt      | Magnetite        |
| Nep     | Nephelin         |
| Pit     | Pitchblend       |
| Plg     | Plagioclase      |
| Py      | Pyrite           |
| Pyx     | Pyroxene         |
| Qtz     | Quartz           |
| Sch     | Scheelite        |
| Scp     | Scapolite        |
| Ser     | Sericite         |
| Si      | Silica           |
| Sid     | Siderite         |
| Syn     | Synchesite       |
| Tour    | Tourmalin        |
| Uran    | Uraninite        |
| Xen     | Xenotime         |

# CHAPTER 1 INTRODUCTION

## 1.1 INTRODUCTION

The Bafq district of Central Iran is the most important Fe metallogenic province in the region and a significant district on a worldwide basis. The district contains reserves of over 2 billion tonnes of Fe (NISCO, 1980) within more than 34 major magnetic anomalies in a 7,500 km<sup>2</sup> area. Among these targets, 14 have been defined as major deposits with over 1 billion tonnes of high grade ore (53-65 % Fe) (Taghizadeh, 1976). The Bafq district magnetite–apatite systems are hosted by a lower Cambrian sequence of lavas, pyroclastic, epiclastic rocks, intercalated carbonates and subvolcanic granites. In addition to magnetite–apatite ores there are several non-ferrous ore bodies containing Pb - Zn, Mn and U.

The origin of the Bafq magnetite–apatite deposits remains controversial and different ore genesis models have been proposed. Within this group of deposits is the Esfordi apatite–magnetite deposit. It is ostensibly a Kiruna-type variant and one of the most P-rich of the Bafq magnetite–apatite occurrences. The ore is an inclined, stratiform, lens-shape body, about 500 m length and with an average width of 120 m.

The Esfordi open-cut mine currently produces 103,000 tonnes of apatite concentrate a year, from a resource of 17 Mt @ 13.5 wt % P<sub>2</sub>O<sub>5</sub>. The surface exposure of Fe-oxide and apatite ore, its REE mineralisation and extensive alteration zones, together with the availability of drill core samples, make Esfordi one of the best examples of Fe–P mineralisation in the Bafq district on which to undertake research.

This project entailed a detailed examination of the mineralogy and petrology of the ore and altered host rocks at Esfordi, together with the geochemical characteristics of the various ore types present. At the local scale the results are intended to assist exploration, mining and mineral processing within the deposit environs. At the broader scale, this study

is designed to improve understanding of the formation of the Bafq deposits and their relationship to Kiruna-type magnetite–apatite and other Fe–Cu–Au deposits around the world.

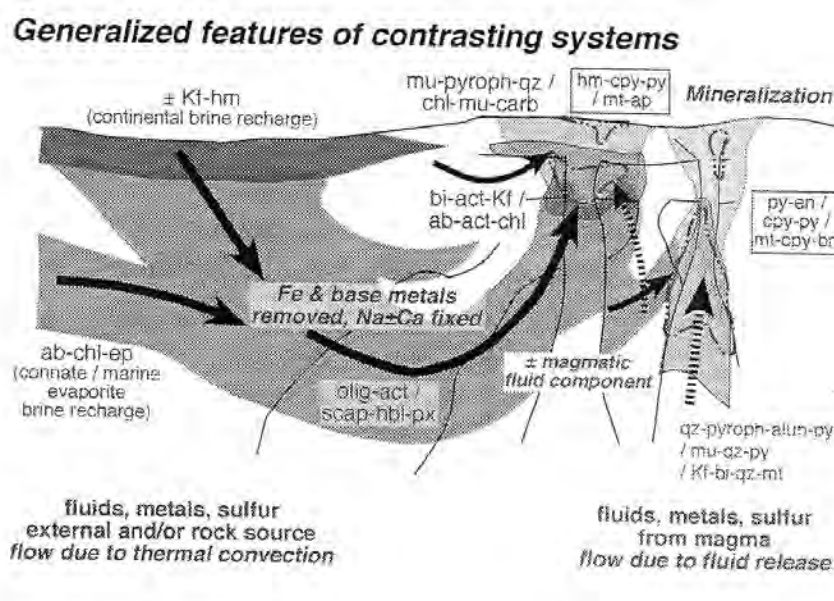
## **1.2 LITERATURE REVIEW: AN INITIAL PERSPECTIVE**

The most important non-sedimentary group of economic Fe-oxide-rich deposits in the world are the Kiruna-type magnetite–apatite and the Fe-oxide–Cu(–Au) deposits. Some of the most famous districts containing such deposits are northern and central Sweden (hosting Kiruna), the Gawler Craton of South Australia (hosting Olympic Dam), the Cloncurry district of northern Queensland, the southern Great Bear magmatic zone in the Northwest Territories of Canada, the St Francois Terrane in southeastern Missouri, the Avnic district of Turkey, the Candelaria systems in the cordillera of Chile and the contrasting El Laco and Carajas districts in Brazil (hosting Alemao, Igarape Bahia, Salobo and Salobo-3 Alpha). Most of these deposits have been subjected to extensive research over the last decade driven by the need for more effective exploration methods, particularly for the Cu–Au bearing variants of such deposit types. The Central Iranian Fe-oxide districts are of equal significance to the districts named but their geological characteristics have been poorly documented.

This group of ore deposits displays highly varied styles of mineralisation, alteration, chemistry and tectonic setting. The distinctive characteristics which differentiate the Fe–P sub-group from the Fe-oxide–Cu(–Au) sub-group are:

- (a) tectonic setting,
- (b) spatial relationship to plutons,
- (c) low Ti abundances in the magnetite and/or hematite and
- (d) association of P in Kiruna-type magnetite–apatite sub-group of deposits, and Cu with  $\text{Au} \pm \text{Ag}$  in the Fe-oxide–Cu(–Au) sub-group, together with a suite of minor elements that include REE, U, Th, Co, Ba and F.

Various genetic models have been proposed for the formation of this group of deposits (and the basis on which they can actually be grouped). Such models have subsequently been used in an attempt to define and differentiate the characteristics of productive systems from those of barren or subeconomic systems. There is, however, no consensus among researchers as to the principle source and characteristics of the fluids responsible for mineralisation or the nature of the contribution of associated magmas (Fig 1.1).



**Figure 1. 1 Schematic model of igneous-driven circulation of fluids causing alteration zoning in mafic and felsic systems (after Barton and Johnson, 1996).**

Magnetite–apatite (Kiruna-type) and Fe-oxide–Cu(–Au) deposits may be considered to form the end-members of a continuum of deposit types within one broad class (Hitzman *et al.*, 1992). The common features are their formation in post-Archean rocks, where thickened and differentiated continental crust had undergone extension and development of a variety of subsequent features including igneous activity associated with mantle underplating, high heat flow and oxidised source rocks that commonly contain evaporites. Nearly all major districts containing these deposits have a geological setting

involving intercratonic extensional tectonics coeval with host rock deposition. In this regard, Hitzman (2000) proposed three major tectonic processes including intracontinental orogenic collapse, intra-continental anorogenic magmatism and extension along a subduction-related continental margins. The magnetite–apatite deposits of different age and geological settings show remarkably similar alteration and mineralisation style, whereas the Fe-oxide–Cu (–Au) deposits are more diverse.

The temporal relationship of the two principle mineral deposit sub-groups is controversial. Hitzman (2000) suggests that they are not coeval, even where in close spatial relationship, but that the magnetite–apatite part of such systems formed prior to any significant Fe-oxide–Cu(–Au) mineralisation. It was also suggested that, despite many shared features, magnetite–apatite (Kiruna-type) and Fe-oxide–Cu(–Au) deposits may have fundamentally different origins (and should, therefore, not be grouped).

A brief review of some of the better documented examples of these sub-groups, together with other style of Fe-oxide mineralization, is presented as a basis for consideration of the characteristics of the Esfordi apatite-magnetite system

### **1.3 IRON OXIDE–CU (–AU) DEPOSITS**

This sub-group of deposits was recognised by Hitzman *et al.* (1992) as a major category of hydrothermal mineralisation in continental crustal environments. This group of deposits is Fe-oxide-rich with variable amounts of Cu sulphides and pyrite. It also contains significant enrichments of Au, REE, Ag, P, F, U, Ba, Mo, Co and, in some cases, Th, B and As (Williams and Pollard, 1998; Pollard 2000; Haynes 2000). The well-developed alteration zones in the majority of deposits are characterised as sodic, potassic, sericitic and siliceous at various depths (Table 1.1).

Fe-oxide–Cu (–Au) mineralisation has different styles, including breccia, stockwork, veins, carbonate replacement and ironstone-hosted deposits. Magnetite is generally

abundant and overprints previous sodic and potassic alteration. Sulphide mineralisation, including chalcopyrite and bornite, commonly overprints the magnetite.

Various depths of mineralisation have been proposed for this sub-group. In deep-seated deposits, such as those of the Cloncurry district, sodic or sodic-calcic alteration (e.g. albite-clinopyroxene-amphibole-scapolite-titanite assemblages) are common. Sericitic alteration and hematite-rich mineralisation are dominant in shallow depositional systems where surface waters contributed to the hydrothermal solution (e.g. Olympic Dam, Susanna or northern Chile) and the main Cu minerals of chalcopyrite, bornite, digenite, covellite and chalcocite are typically in a zoned arrangement (Haynes *et al.*, 1995; Espinoza *et al.*, 1996). A low-grade hematite-quartz or hematite overprint may be developed in the upper most part of these systems (Haynes *et al.*, 1995).

The studies by Menard (1995), Lindblom *et al.* (1996), Rotherham *et al.* (1998), Baker (1998) and Borrok *et al.* (1998) suggest a magmatic-hydrothermal fluid source, whereas Barton and Johnson (2000) believe that non-magmatic brines are the most important component of the hydrothermal system. Evidence of early magmatic-derived fluids and later meteoric fluids at Olympic Dam is presented by Oreskes and Einaudi (1992). Mixing models, involving both magmatic and hydrothermal components to the mineralizing processes, have also been considered (Huston *et al.*, 1993; Gow *et al.*, 1994; Ullrich and Clark, 1998; Barton and Johnson, 2000).

A genetic relationship between alkalic, K-rich magnetite deposits with the evolution of CO<sub>2</sub>-rich phases from metaluminous intrusive rocks has been used as evidence that Fe-oxide-Cu (-Au) deposits are part of a granitoid-related Cu-Au spectrum of deposits (Pollard, 1998; Perring *et al.*, 2001).

### **1.3.1 Olympic Dam**

The Fe-rich Olympic Dam Cu-U-Au deposit is located within the meso-Proterozoic Roxby Downs Granite of the Stuart Shelf region in the northeast Gawler Craton, South

Australia. The Roxby Downs Granite is an undeformed, unmetamorphosed, coarse to medium grained, quartz-poor, biotitic syenogranite with A-type geochemical affinities (high K<sub>2</sub>O, REE, Zr, Y, U, Th and F) (Creaser, 1989).

The Olympic Dam Breccia Complex is an 8 x 6 km zone composed of brecciated and altered granite with clasts of felsic to intermediate ash flow tuffs, lava flows and sediments intersected by zones of hematite-rich breccia that extend more than 1 km below surface (Oreskes and Einaudi, 1990). The brecciation and mineralisation may have postdated granite emplacement by up to 200 Ma (Oreskes and Einaudi, 1990). The breccia has been divided into granite-rich and hematite-rich types (Reeve *et al.*, 1990) with the hematite-rich breccia composed of a mixture of granite, hematite, mafic and felsic intrusive rocks and sedimentary fragments associated with chalcopyrite, fluorite, quartz and carbonate. The outer margin of the breccia complex is mainly granitic with a sericitised and locally hematitised matrix that varies towards the core of the system from matrix-poor types with jigsaw texture to matrix-supported types with increasing hematite replacement (Oreskes and Einaudi, 1990).

**Table 1.1 Olympic Dam-type Fe–Cu–Au deposits.**

|                                 | Main host rock                                                                                              | Host rock age (Ma)                                 | Ore minerals                     | Mineralization style                                                   | Reserve                                                                                  | Confining structure style  | Alteration and alteration assemblage                                            | Reference                                                                            |
|---------------------------------|-------------------------------------------------------------------------------------------------------------|----------------------------------------------------|----------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------------------------------|----------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| Olympic Dam                     | Syenogranite with minor volcanoclastics and felsic/mafic dykes                                              | 1588±4 Ma (U-Pb, zircon, Creaser and Cooper, 1993) | Cpy-Bn- Mt-Hm-Allan-Mon-Gal-Uran | Disseminated sulphides in breccia matrix, Breccia, veins               | 2320 Mt @ 0.5 g/t Au<br>1.3 % Cu<br>0.4 kg/t U <sub>3</sub> O <sub>8</sub><br>2.9 g/t Ag | N-W breccia complex        | Mt±Hm, Chl, Ser, Sid, Py, Cpy, Pit, Ce, Bn, Pit, Bar, Flu, Chl, Qtz             | Reeve <i>et al.</i> (1990); Oreskes and Einaudi (1992); Skirrow <i>et al.</i> (2002) |
| Acropolis                       | Granitoid, gneissic alkali granite                                                                          | Meso-Proterozoic                                   | Mt-Hm±Sid-Cpy-Uran               | Breccia, massive, vein networks                                        | 66 Mt @ 0.7 % Cu                                                                         | Shear zone (fault breccia) | Na-K-Fe metasomatism chloritization, martitization, silicification              | Oreskes and Einaudi (1992); Skirrow <i>et al.</i> (2002)                             |
| Cornwall, Pennsylvania          |                                                                                                             |                                                    | Py-Cpy-pyr-Mt-Hm                 | Massive to disseminated magnetite; vein, replacement, stratiform loads | 100 Mt @ 40 % Fe<br>0.29 % Cu<br>0.04 % Co                                               |                            | Clinopyroxene, garnet, tremolite, exoskarn; chlorite and magnetite metasomatism | Laznicka (2002)                                                                      |
| Batchawana, Ontario             | Felsic volcanics (rhyolites), subvolcanic porphyries and related breccias, dolerite dykes and flood basalts |                                                    | Cpy-Py-Pyr                       | Heterolithic breccia                                                   | 256 Mt @ 0.18 % Cu                                                                       | Rift related breccias      | Na-Ca-Fe metasomatism chloritization                                            | Norman and Sawkins (1985); Laznicka (2002)                                           |
| Prominent Hill, South Australia | Metasediments and felsic volcanics                                                                          | Meso-Proterozoic                                   | Cpy-Bn-Cc-Hm-Uran                | Disseminated sulphides in breccia                                      | 107 Mt @ 1.94 % Cu<br>0.65 g/t Au<br>1.6 g/t Ag                                          | Hematitic breccia          |                                                                                 | Skirrow <i>et al.</i> (2002)                                                         |

The principal minerals are hematite, sericite and chlorite. Magnetite is locally abundant along with pyrite, chalcopyrite and siderite. Hematite-rich breccia core contains considerable amounts of Cu and Fe sulphides, as well as U, Ag and Au mineralisation (Haynes *et al.*, 1995). The sulphide mineralisation shows mineral zoning from chalcocite in the center to bornite to chalcopyrite to pyrite at the outside (Roberts and Hudson, 1983). The deposit contain reserves of over 2 billion tonnes @ 1.6 % Cu, 0.6 kg/t U<sub>3</sub>O<sub>8</sub>, 0.6 g/t Au and 3.5 g/t Ag (Roberts and Hudson, 1983; Reeve *et al.*, 1990).

Hematite-rich breccias are zoned inward from altered granite and hematite fragments in a hematite matrix (heterolithic breccia) to a fine-grained hematite breccia and hematite-quartz microbreccia in a fine hematite matrix (Oreskes and Einaudi, 1992).

Haynes *et al.* (1995) recognize three hematite mineralisation stages at the Olympic Dam Breccia Complex forming a three-level vertical zonation (Table 1.2).

**Table 1.2 Hematite mineralisation stages at the Olympic Dam breccia complex (after Haynes *et al.*, 1995).**

|               |                                                                                                |
|---------------|------------------------------------------------------------------------------------------------|
| Shallow level | Late porous, vuggy or massive hematite, quartz and barite                                      |
| Medium level  | Hematite, sericite, chalcopyrite, bornite, pitchblende, barite, fluorite and chlorite          |
| Deep level    | Early magnetite ± hematite, chlorite, sericite, siderite, pyrite, chalcopyrite and pitchblende |

Oreskes and Einaudi (1990) suggested that the heterolithic breccia, hematite-quartz microbreccia, hematite breccia and their elongate shape and steep dip are the result of the mineralisation forming by hydrothermal brecciation and metasomatism of the Roxby Downs Granite along active faults. Fluidization textures, abraded fragments and sorted rock flours indicate phreatic eruptions were probably important in the formation of the breccia (Oreskes and Einaudi, 1990), although Reeve *et al.* (1990) interpreted the

phreatomagmatic breccia and volcaniclastic rocks associated with felsic and mafic igneous dykes in the central and southeastern part of breccia complex to be diatremes and associated tuffisite dykes.

The model of Oreskes and Einaudi (1992), based on fluid inclusion geothermometry and stable isotope studies, has the magnetite-rich zones at Olympic Dam deposited from high-temperature (400 °C) hydrothermal fluids and the hematite breccia at lower temperatures (190 °C), but the latter may have been the latest of a series of hydrothermal events. The Au mineralisation belongs to a late stage hydrothermal episode responsible for CO<sub>2</sub>-bearing fluorite and quartz veins.

Although the source of the metals at Olympic Dam is still controversial, high  $\delta^{18}\text{O}$  compositions of the fluids suggest a magmatic affinity; probably derived from highly differentiated igneous bodies (Oreskes and Einaudi, 1992; Skirrow *et al.*, 2002).

### 1.3.2 Cloncurry District, Australia

The Cloncurry district of northwest Queensland is another variant of Fe-oxide–Cu(–Au) deposits. Most Cloncurry district Cu-Au deposits are hosted by deformed and metamorphosed Mesoproterozoic (1.8-1.65 Ga) sequences, associated with shear zones and contain high Fe and low S mineral assemblages. The most common alteration assemblage is albite–actinolite–scapolite–magnetite±hematite–diopside–calcite–quartz and can be divided into Na±Ca, Ca±Fe, Fe±K and K-dominated alteration assemblages (**Error! Reference source not found.**).

The Cu±Au±Ag±Co deposits are mainly structurally controlled within a 100 km long corridor hosted by the variably metamorphosed Mary Kathleen and Soldiers Cap Groups and other intrusive rocks. This group of deposits may be sub-divided into Au-dominated deposits (Gilded Rose, Tick Hill, Lorena, Mount Freda, and Wynberg) and Cu-Au±Co±Ag deposits (Ernest Henry, Eloise, Osborn, Mt Cuthbert, Great Australia,

Hampden, Copper Canyon, Greenmount, Lightning Creek, Duchess, Trekellano, Wee MacGregor, Maronan, Monakoff and Starra).

### 1.3.3 Chilean Fe-oxide-Cu-Au (Zn-Ag) deposits

The Chilean Fe-Cu-Au deposits are restricted to a belt 30 km wide and ~1000 km long that follows the Atacama Fault system. This series of deposits is hosted by an intensely altered suite of volcanic and volcanoclastic rocks that are part of an Early Cretaceous continental margin volcanic arc and marine back-arc basin terrane (Perez *et al.*, 1990; Marschik *et al.*, 2000). Most deposits in this region show a close relationship to those within the Early Cretaceous Chilean Coastal Batholith (**Error! Reference source not found.**). The deposits of the Punta del Cobre Belt mainly occur within or near the batholith metamorphic halo. The volcanic host rocks are affected by variously pervasive Na-K-Ca-Fe alteration. The ore mineralogy consists mainly of magnetite and/or hematite with chalcopyrite, pyrite, pyrrhotite, sphalerite and locally REE minerals. Gold is associated with chalcopyrite and pyrite as micron-sized inclusions (Ryan *et al.*, 1995; Marschik *et al.*, 2000). The Cu and Au mineralisation of the major deposits in the district is controlled by the intersection of N-NW and NW trending faults. The mineralisation style is mainly massive veins, networks of veinlets and stringers, breccia fillings, and concordant replacement lenses and mantles within altered volcanic host rocks.

La Candelaria is the largest Fe-oxide-Cu-Au (Zn-Ag) deposit of Chilean Cretaceous continental volcanic arc terrane with reserves of 470 Mt @ 0.95 % Cu, 0.22 g/t Au and 3.1 g/t Ag (Ryan *et al.*, 1995). The other mines in the Punta del Cobre district are Mantos de Cobre, Meleno, Trinidad, Sacovon Rampa, Carola, and Natoco (Marschik *et al.*, 2000).

## 1.4 KIRUNA-TYPE MAGNETITE–APATITE DEPOSITS

Kiruna-type magnetite–apatite rocks are found in various parts of the world and within different geologic environments. This group of deposits is usually closely

associated with igneous rocks that range in composition from mafics to felsic and include both extrusive and intrusive rocks. The origin of Kiruna deposits has long been controversial, particularly those at Kiruna itself (Frietsch, 1995; Martinsson and Weihed, 1999; Nystrom and Henriquez, 1994; Ripa, 1988) and El Laco (Broman *et al.*, 1999; Nystroem and Henriquez, 1995; Sillitoe and Burrows, 2002).

Liquid magmatic models have been ascribed a prominent role, particularly at Kiruna and El Laco. This is based, to a significant extent, on similarities between the magnetite textures and flow and quench textures observed in silicate melts (Foose and McLelland, 1995; Frutos and Oyarzun, 1975; Henriquez and Martin, 1978; Henriquez and Nystrom, 1998). Other workers support a hydrothermal depositional model, particularly for El Laco, based on geologic relationships, fluid inclusion studies, and hydrothermal alteration (Hildebrand, 1986; Hitzman *et al.*, 1992; Rhodes and Oreskes, 1994, 1996, 1999; Rhodes and Larson, 1997; Sheets *et al.*, 1997; Hitzman, 2000; and Barton and Johnson, 2000).

The key characteristics of the main Kiruna-type magnetite–apatite deposits are shown in Table 1.5. Further deposits of the Kiruna, El Laco, Southeastern Missouri are given in the following sections.

**Table 1.3 Cloncurry district (type) Fe–Cu–Au deposits**

|               | Main host rock                                                                     | Host rock age (Ma)              | Ore minerals                                            | Mineralization style                                | Reserve                                                               | Confining structure style                             | Alteration and alteration assemblage                                | Reference                                                              |
|---------------|------------------------------------------------------------------------------------|---------------------------------|---------------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------------------------|-------------------------------------------------------|---------------------------------------------------------------------|------------------------------------------------------------------------|
| Ernest Henry  | Intermediate to felsic volcanics or sub-volcanic sills, mafic volcanics, diorite   | 1746±9 Meso-proterozoic         | Chpy+py+<br>Mt±Allan±<br>Mon±Ap±<br>Sch±Gal±<br>Mo±Uran | Breccia, replacement                                | 166 Mt @<br>0.5 g/t Au<br>1.6 % Cu (500 g/t Co, 180 g/t Mo, 50 g/t U) | Shear zone                                            | Cal-qtz-bio. Mag-bio-gar, k-feld, chl, epi, tour, flu.              | Ryan (1998); Mark <i>et al.</i> (2000)                                 |
| Starra        | Iron stone, metasiliclastic and calc-silicate rocks                                | 1750 Ma                         | Py-Cpy-Au-Mt                                            | Breccia, replacement                                | 6.9 Mt @<br>4.8 g/t Au<br>1.65 % Cu                                   | Shear zone                                            | Na-K-Fe metasomatism chloritization, martitization                  | Davidson <i>et al.</i> (1989); Rotherham <i>et al.</i> (1998)          |
| Osborne       | Amphibolite, pegmatite, qtz-alb-anthophyllite metamorphic rocks, actinolite schist | Meso-proterozoic                | Py-Cpy-Mt-Hm                                            | Veining, replacement, stratiform mineralizing loads | 36 Mt @<br>1.0 g/t Au<br>2.0 % Cu                                     | Stratigraphic unit                                    | K-Mg and Na, Mt-Qtz±Bio, calc-silicate, Bio, Si, carbonate and pyr. | Adshead (1995)                                                         |
| Eloise        | Amphibolite, meta-arkose (Soldiers Cap Group)                                      | Meso-proterozoic (1.67-1.60 Ga) | Pyrr-Cpy-Mt                                             | Localised disseminated and massive sulphide loads   | 3.2 Mt @<br>1.5 g/t Au<br>5.8 % Cu<br>19 g/t Ag                       | N-S trending Shear zone                               | Qtz-Alb., Hor.-Bio.-Qtz Ca-Fe-Mg-K silicate                         | Baker <i>et al.</i> (1998); Baker and Laing (1998)                     |
| Mount Elliott | Amphibolite, metapelite, Carbonaceous schist, trachyandesite                       | Meso-proterozoic (1.67-1.60 Ga) | Pyrr+<br>py±Cpy ±<br>Mt                                 | Skarn (vein, replacement)                           | 3.3 Mt @<br>1.8 g/t Au<br>3.6 % Cu                                    | Steep to moderately dipping faults, veins and breccia | Alb-Bio-Carb, Diop-hed-sc-ap                                        | Little (1997); Fortowski and McCracken (1998) Wang and Williams (2001) |
| Swan          | Calc-silicate rocks and metasilstone                                               | Meso-proterozoic                | Cpy-py-Mt-Allan                                         | Skarn (vein, replacement)                           | 13.5 Mt @<br>0.5 g/t Au<br>0.9 % Cu                                   | Cloncurry mineralisation corridor                     | Skarn-like alteration Amp±Epi±Hed±Mt                                | Wang and Williams (2001)                                               |
| Greenmount    | Altered carbonaceous rocks                                                         | 1660 Ma                         | Py-Cpy-Hm ± Mt ± Sch                                    | Qtz-k-feld veins                                    | 3.6 Mt @<br>0.8 g/t Au<br>1.5 % Cu<br>0.6 % Co                        | Stratigraphic boundary                                | Albite-scapolite Microcline-biotite                                 | Homestake Quarterly Report, March 1995                                 |

**Table 1.4 Chilean-type Fe–Cu–Au deposits**

| Deposit                                       | Main host rock                                                             | Host rock age (Ma)                                                    | Ore minerals                         | Mineralization style                  | Reserve                                        | Confining structure style                     | Alteration and alt. assemblage                                                      | Reference                     |
|-----------------------------------------------|----------------------------------------------------------------------------|-----------------------------------------------------------------------|--------------------------------------|---------------------------------------|------------------------------------------------|-----------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------|
| La Candelaria, Chile                          | Andesitic volcanics, tuff, metasediments (Punta del Cobre Fm.)             | Early Cret.                                                           | Mt-Hm-Pyrr-Py-Cpy                    | Lenses and veins, breccia filling     | 400 Mt @ 1.0 % Cu<br>0.20 g/t Au<br>4.5 g/t Ag | Shear zone, NNW-NNE faults, Volcanic layering | Pyroxene, garnet, actinolite, K-feld., hornblende, scapolite, epidote, calcite, Qtz | Martin <i>et al.</i> (1998)   |
| Manto Verde, Chile                            | Andesitic volcanics, diorite porphyry stock                                | Early Cret.                                                           | Hm-Cpy-Py                            | Breccia filling, stockwork            | 120 Mt @ 0.72 % Cu<br>0.5 g/t Au               | Manto Verde fault (3 breccia zones)           | K-feld., sericite, qtz, calcite alteration                                          | Vila <i>et al.</i> (1996)     |
| Buena Esperanza (and Mantos Blancos), N-Chile | Andesitic volcanics and volcano-sedimentary rocks                          | Early Cret.                                                           | Bor-Cpy-Py-Hm-Gal-Digenite-Covellite | Breccia filling, veins                |                                                | Shear zone, breccia                           | Chlorite, sericite, hematite, albite, calcite, qtz                                  | Espinoza <i>et al.</i> (1996) |
| Alemao Cu-Au-(REE-U) deposit, Brazil          | Acid-intermediate metavolcanics, metavolcanoclastic, metasedimentary rocks | 2350 Ma (Docego 1988); Cu-Au mineralisation 2850 Ma<br>Mougeot, 1996) | Mt-Cpy-Py-Br-Mol                     | Breccia filling, veins and stockworks | 170 Mt @ 1.5 % Cu<br>0.8 g/t Au                | Hydrothermal breccia, Fault shear zone        | Chlorite, biotite, amphibole, carbonates, qtz and Fe-metasomatism                   | Ronze <i>et al.</i> (2000)    |
| Igarape Bahia Au-Cu-(REE-U) deposit, Brazil   | Acid-intermediate metavolcanics, metavolcanoclastic, metasedimentary rocks | 2350 Ma (Docego 1988); Cu-Au mineralisation 2850 Ma<br>Mougeot, 1996) | Mt-Hm-Cpy-Bor-Moly-Dig-Py            | Breccia filling                       | 29 Mt @ 2 g/t Au                               | Heterolithic breccias                         | Chlorite, Fe, carbonate, qtz, tourmaline, biotite, and sulphide metasomatism,       | Tazava and de Oliveria (2000) |
| Cobriza, Peru                                 | Granite                                                                    | 263 Ma                                                                | Cpy-Py-(Ag-Bi-W-Sn)                  | Manto in calcic skarn                 | 100 Mt @ 1.5 % Cu (Ag,Bi)                      | NW reverse faults                             | Diopside, garnet, hornblende skarn type (with actinolite-phlogopite-Qtz)            | Espinoza (2002)               |
| Cobrepampa, Peru                              | Linga Monzonite                                                            | 96 Ma                                                                 | Cpy-Br-Cc-Mt-Py (Au-Ag)              | Multiple veins                        | 5 Mt @ 2-5 % Cu                                | Faults shear zone                             | Magnetite, actinolite, chlorite, albite, K-feld, apatite, qtz, calcite              | Espinoza (2002)               |

**Table 1.5 Kiruna-type deposits**

|                               | Main host rock                                                 | Host rock age (Ma)                                                                                   | Ore minerals                     | Mineralization style                    | Reserve                         | Alteration and alt. assemblage             | Reference                                                                                                          |
|-------------------------------|----------------------------------------------------------------|------------------------------------------------------------------------------------------------------|----------------------------------|-----------------------------------------|---------------------------------|--------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| Kirunavaara, N Sweden         | Felsic to intermediate volcanics (Porphyry Group)              | Mesoproterozoic 1.6-1.9 Ga (Welin <i>et al.</i> 1971)<br>1.89 Ga (Sm-Nd, Cliff <i>et al.</i> , 1990) | Low Ti-Mt. and minor Ap, Hm, REM | Elongate conformable lense              | 2000 Mt @ 60 % Fe<br>0.9 % P    | Mt-Ap-Act-Alb-Cal                          | Geijer (1967)<br>Hitzman (2000)                                                                                    |
| Pea Ridge, Southeast Missouri | Rhyolitic lava flow and tuffs                                  | 1.48-1.45 Ga (Bickford, 1988)                                                                        | Mt and minor Hm-Ap-REM           | Massive, disseminated                   |                                 | Hm-Qtz-K-feld.-Ser-Act-Chl-Carb            | Kerr (1998)                                                                                                        |
| El Laco, Chile                | Felsic to intermediate volcanics (Andesitic and dacitic lavas) | 2.1 Ma (Maksaev <i>et al.</i> , 1988)                                                                | Mt-Ap                            | Massive, lava flow, pyroclastics, dykes | 500 Mt @ 60 % Fe                | Mt-Pyx-sep-Alb-diop (hydrolytic / silicic) | Nystrom and Henriquez (1994); Rhodes and Oreskes (1999); Naslund <i>et al.</i> (2002); Sillitoe and Burrows (2002) |
| Bafq, Central Iran            | Mainly felsic volcanics and volcano-sedimentary rocks          | Lower Cambrian                                                                                       | Mt-Hm-Ap                         | Massive, elongate conformable lense     | 2000 Mt @ 60 % Fe<br>Low->1 % P | Mt-Act-Pyx-Sep-Alb-K-feld-Chl-Cal-Qtz      | NISCO (1971, 1975, 1979, 1980)<br>Daliran (1990, 2002)<br>Förster and Jafarzadeh (1994)                            |

#### 1.4.1 Kiruna District, Sweden

The P-rich magnetite ores of the Kiruna area in northern Sweden are hosted by 1880-1890 Ma Mesoproterozoic rocks (Cliff *et al.*, 1990; Romer *et al.*, 1994). The Svappavaara, Stuor-Ratek and Gullivare areas in northern Sweden and Grungesberg in central Sweden contain voluminous magnetite–apatite ore bodies hosted by alkali rhyolite, trachyte, ash and lava flows. The main deposits are Kiirunavaara, Luossavaara, Haukivaara, Rektorn, Henry and Nukutusvaara (Parak 1975). Except for Kiirunavaara, the other Fe deposits are no longer mined.

The Kiirunavaara deposit is the largest of the Fe deposit in the region and has been studied for over 100 years. The ore body is tabular and broadly conformable with the host rock, dipping 50-60°E. The Kiirunavaara ore consists of mainly low Ti-magnetite with minor hematite and fluorapatite (~2 % P). Actinolite, diopside and calcite occur as minor accessory phases. The main ore body has a length of ~6 km with a typical thickness of 80-100 m. A reserve of 2000 Mt @ 60 % Fe and 0.9 % P has been reported. The ore body is developed between a porphyritic syenite footwall and a rhyolite hanging wall (Romer *et al.*, 1994). The main host rock is the Porphyry Group and is interpreted to be a sequence of acid pyroclastic rocks. The basement is a greenstone sequence with minor shallow water marine sediments. The Palaeo-Proterozoic greenstone basement unconformably overlies Archean granitic gneiss (Frietsch 1984). The volcanic rocks in the Kiruna district are contained within grabens or calderas (Geijer, 1967). The subsidiary Haukivaara, Rektorn, Henry and Nukutusvaara deposits are located at the top of the Porphyry Group and are comparable with the Kiirunavaara and Luossavaara deposits but have higher apatite and hematite contents. Rocks of the Porphyry Group have been metamorphosed to greenschist grade (Harlov *et al.*, 2002).

Based on morphology, mineralogy and composition, several categories of Kiruna ore are recognised and these contain different P contents. Geijer and Magnusson (1944)

recognize two groups using a 0.2 % P cutoff. Other subdivisions, based on morphology and mineral assemblages, have been developed by Geijer and Magnusson (1944), Frietsch (1978) and Harlov *et al.* (2002).

Harlov *et al.* (2002) recognised three broad groupings at Kiirunavaara. The first category is the primary magnetite–apatite ore. This ore forms the so-called skeleton ore (Nystrom and Henriquez, 1989, 1994) and consists of platy magnetite (a few tenths to a few mm thick) in an apatitic matrix. The magnetite has numerous apatite inclusions (10–20  $\mu\text{m}$ ) and the apatites are compositionally zoned and contain monazite inclusions. The second category is the brecciated apatite-magnetite ore. In this ore, angular brecciated fragments of magnetite are contained in an apatite matrix and is interpreted to be the result of brittle deformation at relatively low temperatures. The magnetites again contain numerous apatite inclusions (from  $\sim 500 \mu\text{m}$  to  $< 10 \mu\text{m}$ ). The apatite grains are zoned and contain monazite inclusions with same textural patterns of the primary ore. The monazite also occurs as relatively large interstitial grains (10–100  $\mu\text{m}$ ). The final category is banded magnetite–apatite ore containing fine, alternating, discontinuous apatite and magnetite-rich bands, which are interpreted to be the imprint of plastic deformation. The magnetite grains ( $< 200 \mu\text{m}$ ) are inclusion-free. The apatite is generally fine and contains less monazite inclusions than in the primary ore. Monazite typically occurs as individual crystals (10–150  $\mu\text{m}$ ) along magnetite, apatite, tremolite and quartz grain boundaries.

#### *Kiruna-type genetic models*

Several genetic models have proposed for the genesis of Kiruna deposits. Geijer (1910 et seq.) and Frietsch (1973, 1978, 1984) suggested a magmatic origin related to immiscibility between silicate and Fe-oxide rich magma. They proposed that sub-surface volatile evolution played an important role in separation of ore magma. Geijer (1967), Philpotts (1967), Parak (1975) and Frietsch (1978) supported this concept on the basis of various fabrics within the ore assemblages.

Though accepting a predominantly magmatic model, Frietsch (1973) concluded that the main and P-rich ore facies formed in the magmatic stage(s), whereas the hematite-rich ore was deposited later by oxidizing hydrothermal solutions. Parak (1973) documented high REE contents in some of the apatitic iron ores in northern Sweden and proposed a non-magmatic volcanic-sedimentary origin.

Many of the Kiruna-type deposits in northern and central Sweden are accompanied by replacement and alteration of the host rock (Frietsch, 1978). Hematite (after magnetite), quartz, muscovite, chlorite, calcite, tourmaline, barite, allanite, zircon and fluorite are among the minor alteration products. Geijer (1919, 1967) reported considerable amounts of breccia, composed of magnetite, hematite, apatite and sparse amphibole, particularly at the rim of the main ore body but with a gradational boundary. In some of the Swedish Kiruna-type ores, a cross cutting relations between younger apatite-rich ore and magnetite ore breccia has been reported (Geijer, 1967; Frietsch, 1973). Based on a dominant magmatic model, and using trace element distribution, Frietsch (1970) proposed three stages in the formation of Kiruna-type ores: the Kiruna-type magnetite proper, P-rich ore and late-stage hydrothermal hematite ore. Parak (1975), however, suggested that the ore breccias at Kiruna do not have the same origin as the main ore body and that the ore breccia was formed by mobilization of sedimentary Fe-oxides, which had been mobilised into adjacent fracture systems. In this exhalative-sedimentary model the ore was considered to be contemporaneous with volcanism and sedimentation.

More recent studies of Kiruna-type ores (Broman *et al.*, 1999; Naslund *et al.*, 2000; Bergman *et al.*, 2001) suggest that they are likely to have been deposited from an Fe-oxide melt that was rich in volatiles and P, followed by separation of water-rich fluids and extensive hydrothermal overprint.

#### 1.4.2 Chilean magnetite–apatite deposits

Numerous Fe-oxide deposits and some significant Cu deposits are located in a belt 1000 km long and up to 30 km wide in the Atacama Desert of northern Chile. The mineralisation occurs within late Jurassic–early Cretaceous magmatic arc and back arc sedimentary sequences. Andesite, andesite flows and volcanic breccias with tuff, sandstone, conglomerate and limestone intercalations are developed in the eastern part of the belt, whereas calc-alkaline plutons ranging from gabbroic to granitic compositions are characteristic of the western part of the belt (Espinoza, 1990).

The Fe-oxide bodies occur as pods and dykes in breccias associated with major fault systems. They are mainly composed of magnetite with varying amounts of apatite and actinolite. The host rocks are extensively altered. Bookstrom (1977) reported a variety of secondary assemblages including: albite-oligoclase, scapolite, actinolite, magnetite, biotite, K-feldspar, quartz and calcite.

The archetypal El Laco Fe-oxide deposit occurs in the volcanic arc of the high Andes. It is young (2.1 Ma; Makshev *et al.*, 1988) and is composed of seven discrete ore bodies with an overall resource of 500 million tonnes @ 60 % Fe (Nystrom and Henriquez, 1994). The ore is mainly magnetite and secondary martite within lava flows, dykes and pyroclastic materials. The massive ore contains variable amount of pyroxene and minor apatite and has been cut by several magnetite±pyroxene±apatite veins (Nystrom and Henriquez, 1994; Naslund *et al.*, 2002). The ore bodies occur within a sequence of Plio-Pleistocene andesitic and dacitic lavas with local salinas (Naslund *et al.*, 2002). The host rocks have been pervasively altered to a pyroxene-scapolite-albite assemblage (Rhodes and Oreskes, 1999; Sillitoe and Burrows, 2002).

Whereas there is general agreement about the setting and descriptive characteristics, the origin of the El Laco deposit has been the subject of extensive debate over the last two decades. One group of workers has suggested El Laco is a well-preserved

example of the intrusion and extrusion of volatile-rich ore magma. The main basis for this model is the recognition of apparent quench textures in magnetite, magnetite-rich bombs, pyroclastic Fe-oxides, vesicular structures and presence of high temperature and melt inclusions in apatite and pyroxene (Park, 1961; Rogers, 1969; Frutos and Oyarzun, 1975; Henriquez and Martin, 1978; Nystrom and Henriquez, 1994, 1995; Naslund *et al.*, 1997; Henriquez and Nystrom, 1998; Broman *et al.* 1999; Naslund *et al.*, 2002). Another group supports a metasomatic replacement of host volcanic rocks as the major mineralizing process for massive magnetite–apatite mineralisation. This is based on sub-magmatic temperature of fluid inclusions, alteration of the host rocks, trace and rare earth element geochemistry, stable isotope studies, mineral assemblages and microscopic and microscopic textures (Hitzman, 1992; Larson and Oreskes, 1993; Larson, 1994; Rhodes and Oreskes, 1995a and b, 1996, 1999; Oreskes, 1994, Sheets *et al.*, 1997, Rhodes and Larson, 1997; Rhodes and Oreskes, 1999; Hitzman, 2000)

Strong field evidence has been presented to support the metasomatic replacement of the precursor volcanoclastic sequence at El Laco by Sillitoe and Burrows (2002). They documented a large number of altered andesitic host rock blocks and fragments in the lower most bench of the Laco Sur open pit, which contains pyroxene alteration and cross-cutting magnetite veins. These blocks are altered bedded tuff and tuff breccia with sub-horizontal stratification. Magnetite replaces the block margins and cuts them as small veins and veinlets, giving a jigsaw-like texture (Rhodes and Oreskes, 1999; Sillitoe and Burrows, 2002). Rhodes and Oreskes (1999) reported scapolite-albite alteration that is replaced by coarse-grained diopside in the core of the blocks. At several places the volcanic fragments are entirely replaced by pyroxene prior to magnetite introduction (Sillitoe and Burrows, 2002). Irregular, alternating layers of magnetite and volcanic host rock can easily be interpreted as hydrothermal replacement and deposition rather than a magnetite flow. The layering in magnetite can also be explained as relict original bedding

in the volcanic protolith rather than as flow banding (Rhodes and Oreskes, 1999). Disseminated magnetite is common within the altered volcanic host. Late stage hypogene alteration of altered andesite is widespread. Kaolinite, smectite and talc have replaced the pyroxene (Nystrom and Henriquez, 1994; Rhodes and Oreskes, 1999).

#### **1.4.3 Southeast Missouri iron metallogenic province**

The southeast Missouri Iron Province contains 32 known Fe-oxide bodies associated with Mesoproterozoic rhyolites and granites of the St Francois Terrain (1,480-1,450 Ma; Bickford, 1988). The most important deposits are Pea Ridge (the only active mine in Missouri), Iron Mountain (produced 100 Mt), Bourbon, Kratz Spring, Camels Hump, Pilot Knob, and the low grade Fe-Cu Boss system (Arundale and Martin, 1970).

The St. Francois terrane, which underlies most of the southeast Missouri, is interpreted to be an extensional regime; possibly a failed cratonic rift. Side (1981) suggests that regional uplift and crustal arching associated with mantle upwelling, lead to extension fracturing and partial melting of the lower crust.

The St. Francois Terrain is part of a volcanic belt extending from Michigan and Ohio to Illinois, Missouri and Oklahoma (Kisvarsanyi and Seeger 1993). A range of high level granites with distinctive compositions and modes of emplacement have been recognised including subvolcanic massifs, ring intrusions and central plutons (Kisvarsanyi, 1981, 1984). The subvolcanic massifs are mainly fine grained biotite alkali granites with porphyritic textures. They are granophyric near the contacts and grade into equigranular and coarse-grained rapakivi textures with fluorite, apatite and zircon as accessory minerals (Side, 1981; Kisvarsanyi and Kisvarsanyi, 1989). The ring intrusions contain intermediate to high silica amphibole and biotite granite and quartz monzonites and syenites. These bodies mainly include granophyric, medium and fine-grained porphyritic granite and are interpreted to have formed in ring fractures related to caldera collapse (Kisvarsanyi and Kisvarsanyi, 1989). The central plutons were emplaced in

resurgent calderas composed of medium to coarse-grained high-silica, two-mica granite. There is only one exposure of this granite in the terrane, the Graniteville Granite, which displays a distinctive suite of accessory minerals such as garnet, fluorite, topaz, allanite, monazite and cassiterite. Volcanic rocks are predominantly porphyritic quartz-feldspar rhyolite ash flow tuffs with minor trachyandesite flows (Kisvarsanyi, 1981).

The Fe-oxide bodies have consistent host rocks, mineral assemblage, and associated alteration. Mineralization is typically hosted by volcanic rocks and located near inferred subsidence caldera margins with central granite plutons and trachyte ring intrusions (Seeger and Kisvarsanyi, 1992). Kisvarsanyi and Proctor (1967) and Day *et al.* (1989), interpret the Fe ores as intrusive and/or replacement bodies related to anorogenic rhyolites or trachyte ring intrusions.

Massive, brecciated, and disseminated Fe-oxides have varying proportions of magnetite and hematite. Most hematite is secondary (after magnetite) as specularite and martite, although some bladed hematite with magnetite could be primary. The gangue minerals are typically dominated by quartz and apatite with lesser amounts of amphibole, chlorite, biotite, pyrite, fluorite, barite, garnet, calcite and talc (Nuelle *et al.*, 1991, 1992).

The gangue minerals form interstitial intergrowths, pods and veinlets within the Fe-oxides (Sidder *et al.*, 1993). There is characteristic amphibole-magnetite-quartz alteration in nearly all deposits, with some variation associated with differences in host lithology.

#### **1.4.4 Pea Ridge deposit**

The Pea Ridge Fe ore body is a steeply dipping, discordant magnetite body, within a sequence of subalkaline rhyolitic lava flows and ash flow tuffs. The massive, fine grained magnetite ore body, is 1000 × 200 m and grades into magnetite-rhyolite breccia (Emery, 1968). It contains large apatite crystals and pods of quartz and accessory minerals. The large subhedral apatite crystals contain large monazite inclusion-rich core

and a thin inclusion-free rim. The peripheral heterolithic magnetite-cemented breccia is mainly developed in the hanging wall.

The surrounding rhyolite-hosted alteration envelope includes quartz, K-feldspar and actinolite (Seeger *et al.*, 1989), with accessory epidote, apatite, magnetite, hematite, pyrite, chalcopyrite and calcite (Nuelle *et al.*, 1991).

Various local styles of mineralisation have been recognised based on the occurrences of amphibole, magnetite, hematite, silicification, white quartz veins, REE-bearing breccia pipes and gray quartz veins (Seeger *et al.*, 1989; Sidder *et al.*, 1991; Neulle *et al.*, 1992). Several REE-rich breccia pipes occur within the hematite zone and between the hematite zone and host rhyolite in the northern part of the deposit. The breccia pipes are oval shaped in plan view with maximum diameter of 60 m and steep dips. The breccia pipes are enriched in REE and Th. Clasts are mainly composed of lithic fragments, K-feldspar, quartz, amphibole, magnetite, hematite, and barite. The breccia matrix contains fine-grained monazite, xenotime, allanite, apatite, rutile, thorite, chlorite, hematite and quartz.

The Pea Ridge trace element distributions show a similar element signature to the Iron Mountain, Bourbon and Boss deposits in the St Francois Terrain. Analogies with some aspects of the Olympic Dam Fe-oxide deposit have been proposed by Hitzman (1992) and Kerr (1998), based on the style of mineralisation, metasomatism and development of hematite-REE bearing breccia pipes.

Oreskes and Hitzman (1993) suggested that the Olympic Dam category of deposits formed from hydrothermal processes at shallow crustal levels in which igneous intrusions play an important role in supplying volatile-rich solutions and possibly metal to the system. Oreskes and Hitzman (1993) proposed that Pea Ridge Fe-oxide deposits have formed at somewhat deeper levels, based on high magnetite content associated with potassic alteration.

## **1.5 APATITE RICH ROCKS ASSOCIATED WITH MASSIF ANORTHOSITES**

A wide variety of Fe-Ti and P-rich rock types are found in spatial and temporal association with Proterozoic massif-type anorthosites. Such rocks are known by various names and have unusual compositions compared with more common igneous rock types (Dymek and Owens, 2001). The Fe-Ti oxide-apatite dyke-like bodies are sometimes known as nelsonites and were first reported in the Nelson and Amherst counties of Virginia. It was proposed by Kolker (1982) that most of dyke-like nelsonites are crystallised directly from immiscible oxide-rich melts, many of them reported as layers or dykes within massive magnetite or ilmenite deposits.

A subsidiary group of Fe-Ti oxide-apatite rich rocks are the discordant to concordant, sill-like bodies that occur within the Morin, St. Urbain and Labrieville anorthosite complexes, of the Grenville Province, Quebec (Owens and Dymek, 1992). These rocks are enriched in magnetite, ilmenite and apatite with variable proportions of Ca pyroxene and may be termed oxide-apatite gabbro-norite.

## **1.6 THE PROTEROZOIC FE-OXIDE DEPOSITS OF THE NE UNITED STATES**

Proterozoic hydrothermal Fe-oxide deposits of the northeastern United States (the Adirondack and Mid-Atlantic Belts) display similar mineralogy, host rock and hydrothermal alteration (Friedhauf *et al.*, 2002). These deposits contain low-Ti, P-rich magnetite as irregular massive bodies and stockworks of magnetite veins in amphibole and quartz-K-feldspar gneisses (Leonard and Buddington, 1964; Foose and McLelland, 1995).

Besides these Proterozoic deposits, there are several different types of Fe-oxide deposits in the northeastern US. The Sanford Lake district contains Ti-rich magnetite-ilmenite deposits associated with anorthosite intrusions. There are several Palaeozoic and Mesozoic magnetite bodies in carbonate rocks along the margins of Triassic rift basins, including the Cornwall deposit (Friedhauf *et al.*, 2002). Despite a high concentration of U and REE in many of the Proterozoic Fe-oxide deposits, the Mesozoic magnetite deposits

have very low concentration of U and REE. These criteria, along with the absence of associated granites, have been used by Barton and Johnson (1996) to discriminate this group of deposits for which they proposed a predominantly non-magmatic source for the mineralizing fluids. The high Ti level in Nelsonites is in contrast with low Ti values of Kiruna type Fe oxide-P deposits.

The Adirondack region magnetite deposits form a subgroup of the Proterozoic Fe-oxide deposits. They are hosted by the 1055-1035 Ma Lyon Mountain Granite. These include the Lyon Mountain/Canton County district, Mineville district, Benson Mines deposit and Jayville Mine (McLelland *et al.*, 2001). All of the deposits occur as lenses and veins of magnetite associated with apatite, minor ilmenite and pyrite, within an envelope of hydrothermal alteration (Lindberg and Ingram, 1964). Foose and McLelland (1995) and McLelland *et al.* (2001) compared these deposits with the Kiruna-type and Olympic Dam-type deposits.

The Clinton County District Fe-oxide deposits occur in pyroxene-rich microperthite phases of the Lyon Mountain Granite (Postel, 1952). Sodic and potassic alteration is the main wall rock alteration style associated with Fe-oxide mineralisation. The Benson Mines deposit has close association with metasedimentary rocks and granitic gneisses (Crump and Beutner, 1968). The mineralisation is mainly magnetite with considerable amounts of hematite and traces of molybdenite, chalcopyrite, covellite, fluorite, apatite, sphene, rutile and ilmenite (Crump and Beutner, 1968). The Jayville magnetite mine occurs in strongly altered gneiss with numerous calcite-hematite-pyrite-jasper veinlets (Leonard and Buddington, 1964).

## **1.7 IRANIAN IRON ORES**

Major Fe-oxide districts are located in lower Paleozoic rocks of the Bafq-Posht-e-Badam district of Central Iran, and the Gol-e-Gohar area and Hamedan deposits of the Sanandaj-Sirjan metamorphic belt. These deposits have distinct Kiruna-type

characteristics. The Tertiary Sangam deposit is located in Central East Iran. The P-rich Esfordi deposit, which is the subject of the current study, occurs in the Bafq-Posht-e-Badam district (Figs. 2.2 and 2.4) as the most important Fe province of Iran.

### **1.7.1 Gol-e-Gohar Deposit**

The Sanandaj-Sirjan Metamorphic belt (Fig 2.3) contains two major deposits - the Gol-e-Gohar and Baba Ali and Jalali deposits - and consists of medium to high-grade metamorphic rocks of Neoproterozoic-Paleozoic age exposed along the Main Zagros Thrust Zone (MZTZ). These rocks are overlain by a series of Mesozoic and Cenozoic sediments and volcanics.

The Gol-e-Gohar magnetite-apatite deposit contains ~1.3 billion tonnes of high grade iron ore (Mücke and Golestaneh, 1991; Mücke and Younessi, 1994) and is located 300 km south of Bafq and 50 km southwest of Sirjan (Fig. 2.4). This deposit is situated at the border of the Kheyr-abad Salt Pan Depression, between the Sanandaj-Sirjan Metamorphic Belt and the Urumieh Dokhtar Volcanic Arc. This metamorphic zone developed during the subduction of the Arabian Plate under the Iranian Plate, along the Main Zagros Thrust, during the Cretaceous and subsequent collision during the Pliocene.

The Gol-e-Gohar magnetite deposit consists of five separate ore bodies and is covered by up to 40 m of Neogene conglomerates and Quaternary sediments. An ophiolite mélangé sequence crops out close to the Main Zagros Thrust Zone (MZTZ) and the Gol-e-Gohar deposit. Two granite stocks are situated 15 and 70 km north of Gol-e-Gohar deposit. The ore bodies are hosted by a Neoproterozoic-Cambrian sequence of gneisses, quartz-biotite schists and amphibolites. The major Proterozoic outcrop trend is controlled by NW-SE faults that run parallel to the MZTZ. Massive and brecciated magnetite is accompanied by apatite and is locally martitized. The diverse assemblage of minor sulphides includes pyrrhotite, pentlandite, chalcopyrite, pyrite and sphalerite. Apatite occurs as 10-50  $\mu\text{m}$  euhedral to subhedral isolated veinlets in magnetite (Mücke and

Younessi, 1994). Associated with the Fe-oxides are various minerals including olivine, actinolite, hornblende, phlogopite, carbonates and chlorite.

A range of sedimentary, volcanosedimentary and metasomatic processes have been proposed for Gol-e-Gohar deposit (Valeh and Davoudzadeh, 1977; Moxham, 1990; Mücke and Golestaneh, 1991).

### **1.7.2 Baba Ali and Jalali Deposits**

Baba Ali and Jalali deposits are also situated in the Sanandaj-Sirjan Metamorphic Belt, 40 and 70 km northwest of Hamadan respectively (365 km southwest of Tehran). The ore bodies are hosted by actinolite and calc-schists. Granodiorite and dioritic intrusion cut the schists and produced a skarn halo.

These ore bodies comprise two concordant lenses that are  $250 \times 45$  and  $70 \times 12$  m and  $50$  to  $55^\circ$  toward NE. The ore is high grade with 92-96%  $\text{Fe}_2\text{O}_3$ . The lenses are concordant with the host schists and dip. There are several subsidiary ore bodies around the main lenses (Mück and Younessi, 1994).

### **1.7.3 Sangam Deposit**

The Sangam Fe deposit is located about 18 km NE of Sangam town in Central East Iran (Khorasan Province) and about 500 km NNE of Bafq. The Sangam deposit contains ~500 Mt of high-grade Fe-oxide reserves and is divided into the east, west and central ore bodies. The ore is hosted by carbonates associated with felsic volcanic and intrusive rocks including rhyolite, trachyte, dacite, andesite, granite and monzonite. The granites have a calc-alkaline geochemical signature. The main ore mineral is magnetite with minor hematite, pyrite, chalcopyrite and pyrrhotite. Two types of skarn have been recognised; a Ca-skarn containing garnet, clinopyroxene, calcite, quartz, amphibole, epidote, scapolite and dolomite bearing assemblages and Mg-skarn with forsterite, phlogopite, serpentine, clinocllore, amphibole, talc, magnesite, chlorite, calcite and sulphides (Ebrahimizadeh,

1995). Bagherian Kalat (1996) suggest that the main mineralizing stage is associated with hydrothermal activities that followed the primary stage of skarn development.

Giere and Mohammadi (1977) describe the ore body as pipe-like, with signs of an explosive emplacement. Kermani and Förster (1991) proposed that the ore at Sangam crystallised from an Fe-rich magma.

#### **1.7.4 The Bafq District**

The Bafq mining district contains >2,000 Mt of high-grade Fe ore (NISCO, 1980), which places it among the largest non-BIF type Fe ore districts of the world. This region has attracted geologists for nearly a century due to its complexity and valuable ore deposits. The Bafq mining district contains significant bodies of magnetite mineralisation as reflected by 34 major magnetic targets (Fig 1.1) and several non-Fe systems containing Pb and Zn, Mn, U, P and REE.

The Fe-oxide deposits of the Bafq region mainly consist of magnetite-hematite-apatite and host by Cambrian volcano-sedimentary sequence (also known as Saghand Formation) associated with number of felsic and mafic intrusions. These ore bodies are commonly associated with pervasively altered rhyolitic tuffs and sandstones.

The origin of the Bafq Fe deposits is the subject of a long-standing debate. Among the geological and exploration reports on the region were those of Stahl (1911); Bohne (1928, 1929); Baier (1940); Kumel (1941); Diehl (1944); Walther and Kursten (1958); Venzlaff *et al.* (1961); Molly (1964) and Iwao and Zahedi (1966). Huckriede *et al.* (1962) worked on the geology of the Kerman–Bafq region and attempted to classify its Fe ores.

The National Iranian Steel Corporation (NISCO) initiated several exploration projects. The results of these investigations were compiled in a series of internal reports (NISCO 1969, 1971, 1974, 1975, 1979a,b, 1980). These investigations were oriented toward documenting exploration of the ore field by geophysical exploration and drilling. During these programs over 80 magnetic anomalies were discovered and many of these

were subsequently drilled. Based on the information acquired from these works the style of mineralisation and the geological setting have been documented by geologists of National Iranian Iron and Steel Corporation (NISCO, 1971, 1974, 1975, 1979a,b, 1980).

Most of the early authors proposed a metamorphic origin for the Bafq Fe-apatite deposits, although some geologists who mainly worked on the NISCO projects proposed a metasomatic origin involving metamorphism, volcanic and intrusive activity.

Williams and Houshmand-zadeh (1966) proposed a magmatic origin for the Choghart deposit and compared it with the Kiruna Fe ore deposits. Investigators supporting an immiscible liquid magmatic model of formation included Förster and Borumandi (1971) and Förster and Jafarzadeh (1984) who reported magnetite lava flows and magnetite-bearing pyroclastic rocks at Chador Malu and suggested a carbonatitic affinity for the Fe-oxide melt (a theme amplified in the account of the Bafq district magnetite–apatite deposits by Förster and Jafarzadeh, 1994). Jafarzadeh (1981) interpreted the Chador Malu deposit as an explosive vent filled with magnetite melt. Samani (1988a) classified mineralisation at the Choghart mine and at anomalies 20 and 26 as being of magnetite-carbonatite type.

Darvishzadeh (1983) and Darvishzadeh *et al.* (1996) investigated the mineralogical and geochemical characteristics of the Esfordi Fe–P deposit and noted the alkaline affinity of the igneous rocks, the presence of apatite-rich veins, the size and shape of the apatite crystals and the carbonate-rich matrix. Based on the mineralogical association of magnetite, apatite and carbonate it was concluded that there was a relationship between carbonatitic magmatism and mineralisation, although no situ carbonatites were found at Esfordi.

Haghipour (1977) wrote a geological and petrological report on the stratigraphic correlation of the Bafq host rocks. He had previously suggested a close relationship between Fe ore deposits and metasomatic metamorphism in some deposits but a

volcanogenic or syngenetic origin in other deposits (Haghipour, 1964). Similarly, Momenzadeh (1978, 1982, 1986) proposed a syngenetic submarine volcanogenic origin for Bafq region deposits based on their massive, lenticular, banded and lens-like morphology, their development within a specific lithostratigraphic unit and relation to nearby stratified Mn and Pb deposits. Daliran (1990, 1999, 2002) also concluded that hydrothermal fluids played a prominent role in the evolution of the Bafq magnetite–apatite deposits.

The significance of some of this work in relation to the Esfordi Fe–P system, particularly that of Daliran (1990, 2002) and Förster and Jafarzadeh (1994) is canvassed in the discussion and conclusion chapter of this thesis.

## **1.8 STUDY AREA ENVIRONMENT**

The Bafq region is part of Central Iran Plateau. It is situated on the western margin of Lut Desert, the southern edge of Grate Kavir Desert and is south of Kavir-e-Namak (the Salt Desert). Bafq is the main city of the region, at the south margin of the region, and is accessible by paved road and railway from Yazd, 120 km away.

The Bafq mining district is the largest Fe ore province of Iran and extends from Bafq to Robt-e-Posht-e-Badam located ( $31^{\circ} 30' - 33^{\circ} 15' \text{ E}$  and  $55^{\circ} 00' - 55^{\circ} 50' \text{ N}$ ). The Esfordi apatite-magnetite deposit is located 31 km northeast of Bafq, between the Choghart Fe and Kushk Pb-Zn mines, and is close to the Bafq-Behabad road. The study area is centred at  $31^{\circ} 47' \text{ E}$  and  $55^{\circ} 32' \text{ N}$  on the district magnetic anomaly map (Fig 1.2).

Geomorphologically the area is dominated by a series of Quaternary desert landforms surrounding outcrops of older sedimentary and igneous rocks. The Bafq depression (Kavir-e-Kur) covers  $>1100 \text{ km}^2$  to the north of Bafq and is one of the more prominent desert morphologies in the region. The Esfordi deposit is bounded by elevated dolomite and limestone in the northeast, the Rud-e-Shur seasonal fluvial channel to the south, and an alluvium-covered plain to the west. The Bafq plain is bordered by NNW-

SSE oriented mountain ranges to the west. Most of the elevated points of the region are Mesozoic outcrops, especially Cretaceous limestone. The highest altitude of the region is Mount Ariz (2280 m), and the lowest point is the Bafq Depression (900 m).

The climate is dry with an average annual precipitation of 40-50 mm. The temperature varies from 48°C in summer to -10°C in winter. Because of high evaporation and infiltration rates, there are no permanent surface water features. Rare floods occur after sporadic winter and spring rains and the water drains towards the Bafq salt pan depression. Drinking water is supplied by aquifers, which are usually of poor quality (high K).

The region has sparse vegetation, dominated by saksaul. Due to the vast extents of salt pans and aeolian sand, the area suffers from major sandstorms, especially in summer. The region is thinly populated and locals are mainly involved with shepherding sheep and goats. Most of the population is concentrated in the small towns of Bafq and Behabad, which provide transport and mining infrastructure.

## **1.9 AIMS AND OBJECTIVES**

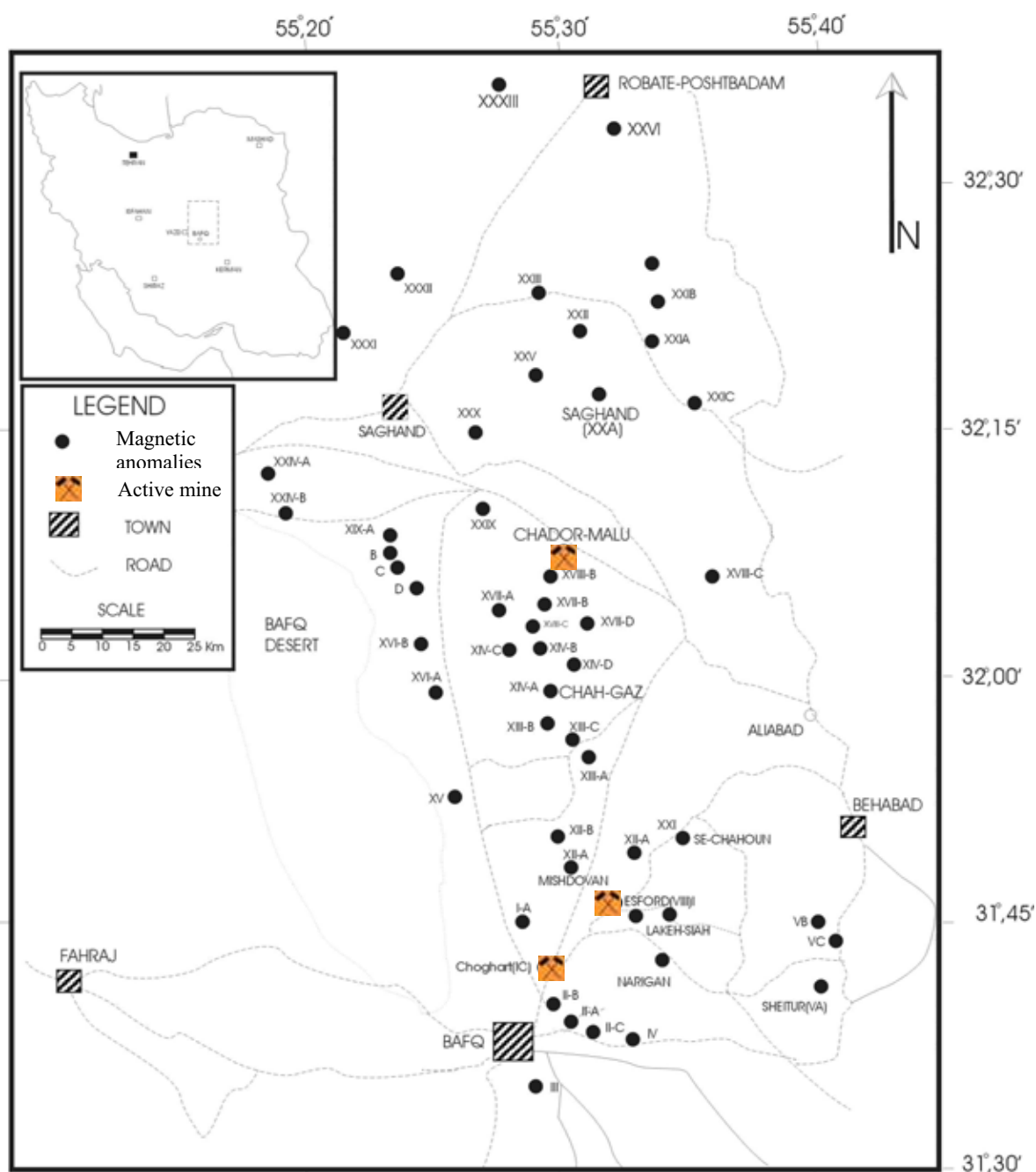
The objectives of this research are to document the geologic, mineralogic, petrographic and geochemical characteristics of both the ore and the host rocks of the Esfordi Fe–P deposit.

To achieve these goals during two field trips a range of geological data have been collected including systematic observation and sampling of Esfordi ore bodies and host rocks, adjacent deposits such as Mishdovan and Choghart; and nearby intrusions. Esfordi geological map and 16 cross sections were prepared based on field observations, mine data, and core logging.

More than 300 samples were selected and transported to UNSW for further studies. 120 thin sections, 70 polished sections and 19 doubly polished sections were prepared to

study the petrography, mineralogy and fluid inclusions. 31 polished thin sections were also prepared for probe analyses. Chemical analyses using XRF and ICP-MS were performed on 60 samples. Several separated mineral and bulk samples were analysed for O, C and S isotopes in CSIRO, Ryde.

**The aim of the study is to constrain potential genetic models for the Esfordi deposit, as part of the magnetite–apatite mineralization system of the Bafq district.**



**Figure 1. 2** Location map of the Bafq–Robat-e-Posht-e-Badam magnetic targets and the Esfordi deposit (after NISCO, 1976).

## **1.10 THESIS STRUCTURE**

This thesis has been structured into eight chapters and four appendices. The general geology, tectonic setting and local geology and lithologic descriptions of the Esfordi deposit are set out in Chapter 2. A more detailed description of the host rocks description, configuration, various host igneous and sedimentary units, based on the current study are presented in Chapter 3. Chapter 4 summarises the ore zone morphology, mineralogy, texture and geochemistry of the various mineralised zones and the characteristics of alteration patterns and their configuration are presented in Chapter 5. Rare earth element mineralogy and geochemistry of the ore and host rocks at Esfordi are provided in Chapter 6 and fluid inclusion and stable isotope studies in Chapter 7. The final chapter of this thesis includes a discussion on the findings of this project and their relevance to an understanding of Fe–P mineralisation in the Bafq district, together with conclusions and suggestions for future research.

## **CHAPTER 2      GEOLOGICAL SETTING**

### **2.1      INTRODUCTION**

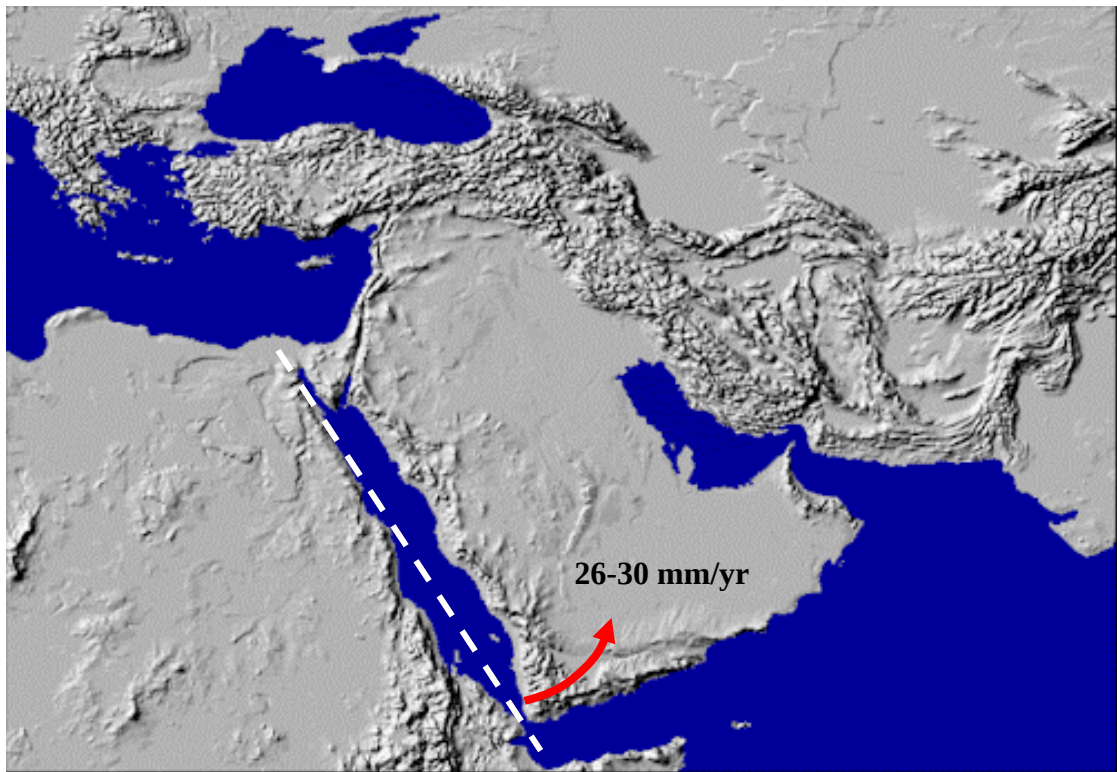
The Iranian Plateau is a tectonically active region within the Alpine-Himalayan orogenic belt. It contains a number of continental fragments that have been welded together along suture zones of oceanic character. The various terranes are bounded by major faults.

Active deformation of Iran is controlled by convergence of the Arabian and Eurasian Plates. The direction of this convergence is about 15° NNE, and stems from the 0.6°/Ma rotation of Africa-Arabia around a pole at 31.63°N and 15.35°E (Jackson *et al.*, 1995) yielding considerable shortening and faulting in the high mountains of the Zagros Fold and Thrust Belt in the south and southeast, the Alborz Range and Kopeh-Dagh Fold Belts in the north and northeast of the region. This yields a linear convergence rate of Arabia-Eurasia of 26–30 mm/year in eastern Iran (Jackson *et al.*, 1995; Walker, 2003). It has been estimated that equal amounts of this compression are consumed in the Zagros Fold and Thrust Belt and in the Alborz Range of Central Iran causing significant right-lateral shearing across eastern Iran (Walker, 2003). There are several indications that the current tectonic configuration dates back to ~5 Ma (Jackson *et al.*, 1995; Walker, 2003; Walker and Jackson, 2004) (Fig 2.1). The complexly deformed terranes of Central Iran and the Lut Block are situated between these two ranges. The surrounding regions to the north and east of the Iranian Plateau are aseismic and appear not to be undergoing deformation.

### **2.2      ZAGROS FOLD BELT AND THRUST ZONE**

The Zagros Fold and Thrust Belt (the “Zagros Belt” or “Zagros Ranges”) is part of the Alpine-Himalayan mountain chain, and extends more than 1,500 km from southeastern

Turkey through northern Syria and Iraq to southwestern Iran (Haynes and McQuillan, 1974; Blanc *et al.*, 2003). The crustal shortening and thickening of the Zagros Belt occurred during the Early to Late Cretaceous.



**Figure 2. 1 Relief map of the Alpine-Himalayan mountain ranges (Basemap from Peakware world mountain encyclopedia).**

The Zagros Belt is bounded to the northeast by the Main Zagros Thrust Fault which is the likely suture zone between the Arabian and Eurasia plates (Dewey *et al.*, 1973; Sengor, 1984). The Zagros Belt is bounded to the east by the Anatolian strike-slip fault and to the west by the Oman Line that is a transform fault inherited from the opening of Neo-Tethys (Fig 2.2) (Falcon, 1969).

The Zagros Belt may be subdivided into three major parallel belts:

- i. *Urumieh Dokhtar Magmatic Arc* – composed mainly of tholeiitic, calc-alkaline and K-rich alkaline intrusive and extrusive rocks and associated volcanics;
- ii. *Zagros Imbricate Zone* and the *metamorphic Sanandaj-Sirjan Zone* – containing slices of metamorphosed and unmetamorphosed Phanerozoic units of the Afro-Arabian passive continental margin and also considerable exposures of ophiolites (Stöcklin, 1968; Stöcklin and Setudehnia, 1977);
- iii. *Zagros Folded Belt* – forming the less severely strained external part of the orogen, and consisting of a succession of folds and thrust sheets (Alavi, 2004). The upper 7-12 km is composed of Neoproterozoic and Phanerozoic sedimentary strata (Alavi, 1991 and 1994).

The Main Zagros Thrust Fault is also the southern margin of the Sanandaj–Sirjan zone which, on the basis of structural history, belongs to the central and northern Iranian tectonic provinces (Stöcklin, 1968). The Sanandaj–Sirjan zone is a region of polyphase deformation and was the last terrane to develop in the Zagros Belt, and its formation was due to the collision between Arabia and Eurasia (Figs. 2.2 and 2.3) (Alavi, 1994). The Urumieh Dokhtar Magmatic Arc, which is interpreted to be an Andean type magmatic arc, is situated at the northeastern edge of this metamorphic belt (Alavi, 1980; Berberian and King, 1981).

The stratigraphic succession within the Zagros Belt ranges in age from late Cambrian to Pliocene (Stöcklin, 1968; Falcon, 1969). The oldest sedimentary unit is believed to be the late Neoproterozoic to early Cambrian Hormoz Formation (Falcon, 1969; Stöcklin, 1977; Kent, 1979). The Hormoz Formation is overlain by 6–10 km of platform deposits (predominantly sandstone, shale and dolomite) in the Cambrian-Triassic sequence and limestone and shale intervals with subordinate evaporites in the Jurassic-Lower Miocene section (Stöcklin, 1968, 1977; Koop and Stonely, 1982).

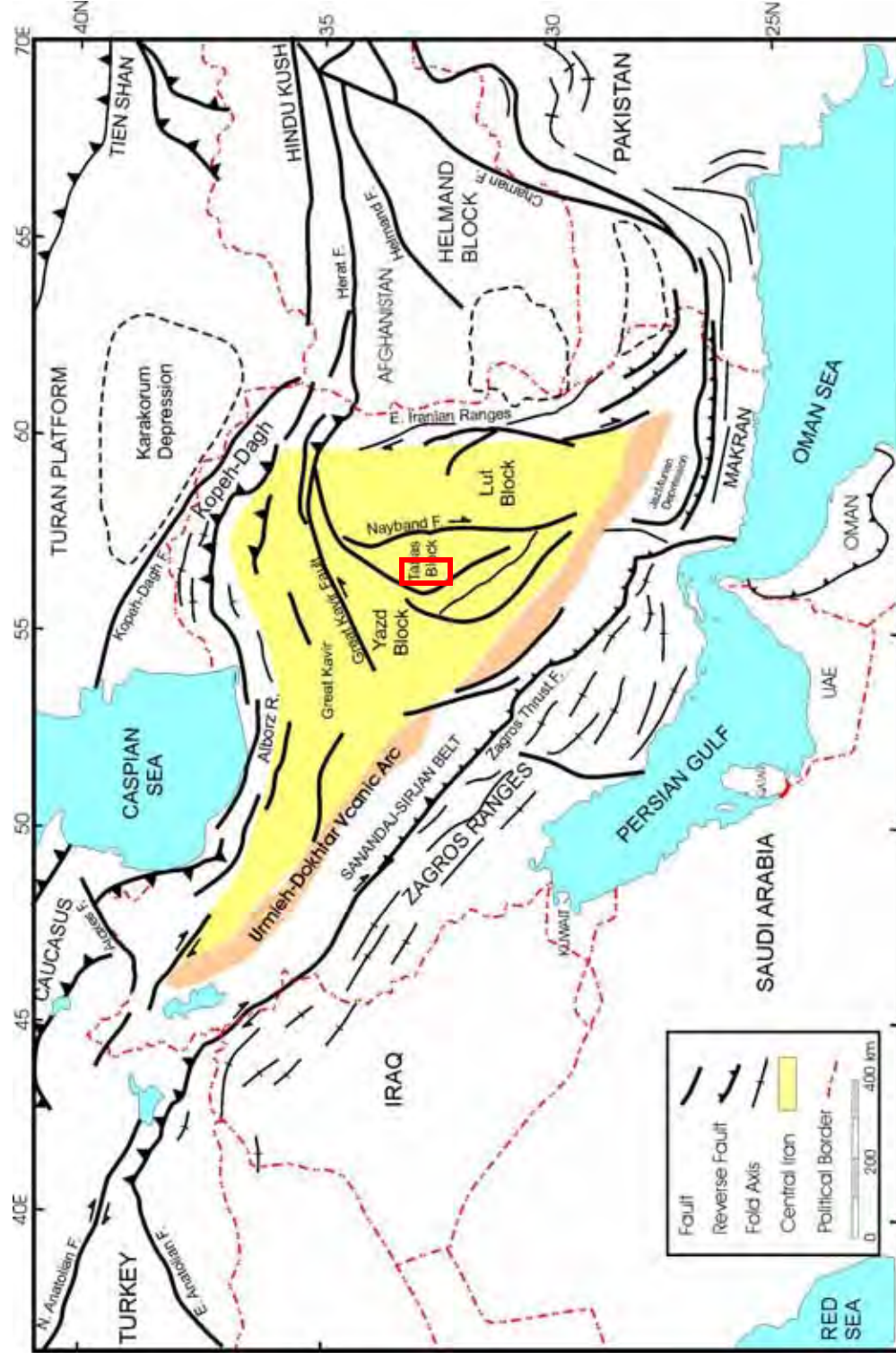


Figure 2. 2 Simplified tectonic map of Iran and adjacent areas. The Central Iran structural zone is divided to different blocks. The Bafq-Posht-e-Badam area is marked by red rectangle (modified after Berberian 1981, Jackson and McKenzie 1984, Haghipour and Aghanabati 1989, Alavi 1991).

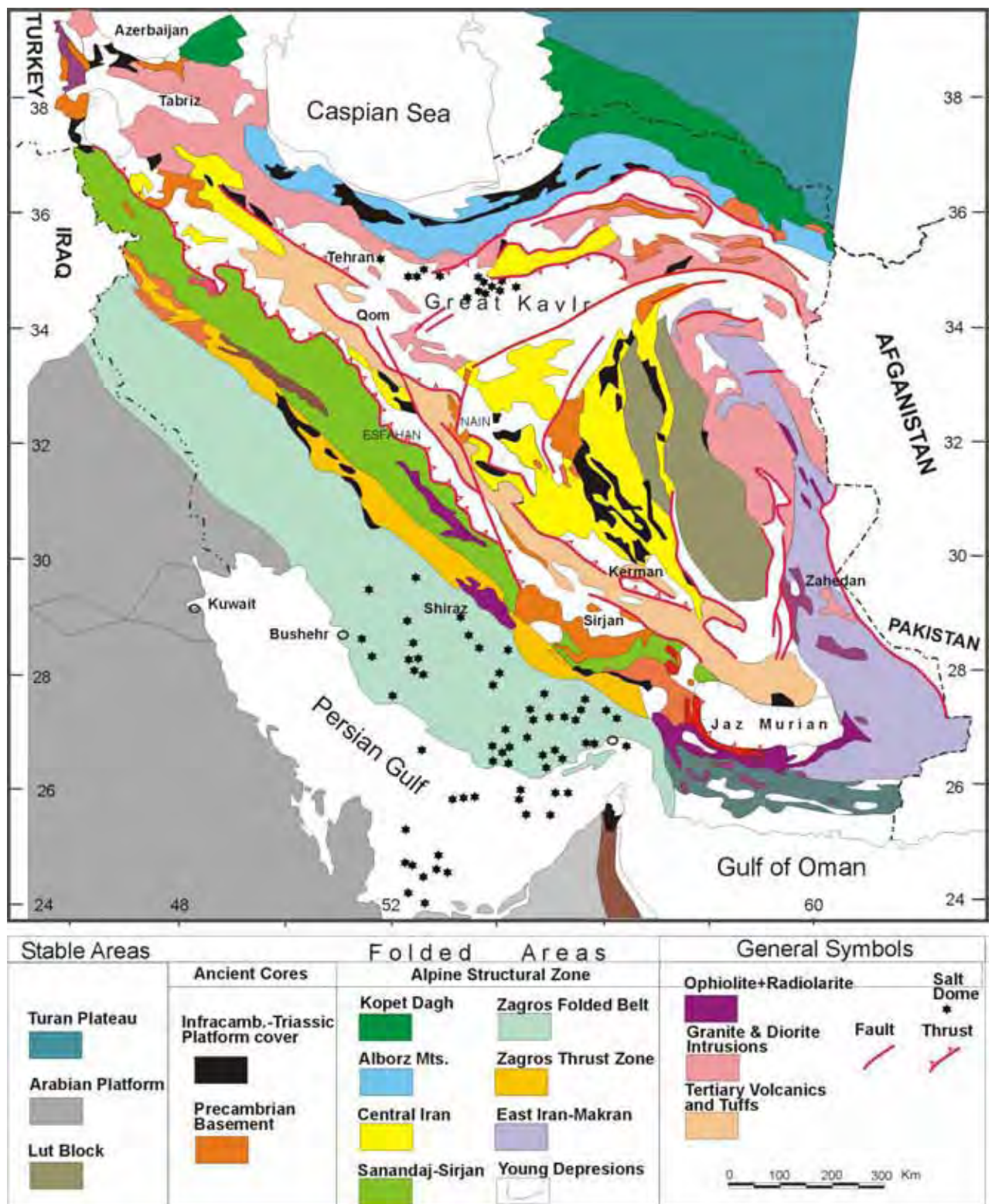


Figure 2.3 Tectonic map of Iran with major structural units (after Stöcklin, 1968).

### **2.3 ALBORZ RANGE AND KOPEH-DAGH FOLD BELT**

The Alborz Range is a narrow mountain belt, 100 km wide, which extends along the Caspian Sea to the northeast of Iran (the Kopeh-Dagh Ranges) and to the northwest into Turkey. The northern flank of the range is steep whereas topographic contrast on the southern flank is less pronounced and progressively connects to Central Iran lowlands. The Alborz Range is an active fold belt, separated from the Caspian Depression in the north by the currently active Talesh and Caspian Faults. It displays a close stratigraphic and structural correlation with Central Iran to the south. The plate boundary between Eurasia (Scytho-Turanian plates) and the remnants of Gondwana (Iranian plate) is a suture line running from the Caucasus to Kopeh-Dagh along the south Caspian boarder (Davoudzadeh and Schmidt, 1983). There is a significant Palaeozoic-Triassic facies changes on both sides of the suture and Palaeozoic ophiolite outcrops along this lineament (Davoudzadeh *et al.*, 1986). Lensch and Davoudzadeh (1982) reported several uplifts of Hercynian and Caledonian basement associated with basic and ultrabasic rocks, which were interpreted by Stöcklin (1977) to be ophiolites derived from Tethys oceanic crust that separated the Gondwanan and Eurasian landmasses until the late Triassic.

The tectonic history of the Alborz Range is divided into two compressional events: a Miocene N-S compression between the Central Iranian Block and south Caspian Basin; and a Pliocene-Quaternary NE shortening oblique to the EW structural trends of the Central Alborz Range (Jackson and McKenzie, 1984; Allen *et al.*, 2003). Precambrian metamorphic rocks are exposed in the northern foot and interior part of the ranges.

The Kopeh-Dagh Range is located in the NE corner of Iran, along the border with Turkmenistan, and is dominated by NW-SE trending folds. It displays a similar trend to the Zagros Belt and is perpendicular to Arabia-Eurasia subduction front. The Kopeh-Dagh Range contains a Jurassic to Oligocene marine succession that is >6,000 m thick (Stöcklin, 1968). A major thrust fault - the Main Kopeh-Dagh Fault - separates the mountain range

from the tectonically stable Turan Platform to the north. Several other thrust faults separate the Kopeh-Dagh from the Alborz Range to the south (Figs 2.2 and 2.3) (Berberian, 1981).

## **2.4 MAKRAN RANGES**

The Makran Ranges are a region of east-west trending folds and shallow thrust faults extending from the Oman Line (the south east border of the Zagros Belt) to the N-S trending Ornach-Nal and Chaman strike-slip faults in SW Pakistan. Behind the Makran Accretionary Prism, ophiolites and microcontinental blocks of Lower Palaeozoic or older metamorphic basement are exposed (McCall, 1995, 2002). Unlike the rest of the Iranian platform, The Makran region was not subject to crustal shortening by the Arabian-Eurasia convergence (Byrne *et al.*, 1992).

A 350 km wide, 8,000 m thick, Cenozoic accretionary prism fronts the Makran Ranges, with active subduction in the Oman Sea 150 km to the south (McCall, 2002). This thick accretionary wedge formed at the active margin of the Oman Sea oceanic crust (a remnant of Tethys oceanic crust) at low angle under Eurasia has occurred since the Cretaceous (Hosseini-Barzi and Talbot, 2003; Vernant *et al.* 2004). The active Bazman and Taftan volcanoes are part of the related volcanic arc.

## **2.5 CENTRAL IRAN**

The Central Iran terrane is a triangular shaped complex of moderate relief within the Alpine-Himalayan Orogenic Belt. It is generally an arid region consisting of narrow mountain ranges and sparse outcrops separated by alluvium-filled depressions.

Based on seismological observations, Jackson and McKenzie (1984, 1988) consider the interior parts of Central Iran (including the Lut Block) to be a rigid body without broad-scale thrust faulting. GPS-based studies indicate that the rate of internal deformation of Central Iran is <2 mm/year which, along with the absence of recently developed tectonic landforms, suggests the rigid behaviour of this block (Vernant *et al.*, 2004;

Walker and Jackson, 2004). Central Iran remains a well preserved area of pre-collisional tectonic evolution of Alpine-Himalayan system, compared with the adjacent Alborz Range and Zagros Belt.

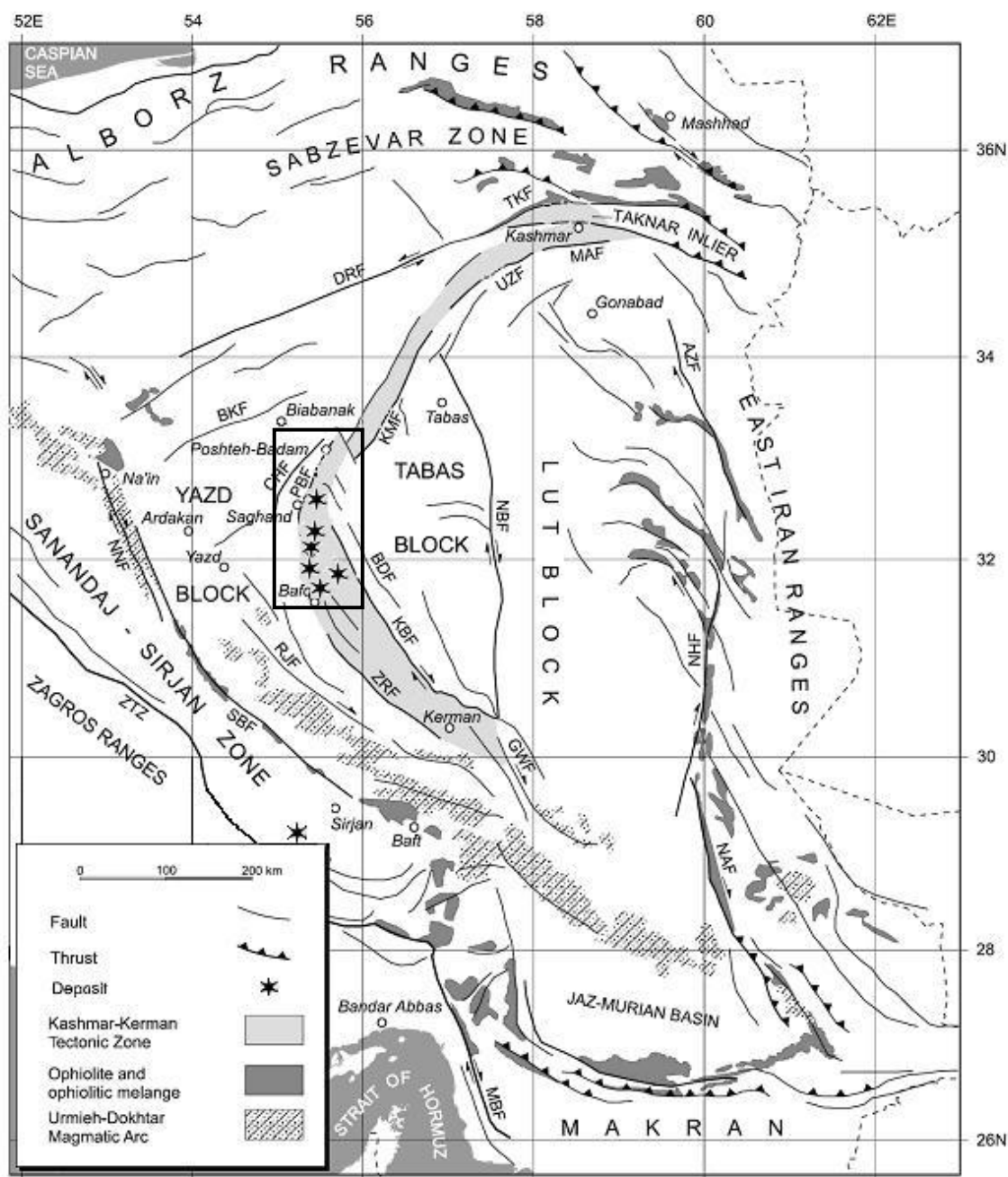
The Central Iran terrane is bounded by the Alborz Range to the north, the East Iranian Ranges to the east, and the Zagros Belt (including the subordinate Sanandaj-Sirjan Belt) and Makran Ranges in the southwest and south (Stöcklin 1968). Along the Zagros Belt border, a series of depressions that include Lake Urmieh, the Tuzlu Gol and Gavkhuni Depressions and the Urumieh Dokhtar Magmatic Arc, which is a distinct morpho-tectonic feature produced by the ongoing convergence between the Arabian (Gondwanan) and Turan (Eurasian) plates. An active subduction along the southern margin of Central Iran is also responsible for the Jazmurian Depression, Makran Accretionary Wedge and the active volcanoes Taftan and Bazman. Based on the deduced Gondwanan provenance of the various Asiatic terranes, it has been proposed that the underlying basement to Central Iran is probably similar to those in the Arabian Shield (Stöcklin, 1974; Berberian and King, 1981).

In contrast to interior rigid body (Jackson and McKenzie, 1984, 1988), Ramezani (1997) described the Central Iran terrane as being situated between two syntaxes of the Alpine-Himalayan Belt including the Arabia-Eurasia collision line in the Lake Van area in Turkey and the India-Eurasia collision line in northeast Afghanistan. These syntaxes are regions, with extensive crustal shortening and a complex system of conjugate thrust and strike-slip faults due to the Cenozoic collision of Eurasia with the Arabian and Indian plates (Ramezani, 1997). The compression produced by this collision caused progressive continental deformation in Central Iran. The influence of dominant structural trends of the surrounding zones (W-E trend of Alborz Range, N-S trend of Lut Block, NW-SE trend of the Sanandaj-Sirjan Metamorphic Belt) produced a very complex, mosaic-like structural pattern in Central Iran (Stöcklin, 1968).

Several major faults divide the eastern half of Central Iran into structural zones and blocks including (from east to west): the Lut and Tabas Blocks, the Kashmar-Kerman Structural Zone, and the Yazd Block (Fig 2.4) (Stöcklin, 1968; Berberian and King, 1981; Alavi, 1991). The Sabzevar zone and Great Kavir (Doruneh) Fault separate Central Iran from the Alborz and Kopeh-Dagh ranges to the north.

The Lut Block is an 800 km by 200-250 km, N-S trending, rigid mass in the eastern part of the Central Iran. It is bounded by the Great Kavir Fault to the north, the Nayband Fault to the west and the East Iran Ranges and Nehbandan Fault to the east (Stöcklin, 1968; Alavi, 1991). The north-south trend of the surrounding ranges is probably due to the rigid behaviour of this block (Stöcklin, 1968) which is generally weakly deformed in comparison with other parts of the Iranian Platform. The Lut Block is mainly covered by a veneer of Tertiary dacite, andesite and associated tuffs and Neogene-Quaternary deposits. Scattered pre-Tertiary outcrops are generally associated with fault structures. The Nayband Fault and the associated Shotori Range separate the Lut Block and the Tabas Block; the latter characterised by gentle fold structures and deposition of ~6,000 m of undisturbed sequences of Upper Triassic to Cretaceous limestone, dolomite and shale.

The East Iranian Ranges are truncated and rimmed by several NS to NNE-SSE trending active faults. These faults are generally tilted toward the NW-SE trend in the northern part of the ranges and generally terminate in thrust faults in the north and merge with Makran Thrust Fault in the south (Walker and Jackson, 2004). The rocks within this mountain range form the Sistan Suture Zone including two accretionary prisms (the Neh and Ratuk Complexes), emplaced during the closure of a narrow arm of the Neo-Tethys basin, that separated the Lut and Afghan Blocks during the Cretaceous-Paleocene (Tirrul *et al.*, 1983).



**Figure 2. 4 Tectonic map of Central–East Iran and major Fe oxide deposits (Revised after Ramazani and Tucker, 2003) The Bafq–Posht-e-Badam area is marked by a rectangle.**

(AZF: AbizFault, BDF: Behabad Fault, BKF: Biabanak Fault, CHF: Chapedony Fault, DRF:Dorouneh Fault, GWF: Gowk Fault, KBF: Kuh-Banan Fault, KMF: Kalmard Fault, MAF: Mehdiabad Fault, MBF: Minab Fault, NAF: Nosratabad Fault, NHF: Nehbandan Fault, NNF: Nain Fault, RJF: Rafsanjan Fault, RVF: Rivash Fault, SBF: Shahre Babak Fault, SJMF: South Jazmurian Fault, UZF:Uzbak-kuh Fault, ZRF: Zarand Fault, ZTZ: Zagross Thrust Zone)

The Yazd Block is bounded by the Chapedony Fault and Kashmar-Kerman Structural Zone (KKSZ), and the Great Kavir (Doruneh), Na'in and Shahre-Babak Faults. The Paleocene Urumieh Dokhtar Magmatic Arc is also situated on the southwest part of this

block with similar a orientation to the KKSZ. The northern part of the Yazd Block shows NW trending faults whereas the southern part is dominated by NE trending faults (Alavi, 1991; Ramezani, 1997). The stratigraphy of the Yazd Block is generally similar to the other parts of Central Iran, and contains sequences of Neoproterozoic–Middle Triassic sedimentary rocks covered by extensive coal-bearing Upper Triassic–Mid Jurassic sandstone, siltstone and shale. The Upper Jurassic movements are associated with emplacement of the Shir-Kuh Granite and associated sedimentary hiatus. Cretaceous conglomerates, shales and limestones unconformably overly the older sequences. Tertiary volcanics and conglomerates have limited exposures in the Yazd Block.

## **2.6 GEOLOGY AND TECTONIC SETTING OF THE BAFQ DISTRICT**

Proterozoic rocks generally crop out in horst-like uplifts in many parts of the Central Iran terrane. Ramezani and Tucker (2003) consider these to be the basement to a Gondwanan fragment situated between the Indian and Arabian plates during the early Cambrian. The tectonic affinity of the metamorphic and associated rocks has long been controversial, due to the sparsity of reliable age dates. The deformation events have been attributed largely to the Pan African Orogeny (also known as the Assyntian, Katangan or Baikalian orogenies) (Huckriede *et al.*, 1962; Stöcklin 1968, 1974; Stöcklin and Nabavi 1973; Berberian and King, 1981). This orogenic phase is considered by Brown and Coleman (1972), Al-Shanti and Mitchell (1976), Greenwood *et al.* (1975, 1976), Neary *et al.* (1976) and Frisch and Al-Shanti (1977) to be an episode of plate collisions and arc magmatism terminating about 600-550 Ma in Arabia.

The post-Assyntian magmatism generated the extensive Doran Granite in NW Iran, which intrudes Upper Precambrian rocks. The Doran Granite is overlain by Lower Cambrian sediments and is considered to be equivalent to the Chador Malu, Zarigan and Narigan Granites of the Saghand-Bafq district, which intruded into the lower parts of

Neoproterozoic beds and are thought to be the plutonic equivalents of the adjacent interbedded acid extrusive rocks (Stöcklin *et al.*, 1977).

Similarities in the characteristics of Late Neoproterozoic sequences and the lithological uniformity of lower Palaeozoic sedimentary facies in Iran (such as the Tashk Formation), Oman (Hugf Group) and the Himalayas (Purana Sequence), suggest the conjunction and geological continuity of Arabia, Iran and India during these periods. This continuity is best demonstrated by the distribution of early Cambrian evaporite-carbonate units found in Central Iran (Rizu-Desu Series and equivalent Cambrian Volcano Sedimentary Unit), the Zagros Belt (Hormoz Formation), Oman (Ara Formation) and the Salt Ranges of Pakistan (Punjab Series) (Husseini, 1989; Talbot and Alavi, 1996).

Samani (1988a,b) suggested that the uppermost Proterozoic-Vendian (Infracambrian) consists of three facies including Bayondor, Soltanieh, Barut and Zagun Formations in Central Iran and the Alborz Range. These formations are mainly consist of cherty dolomites, shales and sandstones respectively (Stöcklin *et al.*, 1965; Assereto, 1963 and Samani, 1988a). The equivalent formation in the Zagros Belt is the Hormoz Formation, and it contains halite, gypsum, various volcanic units and exotic blocks of various sizes. The equivalent formation in Central Iran consist of sedimentary material such as black laminated limestone, dolomite, sandstone, shale, basalt, rhyolite, and trachyte (Stöcklin *et al.*, 1977), and a volcano-sedimentary complex, which covering the area between Robat-e-Posht-e-Badam and Zarand (Fig 2.5).

Palaeomagnetic evidence, regional stratigraphic constraints and a gap between the Salt Ranges of Pakistan and eastern Arabia (Oman) suggest that Central Iran was most likely situated between India and Arabia along the Proto-Tethyan margin of Gondwana during the Early Cambrian (Fig 2.6) (Becker *et al.*, 1973; Sofel and Förster, 1984; McKerrow *et al.*, 1992; Unrug, 1997; Ramezani and Tucker, 2003).

Following Stöcklin (1968) and Stöcklin and Setudehnia (1977), both Berberian and King (1981) and Hussein (1989) interpreted the evaporitic deposits of the Hormoz Formation, the Ara Formation, the Rizu-Desu Series in Central Iran and the Salt Ranges as rift basin deposits spatially associated with post-orogenic, extensional alkaline granites and volcanics.

Late Neoproterozoic-Cambrian magmatism in the Himalayas (Mandi Granite) and Zagros Belt (the igneous enclaves in the Hormoz Formation equivalent to the CVSU in Central Iran) have been correlated and indicate an active continental margin environment along the northern edge of the proto-Tethys (Jaeger *et al.*, 1971; Mehta, 1977; Jackson and McKenzie, 1984; Ramezani, 1997; Ramezani and Tucker, 2003). Extensive geochronologic dating on Bafq-Saghand intrusions, volcanics and basement rocks yield a Neoproterozoic age for units such as the Boneh-Shurow Complex (542 Ma) and Tashk Formation (627-533 Ma) (Ramezani, 1997). The regional deformation of the Boneh-Shurow Complex in the Kashmar-Kerman Structural Zone, the geochemical character of non-alkaline Cambrian granites and associated volcanics and late stage trondhjemite intrusions of the Saghand area, suggest Early Cambrian subduction of oceanic crust in a continental margin regime. Coeval evaporite deposition in contiguous Arabia-Iran-India is consistent with an extensional, back-arc basin (such as the Najd System, Arabia) running parallel to the proto-Tethyan continental margin (Ramezani and Tucker, 2003).

Geological units in the Esfordi area of the Bafq-Biabanak district can be temporally divided into Neoproterozoic, Cambrian, and younger sequences. The Bafq-Biabanak district contains exposures of metamorphic crystalline basement such as the Boneh-Shurow Complex as well as overlying Neoproterozoic–Lower Palaeozoic sequences. This district is located between major fault structures - the Chapedony, Posht-e-Badam, Kalmard and Kuhbanan Faults - and has been interpreted as a series of horst and grabens

(Figs. 2.7 and 2.8) (Haghipour 1977, 1978; Huckriede *et al.*, 1962). The lithostratigraphic subdivisions in the region and their nomenclature have been summarised by Valeh and

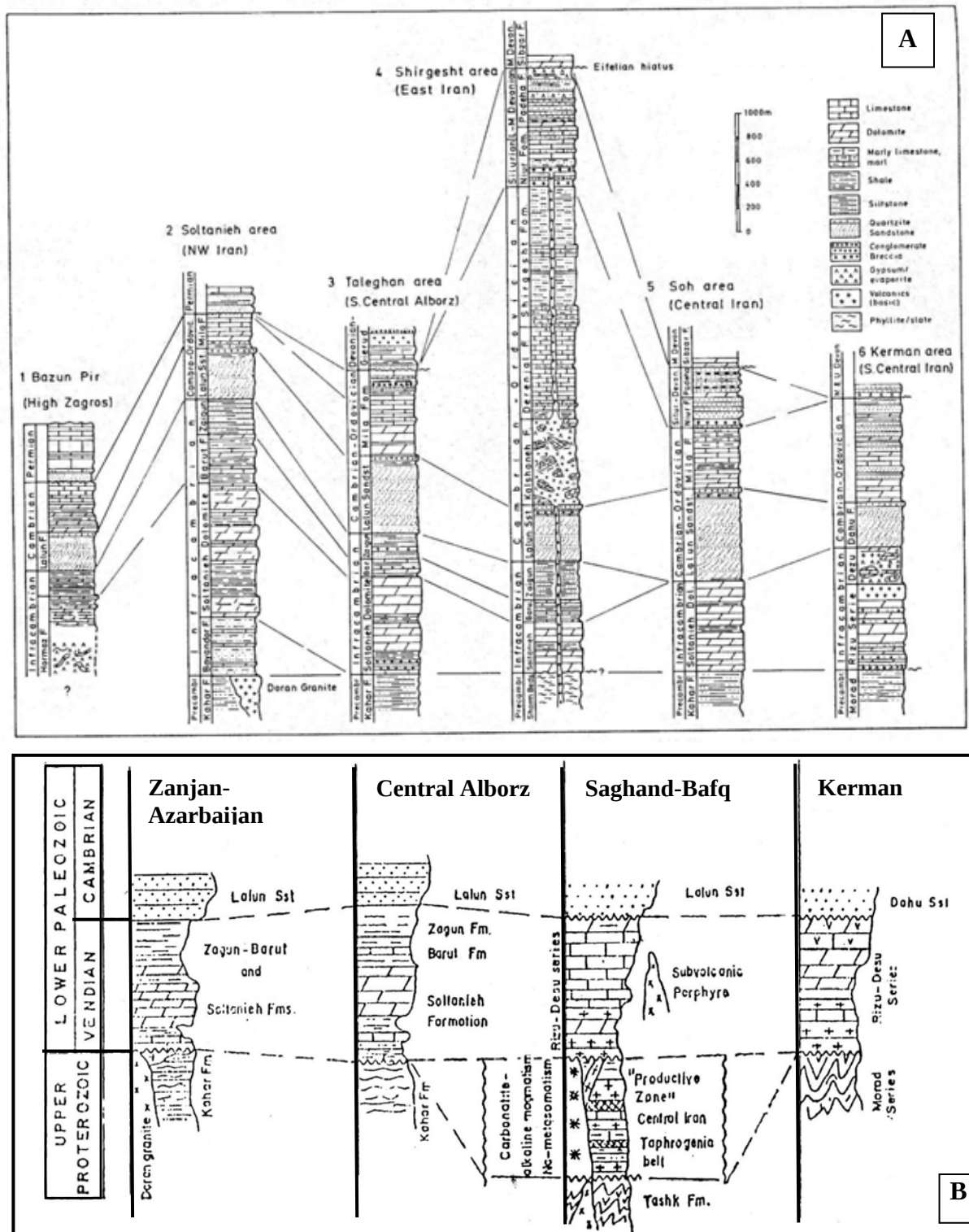
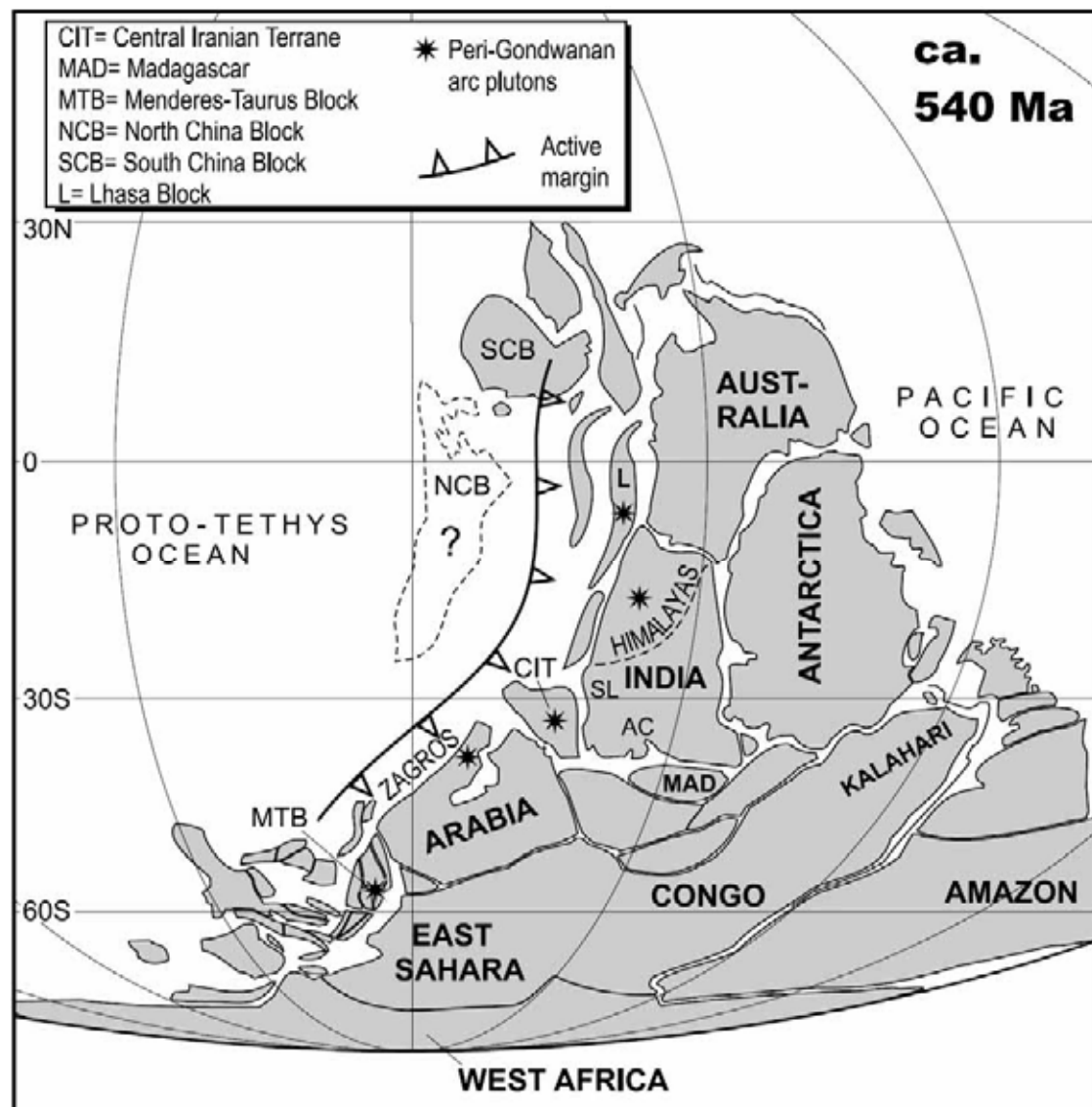


Figure 2. 5 Stratigraphic correlation of Neoproterozoic-Palaeozoic sequences within different part of Iran (A: Stöcklin and Setudehnia, 1977; B: Samani, 1988a).

Haghipour (1970), Haghipour (1977), Haghipour and Pelissier (1977a,b) and more recently by Samani (1993).



**Figure 2. 6 A reconstruction of Gondwana in the Early Cambrian. Precambrian cratons in bold letters, Aravalli Craton (AC) and Salt Range (SL). (After Ramezani and Tucker, 2003).**

Proterozoic rocks of Central Iran are largely restricted to the Kashmar-Kerman Structural Zone (Fig 2.4). Until recent provision of more reliable age dating, rocks exposed in many ancient horst-like uplifts in Central Iran were assigned a late Neoproterozoic age, with correlation between blocks mainly based on lithological

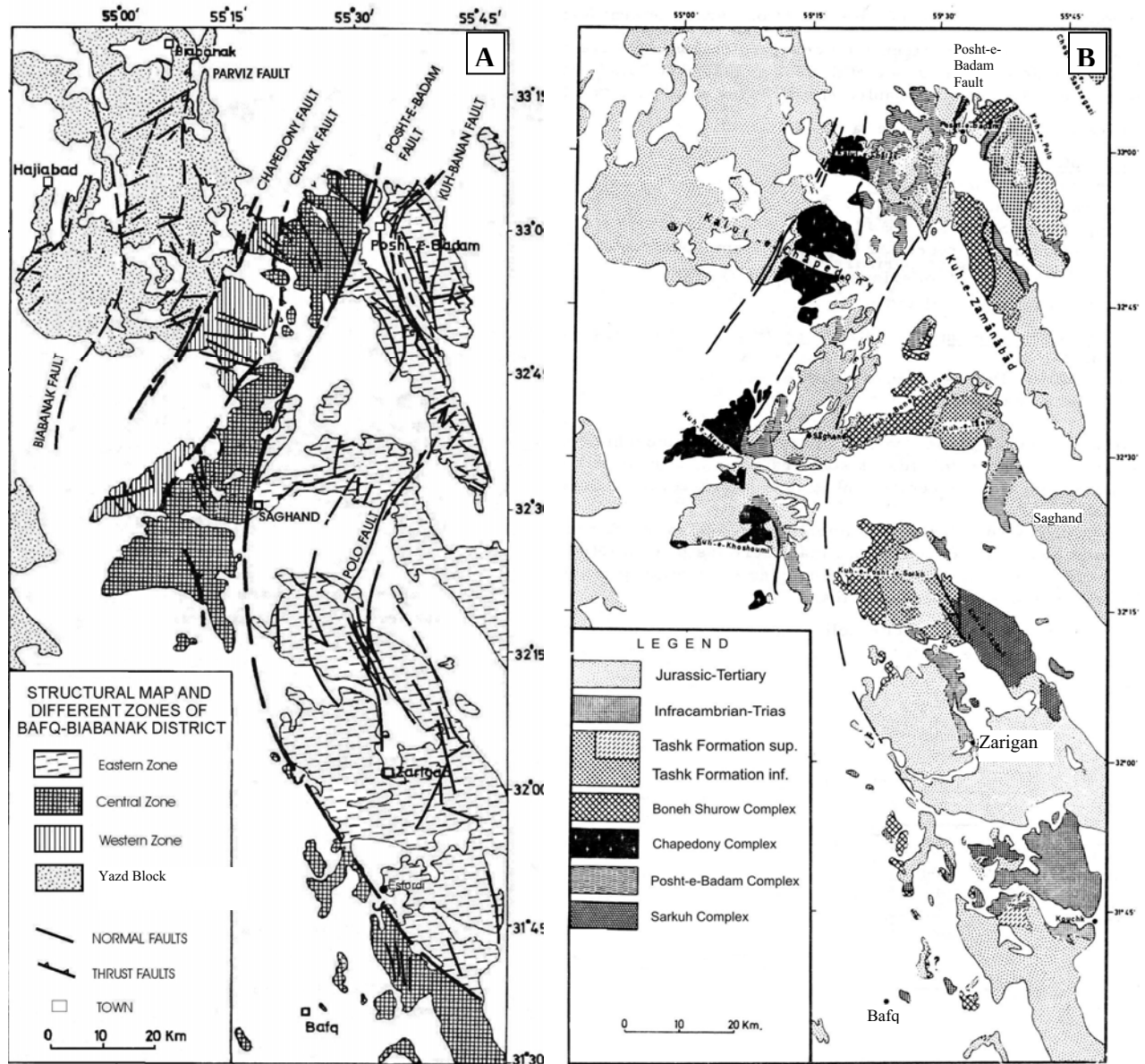
associations and metamorphic grade. Extensive faulting however, makes regional correlation of lithostratigraphic units difficult (Ramazani, 1997).

The Kashmar-Kerman Structural Zone (or Bafq-Kerman Horst) is a relatively narrow, arcuate zone dominated by fault structures (Huckriede *et al.*, 1962). This zone is defined by the Posht-e-Badam, Kalmard, Uzbek-Kuh and Kashmar faults in the north and the Kuhbanan and Zarand Faults in the south (Figs. 2.7 and 2.8). Rocks of Neoproterozoic to Quaternary age are exposed within this zone. The horst-like structure of this zone has exposed the most extensive outcrops of crystalline basement in Central Iran together with overlying Neoproterozoic to Carboniferous sequences (Stöcklin and Setudehnia, 1977). The Bafq area (and Esfordi mineralising system) is situated in this structural zone. The large adjacent troughs are filled with thick Jurassic and Cretaceous sedimentary sequences (Fig 2.7 and 2.8) (Huckriede *et al.*, 1962; Stöcklin, 1968; Haghipour, 1977).

Neoproterozoic exposures in the Bafq-Biabanak district can be subdivided into three lithotectonic domains, separated by the Posht-e-Badam Fault, Chatak Fault and Chapedony Faults (Figs. 2.7 and 2.9) (Haghipour, 1978; Ramezani, 1997). The eastern Neoproterozoic lithostratigraphic domain contains the Sarkuh and Boneh-Shurow Complexes, the Tashk Formation, various Cambrian volcano-sedimentary units and a number of felsic to mafic intrusive rocks. This domain is generally considered to be part of the Tabas Block (Haghipour, 1977; Ramezani and Tucker, 2003).

Metamorphic rocks in the southern parts of the Bafq-Biabanak district, including the basement exposures nearest to Esfordi, are generally correlated with metamorphic complexes east of the Posht-e-Badam Fault and, hence, the Boneh-Shurow Complex (Figs. 2.7 and 2.8). The western domain rocks are dominated by the amphibolite-grade metamorphic Chapedony Complex and are intruded by Mid-Eocene granites and diorites. The central domain is a narrow zone of extensive faulting restricted between Posht-e-Badam Fault and Chatak Fault (Fig 2.7) and mainly contains metamorphic rocks of the

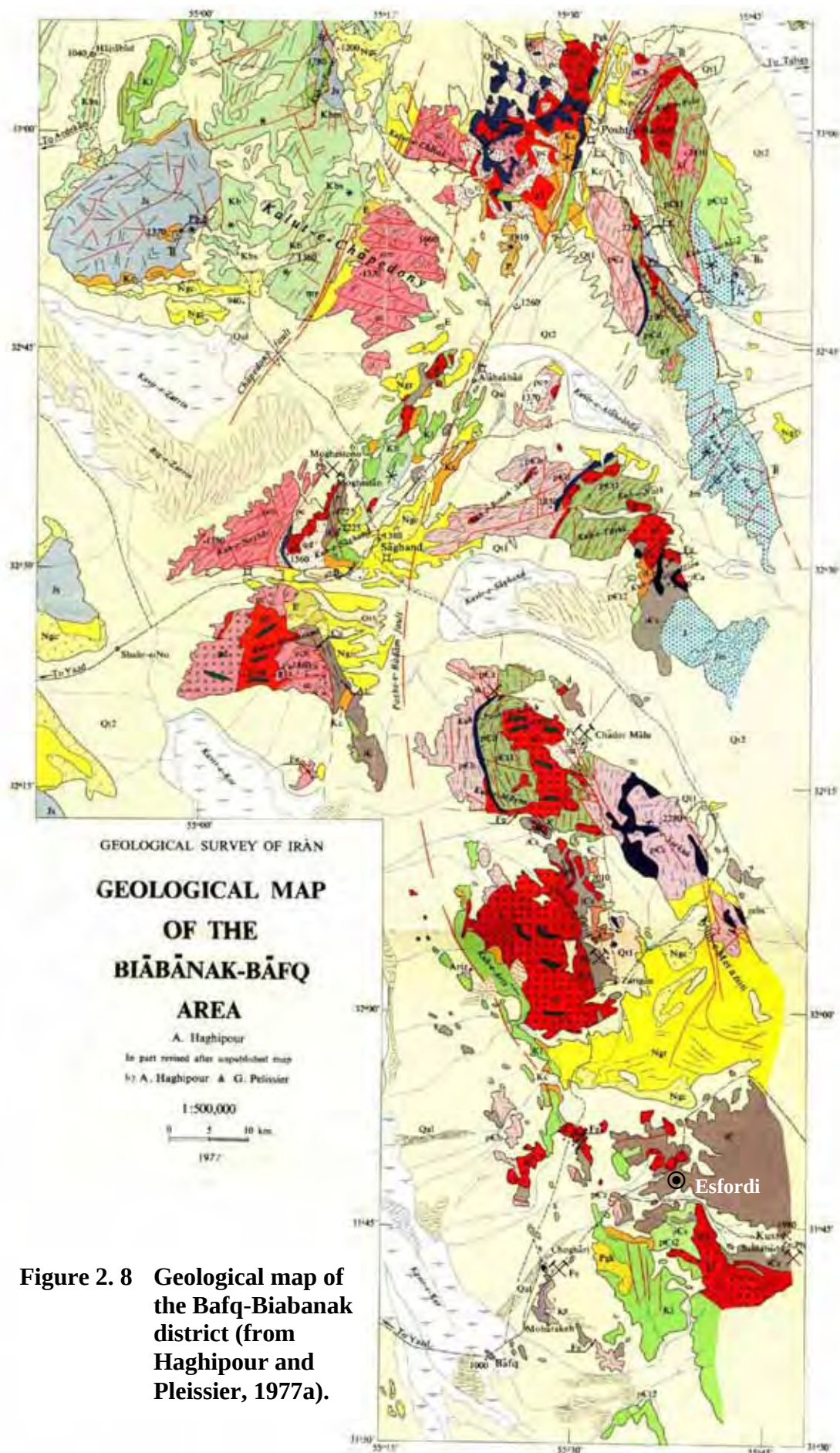
Posht-e-Badam Complex together with several granitic to tonalitic intrusions and allochthonous blocks of Cambrian Volcano-Sedimentary Unit (Ramezani and Tucker, 2003).



**Figure 2.7 Geology of the Bafq-Biabanak district.**

**A: Structural map, including major faults (revised after Haghypour, 1978).**

**B: Distribution of different rock units (from Haghypour 1978).**



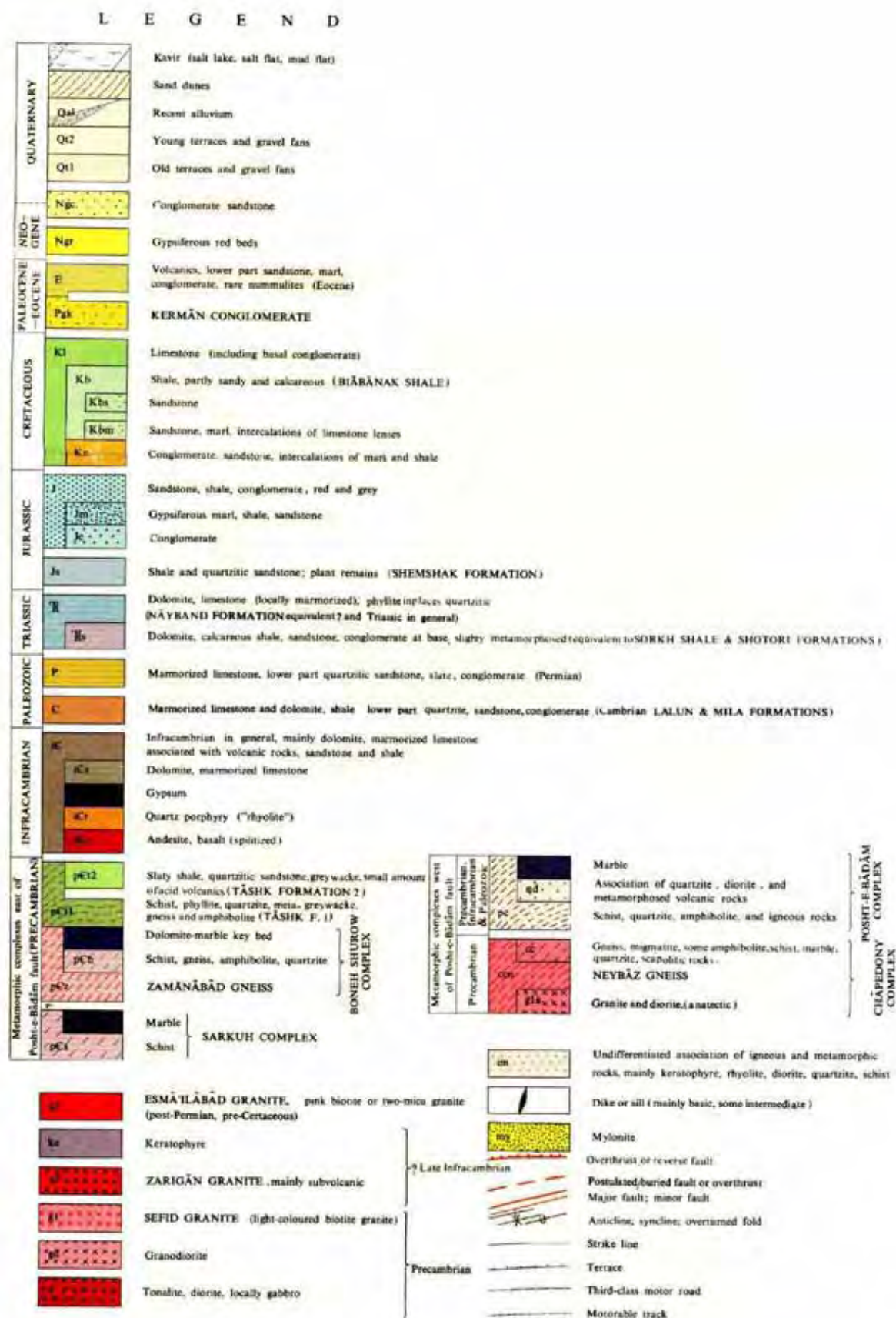


Figure 2.8 Continued.

### WESTERN LITHOSTRATIGRAPHIC DOMAIN

Neogene and Quaternary

Khoshoumi Granite

Coarse-grained two-feldspar granite

Daranjir Diorite

Medium- to coarse-grained hornblende-diorite  
Abundant medium to felsic dikes.

Chapedony Complex

Migmatite and anatexite  
Granitic gneiss, amphibole-gneiss  
Grey porphyroblastic biotite-gneiss

MIDDLE EOCENE

### CENTRAL LITHOSTRATIGRAPHIC DOMAIN

Neogene and Quaternary

Cambrian Volcano-Sedimentary Unit

Tertiary

Reddish volcanic rocks, mainly andesite  
Sandstone, gypsiferous marls with nummulite  
fossils (Eocene), Kerman Conglomerate

Cretaceous (Undifferentiated)  
Massive Orbitolina limestone.  
Conglomerate and sandstone

Olive-green shale and sandstone (Biabanak Shale)

Permian

Fusulin limestone, weakly metamorphosed.

LATE TRIASSIC

Granite-Tonalite

Composit granite to tonalite intrusions.  
(Chamgou and Anarg Granodiorite)

Esmailabad Granite

Coares- grained two-feldspar granite

Marble

Massive crest-forming marble (limestone)

Posht-e-Badam Complex

Greenstone, phyllite, mica-schists.  
Granitic gneiss, amphibolite, locally ultrabasics.  
Dolomitic marble interlayers.

NEYBAZ-CHATAK FAULT

POSHT-E-BADAM FAULT

### EASTERN LITHOSTRATIGRAPHIC DOMAIN

Neogene and Quaternary

Unconsolidated alluvial gravel deposits, sand dunes,  
Kavir (playa-type deposits) (Quaternary)  
Gypsiferous shale and sandstone (Neogene Red Beds).

Triassic

Quartzite and sandy shale.

Weakly metamorphosed dolomite and limestone.

Red shale, sandstone and conglomerate (Sorkh Shale Fm.)

Cambrian

Red sandstone, siltstone and conglomerate  
(Lalun Formation).

Sarkuh Complex

Porphyroblastic mica-schists  
(garnet-andalusite and sillimanite schist)  
Marble interlayers

Cambrian Volcano-Sedimentary Unit

Rhyodacite to andesite flow and tuffs.  
Locally basalt. Dolomitic limestone with  
gypsiferous horizons.

Leucogranite

Shallow-intrusive leucogranites (mainly trondhjemite)  
Abundant mafic dikes (Zargan Leucogranite,  
Douzakh-Dareh Leucogranite and Sefid Granite)

Granite-Tonalite

Composit granite to tonalite intrusions, locally diorite  
(Anz Granodiorite and Polo Mountain Granodiorite).

Tashk Formation

Greywack, arkosic sandstone, shale, volcanoclastic tuff  
with basalt interlayers, weakly metamorphosed

Boneh-Shurow Complex

Mica schists, granitic gneiss, amphibolite.  
Dolomitic marble interlayers.

EARLY CAMBRIAN

NEOPROTEROZOIC

Figure 2. 9 Distribution of lithostratigraphic units in the Bafq-Biabanak district (after Ramezani, 1997).

### **2.6.1 The Boneh-Shurow Complex**

The main exposure of this complex is near Kuh-e-Boneh-Shurow ~10 km northeast of Saghand (Haghipour and Pleissier, 1977a). The other significant exposures in the region are at Kuh-e-Zamanabad, south of Posht-e-Badam, Kuh-e-Nayon and Posht-e-Sorkh, southwest and west of the Chador Malu mine and Kuh-e-Ariz (Fig 2.8). The main lithological groups are quartzo-feldspathic gneisses, mica-schists, amphibolite and dolomitic marble. The Boneh-Shurow Complex is at least 2000 m thick and conformably overlain by the Neoproterozoic Tashk Formation (Haghipour, 1978), however, Ramezani and Tucker (2003) suggest this contact is a structural one. Around the Mishdowan Fe deposit, 15 km northwest of Esfordi, a package of equivalent metamorphic rocks was given the name Mishdowan Complex by Soheili and Mahdavi (1991). A similar range of lithological variants is also reported by Daliran (1990) from that location. In the southern part of the Bafq-Biabanak district, the Zamanabad Gneiss is exposed 22 km NW and 8 km SE of Esfordi (Figs 2.7 and 2.8) and it is inferred to be the local metamorphic basement at Esfordi.

The Zamanabad Gneiss forms the lower part of the Boneh-Shurow Complex and is mainly composed of quartz, K-feldspar and plagioclase with lesser amounts of biotite, epidote, garnet and accessory allanite, apatite, zircon and sericite. This gneiss is generally fine-grained and shows various augen fabrics with local development of anatexite and pegmatite (Daliran 1990). Haghipour (1978) considered that most of the felsic bodies intruding into the overlying Tashk Formation are the result of migmatitization of these gneisses, whereas Ramezani and Tucker (2003) suggest they are metamorphosed felsic sills.

Mica schists within the Boneh-Shurow complex contain dolomitic marble and quartzite lenses. The more biotite-rich schists contain minor feldspar and tourmaline. They mainly occur in the upper part of the complex under dolomitic marble lenses, where they have locally retrogressed to chlorite-rich assemblage. Garnet, staurolite, andalusite and sillimanite bearing assemblages are reported in places (Haghipour, 1978). Iron oxides, zircon, apatite,

sericite and epidote are the common accessory minerals. Texturally these schists contain a range of overprinted granoblastic, poikiloblastic and lepidoblastic fabrics. A dominantly semi-pelitic protolith with probably polymetamorphic character is proposed by Williams *et al.* (1985).

Dark-coloured, garnet-bearing, granoblastic amphibolite horizons, of cm to m-thickness, are a visually distinctive part of the Boneh-Shurow Complex. Haghipour (1978) recognised various hornblende, plagioclase, garnet, biotite and scapolite bearing amphibolites with quartz, apatite, calcite, zircon and Fe-oxide as accessory minerals.

The marbles occur as brown to grey lenses, <100 m thick, and consist of up to 90 % dolomite (Haghipour 1978). White quartz-carbonate veins and veinlets along with cherty nodules are widespread. Typically they contain a mosaic of twinned dolomitic crystals and minor quartz, with accessory phlogopite, scapolite and plagioclase.

A lower amphibolite grade of metamorphism is proposed by (Ramezani and Tucker 2003) and they reported post peak metamorphic zircons dates of  $547 \pm 2$  Ma.

### **2.6.2 The Tashk Formation**

The Tashk Formation is a 2000 m thick sequence of weakly metamorphosed dark green-grey phyllite, quartzite and slates with mafic lavas and associated volcanoclastic rocks (Haghipour and Pelissier 1977a,b, Stöcklin and Setudehnia 1977). The type locality is Kuh-e-Tashk, 25 km east of Saghand. The main outcrops in the region are at Kuh-e-Polo and Zamanabad, east and south of Posht-e-Badam, and Kuh-e Posht-e-Sorkh west of the Chador Malu deposit. There is no outcrop of this formation in the immediate vicinity of Esfordi, the nearest being in hills 3 km south (Fig 3.1) or also near Saghandy mountains, 15 km northwest of Esfordi.

Most of the upper contacts of the Tashk Formation are obscured by granitic intrusions and hydrothermal alteration, however, a few outcrops show a clear conformable relation with the overlying cherty, gypsum bearing dolomites and rhyolitic volcanic rocks attributed

to the Cambrian Volcano-Sedimentary Unit (CVSU) (Haghipour, 1978; Ramezani, 1997). Greenschist grade of metamorphism developed in the lower part of the Tashk Formation, where it is made up of fine-grained mica schists, quartzite schists, phyllite, gneiss, amphibolite and metagreywackes with tuffaceous interlayers (Haghipour, 1978). The upper part of the Tashk Formation is weakly metamorphosed, and composed of greywacke, sandstone and shale and small amounts of acid and mafic volcanics. The mafic volcanics are mainly thin basaltic lavas, alternating with greywacke (Ramezani 1997).

On the basis of detrital zircons from a volcaniclastic tuff horizon Ramezani and Tucker (2003) constrained the depositional age of the Tashk Formation to  $627 \pm 19$  Ma, although zircons from the oldest known intrusion (the Ariz Granodiorite) gave an age of  $533 \pm 1$  Ma.

### **2.6.3 Cambrian Volcano-Sedimentary Unit (CVSU)**

The CVSU is a sequence of unmetamorphosed mafic to felsic volcanics, carbonates, sandstone and evaporitic intercalations exposed in central and southern part of the Bafq–Biabanak district on both sides of Posht-e-Badam Fault (Fig 2.7). The age and stratigraphic nomenclature of these rocks have long been controversial. This sequence has also been termed the Rizu-Dezu Series, Esfordi or Saghand Formations in different parts of the area between Posht-e-Badam and Kerman (Huckriede *et al.*, 1962; NISCO, 1969-1975; Stöcklin and Setudehnia, 1977; Haghipour, 1978; Samani, 1988, 1993).

The most important exposures are in the Esfordi, Zarigan, Saghand, and Khoshoumi areas (Figs 2.7 and 2.8). Previously this sequence and its equivalents in Central Iran were assigned to the “Infracambrian” (Stöcklin 1968; Haghipour 1978; Haghipour and Pelissier 1977a; Samani 1988, 1993; Daliran 1990). Recently Ramezani (1997) and Ramezani and Tucker (2003) reported an Early Cambrian age for the volcanic rocks of this sequence by U-Pb dating of zircons in rhyolitic units in the Bafq region. Ramezani (1997) therefore suggested that the term Infracambrian should be abandoned and proposed the unit be known as the Cambrian Volcano-Sedimentary Unit (CVSU).

The lower contact of the CVSU and Tashk Formation is generally obscured by granite intrusions or hydrothermal alteration, however Ramezani and Tucker (2003) recognised a disconformable contact between these two units at Douzakh-Darreh. The upper boundary of the CVSU in the Esfordi area is obscured by Neogene debris and faulting. Förster and Jafarzadeh (1994) reported a disconformable contact between CVSU and Cambrian Lalun Formation in the southern part of the Bafq region. A conglomerate with reworked fragments of Fe-oxide and metasomatic rocks also marks the upper limit of the sequence (Daliran, 2002). In the Zarigan area, red conglomerates and sandstones of Lalun or equivalent Dahu Formation unconformably overly the top carbonate horizons of the CVSU (Ramezani, 1997).

Haghipour (1978) measured the thickness of the CVSU to be ~900~1000 m in the Saghand and Zarigan area, although Samani (1993) reported a composite measurement of ~1200-1500 m from a similar locality. In the southern part of the region, near the Kushk deposit, the exposed thickness is ~800 m (Haghipour and Pelissier, 1977a; Samani 1993). Stöcklin and Setudehnia (1977) also measured the equivalent Rizu Series at Ab-Morad, 20 km northwest of Kerman, as having a thickness of 800 m. Ramezani (1997) report a thickness of more than 1500 m for this unit near Zarigan.

These measured sequences consisted of several horizons of mafic to felsic lavas and sub-volcanic intermediate to felsic intrusions intercalated with various pyroclastic and epiclastic rocks and dolomitic limestone with local evaporitic facies. At Ab-Morad it contains a basal conglomerate followed by 100 m of alternating sandstone and dolomite, 500 m of volcanoclastic rocks and 150-200 m of felsic lavas and has been termed the Rizu Series by Stöcklin and Setudehnia (1977). A ~200 m thick unit of overlying gypsiferous dolomite (including the Esfordi Dolomite) with felsic and mafic intrusions and volcanics was termed the Dezu Series. Samani (1993) subdivided the sequence into two stratigraphic units – the lower one, predominantly volcanic in character, was defined as the Saghand Formation (“the

productive zone of Central Iran taphrogenic belt”) hosting the Bafq district Fe–P systems; and the upper sedimentary-dominated part of the sequence was defined as the Rizu-Dezu Series. The contact of the Rizu-Dezu Series and Saghand Formation is an angular unconformity and contains a basal conglomerate with altered volcanic clasts. The stratiform Kushk Pb-Zn and Narigan Fe-Mn deposits occur in this unit. Lithologies of the five members of the Saghand Formation are summarised in Fig 2.10.

Daliran (2002) adopted Samani’s subdivisions and suggested that the lower volcanic unit had a continental to epicontinental affinity dominated by felsic welded and unwelded tuffs, whereas the upper unit dominated by sedimentary dolomite represented a shallow-water marine depositional environment in the southern part of the Bafq district, near Mishdovan. Mafic and intermediate lithologies, variously reported as trachybasalt, andesite and trachyte (Stöcklin and Setudehnia, 1977; Haghipour and Pelissier, 1977a,b; Haghipour, 1978; Förster and Knittel, 1979; NISCO, 1980) are intercalated or intrusive into the felsic volcanics. Daliran (1990) identified a spilitic affinity for these rocks at Mishdovan derived from shallow subaquatic caldera eruptions with ring structures producing welded and nonwelded tuffs intercalations in the lower unit. Predominantly shallow water dolomites were deposited during the subsequent period of low volcanic activity.

The lower unit of the CVSU at Mishdovan is mainly composed of unwelded fine grained tuffs without great lateral continuity. These tuffs are generally sparsely porphyritic and contain some stratiform and stratabound hematite deposits. The massive tuffs contain intra formational monogenic agglomerates which indicate local reworking and redeposition in an aqueous environment (Daliran, 1990). The advanced welded and compacted felsic rocks also contain collapsed pumice fragments and a matrix of welded glass shards and dust. The dense, lava-like appearance is mainly the result of welding and compaction of vitroclastic fragments. The Mishdovan welded ash flow tuffs are characterised by low contents of crystals and foreign fragments and this is considered evidence of high

temperature emplacement. Recrystallization has generally converted the primary glassy character of welded ash flow tuffs into rocks with a felsic fabric (Daliran, 1990).

#### **2.6.4 Zarigan and Narigan Granites**

A range of granitic rocks – Boneh-Shurow Complex, Tashk Formation and CVSU – are reported in the Bafq-Biabanak district (Haghipour and Pelissier, 1977a) (Fig 2.8). The age of some of these intrusions is uncertain, but recent zircon dating by Ramezani (1997) indicates an age of  $526 \pm 3$  Ma for the Zarigan, Douzakh-Darreh and Sefied Granites. The Zarigan Granite is the largest of these and covers  $>130 \text{ km}^2$  west of Zarigan.

The Zarigan Granite is a creamy-white to gray coloured leucogranite intruded into the Tashk Formation and CVSU and forms numerous small and large pendants. The Zarigan Granite is a shallow level intrusion with both crystalline granitic to a subextrusive porphyritic textures, with tonalitic or trondhjemitic affinities (Ramezani and Tucker, 2003).

The Chador Malu Granite ( $\sim 60 \text{ km}^2$ ) is the second largest intrusion in the central part of the Bafq-Biabanak district, and has similar characteristics to the Zarigan Granite. To the south and west of Mishdovan, a similar granitic body is intruded into the Tashk Formation and CVSU. Haghipour and Pelissier (1977a) considered this to be equivalent to the Zarigan Granite. Daliran (1990) ascribes a subvolcanic character to the Mishdovan intrusion with fine grained porphyroblastic fabric and notes the presence of secondary albite. The intrusion is dominantly granite and granodiorite with local diorite in the south and southwest, grading into rhyolite and rhyolitic tuff in the north (Soheili and Mahdavi, 1991). Some 6 km south and south-east of the Esfordi deposit, a  $\sim 50 \text{ km}^2$  elongate granitic body intrudes into the CVSU, which is locally known as Narigan Granite (Fig 2.8).

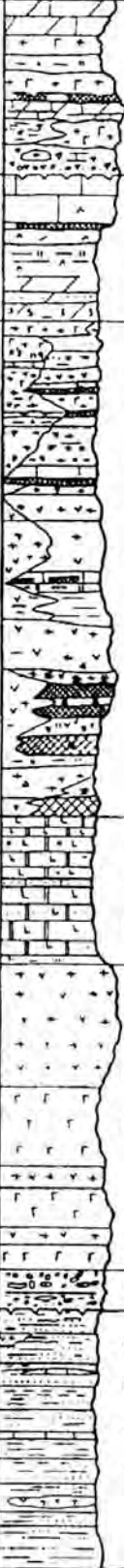
| AGE           |               | ROCK Units                      | Lithology                                                                           | DESCRIPTION                                                                                                                                                                                                                                                                      | Alteration & Deformation            |                                                | Geological Setting                |
|---------------|---------------|---------------------------------|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|------------------------------------------------|-----------------------------------|
| U P P E R     | V E N D I A N | S A G H A N D F O R M A T I O N |   | Alternation of High K Volcanics and Carbonate with Minor Clastics, Evaporites Mn-Fe-Pb-Zn Hosted.                                                                                                                                                                                | No Deformation                      | Locally K-Metasomatism                         | Subsidiary Rift ended to Platform |
|               |               |                                 |                                                                                     | Mostly Carbonate, Evaporates with Intracalations of Tuff, and Lava, Some Fe-Ore, (Rift Salt-Lake Facies.)                                                                                                                                                                        | METASOMATIC<br>LOCALLY<br>EXTENSIVE | GRANITOID<br>CONTACT<br>ALKALI<br>METASOMATISM | MAJOR INTRACONTINENTAL RIFT       |
|               |               |                                 |                                                                                     | Main Ore Bearing Member, Mostly Volcanogenic Consisting of Agglomerate, Breccia, with Intracalations of Carbonate in Upper Part, Extensively Metasomatized, Transformed into Different Metasomatic Rocks, Hosting Fe, U-Th-REE and Apatite Ores (Main Eruptive Volcanic Facies). |                                     |                                                |                                   |
|               |               |                                 |                                                                                     | Rhythmic Clastic-Hydrothermal Albitic Sandston and Slate (Exhalative Sediment Facies)                                                                                                                                                                                            |                                     |                                                |                                   |
|               |               |                                 |                                                                                     | Alternation of Acidic-Intermediate Lava, Lower Part More Acidic, and Upper Part Mainly Basic (Bimodal Continental Lava Facies)                                                                                                                                                   |                                     |                                                |                                   |
|               |               |                                 |                                                                                     | Basal Conglomerate, (Debries Flow Acc. Facies)                                                                                                                                                                                                                                   |                                     |                                                |                                   |
| Upper RIPHEAN |               | N A T K F O R M A T I O N       |  | Greenschist Metamorphosed F. Grained Flyschoid Clastics Minor Intracalations of Carbonate and Basic Volcanic Lava, Locally Metasomatized.                                                                                                                                        | METAMORPHISM<br>Greenschist Facies  | Locally No Metasomatism                        | Continental Slope                 |

Figure 2. 10 Stratigraphic column of the Saghand Formation (after Samani, 1993).

The Narigan Granite near Esfordi is a white to gray leucogranite with a wide variety of grain sizes (Fig 2.11). It contains 1-10 % ferromagnesian minerals, usually in the form of biotite and Fe-oxide. The intrusion has variable textures ranging from subhedral granular to porphyritic and subvolcanic (Fig 2.12).



**Figure 2. 11 Outcrop of Narigan Granite cut by a doleritic dyke, 12 km south of the Esfordi deposit.**

The Narigan Granite is characterised in thin section by a granoblastic to granophyric texture of quartz, K-feldspar and plagioclase (albite) in a xenomorphic granular or porphyritic groundmass. In the granoblastic to granophyric textures plagioclase and alkali feldspar tend to form subhedral, or less commonly euhedral crystals. Anhedral quartz along with fine-grained alkali feldspar occupy intergranular spaces. Some of the K-feldspar crystals contain quartz crystals forming a micrographic texture (Fig 2.12). The marginal zones and isolated outcrops of Narigan Granite may be rich in mica and show alignment of minerals, yielding a distinct flow lineation in hand specimens.

In porphyritic variants (porphyry rhyolite), large phenocrysts of albite, K-feldspar and quartz are embedded in an aphanitic to fine-grained, quartzo-feldspathic groundmass. Some of the K-feldspar and quartz crystals have micrographic textures. The porphyritic granite (or

rhyolite) contains abundant Fe-oxide and embayed and round quartz grains. Muscovite and biotite are also present in minor amounts. The other minor phases are typically amphibole, epidote, chlorite, apatite and zircon. Locally, the wall rock of the Narigan Granite body shows hydrothermal alteration, with the development of amphibole, chlorite, sericite and clay-rich mineral assemblages.

The Zarigan and Narigan Granites are intruded by swarms of doleritic dykes with transitional contacts. The dykes show large variation in thickness, and are commonly subparallel and curved in shape. Ramezani and Tucker (2003) suggest that the dykes intruded the granite in the syn- to late stages of crystallization.

### *Geochemistry*

The result of major and trace element analyses of Narigan Granite samples are listed in Table 2.1. Data from previous studies in the region are included in the various petrochemical diagrams; Zarigan Granite (ZG) and Chador Malu Granite (ChG) from Esmaili *et al.* (1999), Narigan Granite (NG) this study, Saghand Granite (SG) from Ramezani, 1997, Mishdovan Granite (MG) from Daliran (1990). Scattering on some geochemical plots, particularly those involving alkali elements, are partly attributed to the effect of hydrothermal alteration on the more mobile elements, however, general trends and classifications are still coherent and consistent with compositional evolution.

The alumina saturation index values (Shand, 1927) are plotted in Fig 2.13 and show that the least altered Cambrian granites and rhyolites in the region are both Al-oversaturated (peraluminous) and Al-undersaturated (metaluminous) with most samples plotting in the peraluminous region. The molar and normative data are presented in Appendix 3.

**Table 2. 1 Major and trace element composition of the Narigan Granite (XRF).**

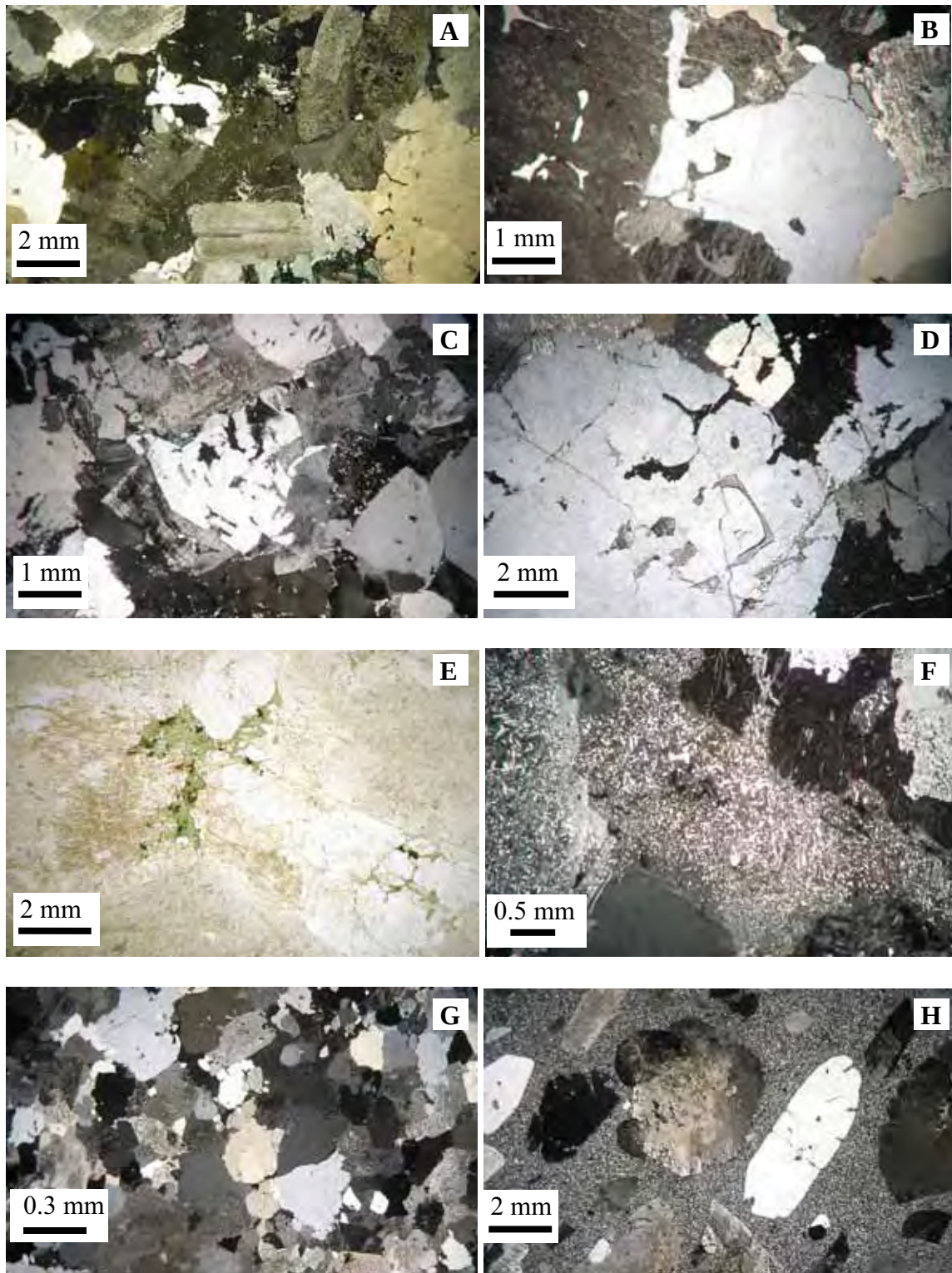
| Major elements (wt %)            |        |       |       |        |       |       |
|----------------------------------|--------|-------|-------|--------|-------|-------|
| Sample                           | 89-1   | 93    | 91-2  | NG1    | NG2   | NG3   |
| SiO <sub>2</sub>                 | 74.06  | 79.39 | 72.43 | 76.8   | 75.4  | 76.25 |
| TiO <sub>2</sub>                 | 0.25   | 0.32  | 0.34  | 0.22   | 0.13  | 0.02  |
| Al <sub>2</sub> O <sub>3</sub>   | 13.71  | 11.05 | 14.26 | 14.52  | 12.71 | 13.26 |
| Fe <sub>2</sub> O <sub>3</sub> T | 1.07   | 0.94  | 1.72  | 0.71   | 1.02  | 0.29  |
| MnO                              | 0.02   | 0.02  | 0.02  | 0.04   | 0.02  | 0.03  |
| MgO                              | 0.55   | 0.36  | 0.79  | 0.35   | 0.14  | 0.05  |
| CaO                              | 1.15   | 0.68  | 0.9   | 1.27   | 0.73  | 0.92  |
| Na <sub>2</sub> O                | 4.02   | 5.77  | 7.02  | 4.76   | 5.31  | 4.95  |
| K <sub>2</sub> O                 | 4.28   | 0.33  | 0.46  | 0.42   | 3.43  | 3.28  |
| P <sub>2</sub> O <sub>5</sub>    | 0.06   | 0.04  | 0.07  | 0.01   | 0.03  | 0.02  |
| LOI                              | 1.15   | 0.96  | 1.68  | 1.21   | 0.86  | 0.91  |
| total                            | 100.34 | 99.89 | 99.69 | 100.31 | 99.78 | 99.98 |

| Trace elements (ppm) |       |       |       |     |     |     |
|----------------------|-------|-------|-------|-----|-----|-----|
| Ba                   | 778.3 | 56.9  | 57.5  | 265 | 250 | 257 |
| Ce                   | 36.55 | 44.41 | 45.57 | 20  | 23  | 26  |
| Ga                   | 15.9  | 10    | 14.8  | 11  | 18  | 19  |
| Nb                   | 5.7   | 6.1   | 5.6   | BLD | 8   | 8   |
| Ni                   | 5.8   | 9     | 5.4   | 4   | 5   | 4   |
| Pb                   | 8.9   | 7     | 5.5   | 8   | 16  | 20  |
| Rb                   | 95.6  | 22.4  | 28    | 12  | 134 | 142 |
| Sc                   | BLD   | BLD   | BLD   | 4   | BLD | BLD |
| Sr                   | 99.8  | 58.5  | 56.6  | 287 | 65  | 61  |
| Th                   | 8.9   | 4.5   | 9.3   | 8   | 11  | 11  |
| U                    | 2.8   | BLD   | 5     | BLD | BLD | BLD |
| V                    | 40.1  | 48.1  | 48.1  | 1   | BLD | BLD |
| Y                    | 23    | 3.7   | 12.7  | 4   | 22  | 40  |
| Zn                   | 18.3  | 14.7  | 17    | 22  | 15  | 15  |
| Zr                   | 125.4 | 121.2 | 119.2 | 28  | 29  | 54  |

BLD: Below level of detection

The Early Cambrian granites of the region are generally rich in silica and have apparently solidified from well-differentiated magmas. The total alkali versus silica plots (TAS; Irvine and Bargar, 1971) indicate a sub-alkaline or calc-alkalic character of the plutonic and volcanic rocks of the region (Fig 2.14) but some high-K granites and the majority of felsic volcanics plot in the alkalic field as defined by Le Maitre (1989) (Fig 2.15).



**Figure 2. 12 Micrographs of Narigan (leuco)Granite.**

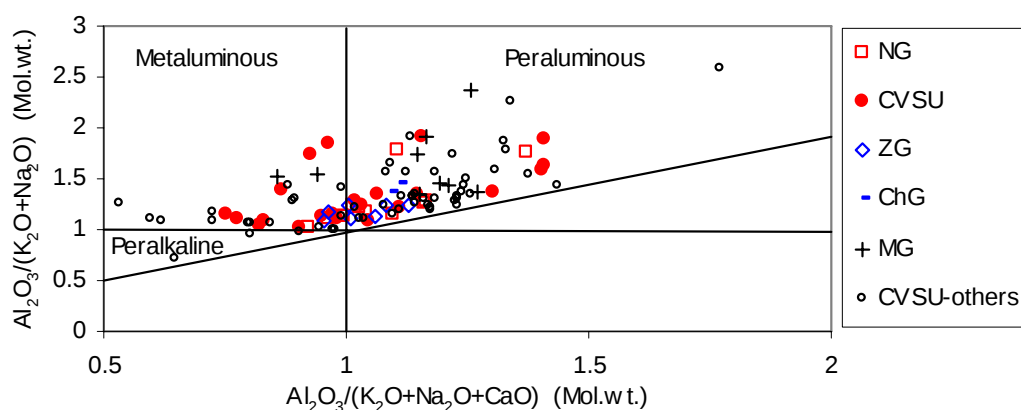
- A & B: Plagioclase, orthoclase and quartz interlocked in a coarse granular fabric (XPL).
- C & D: Dusty plagioclase and orthoclase with graphic and perthitic textures (XPL).
- E: Chlorite-sericite alteration as intergranular and replacing crystals (PPL).
- F: Dusty feldspar, sericite replaced plagioclase (XPL).
- G: Local aplite variant (XPL).
- H: Porphyry granite with large phenocrysts of albite, K-feldspar and quartz embedded in an aphanitic to fine grained quartzo-feldspathic groundmass (XPL).

These felsic plutonic rocks of the region plot in the granite and alkali granite field of the plutonic rock classification diagram (Wilson, 1989). The major oxide plot shows limited compositional variations with close relation of the major intrusive bodies in a general trend of decreasing major oxides with increasing silica (Fig 2.16).

The Narigan Granite is enriched in LREE with high  $(La/Yb)_{CN}$ . The depletion of Sr and Eu is probably related to feldspar fractionation under reduced condition in the parent magma. Sample #23 is a syenitic rock exposed 2 km north of Esfordi and displays a similar trace element pattern to the Narigan Granite but with relative higher REE and Zr concentrations (Fig 2.17). The high concentration of Th is interpreted as the result of selective LILE and LREE enrichment in the mantle source above a subduction zone (Ramezani, 1997).

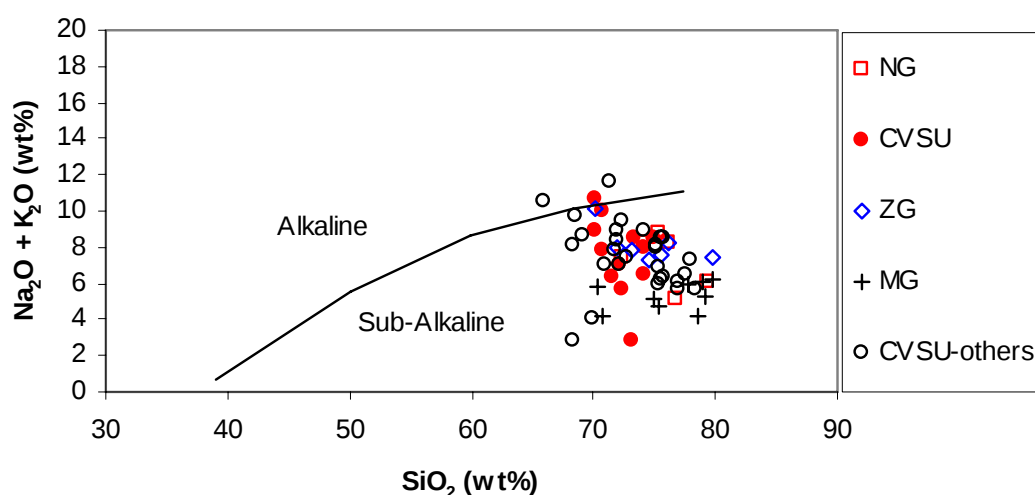
The majority of CVSU samples have a rhyolitic affinity and few samples plotted in dacite and trachy-dacite fields (Fig 2.18). To minimize the hydrothermal alteration effect on the TAS classification CVSU volcanics were plotted in immobile element discrimination diagram ( $SiO_2$  versus  $Zr/TiO_2$  and  $Zr/TiO_2$  versus  $Nb/Y$ ) (Fig 2.19). These diagrams show a more basic character of the CVSU volcanics, with a considerable number of samples plotting in the rhyodacite/dacite field. The  $Zr/TiO_2$  versus  $Nb/Y$  diagram shows two samples in the andesite and one in the trachyte fields.

In an attempt to clarify the tectonic setting of the Cambrian granitic suits, several samples of Narigan Granite and other intrusions Nb versus Y and Rb versus  $Y+Nb$  discrimination diagrams (Pearce *et al.*, 1984) are plotted in Fig 2.20. It is considered that Rb is unexchanged by later alterations. These plots show evolution in a typical destructive plate margin setting. Ramezani (1997) used the same plotting procedure but acknowledged problems due to anomalous trace element abundances and MREE depletion with respect to the LREE and HREE in the Cambrian leucogranites. The Narigan trace elements plot show similar pattern to Saghand leucogranite pattern plotted by Ramezani (1997).

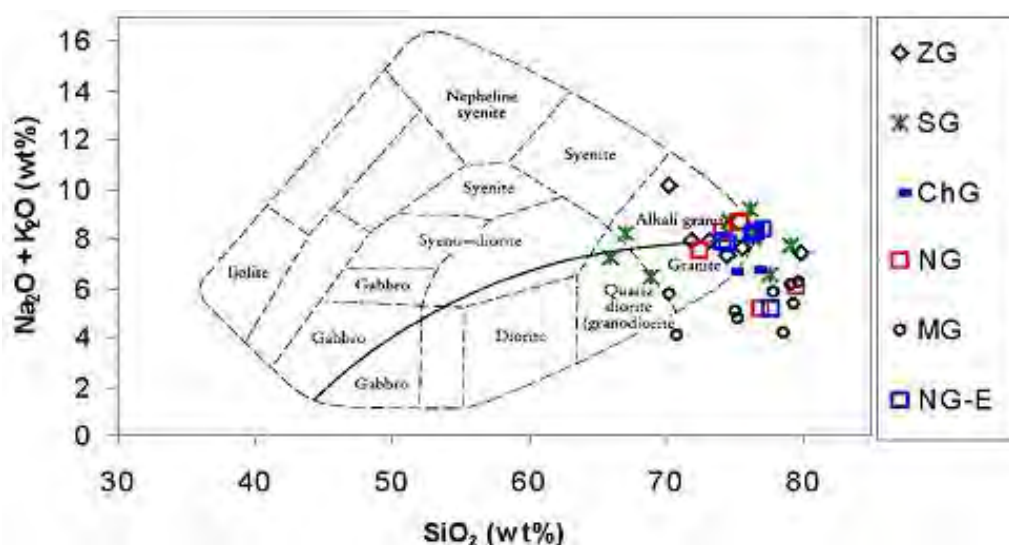


**Figure 2. 13 Al-saturation plot for Bafq region granites and volcanics.** [ChG: Chador Malu Granite, CVSU: Cambrian Volcano-Sedimentary Unit, MG: Mishdowan Granite, NG: Narigan Granite, SG: Saghand Granite, ZG: Zarigan Granite,]

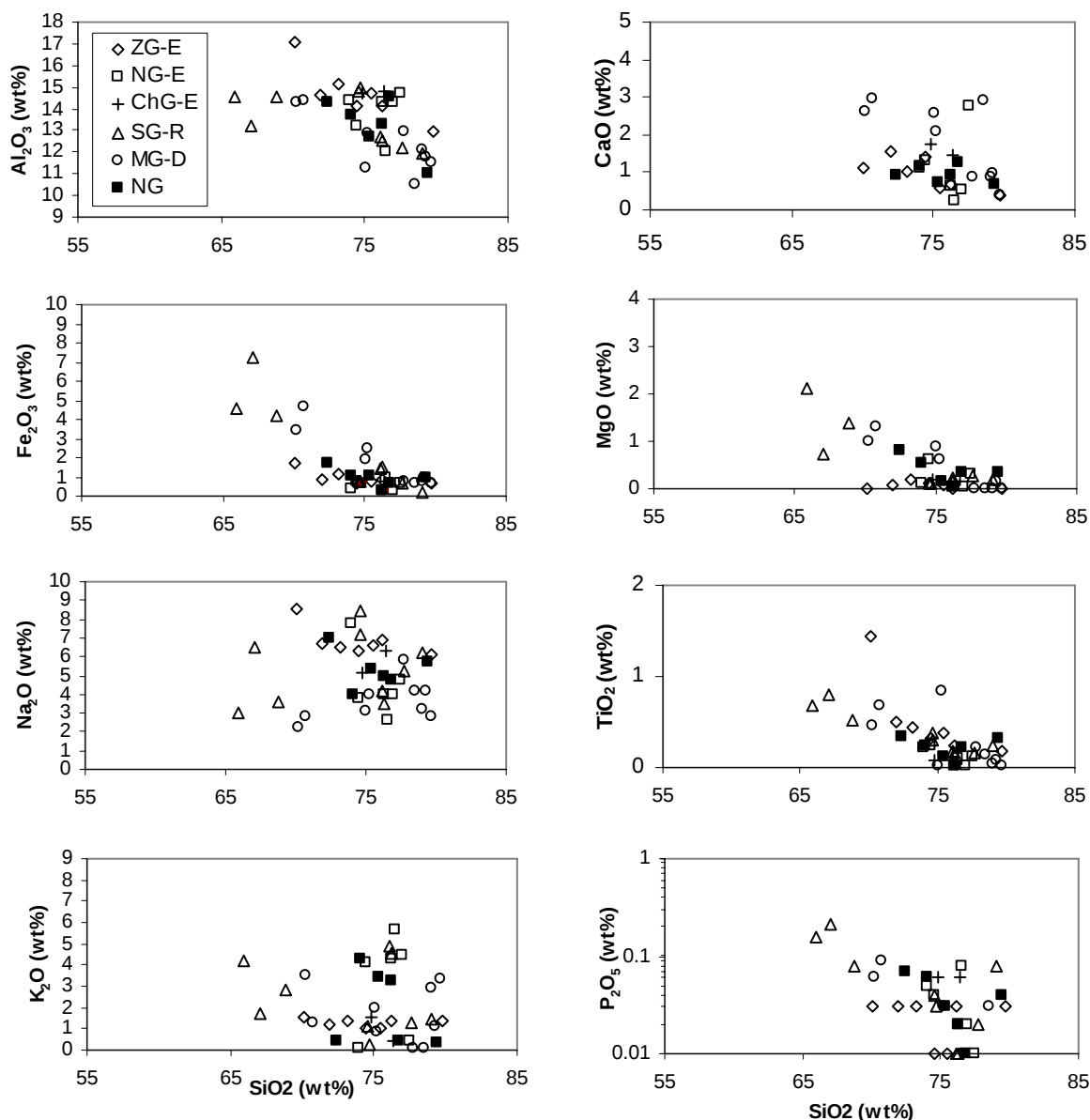
(Data: CVSU-others, ZG, ChG and MG from Esmaili *et al.* (1999); Daliran (1990); Ramezani (1997), Haghipour (1978), Darvishzadeh and Altaf Kohbanani (1996), Mehrabi (1991) and Boroumandi (1973). NG and CVSU from current study).



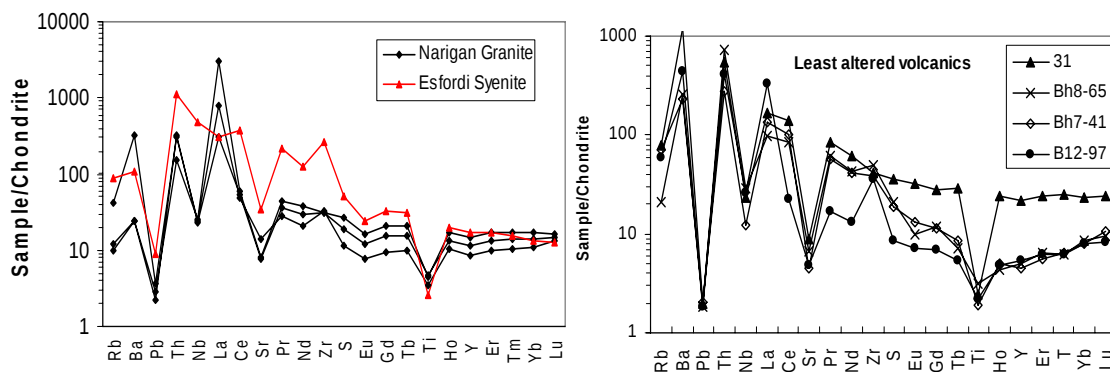
**Figure 2. 14 Total alkali versus silica plot (TAS) for felsic plutonic and volcanic rocks of the Bafq region** (Abbreviations same as Fig 2.13).



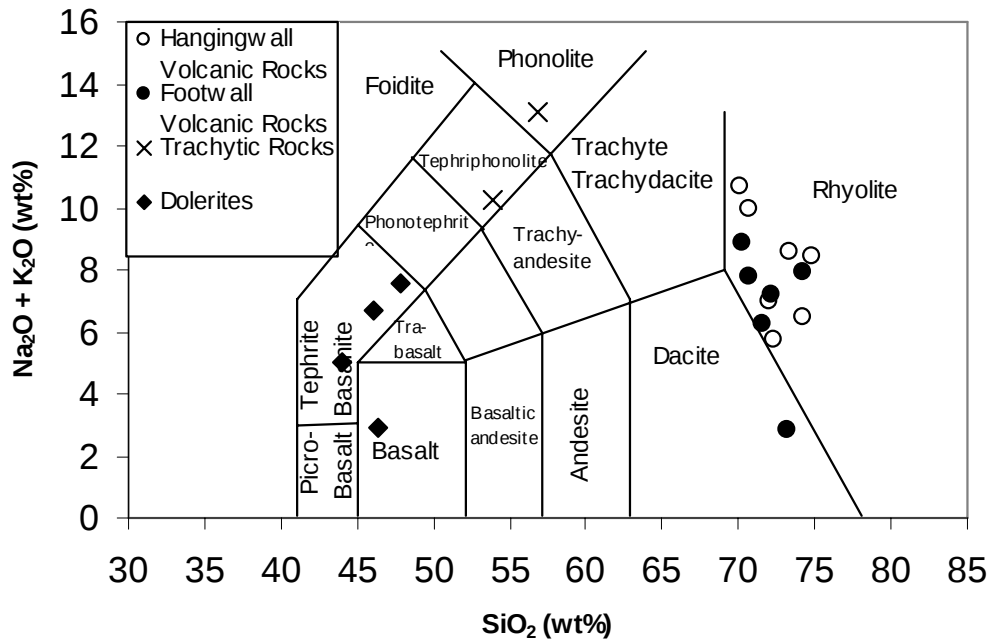
**Figure 2. 15 Chemical classification of Bafq-Biabanak Cambrian granites** (Abbreviations same as Fig 2.13, NG-E from Esmaili *et al.* (1999), classification adapted from Wilson, 1989).



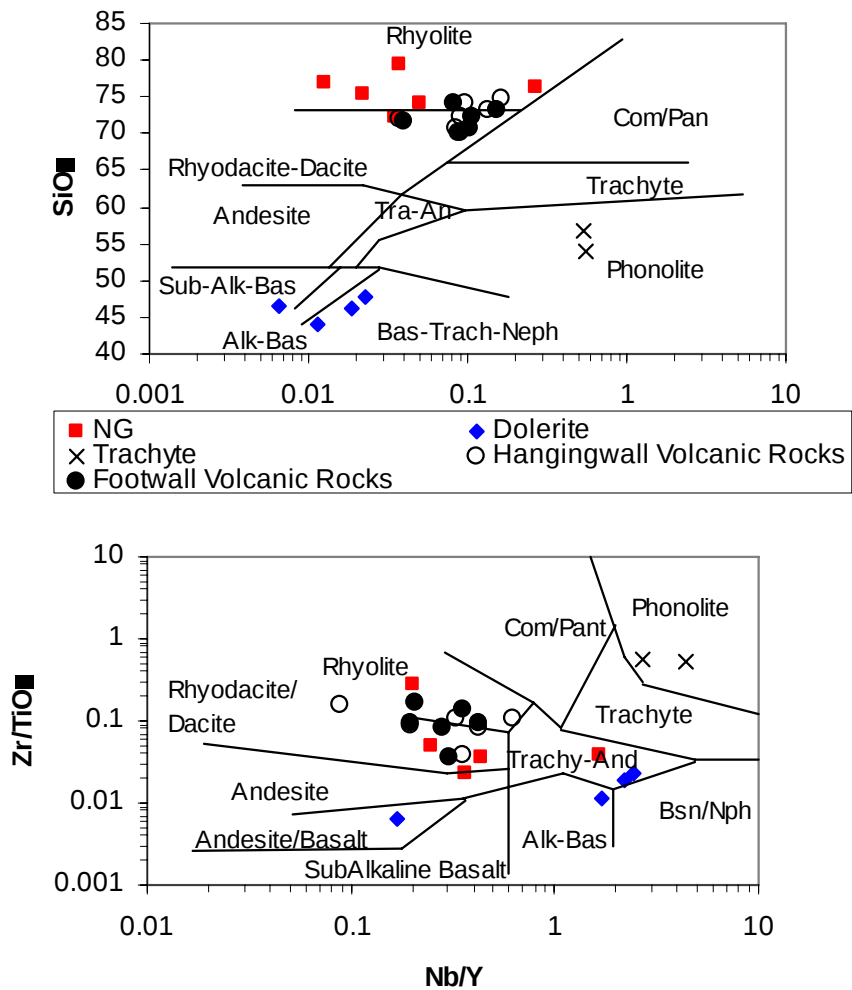
**Figure 2. 16 Major oxide variation diagrams (Harker plots) of the Neoproterozoic-Cambrian granitoids of the Bafq-Biabanak district.**



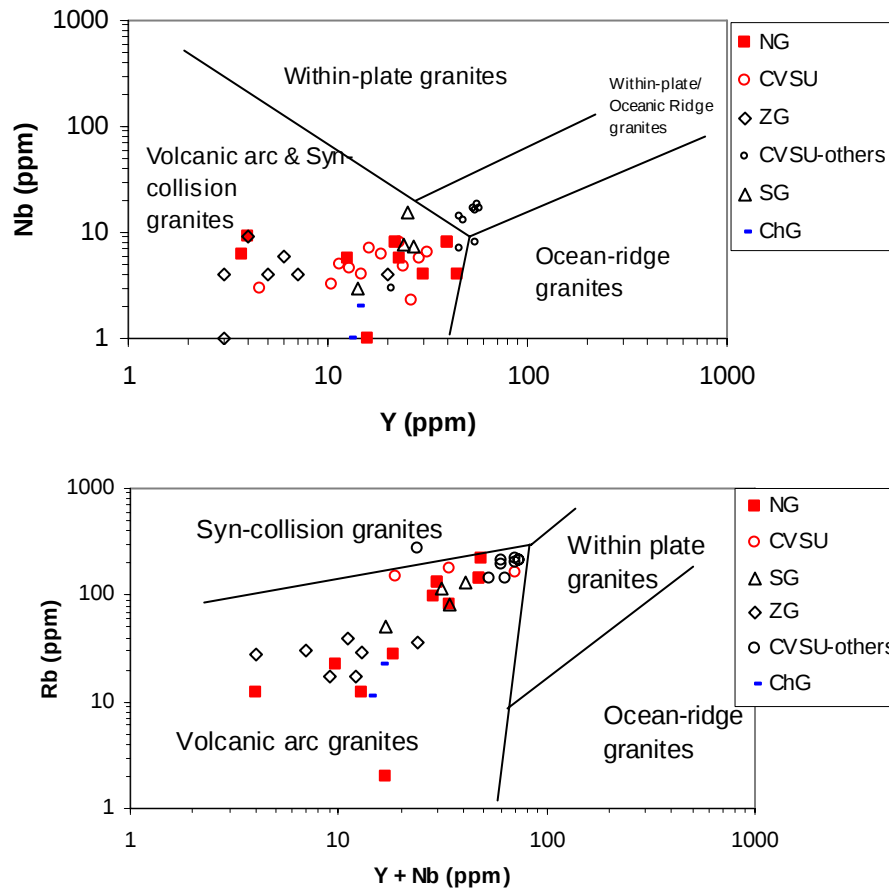
**Figure 2. 17 Chondrite normalised trace element plot of the Narigan Granite and Esfordi Syenite (Data from current study).**



**Figure 2. 18 Plots of the least altered volcanics of the CVSU and dolerites (Dol) of the Bafq-Biabanak district in the TAS diagram (Data: from current study).**



**Figure 2. 19 Classification of felsic and intermediate rocks of the Bafq-Biabanak district. (Data: from current study).**



**Figure 2. 20 Nb/Y and Rb/(Y+Nb) discrimination diagrams for granitic intrusions of the Bafq-Biabanak district. (Abbreviations same as Fig 2.13).**

### 2.6.5 Overlying sedimentary units

The Neoproterozoic and Cambrian units are covered by a series of Palaeozoic to Quaternary sedimentary strata with various lithologies. The oldest sequence is an unmetamorphosed sequence of red sandstone and conglomerate overlying the dolomites and volcanics of the CVSU. The contact has been reported as unconformable in the Zarigan Mountains and conformable in Bafq area (Haghipour, 1978; Förster and Jafarzadeh, 1994). This well-stratified sandstone is equated with the red arkosic sandstone and conglomerates of the Lower Cambrian Lalun Formation in Central Iran and the Alborz Range. It consists of angular grains of quartz and feldspar and lithic clasts of volcanic provenience with zircon, muscovite and tourmaline as accessory phases (Haghipour, 1978). A 100 m thick sequence of shale and dolomite above the top quartzite member of the Lalun Formation in the Nord area close to Zarigan is correlated with the Middle Cambrian Mila Formation in the Alborz

Range (Haghipour, 1978). The only Permian sequence exposed is at Kuh-e-Sefid Donbeh in the Posht-e-Badam area and consists of 450 m of conglomerate, sandstone, slate and limestone and dolomite overlying the Posht-e-Badam Complex above a disconformity (Haghipour and Pelissier, 1977a).

In the northern part of the district, east of Posht-e-Badam and Zamanabad, there are a few exposures of Triassic dolomites, limestones, sandstones and shales, that are correlated with the Lower Triassic Sorkh-Shal, Middle Triassic Shotori and Upper Triassic Nayband Formations in Central Iran (Haghipour, 1978; Stöcklin and Setudehnia, 1977). Haghipour (1978) correlated a sequence of red and gray shales, and quartzitic sandstones to Liassic Shemshak Formation in Central Iran and the Alborz Range.

The Cretaceous conglomerates, sandstones, shales and limestones unconformably overlie various lithologies in the region including the Zarigan and Narigan Granites, CVSU and the older Mesozoic sequences. To the south of the Esfordi deposit and west of the Narigan Granite a >500 m thick section of limestone is exposed (Haghipour, 1978).

The Cretaceous limestone is locally overlain by a conglomerate correlated with the Paleocene to Eocene Kerman Conglomerate (Huckriede et al, 1962). This sequence is followed by Eocene volcanics and a series of Neogene lagoonal deposits of red, poorly consolidated shales, marls and sandstones with evaporitic intercalations.

Vast areas of the district, particularly intermountain depressions controlled by N-S and NE-SW faulting are covered by unconsolidated Quaternary deposits, including fluvial deposits, alluvial fans, playa type deposits and sand dunes. Locally these may be in excess of several tens of metres thick.

## **CHAPTER 3      GEOLOGY OF THE ESFORDI AREA**

### **3.1      INTRODUCTION**

The Esfordi Fe–P deposit is exposed in an area between Mishdowan and Kushk and is hosted within a volcanoclastic section of the Cambrian Volcano-Sedimentary Unit (CVSU) (Fig 3.1). The lower parts of the Saghand Formation, as defined by Samani (1993), are absent near Esfordi. Fe–P mineralisation is hosted by felsic volcanics and intercalated shallow water sediments in the middle of the Saghand Formation (Fig. 2.10), and is intruded by irregular trachytic and doleritic bodies.

Esfordi is situated in the central part of the Kashmar-Kerman Structural Zone (KKSZ) within ~2 km of the projected position of the Posht-e-Badam Fault (a major structural domain boundary within the KKSZ). Some 3 km to the south of Esfordi an upthrown block of Tashk Formation is intruded by the Narigan Granite. The Narigan Granite intrudes the CVSU some 3–5 km to the northwest of Esfordi, but is not exposed at Esfordi. Deformation is locally associated with block faulting and tilting. The host sequence at Esfordi dips gently to the northeast at 35–60°.

The CVSU sequence in the Esfordi area has been studied using surface exposures in the Esfordi mine and surrounding areas and through drill-hole logging. Data from mine geology maps has been incorporated at the interpretive stage.

The CVSU locally contains a ~600 m thick volcanic dominated sequence, and an upper series of relatively thick bedded carbonate-rich sediments (Fig 3.2). The exposed stratigraphic sequence of the CVSU at Esfordi is presented in Fig 3.3. The rock exposures around Esfordi belong predominantly to the hanging wall sequence and show hydrothermal overprints that commonly obscure original rock textures. The footwall sequence is covered

by Neogene deposits and exposures are limited to a few isolated outcrops close to the Esfordi mineralisation. Both hanging wall and footwall sequences are laterally truncated by N-S and NE-SW trending local faults and are generally covered by recent deposits. Several small scale faults also displaced and tilt the limited outcrops.

A series of shallow drill-holes (30-150 m) were drilled within a small area ( $< 0.3 \text{ km}^2$ ) surrounding the deposit (Fig. 3.4). Due to the barren nature of the footwall, only a few drill-holes penetrated the footwall sequence. The core was generally in poor condition, due to exposure, but 30 core segments that were relatively well-preserved were logged and sampled. A general lack of distinctive mesoscopic features meant that differentiation of individual flow units among the rhyolitic pyroclastics was not possible except where well-defined sedimentary intercalations were present. Primary characteristics of such units were barely discernable under thin section examination even where the impact of hydrothermal alteration was less pronounced.

In the following sections, the characteristic of the footwall and hanging wall sequences and associated mafic volcanic rocks of Esfordi will be presented.

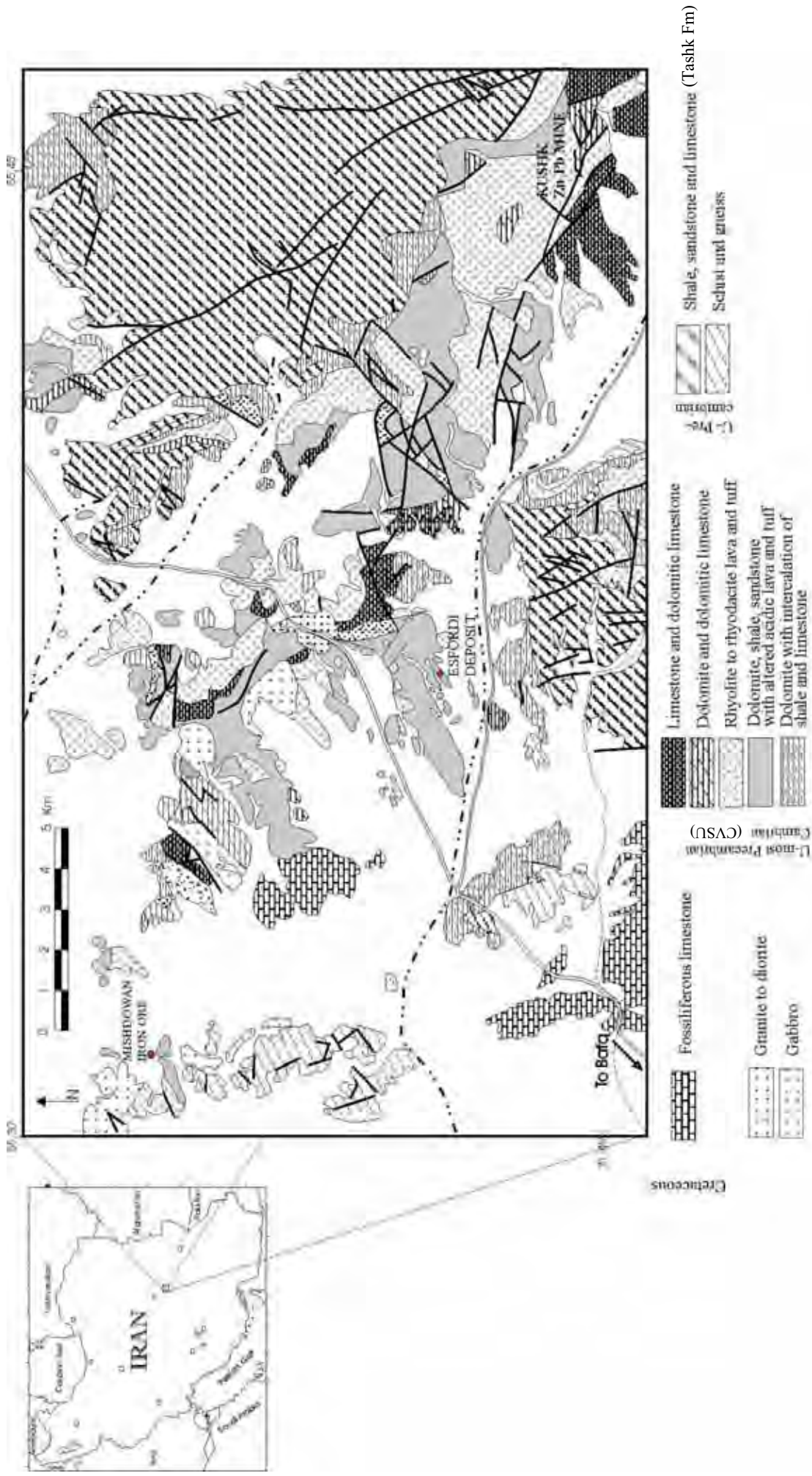
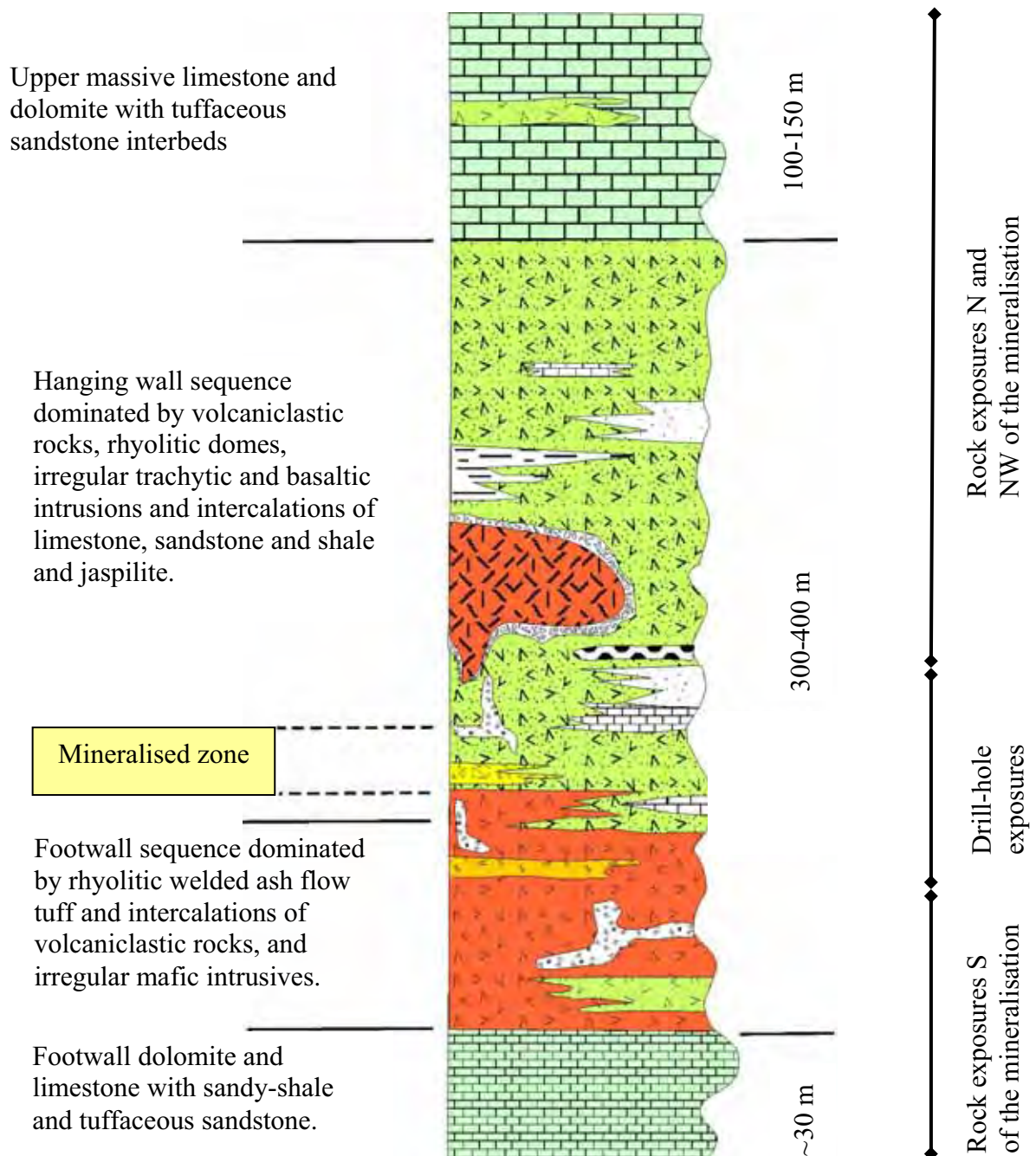
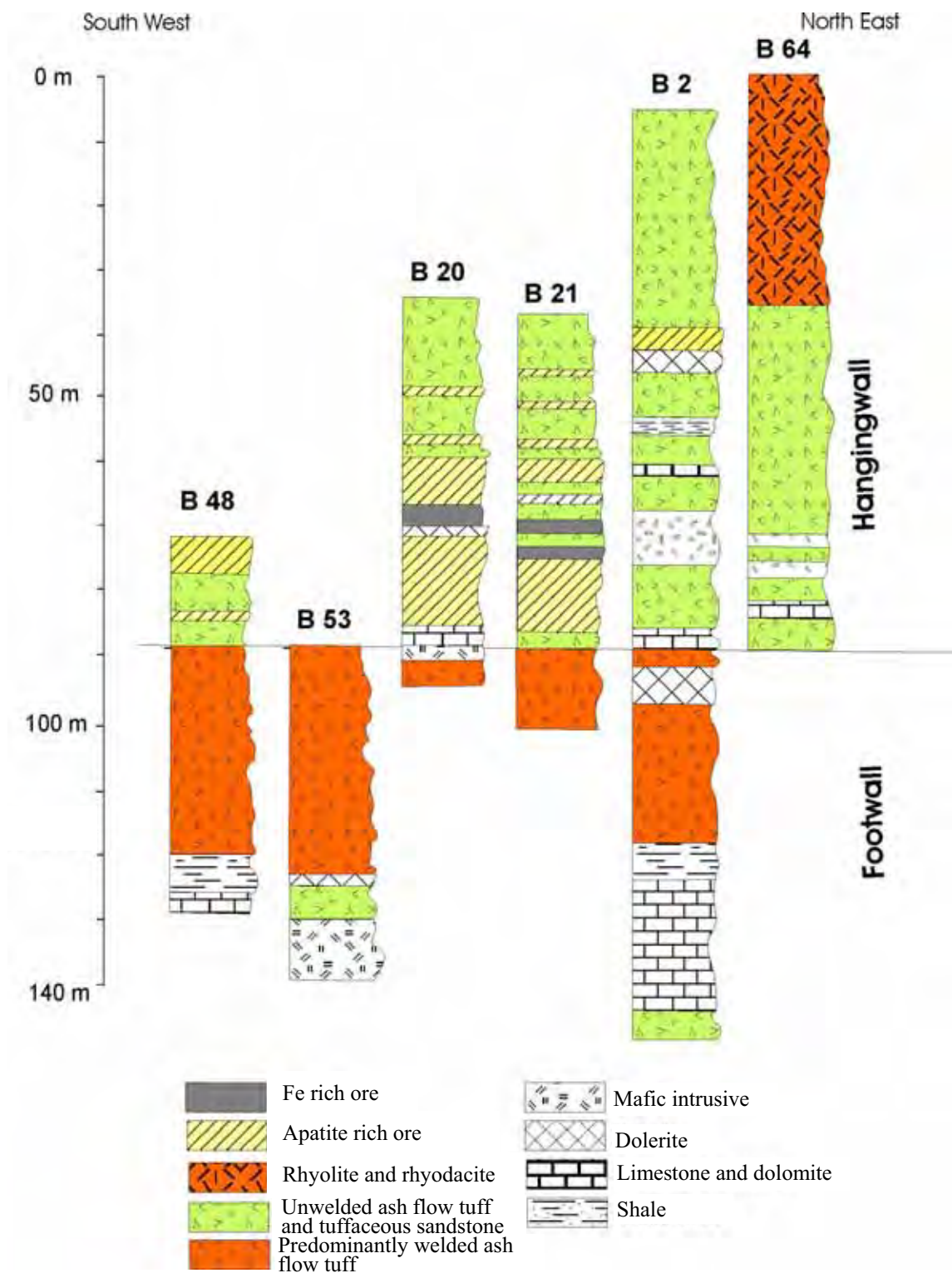


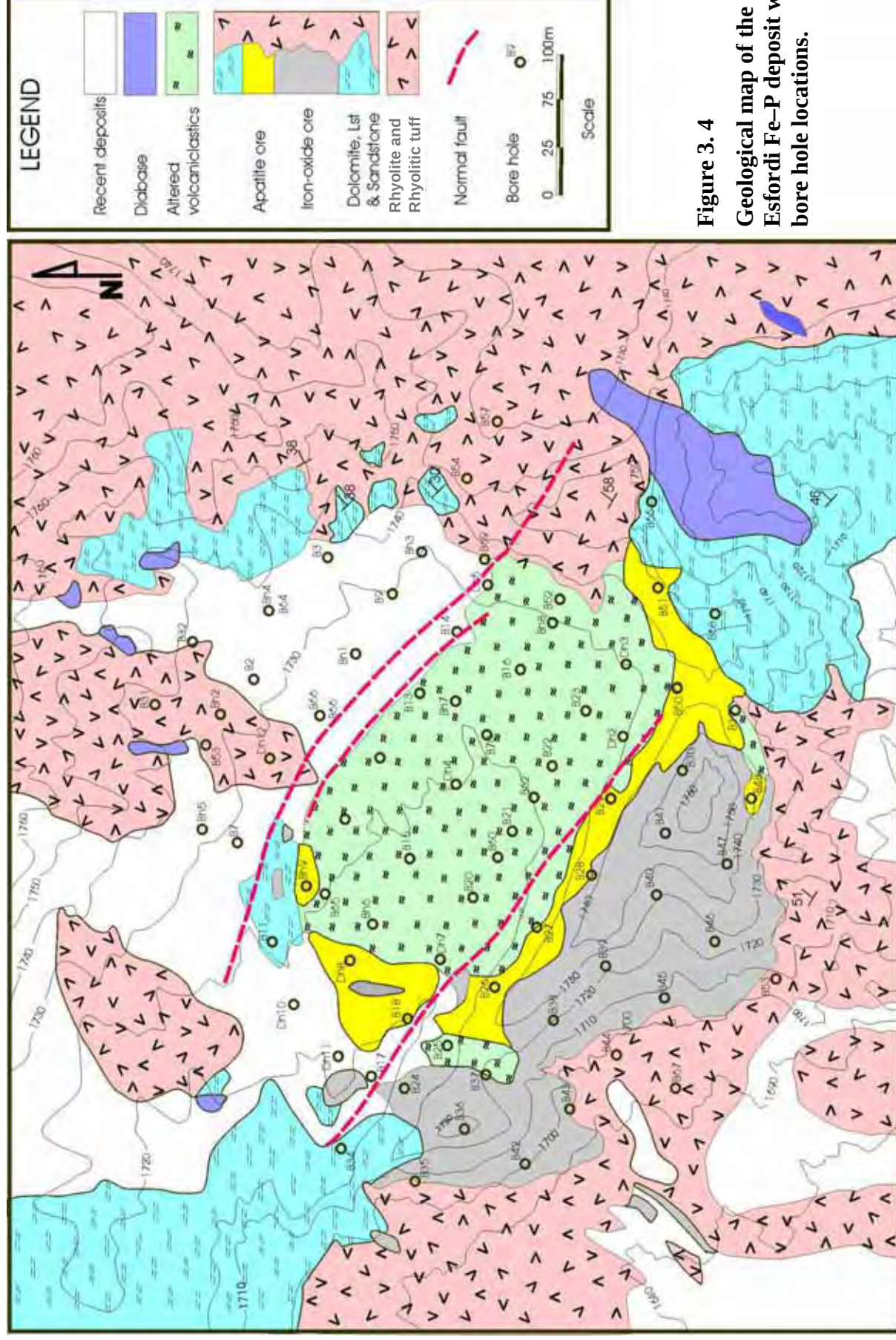
Figure 3. 1 Geological Map of the Esfordi area including the Esfordi, Mishdovan and Kushk deposits (after Soheili and Mahdavi 1991).



**Figure 3. 2 Schematic stratigraphic sequence of the Esfordi volcanic succession (not to scale, Key to lithologies is same as Fig. 3.3).**



**Figure 3. 3** Litho-stratigraphic columns of six bore holes showing typical hanging wall and footwall lithologies.



**Figure 3. 4**  
Geological map of the  
Esfordi Fe-P deposit with  
bore hole locations.

### **3.2 FOOTWALL SEQUENCE OF ESFORDI**

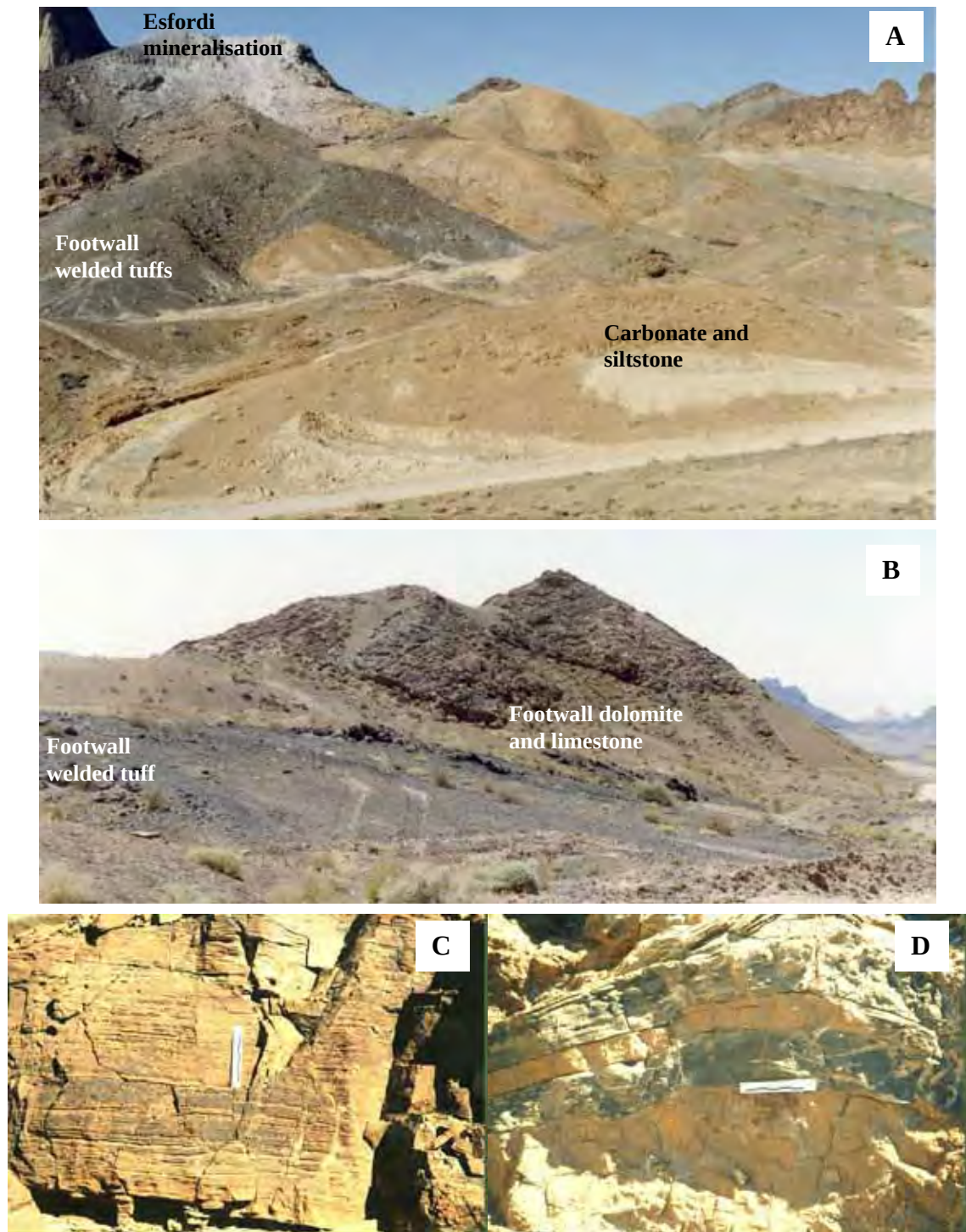
The footwall sequence is mainly covered by recent alluvium and is only exposed in a limited number of outcrops (Fig 3.5) where weathering masks most of the rock fabric. Therefore, the majority of samples were collected from drill-holes.

The footwall sequence is mainly composed of a varied assemblage of volcanic facies that were probably deposited in a shallow water environment. The sequence has vertical variability in grain size and the degree of recrystallization, welding and alteration. Lower in the sequence the footwall tuff is underlain by a ~30 m thick laminated dolomite and limestone with 0.5-2 m interbeds of sandy shale, tuffaceous sandstone and siltstone. Two trachytic bodies are observed in bore holes 20 and 53; the latter containing an intersection more than 10 m thick.

In the footwall sequence a 4 m thick dolomite and limestone bed is exposed within the welded ash flow tuff sequence, close to mineralisation (Fig 3.6 a). Underlying the welded ash flow tuffs is another 40 m of shale and carbonate including 6-9 m of sandy shale and ~30 m of dolomite and minor limestone exposed in a small outcrop east of the Esfordi mineralisation (Figs. 3.2 and 3.6 b). The contact between the sandy-shale and overlying tuff is relatively sharp but gradational with the underlying dolomite. The sandy shale contains planar laminated beds of siltstone and mudstone (Figs. 3.6 and 3.7). The underlying dolomite is medium to thinly-bedded with intervals of colour-banded limestone. Under microscope, the dolomite and limestone have relatively uniform microsparite to sparite matrix textures without any recognizable fossils. The carbonate sequence contains minor amounts of sand and silt-sized quartz clasts, which are locally abundant at contacts with detrital horizons.



**Figure 3.5** Limited outcrops of the Esfordi footwall sequence (A: looking south, B: view from bore hole 47, looking east).



**Figure 3.6 Carbonate layers of the Esfordi footwall.**

- A: Limited exposures of footwall welded ash flow tuff (gray tuff) and underlying sedimentary rocks at the vicinity of the mineralisation (view from south of hole B42, looking south east).
- B: Lower carbonate unit of the footwall sequence (20 m west of hole B67, looking south).
- C: Lamination of siltstone and mudstone in the shale-dominated beds overlying carbonates (scale=5 cm).
- D: Intercalation of thin bedded limestone (light color) and dolomite (dark color) in the lower carbonate sequence of Esfordi (scale=5 cm).

The immediate footwall to the Esfordi deposit consists of 20-40 m of welded rhyolitic to dacitic ash flows with some thin, unwelded intervals. This sequence shows a variety of colouration from gray, grayish green to pink. The ash flow is locally brecciated within ~2 m of mineralisation. Breccia clasts are angular and set in a finer matrix in which locally intense hydrothermal alteration has developed.

The whole-rock major and trace element geochemical composition of selected felsic volcanic rocks are presented in Table 3.1. The IUGS classification scheme for normative *quartz-albite-orthoclase* places the ash flows into the rhyolitic compositional field (Fig 3.8). This is in agreement with the TAS plot classification (Fig 3.9). The immobile element classification scheme of Winchester and Floyd (1978), however, suggests the composition of these units is rhyolitic to dacitic (Fig 3.10). Despite efforts to select unaltered samples, a degree of hydrothermal alteration is present, which could impact such classification schemes.

Welding and compaction of the footwall ash flow tuff produced a relatively dense and massive rock with varying contents of fine quartz crystals and flattened pumice. The flattened pumice fragments locally give an appearance of parallel foliation to the rock (Fig 3.11 b). The welded units generally are gray with pervasive evidence of devitrification and recrystallization of quartz and sericite.

Welded tuffs consist predominantly of quartz, minor feldspar crystals and crystal fragments, set in a fine quartzo-feldspathic matrix (Fig 3.12). The groundmass of the welded ash flow tuffs is extensively devitrified and recrystallized, which has transformed a vitroclastic texture to a fine crystalline matrix of anhedral quartz and alkali feldspar.

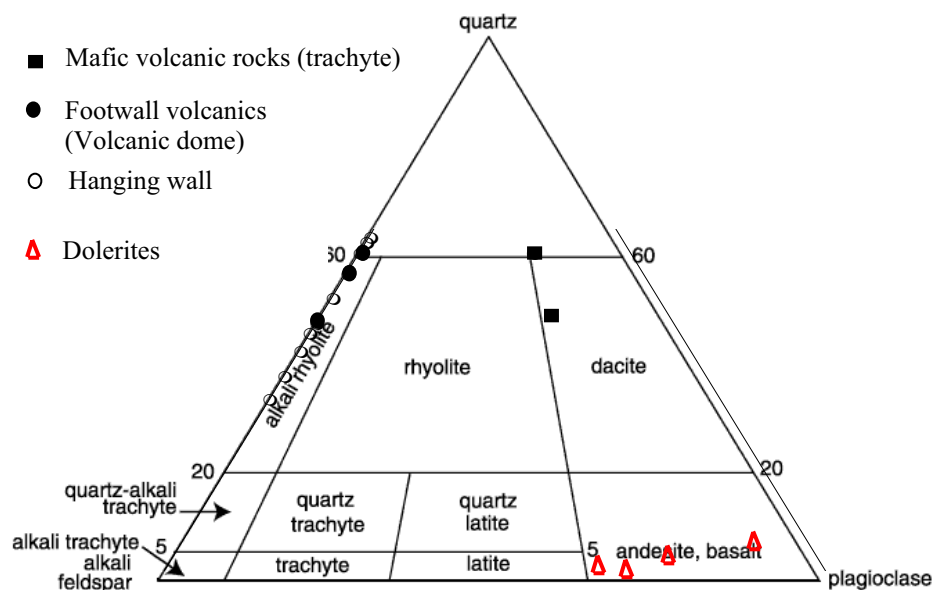
The generally equidimensional fine quartz crystals have grown and interlock in the groundmass. Fine grained sericite and chlorite locally overprint the devitrified matrix of

the ash flows by up to 10 % and is generally associated with devitrified quartz aggregates and the rims of quartz grains.



**Figure 3. 7 Polished slabs of the footwall carbonates and sandstone.**

- A: Footwall limestone with pebbly, sand and silt size clasts of quartz (hole B2-135 m).
- B: Tuffaceous silt banding (dark laminations) in sparitic limestone (hole B2-149 m).
- C: Interbed of calcareous siltstone and sandstone with a dolomite clast in the footwall carbonate unit, east of hole B35.



**Figure 3. 8 Plot of normative composition of hanging wall and footwall volcanic rocks of the Esfordi mineralizing system.**

Quartz crystals (0.1-3 mm) are generally embayed (Fig 3.12 a, i and j). The proportions of crystals and crystal fragments, pumice fragments and lithic fragments each vary from 0 to 15 %. The majority of samples have very low content of lithic fragments. The quartz grains are commonly overgrowth by fine grained quartz-sericite.

Flattened pumice clasts or fiamme, ranging from 0.1-4 mm, are generally filled by sericite and quartz (Fig 3.12 e, f and m). The flattening orientation of the pumice is indicative of the diagenic compaction orientation of the ignimbrites.

In some samples, the matrix contains euhedral to subhedral albite and K-feldspar phenocrysts with anhedral quartz crystals (Fig 3.12 d, l and m). Some feldspar phenocrysts have a pale, narrow rim interpreted to be an overgrowth of a later generation of alkali feldspar. Quartz crystals are generally corroded and have a thin overgrowth of quartz and sericite.

**Table 3.1 Whole rock major and trace element geochemical compositions of igneous rocks in the Esfordi host rock sequence.**

| Footwall sequence                |          |          |             |             |             |             |             |             |
|----------------------------------|----------|----------|-------------|-------------|-------------|-------------|-------------|-------------|
| Sample                           | Bh10-82  | 82-      | Bh8-65      | Bh7-41      | 31-         | ER4         | ER5         | ER6         |
| Rock type                        | Trachyte | Trachyte | Welded tuff | Welded tuff | Welded tuff | Welded tuff | Welded tuff | Welded tuff |
| SiO <sub>2</sub>                 | 46.98    | 53.84    | 74.17       | 70.76       | 70.19       | 73.16       | 71.62       | 72.21       |
| TiO <sub>2</sub>                 | 1.19     | 0.17     | 0.23        | 0.14        | 0.18        | 0.18        | 0.15        | 0.14        |
| Al <sub>2</sub> O <sub>3</sub>   | 15.53    | 16.52    | 12.62       | 10.48       | 11.18       | 12.28       | 11.84       | 11.02       |
| Fe <sub>2</sub> O <sub>3</sub> T | 10.73    | 6.64     | 2.56        | 1           | 1.5         | 2.71        | 2.84        | 3.12        |
| MnO                              | 0.08     | 0.08     | 0.01        | 0.04        | 0.05        | 0.02        | 0.04        | 0.06        |
| MgO                              | 3.56     | 0.59     | 0.68        | 2.35        | 0.87        | 1.24        | 0.92        | 0.94        |
| CaO                              | 5.2      | 5.93     | 0.79        | 2.41        | 2.78        | 2.29        | 3.26        | 2.61        |
| Na <sub>2</sub> O                | 5.33     | 3.54     | 5.27        | 0.36        | 0.34        | 0.51        | 0.69        | 0.21        |
| K <sub>2</sub> O                 | 1.12     | 6.7      | 2.64        | 7.45        | 8.53        | 5.18        | 5.27        | 7.02        |
| P <sub>2</sub> O <sub>5</sub>    | 0.2      | 0.11     | 0.06        | 0.03        | 0.05        | 0.18        | 0.05        | 0.04        |
| LOI                              | 10.33    | 6.19     | 1.81        | 4.57        | 3.32        | 2.13        | 3.61        | 3.25        |
| Total                            | 100.29   | 100.31   | 101.2       | 99.62       | 98.99       | 99.88       | 100.29      | 100.62      |
| Ba                               | 147.9    | 283.9    | 612.9       | 550.5       | 2888.5      | NA          | NA          | NA          |
| Cd                               | BLD      | BLD      | BLD         | BLD         | BLD         | NA          | NA          | NA          |
| Co                               | 24.8     | 9.5      | 3.3         | BLD         | 0.7         | BLD         | BLD         | BLD         |
| Cr                               | 153.2    | 65.2     | 146.9       | 100.3       | 85.3        | BLD         | BLD         | BLD         |
| Cu                               | 8.40     | 11.6     | 9.6         | 9.5         | 31.8        | NA          | NA          | NA          |
| Ga                               | 20.3     | 28.8     | 13.8        | 13.3        | 11.9        | NA          | NA          | NA          |
| Mo                               | 1.8      | 10.3     | 5.4         | BLD         | 2.6         | NA          | NA          | NA          |
| Nb                               | 8.6      | 128.3    | 7           | 2.9         | 5.6         | 2.3         | 4.5         | 6.1         |
| Ni                               | 39.9     | 7.1      | 8.7         | 10.6        | 8.3         | 2.2         | 12.1        | 10.8        |
| Pb                               | 5.8      | 6.3      | 4.6         | 5           | 4.9         | NA          | NA          | NA          |
| Rb                               | 40.2     | 156      | 48.9        | 162.9       | 179.9       | NA          | NA          | NA          |
| Sb                               | BLD      | BLD      | BLD         | 5.2         | 4.3         | NA          | NA          | NA          |
| Sn                               | BLD      | 6.9      | 2           | 7.8         | BLD         | NA          | NA          | NA          |
| Sr                               | 70.9     | 148.5    | 47.5        | 32.4        | 64.8        | NA          | NA          | NA          |
| Th                               | BLD      | 15.4     | 21.1        | 7.9         | 16          | NA          | NA          | NA          |
| U                                | 2.1      | 4.5      | 4.9         | 3.3         | 2.9         | NA          | NA          | NA          |
| V                                | 196.9    | 14.5     | 33          | 25.2        | 34.3        | 14.6        | 34.2        | 24.8        |
| Y                                | 34.08    | 29.04    | 16.4        | 4.6         | 28.7        | 26.1        | 12.8        | 18.6        |
| Zn                               | 32.9     | 21.6     | 10.7        | 9.9         | 10.3        | NA          | NA          | NA          |
| Zr                               | 183.3    | 946.5    | 189.3       | 144.9       | 159         | 274.5       | 59.1        | 149.2       |
| La                               | 20       | 156.5    | 23.5        | 31.5        | 39.3        | NA          | NA          | NA          |
| Ce                               | 30.8     | 276.8    | 52.5        | 61.5        | 84.3        | NA          | NA          | NA          |
| Pr                               | 3.7      | 24.7     | 5.6         | 5.2         | 7.8         | NA          | NA          | NA          |
| Nd                               | 15.3     | 85.1     | 19.4        | 18.7        | 27.8        | NA          | NA          | NA          |
| Sm                               | 3.7      | 12.9     | 3.1         | 2.8         | 5.3         | NA          | NA          | NA          |
| Eu                               | 1.2      | 2.5      | 0.6         | 0.7         | 1.8         | NA          | NA          | NA          |
| Gd                               | 4.6      | 10.8     | 2.3         | 2.2         | 5.6         | NA          | NA          | NA          |
| Tb                               | 0.7      | 1.4      | 0.3         | 0.3         | 1.1         | NA          | NA          | NA          |
| Dy                               | 5.4      | 7.5      | 1.4         | 1.3         | 5.9         | NA          | NA          | NA          |
| Ho                               | 1.1      | 1.1      | 0.2         | 0.3         | 1.3         | NA          | NA          | NA          |
| Er                               | 3.8      | 3.1      | 1.0         | 0.9         | 3.9         | NA          | NA          | NA          |
| Tm                               | 0.5      | 0.3      | 0.2         | 0.2         | 0.6         | NA          | NA          | NA          |
| Yb                               | 3.7      | 1.8      | 1.4         | 1.8         | 3.8         | NA          | NA          | NA          |
| Lu                               | 0.5      | 0.2      | 0.2         | 0.3         | 0.6         | NA          | NA          | NA          |

Trace elements of samples with ER prefix were analysed by NAA, other sample analysed by XRF and ICP-MS, BLD: Below level of detection, NA: not analysed.

**Table 3.1 continued**

| Hanging wall sequence            |                  |          |          |          |          |          |                |                |
|----------------------------------|------------------|----------|----------|----------|----------|----------|----------------|----------------|
| Sample                           | 23-N.<br>Esfordi | RT3      | 105      | ER1      | ER2      | ER3      | ER7            | ER8            |
| Rock type                        | Syenite          | Rhyolite | Rhyolite | Rhyolite | Rhyolite | Rhyolite | Welded<br>tuff | Welded<br>tuff |
| SiO <sub>2</sub>                 | 56.89            | 70.14    | 70.69    | 72.06    | 74.85    | 74.21    | 73.3           | 72.35          |
| TiO <sub>2</sub>                 | 0.19             | 0.191    | 0.19     | 0.25     | 0.15     | 0.16     | 0.09           | 0.2            |
| Al <sub>2</sub> O <sub>3</sub>   | 19.33            | 12.14    | 11.98    | 12.36    | 9.72     | 11.57    | 10.37          | 11.58          |
| Fe <sub>2</sub> O <sub>3</sub> T | 4.77             | 1.72     | 2.05     | 3.14     | 2.88     | 2.16     | 0.531045       | 0.815092       |
| MnO                              | 0.13             | 0.005    | 0.03     | 0.04     | 0.02     | 0.02     | 0.09           | 0.04           |
| MgO                              | 1.01             | 0.21     | 0.63     | 0.59     | 0.41     | 0.61     | 0.44           | 1.43           |
| CaO                              | 1.11             | 1.7      | 1.83     | 0.86     | 0.92     | 1.29     | 2.21           | 3.15           |
| Na <sub>2</sub> O                | 7.05             | 0.31     | 0.45     | 6.03     | 2.82     | 1.23     | 0.15           | 0.14           |
| K <sub>2</sub> O                 | 6.05             | 10.369   | 9.54     | 2.02     | 3.64     | 6.46     | 8.4            | 5.59           |
| P <sub>2</sub> O <sub>5</sub>    | 0.11             | 0.028    | 0.04     | 0.08     | 0.09     | 0.06     | 0.12           | 0.06           |
| LOI                              | 3.04             | 2.17     | 2.07     | 3.11     | 3.83     | 2.47     | 3.69           | 4.81           |
| Total                            | 99.68            | 98.983   | 99.5     | 100.54   | 99.33    | 100.24   | 99.39104       | 100.1651       |
| Ba                               | 259.2            | 668.9    | 550.5    | NA       | NA       | NA       | NA             | NA             |
| Cd                               | BLD              | BLD      | BLD      | NA       | NA       | NA       | NA             | NA             |
| Co                               | 5.7              | BLD      | 1.5      | BLD      | BLD      | BLD      | BLD            | BLD            |
| Cr                               | 55.8             | NA       | 121.4    | NA       | NA       | NA       | NA             | NA             |
| Cu                               | 10.2             | NA       | 16.9     | NA       | NA       | NA       | NA             | NA             |
| Ga                               | 38.9             | NA       | 20.9     | NA       | NA       | NA       | NA             | NA             |
| Mo                               | 6.3              | BLD      | 3        | NA       | NA       | NA       | NA             | NA             |
| Nb                               | 117.7            | NA       | 4.1      | 3.2      | 6.5      | 4.8      | 8.2            | 4.9            |
| Ni                               | 6.3              | BLD      | 15.9     | 2.89     | 2.75     | 1.66     | BLD            | BLD            |
| Pb                               | 22.4             | 4.4      | 4.5      | NA       | NA       | NA       | NA             | NA             |
| Rb                               | 205.7            | 161.2    | 152.6    | NA       | NA       | NA       | NA             | NA             |
| Sb                               | BLD              | NA       | BLD      | NA       | NA       | NA       | NA             | NA             |
| Sn                               | 15               | BLD      | BLD      | NA       | NA       | NA       | NA             | NA             |
| Sr                               | 243.9            | 62.5     | 39.6     | NA       | NA       | NA       | NA             | NA             |
| Th                               | 32.5             | 9.4      | 17.7     | NA       | NA       | NA       | NA             | NA             |
| U                                | 7.8              | 4.4      | 6.9      | NA       | NA       | NA       | NA             | NA             |
| V                                | 17.7             | 19.2     | 27.1     | 13.5     | 16.2     | 27.3     | 21.4           | 11.6           |
| Y                                | 26.5             | 70.8     | 14.7     | 10.5     | 31.4     | 24.2     | 23.1           | 11.5           |
| Zn                               | 195.1            | 8.3      | 11.7     | NA       | NA       | NA       | NA             | NA             |
| Zr                               | 1014.3           | 173.7    | 159.1    | 92.3     | 246.7    | 153.8    | 121.6          | 182.5          |
| La                               | 71.8             | 91.4     | 118.8    | NA       | NA       | NA       | NA             | NA             |
| Ce                               | 224.7            | 37.1     | 47.8     | NA       | NA       | NA       | NA             | NA             |
| Pr                               | 20.4             | 4.1      | 4.2      | NA       | NA       | NA       | NA             | NA             |
| Nd                               | 57.0             | 15.2     | 14.5     | NA       | NA       | NA       | NA             | NA             |
| Sm                               | 7.6              | 2.5      | 2.9      | NA       | NA       | NA       | NA             | NA             |
| Eu                               | 1.4              | 0.4      | 0.6      | NA       | NA       | NA       | NA             | NA             |
| Gd                               | 6.5              | 3.5      | 2.8      | NA       | NA       | NA       | NA             | NA             |
| Tb                               | 1.1              | 0.5      | 0.5      | NA       | NA       | NA       | NA             | NA             |
| Dy                               | 5.3              | 2.1      | 2.9      | NA       | NA       | NA       | NA             | NA             |
| Ho                               | 1.1              | 0.5      | 0.7      | NA       | NA       | NA       | NA             | NA             |
| Er                               | 2.8              | 1.6      | 2.1      | NA       | NA       | NA       | NA             | NA             |
| Tm                               | 0.4              | 0.3      | 0.3      | NA       | NA       | NA       | NA             | NA             |
| Yb                               | 2.1              | 1.8      | 2.4      | NA       | NA       | NA       | NA             | NA             |
| Lu                               | 0.3              | 0.4      | 0.4      | NA       | NA       | NA       | NA             | NA             |

**Table 3.1 continued.**

| Hanging wall mafic intrusions    |          |          |          |          |
|----------------------------------|----------|----------|----------|----------|
| Sample                           | 24       | 28-2     | 90       | 103      |
| Rock type                        | Dolerite | Dolerite | Dolerite | Dolerite |
| SiO <sub>2</sub>                 | 47.77    | 46.12    | 44       | 46.41    |
| TiO <sub>2</sub>                 | 2.59     | 2.72     | 3.21     | 1.243    |
| Al <sub>2</sub> O <sub>3</sub>   | 14.89    | 13.65    | 13.35    | 15.98    |
| Fe <sub>2</sub> O <sub>3</sub> T | 11.72    | 12.83    | 14.27    | 9.64     |
| MnO                              | 0.16     | 0.18     | 0.14     | 0.18     |
| MgO                              | 5.9      | 6.84     | 8.62     | 8.42     |
| CaO                              | 5.38     | 6.2      | 6.16     | 11.16    |
| Na <sub>2</sub> O                | 4.63     | 3.87     | 3.53     | 2.05     |
| K <sub>2</sub> O                 | 2.96     | 2.84     | 1.51     | 0.836    |
| P <sub>2</sub> O <sub>5</sub>    | 0.89     | 0.93     | 0.95     | 0.12     |
| LOI                              | 2.75     | 3.51     | 3.87     | 3.97     |
| Total                            | 99.65    | 99.78    | 99.61    | 96.3     |
| Ba                               | 772.5    | 627.3    | 631.7    | 660.3    |
| Cd                               | 3.3      | 2        | 2.7      | 6.8      |
| Co                               | 33.5     | 37.7     | 38.2     | 60.6     |
| Cr                               | 233.1    | 260.3    | 356.9    | 423.9    |
| Ga                               | 26.2     | 23.9     | 23.7     | 16.8     |
| Nb                               | 81.6     | 78.2     | 66       | 3.8      |
| Ni                               | 103.8    | 133.9    | 214.2    | 131.9    |
| Pb                               | 15.3     | 16.3     | 6.1      | 10.4     |
| Rb                               | 78.5     | 83.4     | 44.7     | 22.6     |
| Sb                               | 0.01     | 0.01     | 0.01     | 3.3      |
| Sn                               | 11.9     | 5.1      | 9.8      | BLD      |
| Sr                               | 747.9    | 739      | 378.2    | 399.8    |
| Th                               | 14       | 16.7     | 8.5      | BLD      |
| U                                | 2.9      | BLD      | 4.3      | BLD      |
| V                                | 204      | 221.4    | 263.5    | 197.8    |
| Y                                | 33.8     | 35.3     | 38.5     | 22.3     |
| Zn                               | 149.4    | 190.7    | 115      | 91.5     |
| Zr                               | 580.6    | 501.7    | 371.8    | 80       |
| La                               | 156.4    | 105.4    | 62.4     | 11.7     |
| Ce                               | 179.4    | 191.7    | 144.2    | 30       |
| Pr                               | 16.9     | 21.2     | 14.5     | 3.7      |
| Nd                               | 65.1     | 76.9     | 59.4     | 16.5     |
| Sm                               | 11.1     | 13.4     | 11.0     | 3.7      |
| Eu                               | 3.8      | 4        | 3.6      | 1.3      |
| Gd                               | 10.6     | 12.5     | 10.3     | 4.6      |
| Tb                               | 1.6      | 1.9      | 1.5      | 0.7      |
| Dy                               | 7.7      | 8.9      | 7.4      | 4.2      |
| Ho                               | 1.5      | 1.8      | 1.4      | 0.8      |
| Er                               | 3.7      | 4.3      | 3.4      | 2.3      |
| Tm                               | 0.5      | 0.6      | 0.4      | 0.3      |
| Yb                               | 2.9      | 3.3      | 2.5      | 1.9      |
| Lu                               | 0.4      | 0.6      | 0.4      | 0.3      |

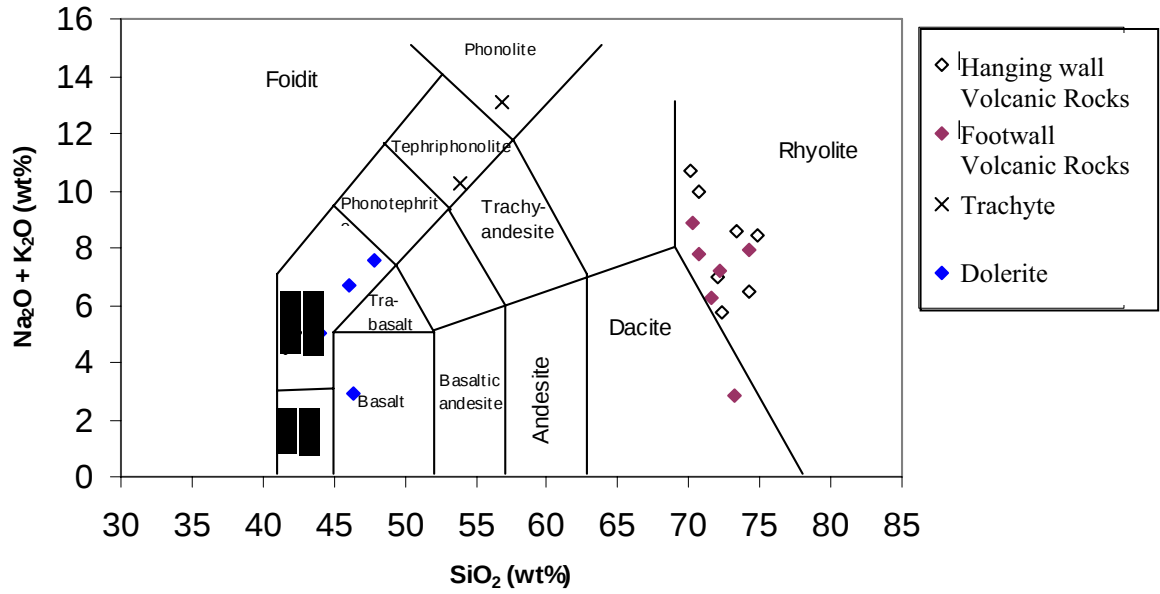


Figure 3. 9 Plots of the Esfordi host rock volcanic rocks in the TAS diagram.

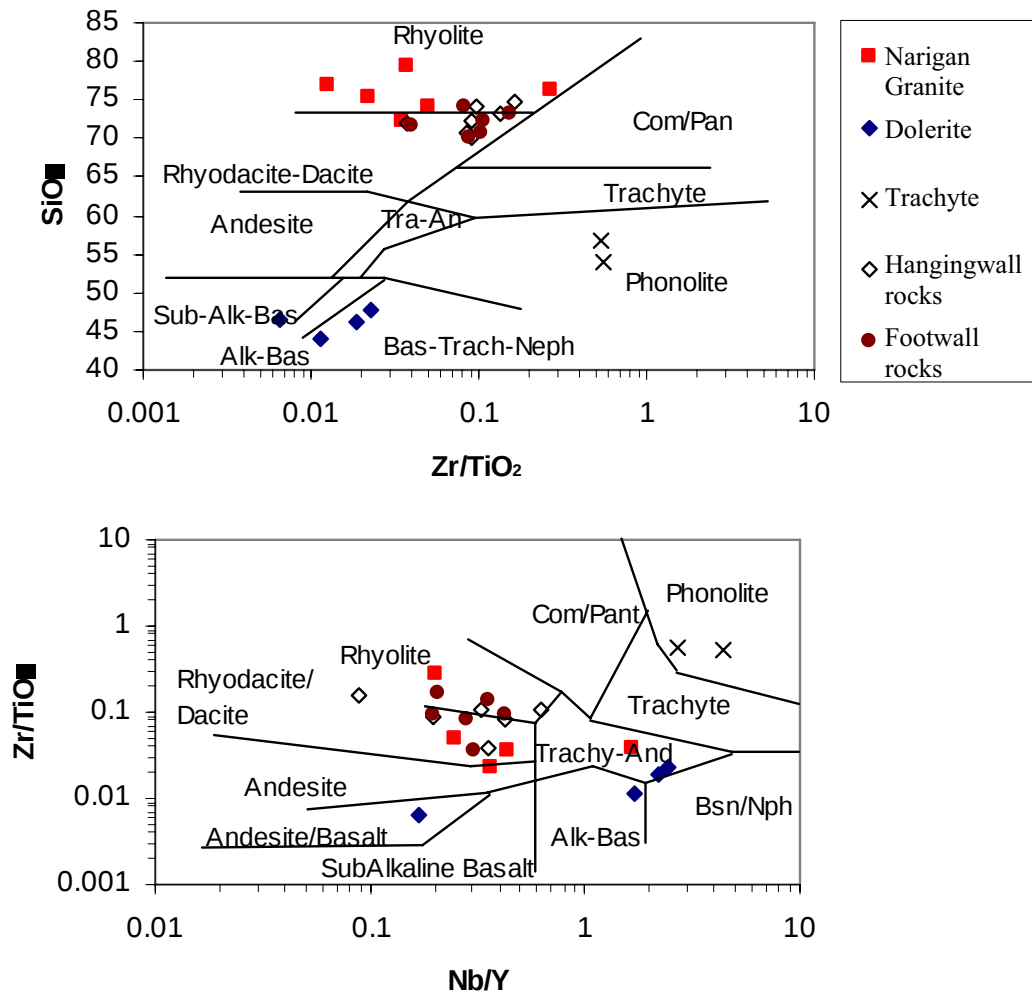
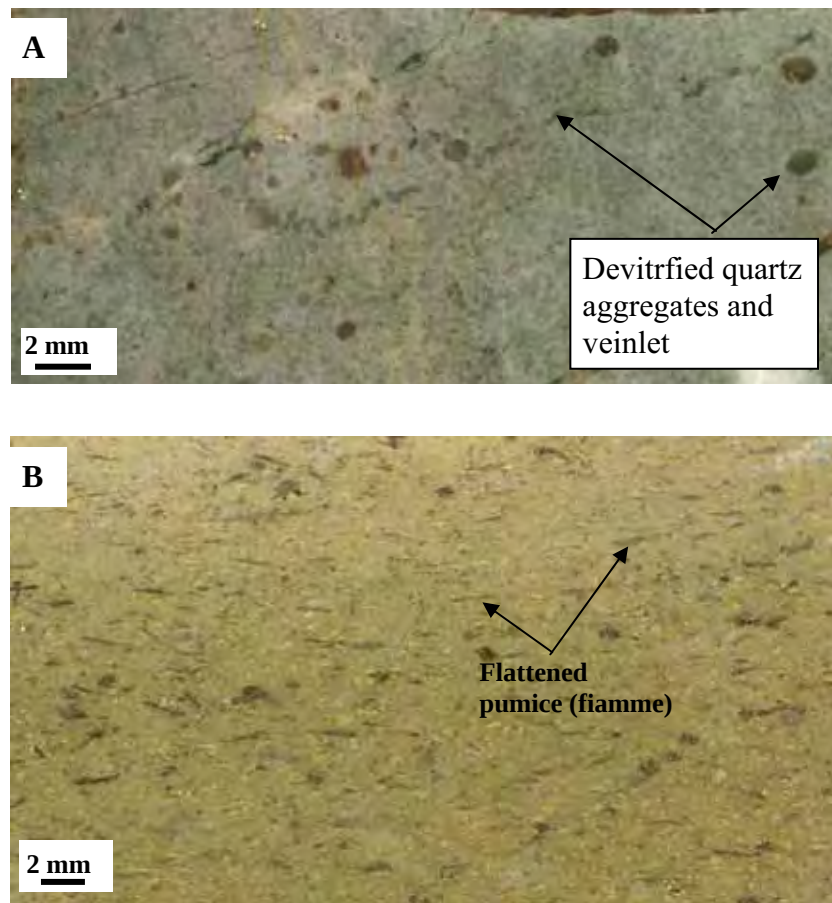
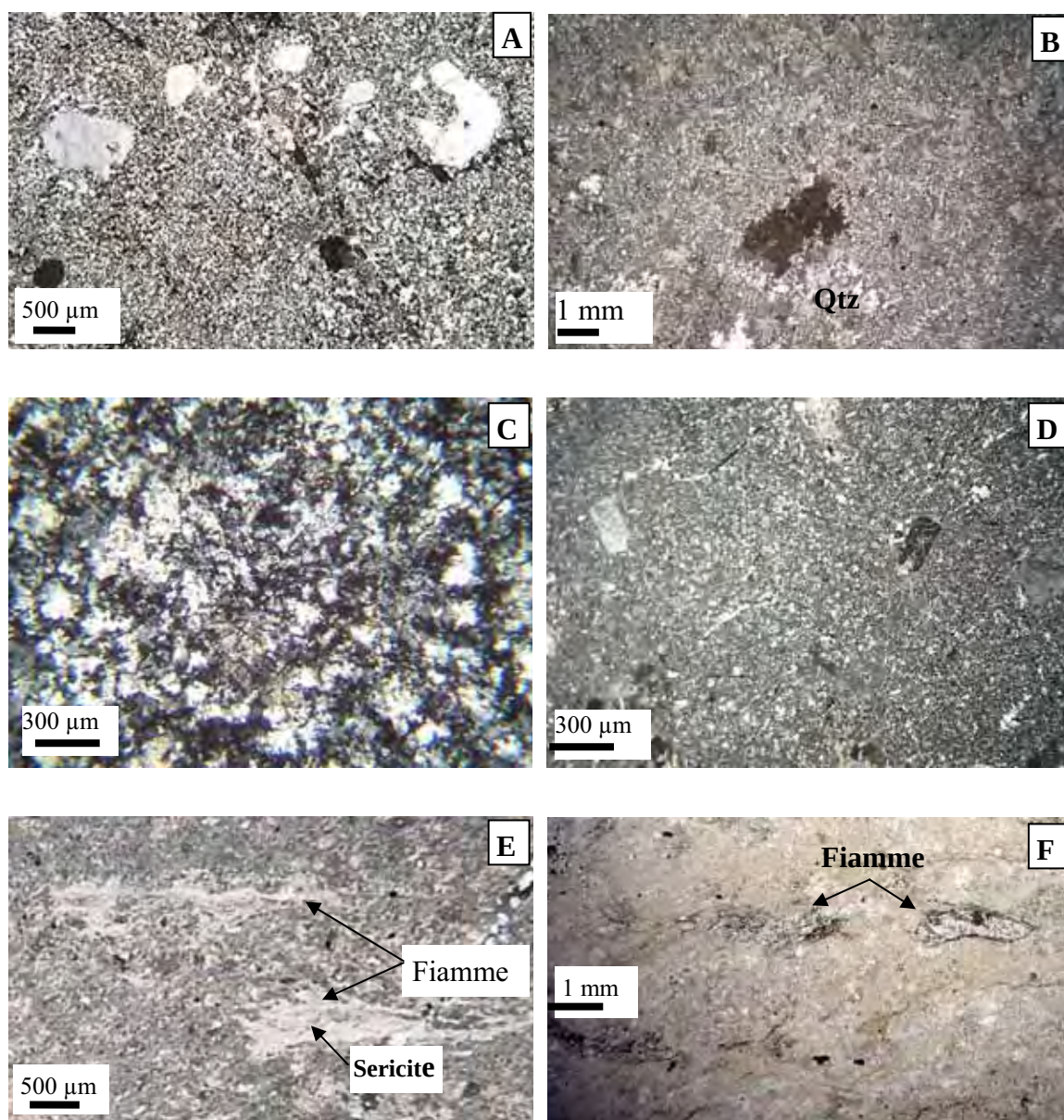


Figure 3. 10 Plot of Esfordi hanging wall and footwall volcanics and mafic intrusives using immobile element discrimination diagrams.



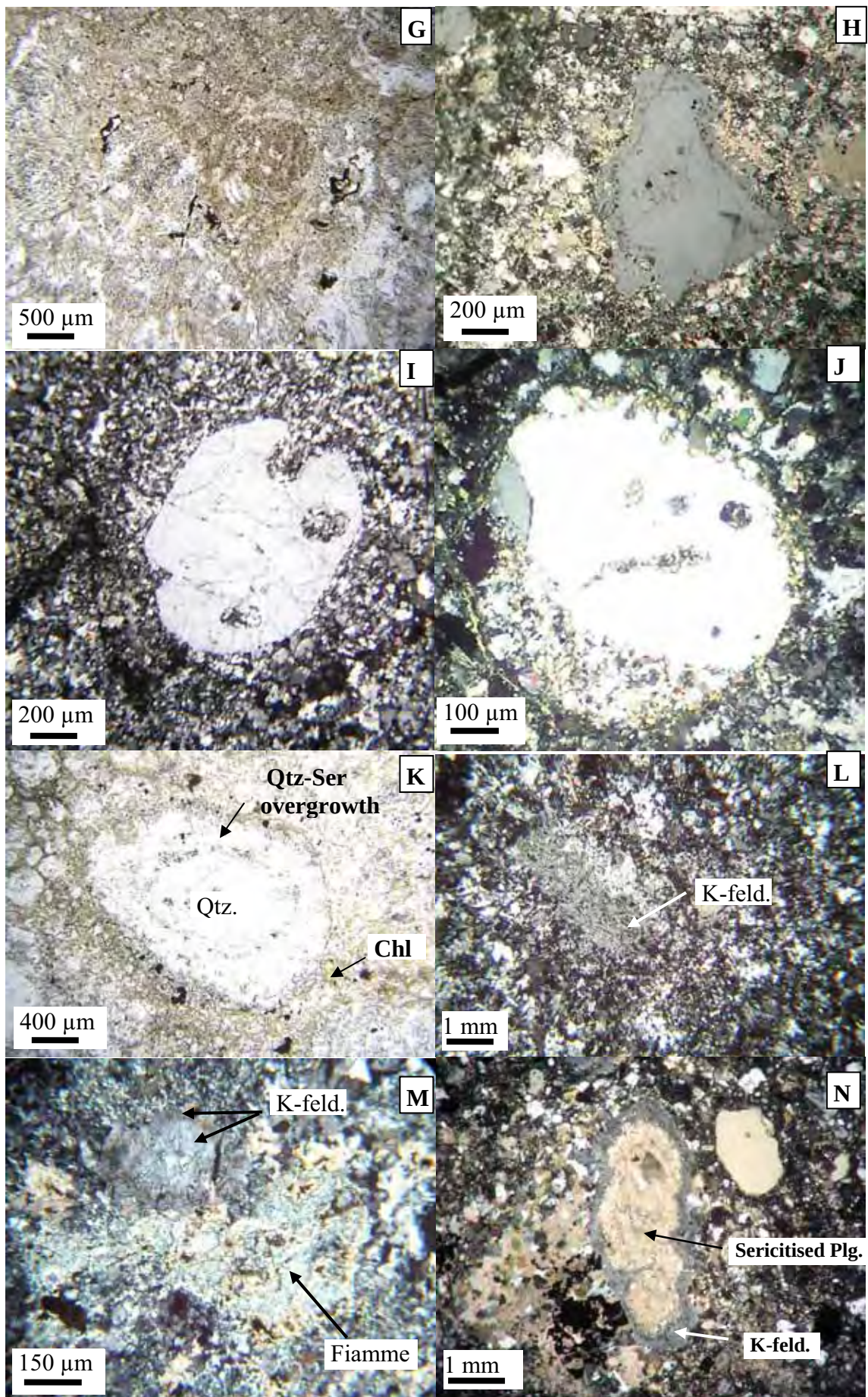
**Figure 3. 11 Two polished slab of the footwall welded ash flow tuff.**

- A: Quartz phenocryst in a fine devitrified matrix with late quartz veins.
- B: Flattened pumices (fiamme) in a fine devitrified ash tuff. A late epidote alteration overprints the fabric (hole B20-75 m).



**Figure 3. 12 Photomicrographs of Esfordi footwall welded ash flow tuffs.**

- A: Welded ash flow tuff with embayed quartz clasts (Bh8-65m, PPL).
- B: Welded ash flow with devitrified quartz and late carbonate overprint (Bh3-68 m, XPL).
- C: Devitrified quartzo-feldspatic matrix of welded ash flow tuff (Bh8-65m, XPL).
- D: Feldspar phenocryst in footwall welded ignimbrite with crystal, pumice and lithic fragments ( B64-108m, XPL).
- E and F: Flattened pumice (Fiamme) in a devitrified fine grained welded ash, oriented parallel to layering. Fiammes are filled by quartz and carbonates, (B20-75, PPL).



**Figure 3.12 Continued.**

- G: Vitroclastic groundmass of a rhyolitic ash flow with perlitic fractutres, the glass has been replaced by quartz, sericite and chlorite (B2-110 m, PPL).
- H: A overgrowth on quartz fragment in welded ash flow tuff (B9-99 m, XPL).
- I: Embayed quartz phenocryst in a devitrified matrix of ash flow (B2-110 m, XPL).
- J & K: Quartz with an overgrowth of the younger generation of quartz and sericite in footwall welded tuff (Bh9-99 m, XPL).
- L: K-feldspar crystal overgrowth the fine vitroclastic fabric of the footwall welded tuff (Bh7-41 m, XPL).
- M: Overgrowth of K-feldspar associated with a partially flattened pumice. The pumice filled with sericite and quartz in a vitroclastic fabric of a welded ash flow (B2-97 m, XPL).
- N: K-feldsar overgrowth on a sericitized and chloritized plagioclase crystal in footwall welded tuffs (Bh11-54 m, XPL).

A number of studies have suggested that a range of welded and unwelded tuffs can form by direct subaqueous eruption and subsequent water and/or gas-supported transport and deposition. These are usually interpreted to have formed as pyroclastic flow and surges and indirect remobilization and redeposition of material (Fisher and Schmincke, 1984; Cas and Wright, 1987; McPhie *et al.*, 1993). The association of intercalated carbonates and tuffaceous sandstones with traction current bedding is consistent with deposition in a shallow marine environment. The less pumiceous fragments would not be as prone to collapse and these show a granophyric growth of quartz and feldspar which seem to be related to higher porosity during fluid-vapor phase circulation (Schmincke and Swanson, 1967).

In some cases fiamme may have originally been unvesiculated juvenile clasts (Gibson and Tazieff, 1967). Fiamme usually indicate a single compactional flattening, however, in some welded tuffs the fiamme are stretched and show a lineation parallel to flow foliation, which indicates secondary mass flowage of the tuff during welding (rheomorphism) (Cas and Wright, 1987). Drusy quartz and feldspar infills in the matrix, pumice cavities and reticulated veinlets probably formed during percolation of fluids through ignimbrites during devitrification rather than later hydrothermal alteration. Daliran (1990) observed similar textures at Mishdovan and interpreted them to be indicative of high temperature processes in a welded ash flow.

Micropoikilitic quartz and alkali feldspar commonly form as the products of devitrification of rhyolitic glass in welded tuffs or rhyolitic flows (3.13 c and d). Lofgren (1971) originally suggested that micropoikilitic textures composed of fine-grained quartz and feldspar are characteristic products of high-temperature (above 300°C) devitrification of silicic glass, but that spherulitic structures and perlitic fractures are the result of rapid and low temperature (200°C) devitrification. The existence of all these features in the

welded tuff in the Esfordi footwall suggests both high and low temperature devitrification of their vitroclastic matrix.

The footwall sequence contains conformable trachytic bodies and a series of doleritic dykes. Several outcrops of gabbro and basalt also occur in the lower Tashk Formation, 5 km south-west of Esfordi. Despite, lack of chilled margins observation, the stratabound nature and microscopic features of trachytic rocks, suggest either intrusion as sill-like bodies or flows in the volcano-sedimentary sequence. The trachytic bodies are not exposed at the surface in the vicinity of Esfordi but is intersected in boreholes 10 and 53 (Fig. 3.4) and an exposure 2 km west of Esfordi. The contacts with the welded ash flows are sharp and linear. The trachytes are medium to fine grained weakly porphyritic rocks that are generally altered to chlorite-epidote-sericite assemblage with a light to dark greenish colour. Using the IUGS normative plot a composition of dacite is indicated, which probably is due to mild alteration whereas TAS and immobile element plots suggest phonolite to tephriphonolite composition (Figs. 3.8 to 3.10).

### **3.3 HANGING WALL SEQUENCE**

Some 350 m of volcanic, subvolcanic and sedimentary rocks of the CVSU have been documented in the hanging wall to the Esfordi mineralisation (Figs 3.3, 3.4, 3.13 and 3.19).

Fe–P mineralisation at Esfordi is part of a varied package of volcanoclastic and chemical sediments some ~200 m thick. The low-grade mineralization extends up into the hanging wall. This package is known by mine geologists as the “productive zone” or as “green rock”, due to amphibole-rich alteration. Other horizons, patches and veins are grey, cream, pink or purple due to the development of secondary quartz, carbonate, K-feldspar and hematite, particularly in the rock matrices and overgrowths (Figs 3.15 and 3.17). The rocks in this interval are interbedded polymictic pebbly sandstones, unwelded

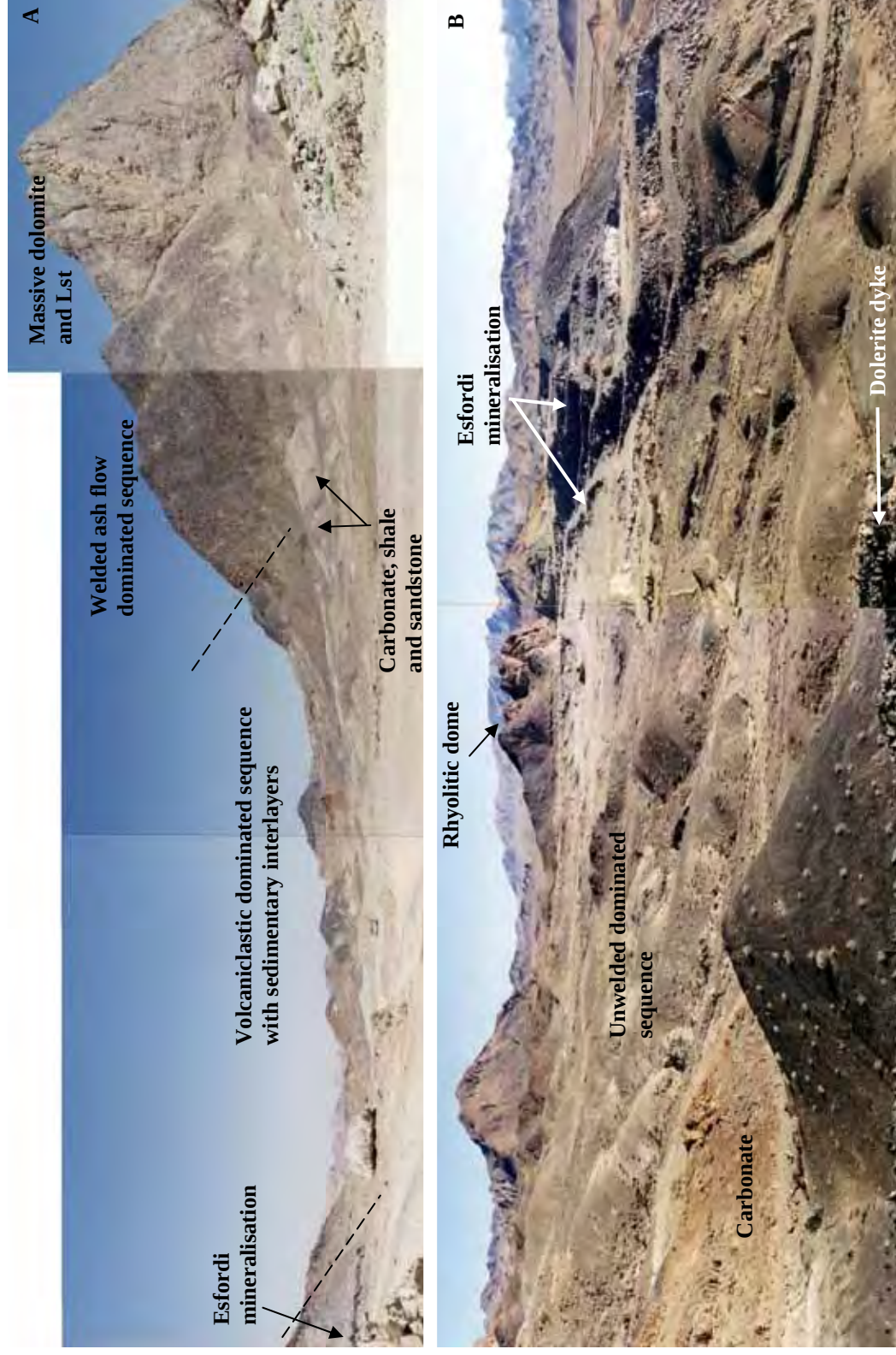
ash flows, shales, limestones and jaspilite without great lateral continuity between drill holes (~600 m). The package is intruded by irregular trachytic and doleritic bodies, similar to those in the footwall.

The most distinctive lithology is a polymictic pebbly sandstone, which forms a series of poorly bedded units up to 10 m thick. It also contains thinly bedded interbeds of ash up to 50 cm thick (Fig 3.19). The clasts in the polymictic pebbly sandstone are generally poorly sorted (<1 - >30 mm) and variously rounded (Figs. 3.14 A-G and 3.16A-J). The clasts are predominantly lithic (10~60 %) with lesser amounts of crystal fragments (<25 %). The matrix is now silt-sized but may have originally been coarser glass shards. A calcareous matrix may be locally prominent. The nature of this matrix is often obscured by subsequent hydrothermal fluid interaction.

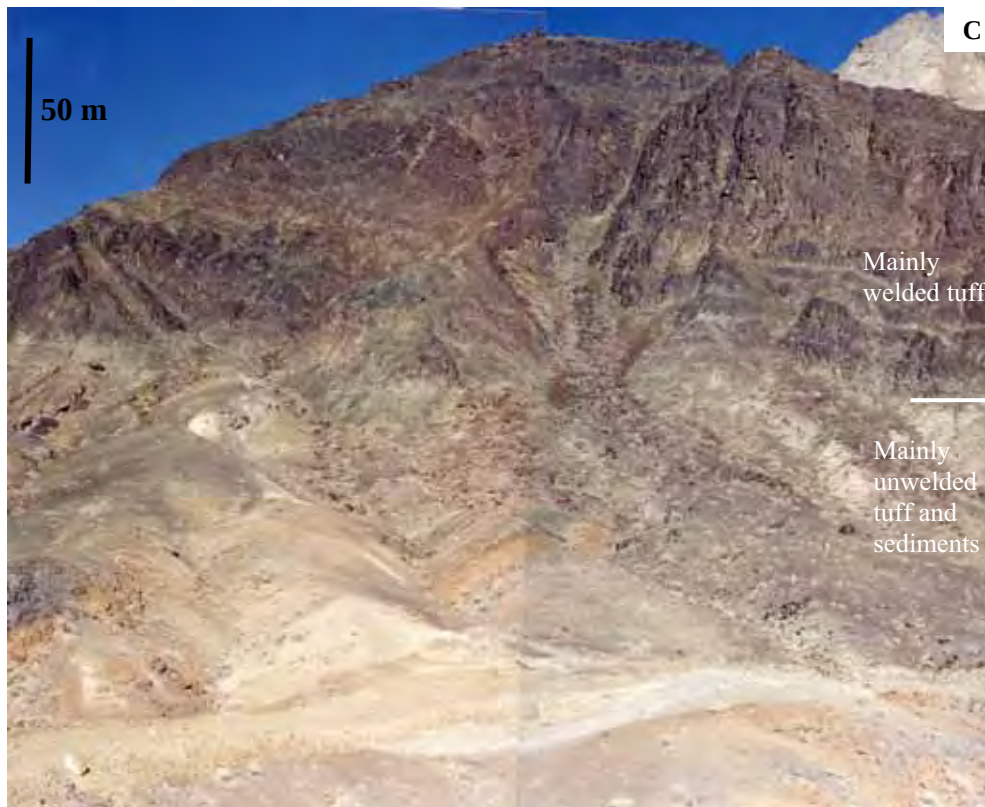
A persistent 15 m thick limestone bed is exposed at the base of the sequence. The carbonate horizons are generally thinly bedded with sand and silt size clastic fragments and interbeds of mudstone and sandstone.

Macroscopic and microscopic evidences of the Esfordi host rocks point to a shallow marine environment (Cas and Wright 1987; McPhie et al., 1993). Among these evidences, geometry of sedimentary units, lithology, and sedimentary structures are more characteristic. The conglomerate and pebbly sandstone contain distinctive lithic fragments and interbeds of sandstone, siltstone, mudstone and carbonate (Fig 3.14 A-E and Fig 4.21). The thickness of these sedimentary beds varies and sometimes pinch out. Interbeds of welded ash flows within the sequence are also evident of terrestrial or shallow depositional environment.

Sedimentary structures such as cross stratification, imbrications and sole structures such as flutes can interpreted as shallow marine environment (Fig 3.19).



**Figure 3.13** (see next page for caption).



**Figure 3. 13 Outcrop pattern of volcanic and volcanoclastic sequence of the Esfordi hanging wall.**

A and C: The Esfordi hanging wall sequence including unwelded lapilli tuffs, tuffaceous pebbly sandstone and siltstone, and intercalated limestone, dolomite and marl in the lower part, and dominated welded ash flow tuff sequence with unwelded intervals in the upper part. The massive carbonate sequence overlies the volcanic and volcanoclastic sequence (looking N). B: The volcanoclastic dominated sequence overlying the Esfordi mineralisation. Note the felsic volcanic dome at the back of the image (looking SE).

Prominent among the lithic clasts are rhyolitic volcanic rocks with distinctive embayed quartz crystals. Among these are welded and unwelded ash flow fragments (Fig 3.14 A-G) as well as rhyolitic lavas with devitrification textures (Fig 3.16). Tuffaceous sandstones, limestone and siltstone clasts are common. Mafic volcanic clasts are also widely distributed, their original fabrics typically obscured by amphibole, biotite and chlorite alteration extending into the adjacent matrices. Fragments of magnetite  $\pm$  hematite  $\pm$  apatite are ubiquitous, ranging from pebbles to sand size grains on which hematite overgrowths are developed (Fig 3.19). Other lithic clasts include hydrothermal alteration assemblages such as vein quartz  $\pm$  sericite.

Whereas many quartz fragments in these sandstones are characterised by embayments suggesting derivation from felsic volcanic rocks, others have features more typical of the metamorphic basement such as undulose extinction. The K-feldspar crystals and crystal fragments typically have a narrow overgrowth of younger generation K-feldspar. Magnetite grains are locally enriched in sedimentary laminae, up to 10 cm thick, within the sandstones and may represent current lag accumulations (Fig 3.19).

Polymictic pebbly sandstone contains localised zones with more monomictic character, particularly those rich in rhyolitic clasts. Such intervals may represent unwelded ash flows or resedimented pyroclastics. Interbeds of shale, carbonate and jaspilite indicate episodes of lower rates of clastic sedimentation. A range of clasts of Fe-oxide  $\pm$  apatite, altered wall rocks and mafic intrusions, widespread matrix alteration and jaspilite horizon suggest episodic unroofing of an active mineralised system and the reworking of this detritus together with unconsolidated volcanic debris under shallow water conditions (a theme revisited in subsequent chapters).

The hanging wall volcanoclastic facies contains various irregular intrusions. The whole rock major and trace element geochemical composition of mafic volcanic rocks of the Esfordi sequence is shown in Table 3.1. The plot of immobile elements classification

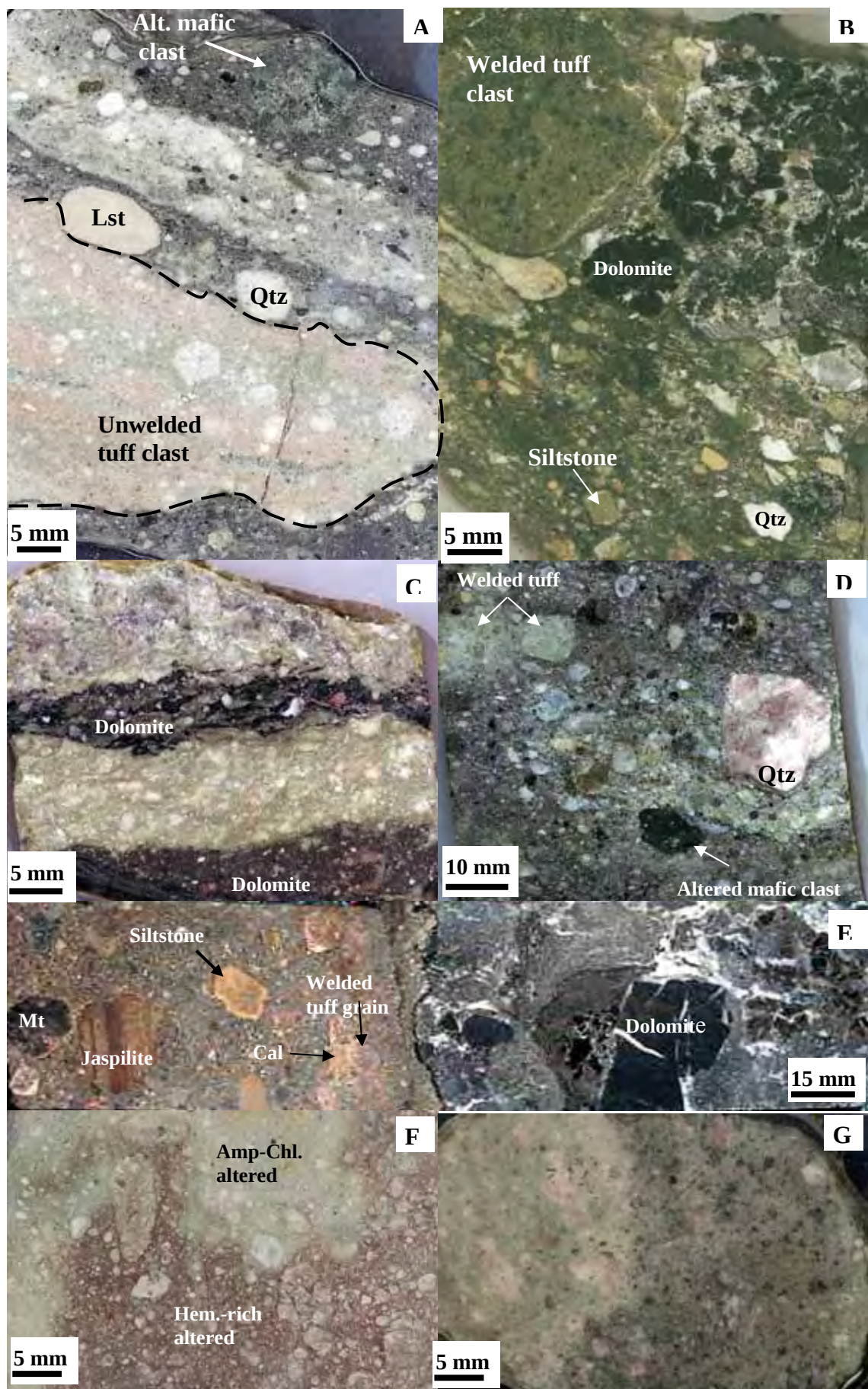


Figure 3. 14 (Caption on next page.)

**Figure 3.14 Polished slab of volcanoclastic rocks of the Esfordi hanging wall.**

- A: Lapilli tuff (dark part) interbedded with tuffaceous pebbly sandstone with various clasts of carbonate, siltstone, mafic igneous rocks and quartz crystals (Hole B21-68 m).
- B: Contact of a polymict breccia and pebbly sandstone. Note the large clast of welded tuff and dolomite.
- C: Interbedded calcareous and non-calcareous tuffaceous sandstone (Hole B2-100 m).
- D & E: Polymict tuffaceous sandstone with angular to subrounded welded, carbonate, jaspilite and magnetite clasts and crystal fragments in a tuffaceous pumice and ash-rich matrix (D) and sand and silt matrix (E). (Hole B64-75 m).
- F & G: Tuffaceous sandstone with pumice and quartz crystal fragments with various greenish tints due to Fe-oxide and amphibole-chlorite enrichments (Hole B54-60 m).

scheme indicates that these rocks have a phonolite composition (Fig 3.10). These bodies appear stratabound but with a poor continuity and have trachytic textures. Alkali feldspar, plagioclase, amphibole and biotite are common minerals. The fabric is generally hypidiomorphically granular to porphyritic (Fig 3.18). They typically comprise 60-70 % K-feldspar, 10-20 % nepheline, amphibole and biotite, 5-15 % overprinted carbonate and quartz and accessory minerals including opaque minerals chlorite and epidote.

The basal volcanoclastic part of the hanging wall sequence is adjacent to and overlain by rhyolite domes (Fig 3.15), welded ash flows intercalated with lesser unwelded intervals. Given the poorly developed layering in these units exposed adjacent to Esfordi, and lack of drill hole intersections, stratigraphic thickness is poorly constrained. The welded ash flow horizons of the hanging wall sequence are generally gray and have similar textures and fabrics to the footwall welded tuffs.

Rhyolitic flows and domes are common in the upper parts of the Esfordi hanging wall. Whole rock major and trace element composition is shown in Table 3.1. Plots of normative and immobile elements indicate a rhyodacite to dacite composition (Figs. 3.9 and 3.10). A prominent rhyolitic dome located 100 m to the east of the Esfordi mineralisation, is 200 m long with an apparent thickness of ~80 m. The dome interior has a range of aphanitic, porphyritic, spherulitic, and micropoikilitic textures with local flow banding (Fig 3.17).

Vesicles and amygdales are common in rhyolitic lavas at Esfordi (Fig 3.17). The majorities of amygdales are stretched and range from 0.1–2 mm. The Esfordi felsic lavas have flow foliations of varying intensity and generally horizontal in direction. The margins contain flow breccia, and resedimented hyaloclastites. A mixture of lava and sediments is also observed in some exposures and bedding of volcanoclastic rocks peripheral to domes is generally disturbed. These are interpreted as peperites. Phenocrysts in the rhyolitic lavas

and domes have complex assemblages and heterogeneous distributions. Some phenocrysts are primary and crystallised within the felsic magma whereas, others are trapped as xenocrysts. Phenocryst abundances range up to 30 % and are dominantly composed of relatively large quartz (500  $\mu\text{m}$ ), euhedral to subhedral plagioclase and orthoclase. The groundmass is of glassy to microcrystalline quartz and feldspars. Phenocrysts are partially resorbed which results in embayed and rounded outlines. A micropoikilitic rim of fine-grained quartz around quartz phenocrysts is also common.

Based on modern examples of shallow subaqueous silicic eruptions (Reynolds *et al.*, 1980) the emplacement of a rhyolitic dome into unconsolidated sea-floor sediments invariably causes quench fragmentation, auto brecciation and resedimentation. Seawater confining pressures determine whether eruptions are effusive or explosive (Cas and Wright, 1991). The overlying massive rhyolitic pumice and lithic-rich breccia and stratified pumice sandstone in the hanging wall of the Esfordi deposit indicates pyroclastic eruptions. The minor relicts of glass is also observed but the majority of the rhyolites have a very fine ground mass, which is probably a devitrified glassy matrix given its similarity to rocks described by McPhie *et al.* (1993) in the Mount Read Volcanics of western Tasmania.

Förster and Jafarzadeh (1994) recognised several rhyolitic domes (500-1000 m in diameter) west of Kushk, around Mishdovan and Esfordi. These rhyolitic to rhyodacitic lavas and domes (Fig 3.3) together with diverse volcanoclastic rocks and sediments including thin bedded limestone and dolomites, and basement-derived sandstones are the essential elements of the volcanic architecture in the Esfordi sequence. This assemblage of volcanic facies is typical of shallow felsic submarine volcanic successions (McPhie *et al.*, 1993).

A jaspilite layer up to 6 m thick is exposed about 100 m above the mineralizing zone. This jaspilite layer with conformable stratigraphic relation with the enclosing volcano-

sedimentary sequence is well exposed some 500 m NW of Esfordi. The jaspilite layer will be discussed in chapter 4.



**Figure 3. 15 A rhyolitic lava dome in the Esfordi volcanic succession ~100 m east of Esfordi (looking northeast).**

Mafic bodies have a basaltic-andesitic composition under the IUGS classification scheme, but a basalt-andesite and trachyte composition under the classification scheme of Winchester and Floyd (1978) (Figs. 3.9 and 3.10).

The most altered doleritic bodies are extensively brecciated with significant amount of hydrothermal amphibole, apatite and Fe-oxide and are interpreted to be older than fresh dolerite intrusions which were likely emplaced after the mineralization of Esfordi.

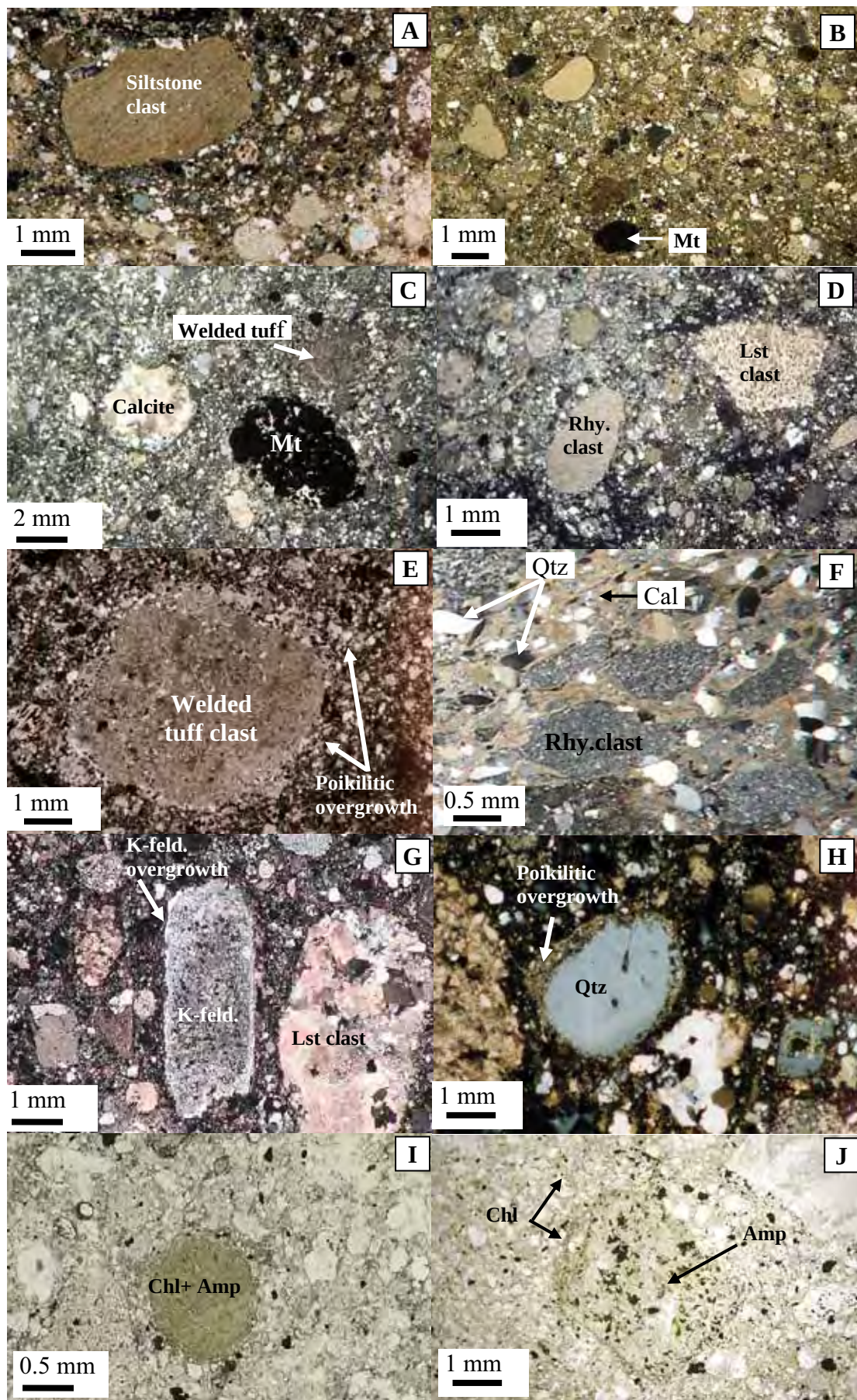
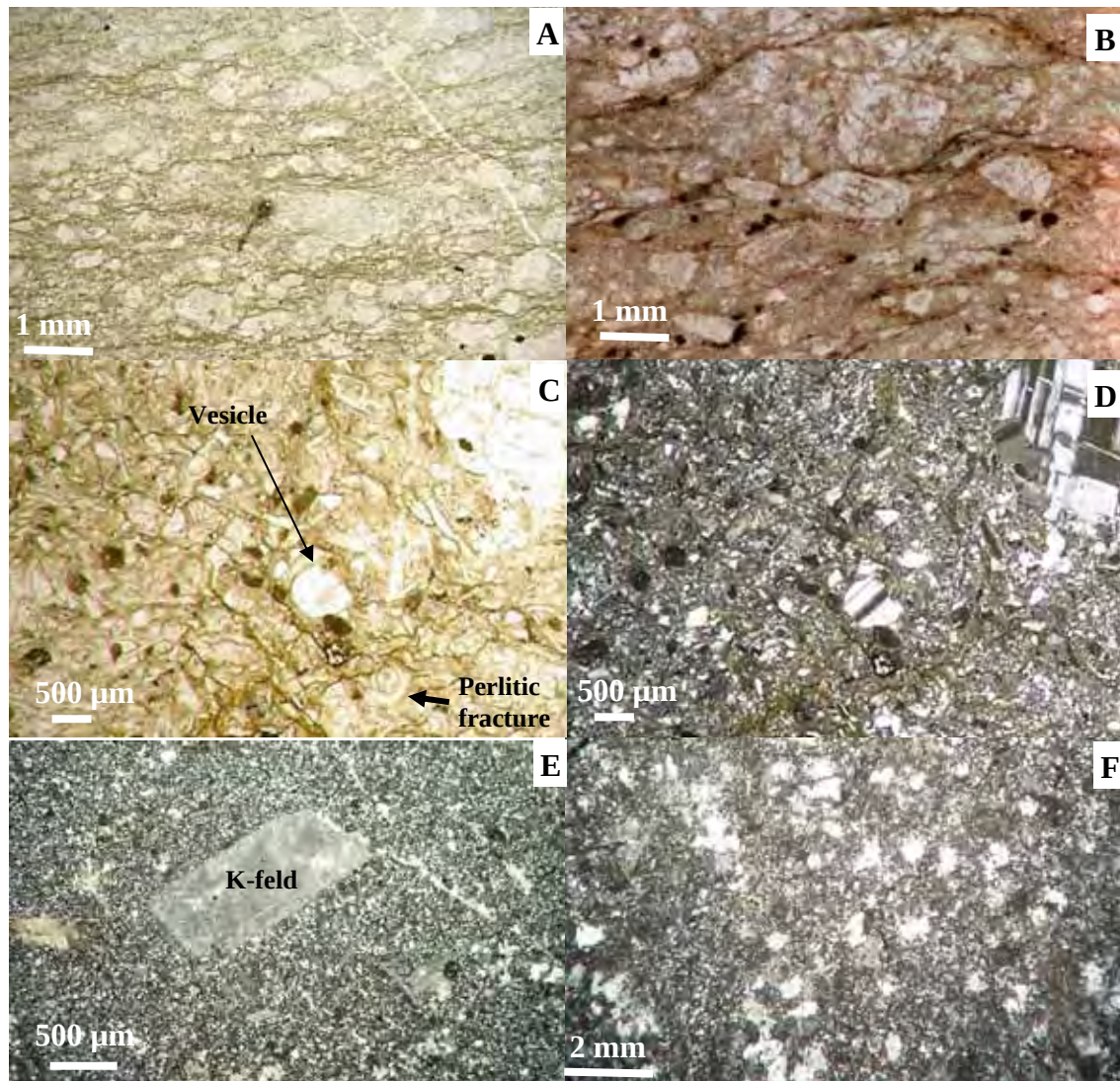


Figure 3. 16 (Caption on next page.)

**Figure 3.16 Photomicrographs of Esfordi hanging wall volcanoclastic rocks.**

- A: Tuffaceous pebbly sandstone with a rounded siltstone clast, matrix is rich in hematite and carbonate (Bh1-68, XPL).
- B, C & D: Polymictic tuffaceous sandstone with various clasts of magnetite, limestone, rhyolite, welded and non-welded ash flow fragments sit in an amphibole-chlorite-rich (B) and finer tuffaceous matrix (C & D). The rhyolite fragment is extensively altered to sericite-quartz, (Bh1-98, Bh5-80, XPL).
- E: Poikilitic overgrowth of a welded ash flow clast (Bh3-48, XPL).
- F: Rhyolitic fragments with angular shape in a matrix rich in quartz clasts and carbonate (Bh4-62, XPL).
- G: A Feldspar crystal with an overgrowth rim, magnetite and carbonate clast in a finer tuffaceous matrix (Bh1-13, XPL).
- H: Poikilitic overgrowth around a quartz grain (Bh1-13, XPL).
- I & J: Mafic volcanic clasts with extensive chlorite alteration in a finer matrix of quartz and carbonate (Bh1-13 & Bh4-65, PPL).



**Figure 3. 17 Photomicrographs of rhyolitic dome and welded ash flow tuffs of the Esfordi hanging wall.**

A & B: Flow banding in rhyolite of Esfordi felsic dome.

C: (PPL) and D (XPL): Vitroclastic texture of rhyolite flow with perlitic fracture and vesicles filled by feldspar, quartz and sericite.

E: Large K-feldspar crystal overgrowth the vitroclastic rhyolite (RT3, XPL).

F: Poikilitic texture of a vitroclastic fabric of Esfordi rhyolite (105, XPL).

Mafic sills, contain sodic to alkali feldspar, both as phenocryst (up to 2 mm) and in the trachytic groundmass (Fig 3.13). Primary fabric and much of the original mineralogy has been destroyed, by pervasive alteration. Biotite, Fe-oxide and apatite (up to 10 %) are common alteration minerals. Numerous subparallel mafic bodies of mainly basaltic composition, up to 15 m thick, intruded both the footwall and hanging wall sequence of the CVSU at Esfordi.

Photomicrographs of mafic intrusions and hanging-wall volcanics are shown in Fig. 3.13. The younger generation of doleritic dykes is relatively fresh and mainly composed of plagioclase and aggregates of brown amphibole (Fig 3.18) and iron oxides with remnants of pyroxene. These dykes have a coarse to medium grained intergranular to ophitic texture. They typically contain 40-50 % plagioclase, and 50-60 % mafic minerals dominated by amphibole. The amphiboles are rimmed by brown biotite (Fig 3.18) which suggest mineral-hydrous silicate melt interaction rather than late stage hydrothermal alteration. Dykes are variably altered by chlorite, sericite and calcite and strongly altered dykes contain a high quantity of Fe-oxide and apatite (Fig 3.18).

The upper part of the hanging wall sequence of the CVSU is marked by 100-150 m of massive limestone and dolomite with tuffaceous sandstone interbeds (Fig 3.13 a). It locally contains thin beds of dark, ash-rich sediments and recrystallised calcite and quartz veins.

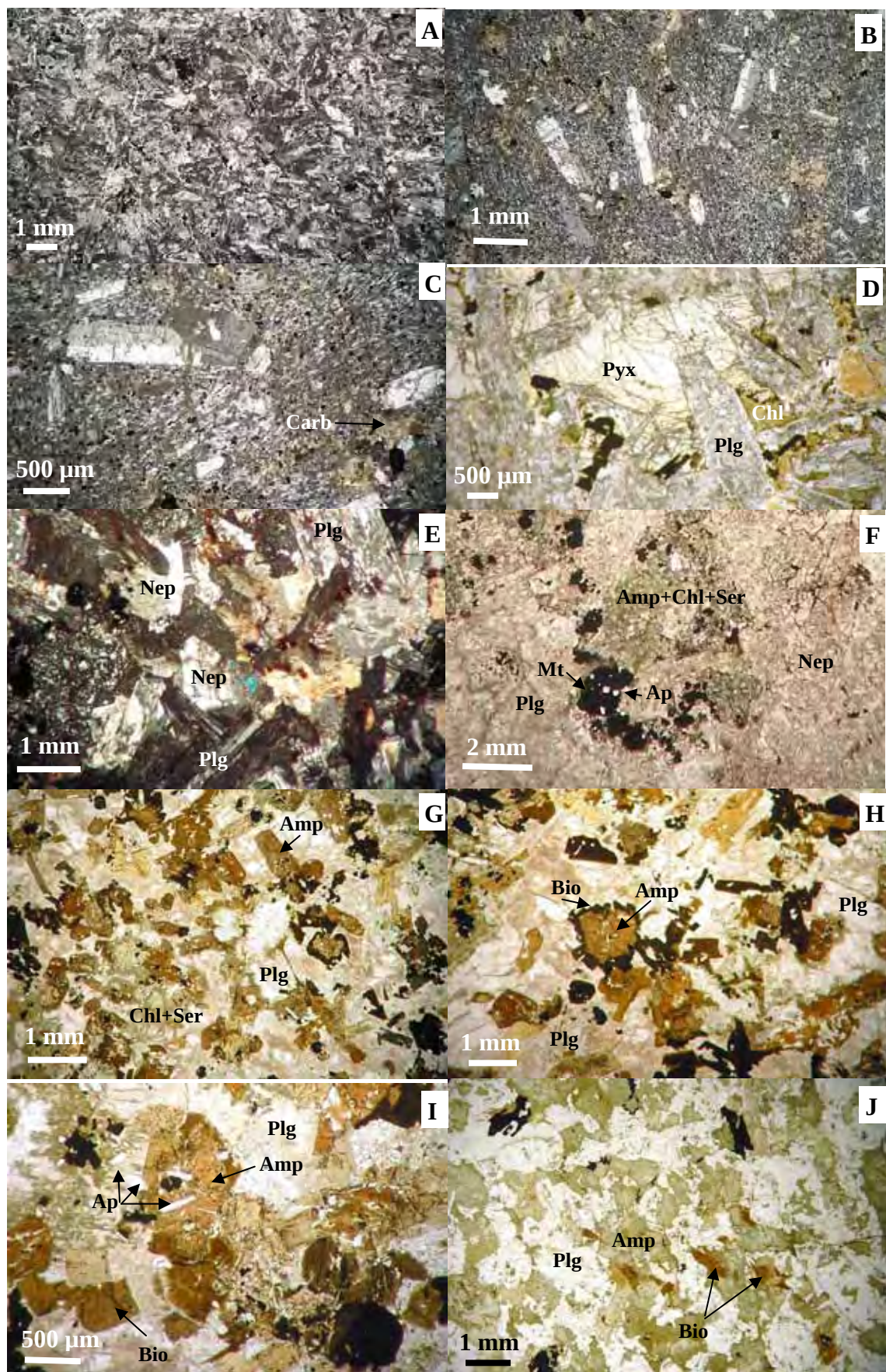
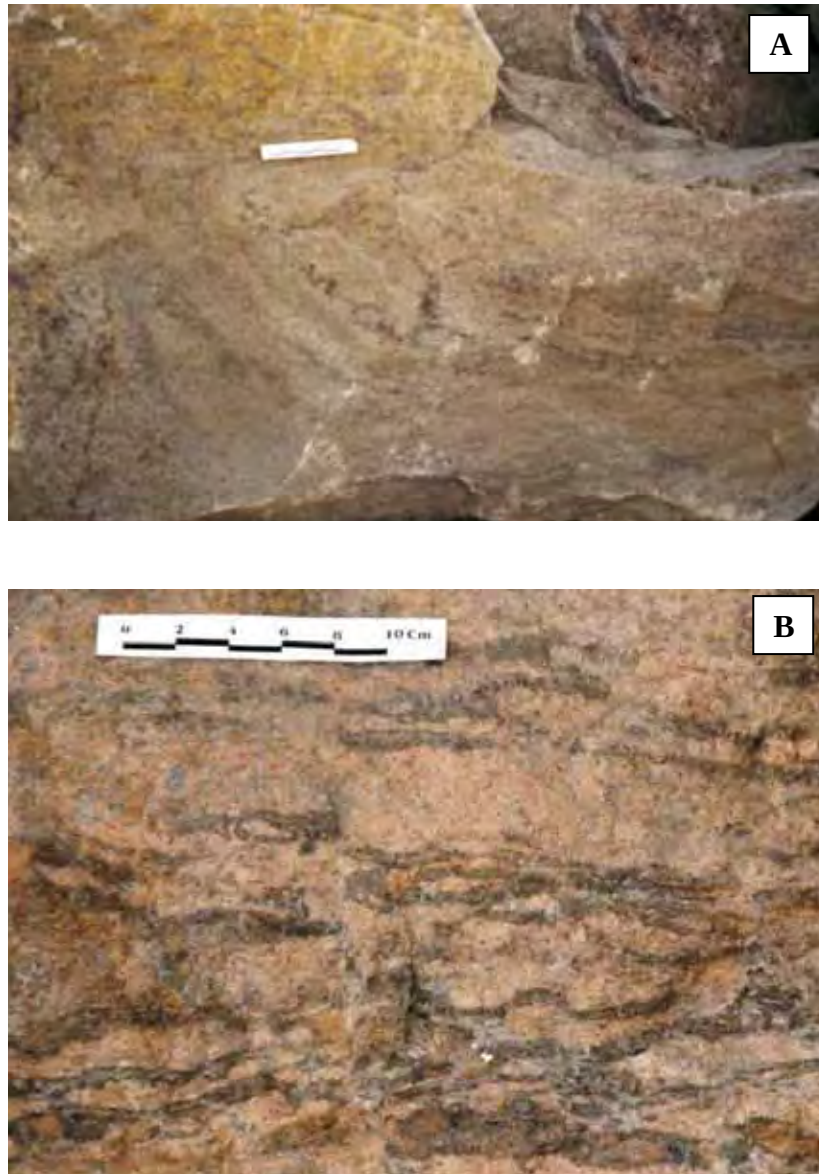


Figure 3. 18 (Caption on next page.)

**Figure 3.18 Micrographs of the mafic sub-volcanic rocks of hangingwall sequence.**

- A: Trachyte with granular texture, XPL.;
- B & C: Two porphyry trachyte from Esfordi footwall with large alkali feldspar phenocrysts, XPL.
- D: Xenomorphic pyroxene and plagioclase in an altered Esfordi dolerite. Chlorite, carbonate and sericite within dusty plagioclases are the products of alteration, PPL.
- E: Nepheline syenite, north of Esfordi with nepheline, plagioclase, amphibole and pyroxene. The Rock is showing K-feldspar, sericite-chlorite alteration, XPL.
- F: Amphibole-chlorite-sericite alteration of north Esfordi nepheline syenite. Magnetite is associated within this altered patch with small apatite crystals, PPL.
- G: Chlorite-sericite alteration of Esfordi dolerite, PPL.
- H: Amphibole rimmed by biotite in a relatively fresh Esfordi dolerite, PPL.
- I: Apatite crystals within amphibole and plagioclase crystals, PPL.
- J: Gabbro intrusion in underlying Tashk Formation with relatively large plagioclases, amphibole and pyroxene with minor biotite, PPL.



**Figure 3. 19 Hanging wall sandstone intercalations.**

A: Cross-bedding (scale is 10 cm)

B: Intervals of fine ash and pebbly sandstone.

## **CHAPTER 4      IRON-OXIDE – APATITE MINERALISATION AT ESFORDI**

### **4.1    INTRODUCTION**

In this chapter the various facies of mineralisation at Esfordi are described, including their geometry, fabric, mineralogy, geochemistry and mineral paragenesis, which leads to an overall paragenetic scheme for the Esfordi system.

Field observations and logging of mineralised core demonstrate that the main apatite–magnetite mineralised system is a gently dipping lens 400 m long and up to 90 m thick. It is broadly conformable with volcanic rocks and intercalated sediments of the CVSU (Fig 4.1). Three main facies of mineralisation are recognised at Esfordi as schematically depicted in Fig 4.2 – (i) the Fe-oxide core of the mineralised system, (ii) an adjacent or overlying zone dominated by apatite which forms the economically significant part of the system and (iii) a prominent zone of more localised Ca-rich alteration, containing low grade apatite mineralisation peripheral to the main apatite ore body. Two subordinate facies of mineralization, a thin magnetite ± hematite ± apatite horizons of detrital character extend into altered peripheral volcanoclastic rocks and a persistent jaspilite horizon less than 5 m thick that is developed some ~100 m stratigraphically above the Fe-oxide core. Interpretation of the different spatial and temporal relationships suggests a sequence of fluid related mineralisation.

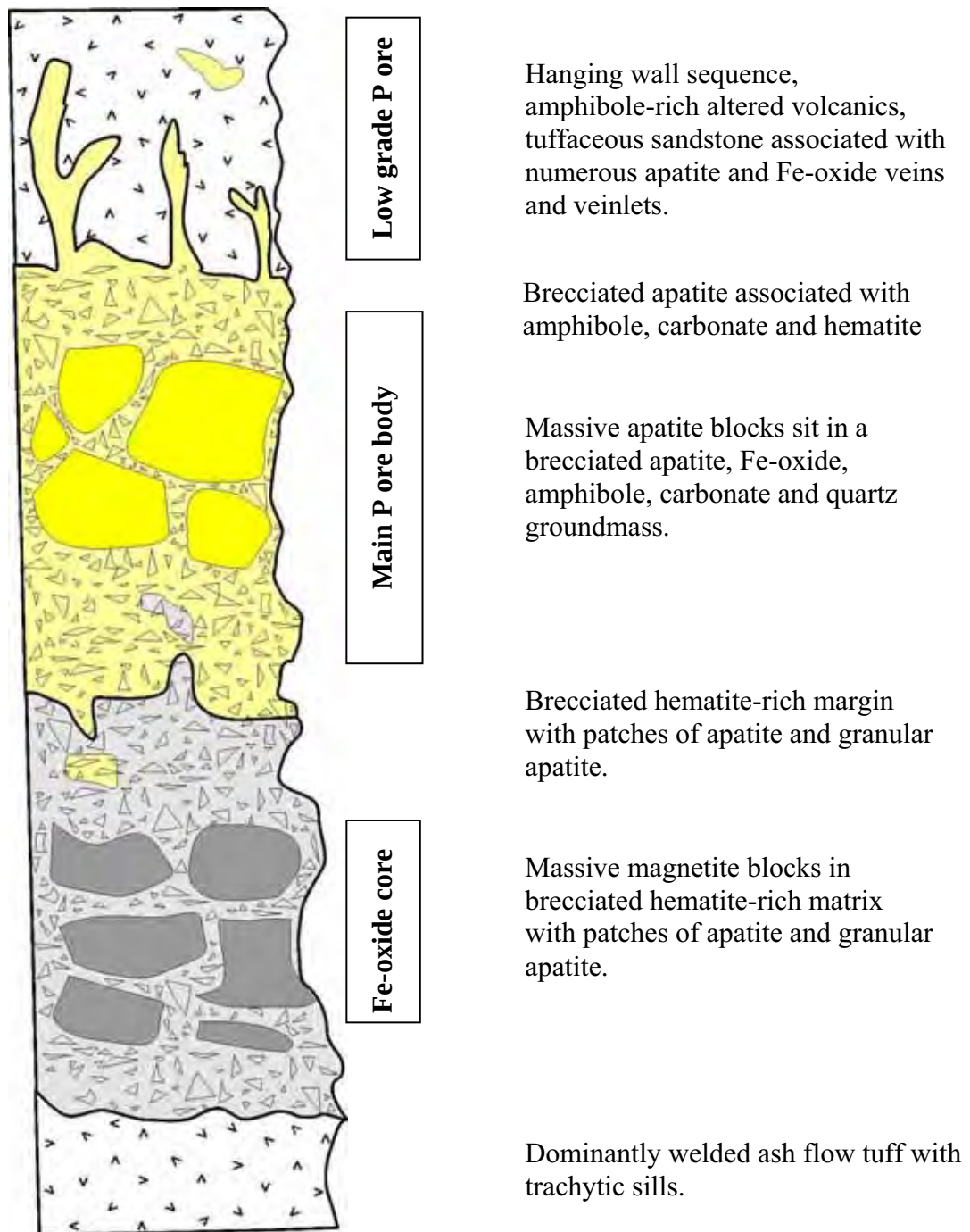
## 4.2 FE-OXIDE CORE

One of the most striking features of the Esfordi system is the lenticular Fe-oxide rich core. Based on drill holes and surface mapping, the upper surface of the Fe-oxide core dips generally between 21° and 72° toward the NE. The thickness varies from around 10 to >60 m. The total length of the Fe ore body is ~420 m with a width of 20 to 150 m (Fig. 4.1). Four cross-sections perpendicular to the strike of the iron ore body are presented in Fig 4.3, and additional sections in Appendix 3.

The magnetite-rich core underlies the apatite-rich zone and pinches out laterally into a highly altered suite of rhyolitic volcanic and volcanoclastic rocks (Figs. 4.2 and 4.3). The contact between the Fe-oxide ore and volcanic host rocks in the footwall is generally sharp but the contact with the overlying apatite-rich zone in hanging-wall may be either sharp or gradational. The gradational contact is mainly observed at the highly brecciated contacts. Several cross-sections have been constructed based on borehole drilling (Appendix 3).

Within the main Fe-oxide body there are gradational textural and mineralogical characteristics from core to margins. The central core is massive and magnetite-rich whereas the marginal zone is more brecciated and with a higher hematite content. The effects of weathering are generally minor with local development of goethite-hematite crusts and leaching of late stage carbonates that extend a maximum 2 m from surface.

Whole rock major and trace element analyses of representative samples of Fe-oxide core are shown in Table 4.1. A standard box plot of the P and Fe contents from 38 holes within typical Fe-oxide rich, P-rich and low-grade ore is illustrated in Fig 4.4.



**Figure 4. 1 Schematic diagram showing the main mineralised zones in the Esfordi mineralised system.**

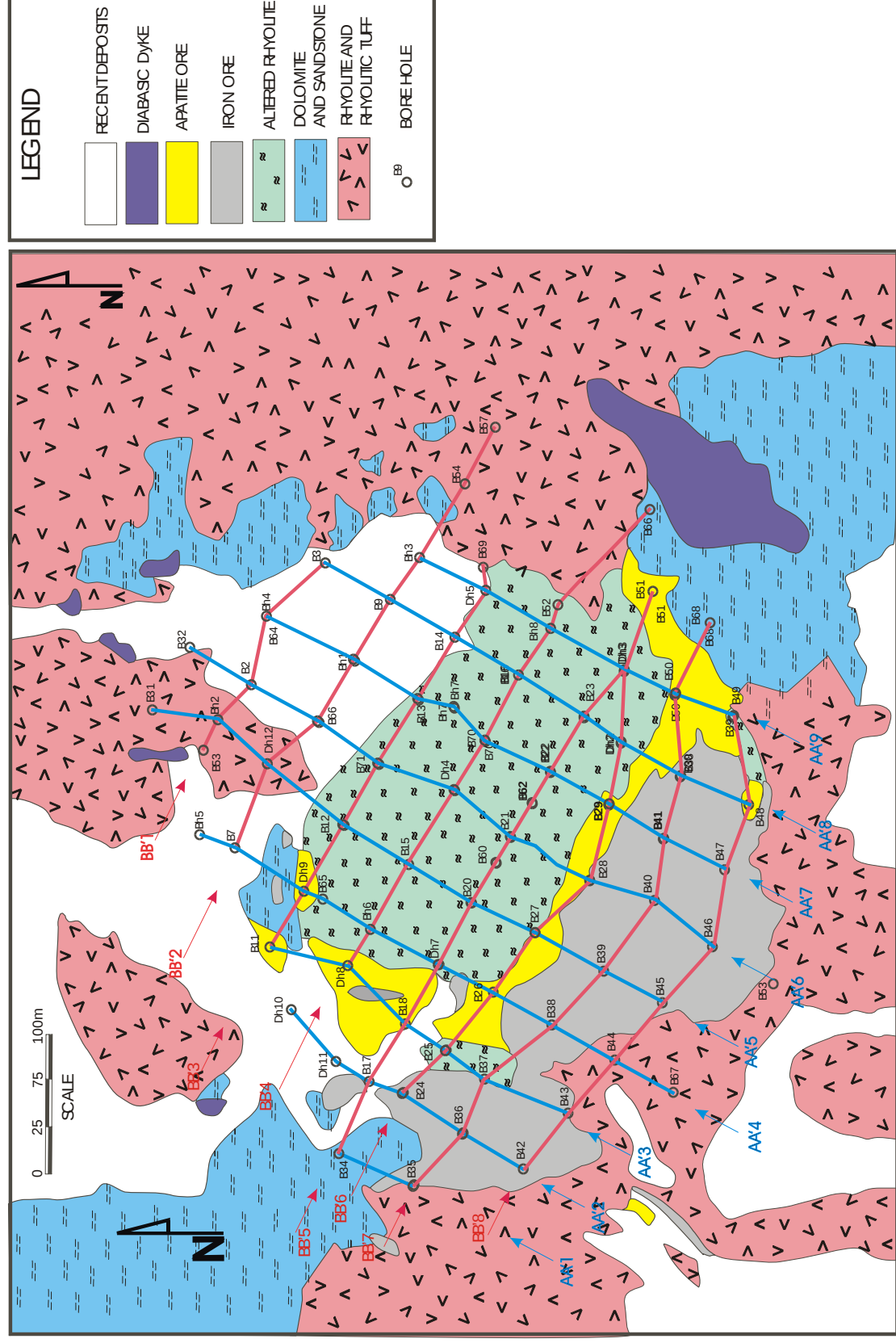
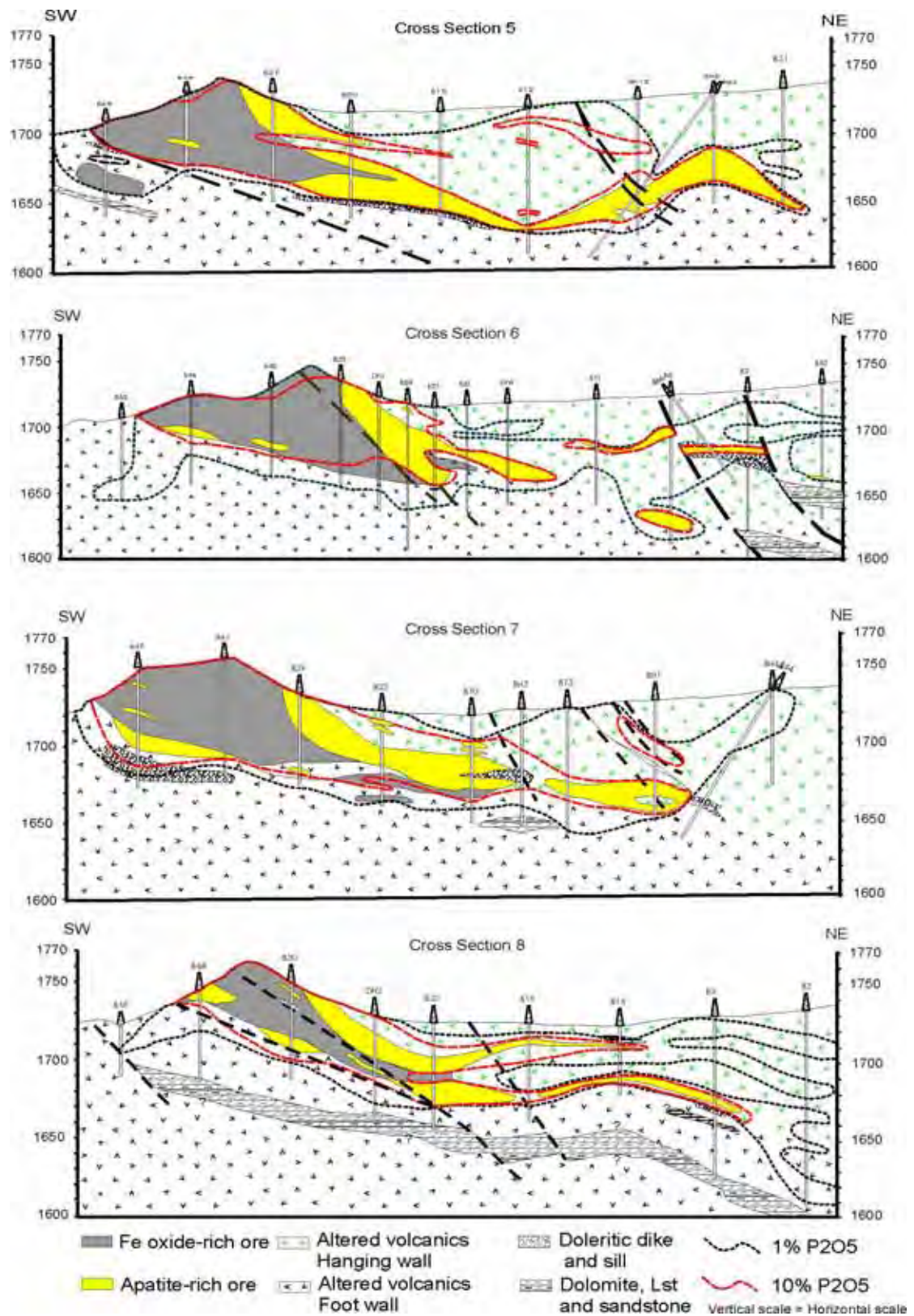
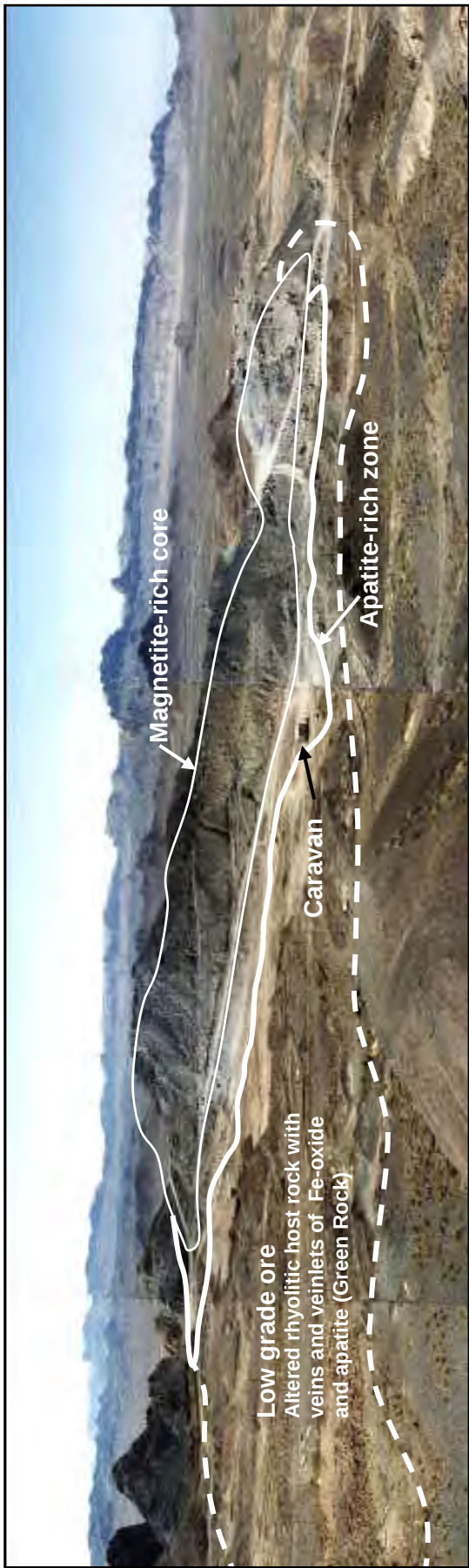


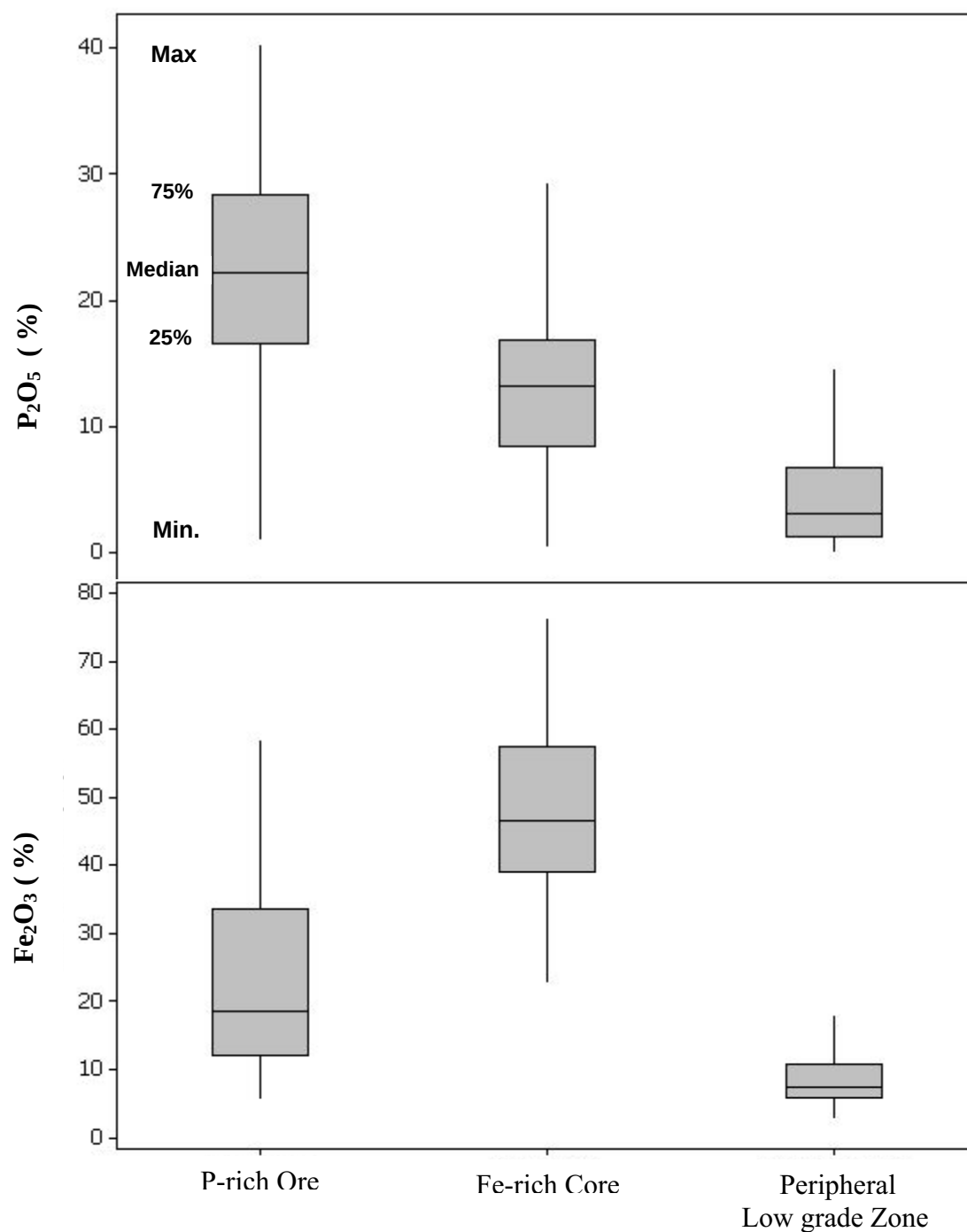
Figure 4. 2A Geological map of Esfordi deposit and location of geological cross-sections.



**Figure 4.2B** Selected cross-sections perpendicular to the strike of the Esfordi Fe-oxide and apatite-rich ore bodies (cross section numbers as per the sequence in Appendix 3).



**Figure 4. 3** Main iron and apatite ore bodies of the Esfordi deposit (looking south).



**Figure 4. 4** Standard boxplot of the  $P_2O_5$  and  $Fe_2O_3$  concentration in high and low grade ores based on 1836 samples from 38 bore holes (data from NIPCO, 1991).

**Table 4.1 Whole rock major and trace element analyses of representative samples of the Esfordi Fe–P ore.**

| Wt %                           | Massive magnetite-rich core |        | Brecciated rim of the Fe-oxide core |        | Massive apatite ore |        | Brecciated apatite ore with carbonate overprint |        |        | Jaspilite |
|--------------------------------|-----------------------------|--------|-------------------------------------|--------|---------------------|--------|-------------------------------------------------|--------|--------|-----------|
| sample                         | B20-43                      | B27-38 | B34-11                              | B40-14 | Bh12-65             | Cx-ap  | 108                                             | B27-22 | R3     | 10        |
| SiO <sub>2</sub>               | 18.33                       | 9.74   | 9.94                                | 9      | 3.47                | 4.07   | 32.96                                           | 2.71   | 16.49  | 29.52     |
| TiO <sub>2</sub>               | 1.58                        | 0.96   | 0.46                                | 0.49   | 0.05                | 0.04   | 0.07                                            | 0.02   | 1.76   | BLD       |
| Al <sub>2</sub> O <sub>3</sub> | 0.16                        | 0.15   | BLD                                 | BLD    | BLD                 | BLD    | BLD                                             | 0.1    | BLD    | 0.26      |
| Fe <sub>2</sub> O <sub>3</sub> | 69.70                       | 66.91  | 22.67                               | 52.97  | 3.23                | 2.14   | 19.52                                           | 7.46   | 16.59  | 62.38     |
| MnO                            | 0.02                        | 0.03   | 0.01                                | 0.05   | 0.07                | 0.08   | 0.06                                            | 0.04   | 0.03   | 0.12      |
| MgO                            | 0.53                        | 0.23   | 0.62                                | 1.21   | 0.99                | 0.95   | 0.96                                            | 0.56   | 1.39   | 0.15      |
| CaO                            | 4.56                        | 11.33  | 37.46                               | 19.85  | 51.27               | 51.59  | 25.02                                           | 50.11  | 35.52  | 3.83      |
| Na <sub>2</sub> O              | 0.12                        | 0.34   | 0.42                                | 0.32   | 0.68                | 0.82   | 0.42                                            | 0.32   | 0.48   | 0.09      |
| K <sub>2</sub> O               | BLD                         | 0.05   | 0.08                                | 0.02   | 0.15                | 0.16   | 0.09                                            | 0.03   | 0.11   | BLD       |
| P <sub>2</sub> O <sub>5</sub>  | 2.47                        | 5.53   | 22.25                               | 11.39  | 32.64               | 33.65  | 16.33                                           | 32.73  | 22.12  | 0.08      |
| SO <sub>3</sub>                | BLD                         | BLD    | 0.19                                | BLD    | 0.44                | 0.46   | 0.24                                            | 0.14   | 0.31   | BLD       |
| L.O.I                          |                             | 3.29   | 4.54                                | 2.82   | 0.39                | 3.55   | 2.63                                            | 4.75   | 4.58   | 2.6       |
| Total                          | 97.47                       | 98.56  | 98.64                               | 98.12  | 93.38               | 97.51  | 98.3                                            | 98.91  | 99.38  | 99.03     |
| Trace elements (ppm)           |                             |        |                                     |        |                     |        |                                                 |        |        |           |
| As                             | 17.3                        | 19.9   | 114.9                               | 83.9   | 109.2               | 88.3   | 24.3                                            | 106.6  | 146.4  | 29.5      |
| Cd                             | 17.5                        | 17.9   | 3.3                                 | 10.5   | 6.6                 | 18     | 7.6                                             | 11     | BLD    | 13.2      |
| Cu                             | 11.3                        | 17.8   | 33.4                                | 20.2   | 36.3                | 31.9   | 27.1                                            | 320.5  | 20.9   | 74.5      |
| Ga                             | 32                          | 22     | 3.5                                 | 16.3   | 2.2                 | 0.01   | 2.2                                             | BLD    | BLD    | 2         |
| Nb                             | 3.6                         | 1.7    | BLD                                 | BLD    | BLD                 | 5.9    | 1                                               | BLD    | 21.6   | 2.9       |
| Pb                             | 5.7                         | 6.1    | 5.3                                 | 6.4    | 6.3                 | 8.1    | 4.2                                             | 8.4    | 7.6    | 6.5       |
| Rb                             | BLD                         | BLD    | 12.9                                | 1.8    | 24.4                | 22     | 11.6                                            | 21.2   | 15.6   | BLD       |
| Sr                             | 34.3                        | 117.2  | 408.6                               | 151.6  | 367.9               | 408.4  | 381.3                                           | 410.7  | 268.7  | 44.3      |
| Sn                             | 45                          | 52.7   | BLD                                 | 44.8   | BLD                 | BLD    | 23.1                                            | BLD    | 43.6   | 55.4      |
| Th                             | 14.7                        | 37     | 64.5                                | 71.2   | 97.3                | 71     | 51.8                                            | 78.7   | 66.5   | 3.6       |
| U                              | 1.74                        | 15.95  | 8.52                                | 6.87   | 14.87               | 8.00   | 8.84                                            | 9.26   | 6.41   | 4.43      |
| V                              | 2189.6                      | 1265.7 | 252.7                               | 749.8  | 128.2               | 34.8   | 315.4                                           | 40.7   | 114.4  | 11.4      |
| Y                              | 131.9                       | 260.3  | 1234.7                              | 1057.8 | 1606.5              | NA     | 611.0                                           | 995.9  | 709.5  | 1.4       |
| Zn                             | 17.8                        | 13.6   | 10.1                                | 15.2   | 9.3                 | 4.2    | 3.6                                             | BLD    | 7.1    | 19.2      |
| Zr                             | BLD                         | BLD    | 22.4                                | BLD    | 28.9                | 30.6   | 26.7                                            | 30.2   | 28.9   | BLD       |
| La                             | 77.3                        | 323.0  | 1145.7                              | 1068.3 | 2551.6              | NA     | 2582.4                                          | 2056.7 | 406.6  | 22.6      |
| Ce                             | 443.5                       | 1060.0 | 3058.8                              | 2553.8 | 6477.6              | 5073.5 | 3469.6                                          | 4721.3 | 1363.4 | 33.5      |
| Pr                             | 54.4                        | 132.6  | 324.8                               | 320    | 599.5               | NA     | 363.7                                           | 444.9  | 158.24 | 1.4       |
| Nd                             | 213.7                       | 495.1  | 1383.4                              | 964.4  | 2282.2              | NA     | 1148.1                                          | 1644.2 | 477.1  | 3.6       |
| Sm                             | 38.0                        | 80.1   | 222.0                               | 234.6  | 362                 | NA     | 243.7                                           | 263.3  | 125.8  | 0.5       |
| Eu                             | 4.3                         | 6.7    | 19.2                                | 15.4   | 35.1                | NA     | 21.7                                            | 45.7   | 16.0   | 0.4       |
| Gd                             | 36.4                        | 78.4   | 239.0                               | 258.7  | 370                 | NA     | 223.6                                           | 282.2  | 161.7  | 0.4       |
| Tb                             | 5.5                         | 11     | 37.1                                | 41.1   | 55.9                | NA     | 30.2                                            | 48.2   | 26.5   | 0.1       |
| Dy                             | 26.4                        | 52.1   | 190.7                               | 216.4  | 264.2               | NA     | 134.7                                           | 176.9  | 142.4  | 0.4       |
| Ho                             | 5.7                         | 11.3   | 43.1                                | 48.2   | 55.2                | NA     | 26.4                                            | 40.6   | 31.7   | 0.1       |
| Er                             | 13.7                        | 27.6   | 110.9                               | 127.1  | 148.9               | NA     | 69.4                                            | 89.5   | 79.2   | 0.2       |
| Tm                             | 1.7                         | 3.4    | 14.3                                | 17     | 19.2                | NA     | 8.4                                             | 13.3   | 10.8   | 0.1       |
| Yb                             | 8.7                         | 18.2   | 76.0                                | 91.3   | 97.8                | NA     | 42.8                                            | 78.7   | 56.5   | 0.2       |
| Lu                             | 1.2                         | 2.6    | 10.3                                | 13     | 12.6                | NA     | 5.4                                             | 8.8    | 7.6    | BLD       |

All major and part of the trace elements have been analysed by XRF except REE, Y and U by ICP-MS.

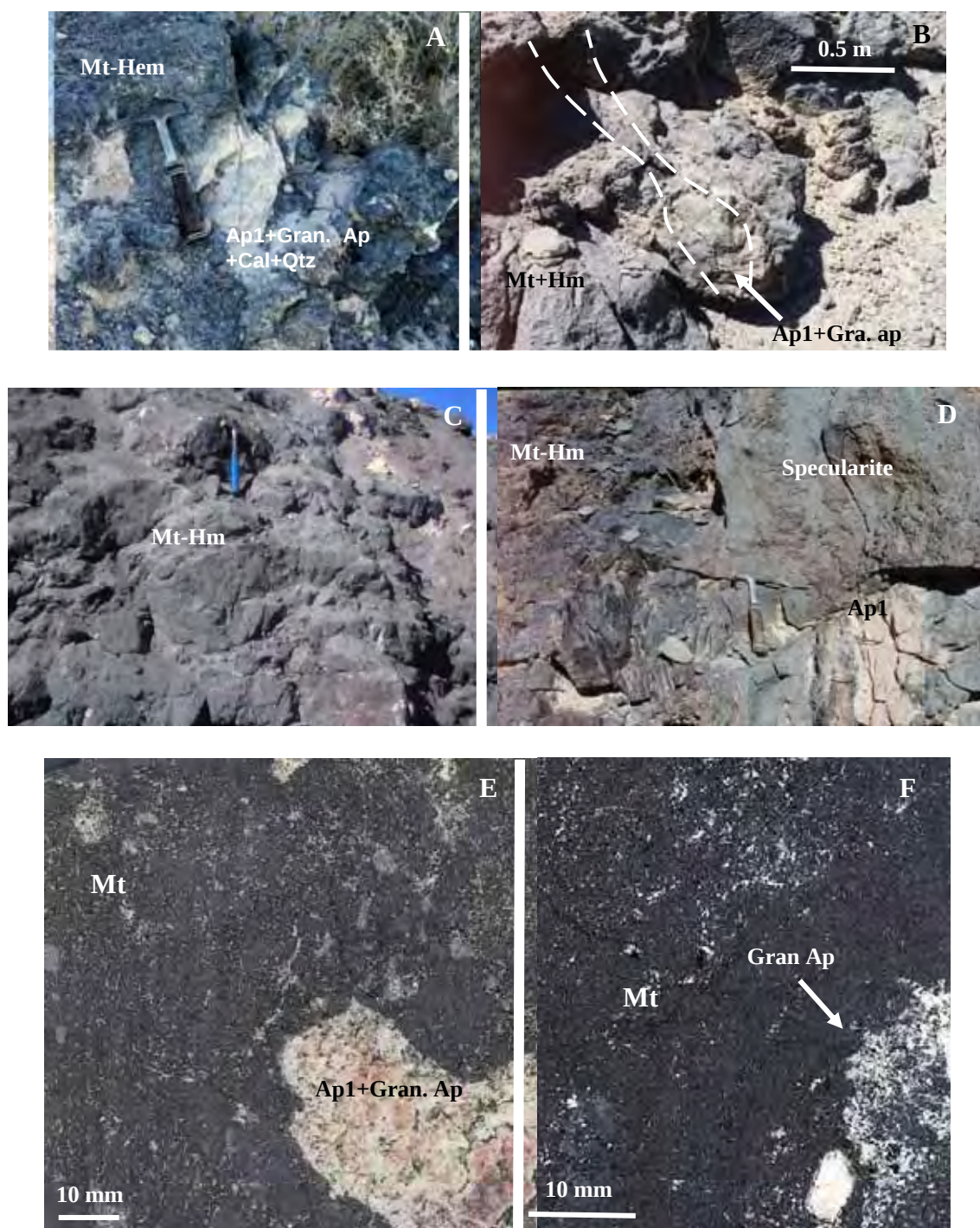
BLD: Below level of detection; NA: not analysed

#### 4.2.1 Massive magnetite

Massive magnetite forms the core of the Fe-oxide lense of the Esfordi mineralized system and has mainly been observed in bore holes and to a lesser extent in mine faces and outcrops. At the mesoscopic scale, the massive Fe-oxide zone is mainly composed of black, massive magnetite and hematite with sparse intergrown patches of apatite-magnetite, veinlets of apatite, ghosted fragmental outlines and healed fractures (Fig. 4.5). The apatite-magnetite patches display various shapes, from lenses to irregular forms with sizes ranging from a few mm to 1 m. The degree of brecciation, porosity and martitization increases gradually from the core of the Fe-oxide blocks to marginal zones. Hematite in the weathered zone is fine-grained and anhedral and has a spongy appearance. The high-grade massive Fe-oxide is almost pure, with irregular conchoidal fractures, and shows minimum apatite intergrowth compared with the brecciated parts of the deposit.

Microscopically, the massive magnetite core has moderate brecciation with some brecciated trails and frameworks (Fig. 4.7). The magnetite grains, 0.05 - 4 mm in size, are subhedral to anhedral in a granoblastic aggregate. The magnetite-rich core typically contains 5-20 % apatite in irregular corridors or disseminations between magnetite grains. Martitization is observed along grain margins and fractures in the magnetite.

Beside the secondary hematites (martite), thick blades of hematite are also present in equilibrium with primary magnetite. The thick hematite laths, as individual crystal or aggregates, sit between the magnetite grains in a finer matrix of secondary hematite. These hematites show range in size from 0.02–2 mm and are typically euhedral to subhedral without any traces of magnetite (Fig. 4.7 G).



**Figure 4.5 Main Fe-oxide zone of the Esfordi deposit.**

A – C: Massive magnetite-rich core with apatite patches;

D: Hematite-rich brecciated margin;

E & F: Two polished slabs of magnetite-rich core with patches of apatite.



Ilmenite is a minor phase in some magnetite grains where it occurs as thin exsolution lamellae and inclusions associated with titanomagnetite grains. A weak but pervasive carbonate overprint occurs in the massive Fe-oxide ore. The calcite forms veins and fissures-fill (Fig 4.11 g). Actinolite is also present as a minor phase in veins and brecciated corridors. Compared with the brecciated Fe-oxide rim, the massive magnetite zone has low amphibole content (< 5 %).

#### **4.2.2 Brecciated hematite-rich marginal zone**

The margin of the main Fe-oxide body is extensively brecciated over 2 to >10 m. The breccia blocks and fragments contain sooty to dull metallic magnetite with localised vuggy specularite. Breccia clasts of more massive magnetite, ranging in size from few mm to 20 cm, are variably replaced by hematite and set in a matrix of bladed and feathery hematite with minor apatite, calcite, actinolite and quartz.

Rounded blocks of massive magnetite are observed mainly at the boundary of Fe-oxide core and volcanoclastic host. Förster and Jafarzadeh (1994) reported similar fabrics in other Bafq district Fe-oxide occurrences which they interpreted as magmatic pillows. At Esfordi these bodies seem to be part of the brecciated zone and occur most commonly as small blocks within more intensely magnetized corridors.

Veins, veinlets and patches of apatite and calcite are present in the brecciated Fe-oxide zone, but are more abundant in the most strongly brecciated margins. These patches and veinlets are discontinuous and offset by other veinlets and fractures, suggesting recurrent fracturing accompanied by the specific mineralogy deposition (Fig. 4.9).

Microscopically the brecciated marginal zone consists of spongy intergrowth of sieve-like, skeletal or feathery hematite grains surrounding a magnetite core, associated with small amounts of apatite, quartz, calcite, siderite, actinolite, albite, chlorite and scapolite.

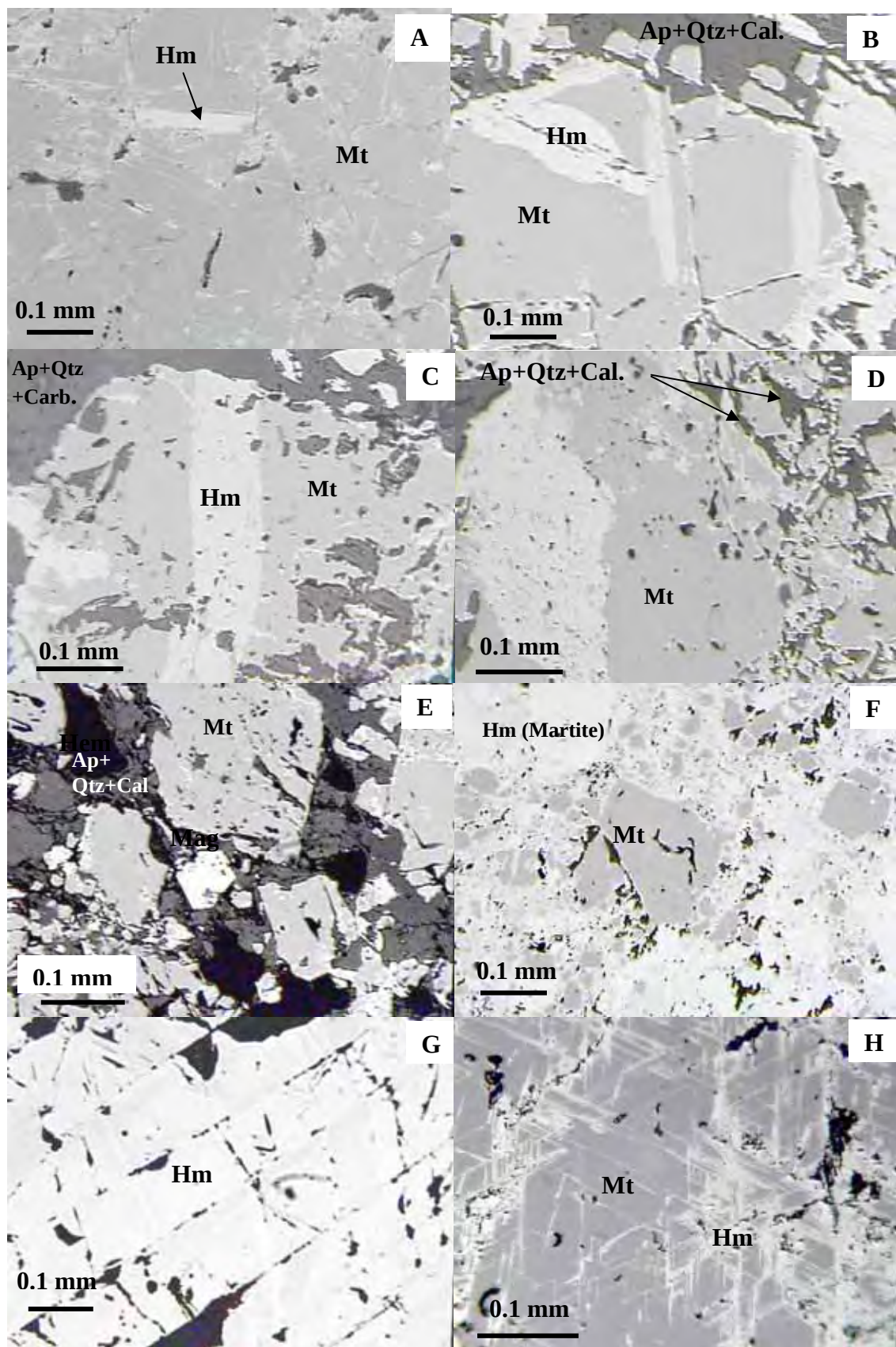


Figure 4. 7 (Caption on next page.)

**Figure 4.7 Photomicrographs of Fe oxide core of the Esfordi system.**

- A: Magnetite rich core of the Fe oxide rich zone with minor hematite. This zone is less brecciated than the peripheral zones.
- B & C: Martitization along the fractures of large magnetite crystals.
- D & E: Brecciation of magnetite and development of hematite, apatite, quartz and carbonate within fractures.
- F: Remnant core of magnetite in heavily martitized Fe-oxide zone.
- G: Large elongate crystals of hematite in brecciated Fe-oxide zone. Hematite replaced magnetite along crystal cleavages.



**Figure 4. 8 Brecciated Fe-oxide rich zone.**

- A: Magnetite with locally apatite-rich patches (sample 108).
- B: Veins and veinlets of apatite 1, granular apatite, hematite and carbonate assemblage in magnetite-rich brecciated rock (mine quarry close to hole B36).
- C: Brecciated magnetite and hematite with interstitial apatite 2 and carbonates from massive Fe-oxide ore zone (Hole B21-43.5 m).

Pseudomorphs of hematite after magnetite and magnetite relicts are common. The preserved magnetite crystals (0.01–2 mm) with fragmented appearance and angular fragments are common in brecciated and semi-brecciated ore.

Hematite crystals are commonly tabular (after [0001]) and developed in plates with intense intergrowths. In most cases the thick tabular crystals show a lamellar twinning along [1011]. There are two distinguishable types of twinning; (i) developed during primary crystallisation and subsequent transformations and (ii) apparently formed through mechanical deformation. The bent structure in tabular hematites and subsequent cracks and brecciation is abundant. Ramdohr (1980) explained this phenomenon as a translation after [0001] which occurs in combination with glide twin formation after [1011] during the non-fracturing deformation of hematite plates (Fig 4.9).

The marginal breccias contain a variable proportion of coarser clasts and finer matrix. Most of the coarse breccia grades into progressively finer assemblages of hematite - magnetite, apatite, calcite, quartz, albite and actinolite microbreccias and fine-grained, massive, semi-homogenous Fe-oxide. The fragments are mainly poorly sorted with angular shapes in a set of fine-grained matrix of the same mineralogy. The magnetite, hematite and at least one generation of apatite show a relict texture with fracturing and corrosion. Unusual fragment types include volcanic host rock, polygenerational breccia fragments, angular and also well-shaped crystals and clasts of magnetite, hematite and apatite are present. Intergrowths of hematite, magnetite, apatite and calcite are common. Small crystals and aggregates of monazite and allanite are also associated with apatite and hematite in breccia matrix. Late sulphide phases including pyrite with sparse chalcopyrite were detected in some breccia samples (Fig 4.10).

The surrounding altered volcanics and tuffs also show localised Fe-oxide enrichment in the form of specularite and late fissure filling hematite that is usually associated with calcite and quartz.

A late magnetite generation (magnetite 2) developed in irregular patches and veins of the brecciated margin of the Fe-oxide rich core, and adjacent brecciated apatite ore. This generation of magnetite typically replaces the blade shape hematite, specularite and martite which were developed after magnetite 1 (Fig 4.10). Adjacent, more massive apatite-rich ore contains bleached patches and veins with aggregates of magnetite 2. These magnetites seem to have developed after removal of thin lamellas of hematite within and between apatite crystals.

#### **4.2.3 Apatite mineralisation associated with Fe-oxide rich core**

Within the Fe-rich, lense-shaped core of the Esfordi system there are P-rich zones. Mesoscopic examination indicates the apatite in the core is of variable grain size and in the form of disseminations or intergrowths with magnetite-hematite veins, veinlets or patches (Figs. 4.5 and 4.11). The monomineralic apatite patches and veins are commonly distorted by subsequent fracturing, dissolution and mineral growth. Overprinting with late calcite and quartz alterations is pervasive and gives a cream-brown tinge. The more brecciated marginal zone contains relatively higher matrix apatite contents than the less brecciated massive magnetite-rich core.

Based largely on microscopic studies, two main generations of core apatites are recognized – an early generation of apatite (“apatite 1”) and finer granular apatite. Apatite 1 typically occurs in three main textural forms; monomineralic mosaics, matrix to magnetite grains and inclusions in magnetite crystals.

Relicts of apatite 1 are preserved as scattered monomineralic patches from 10 to 500  $\mu\text{m}$  inside the magnetite core, and form mosaics containing 200 ~ 3000  $\mu\text{m}$  grains surrounded and cut by corridors of fine granular (<100  $\mu\text{m}$ ) apatite (Fig 4.12). These relicts of apatite 1 are usually rich in solid inclusions (mainly monazite). The apatite 1 crystal aggregates also occur as the matrix to magnetite grains.

**Table 4. 2 Characteristics of the different types of apatites in the Esfordi system.**

|                              | <b>Stage 2 (Brecciation)</b>                                                                               |                                                                                                                                                                                                                                                                 |                                                                                                                            | <b>Stage 3 (Late)</b>                                                                                               |
|------------------------------|------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
|                              | <b>Apatite 1</b>                                                                                           | <b>Apatite 2</b>                                                                                                                                                                                                                                                | <b>Granular apatite</b>                                                                                                    | <b>Apatite 3</b>                                                                                                    |
| <b>Morphology and colour</b> | Mosaic of anhedral crystals<br>Granoblastic texture<br>Usually white in color<br>With REM solid inclusions | Large, green, euhedral to subhedral crystals with low solid inclusions and sparse fluid inclusions<br>Brecciated with deformation tracks and corridors; white, pink or purple anhedral to subhedral crystals<br>Veins and veinlets of hematite and/or magnetite | Granular fine-grained crystals after apatite 1 and 2.<br>White and anhedral crystals in corridors or around apatite grains | Small clear, euhedral to subhedral crystals<br>Always occurred within late stage, quartz or carbonate               |
| <b>Mineral assemblage</b>    | Magnetite, pyroxene, amphibole I, hematite                                                                 | Hematite, amphibole 2, chlorite, albite, K-feldspar                                                                                                                                                                                                             | Hematite, pervasive quartz and carbonate, amphibole II, chlorite                                                           | Within quartz and carbonate veins; amphibole 3, talc, chlorite, epidote, Fe-hydroxides                              |
| <b>Zone of occurrence</b>    | Main apatite and Fe-oxide zones                                                                            | Main apatite ore zone<br>Border of main Fe-oxide main ore zone<br>Apatitic veins and stockworks in overlying altered host rocks                                                                                                                                 | Corridors in apatite 1, brecciated main apatite 2 and apatite veins and veinlets in altered host rock                      | Overprint the older stages specially brecciated main apatite ore<br>Apatite veins and veinlets in altered host rock |

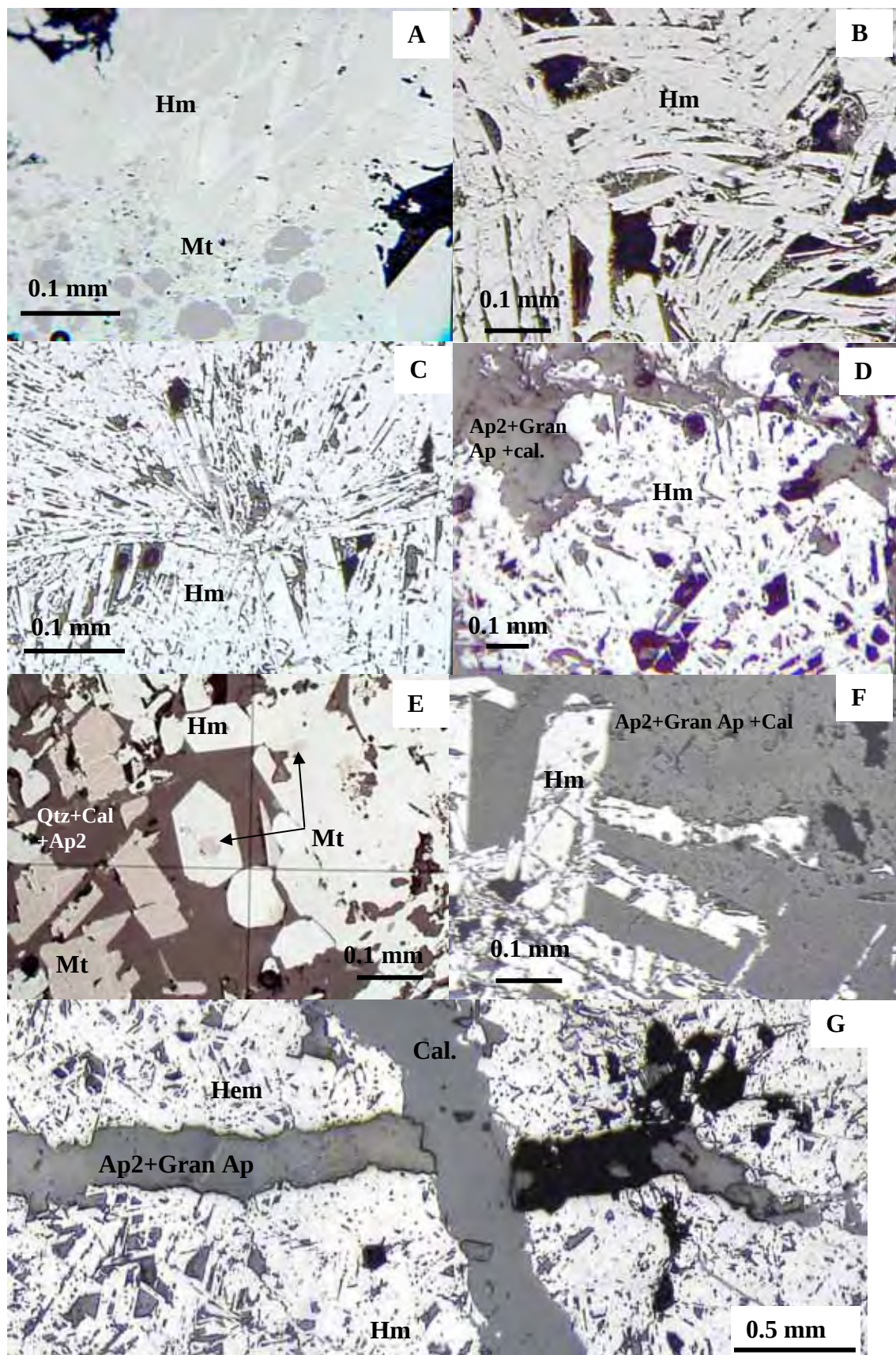
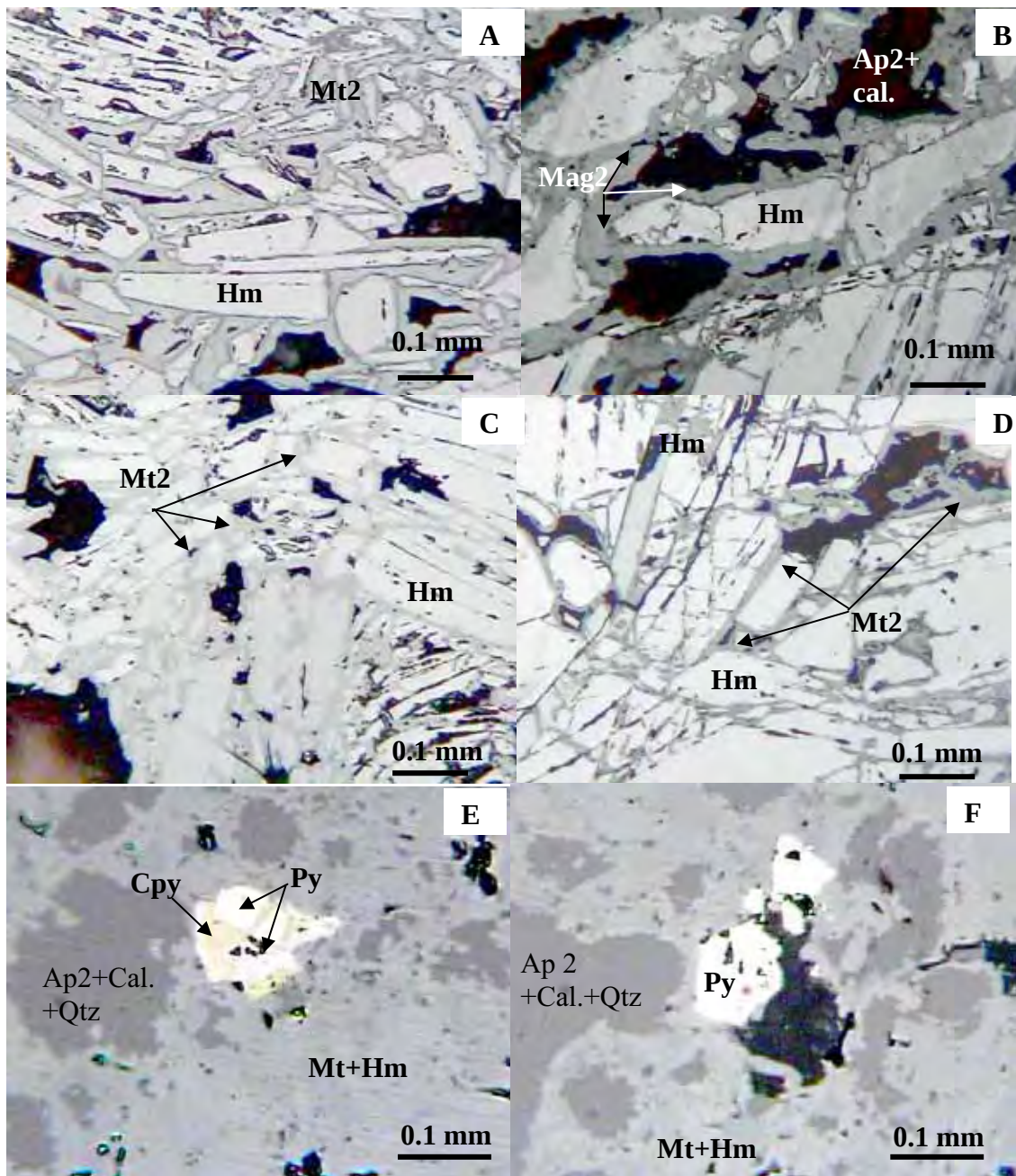


Figure 4. 9 (Caption on next page.)

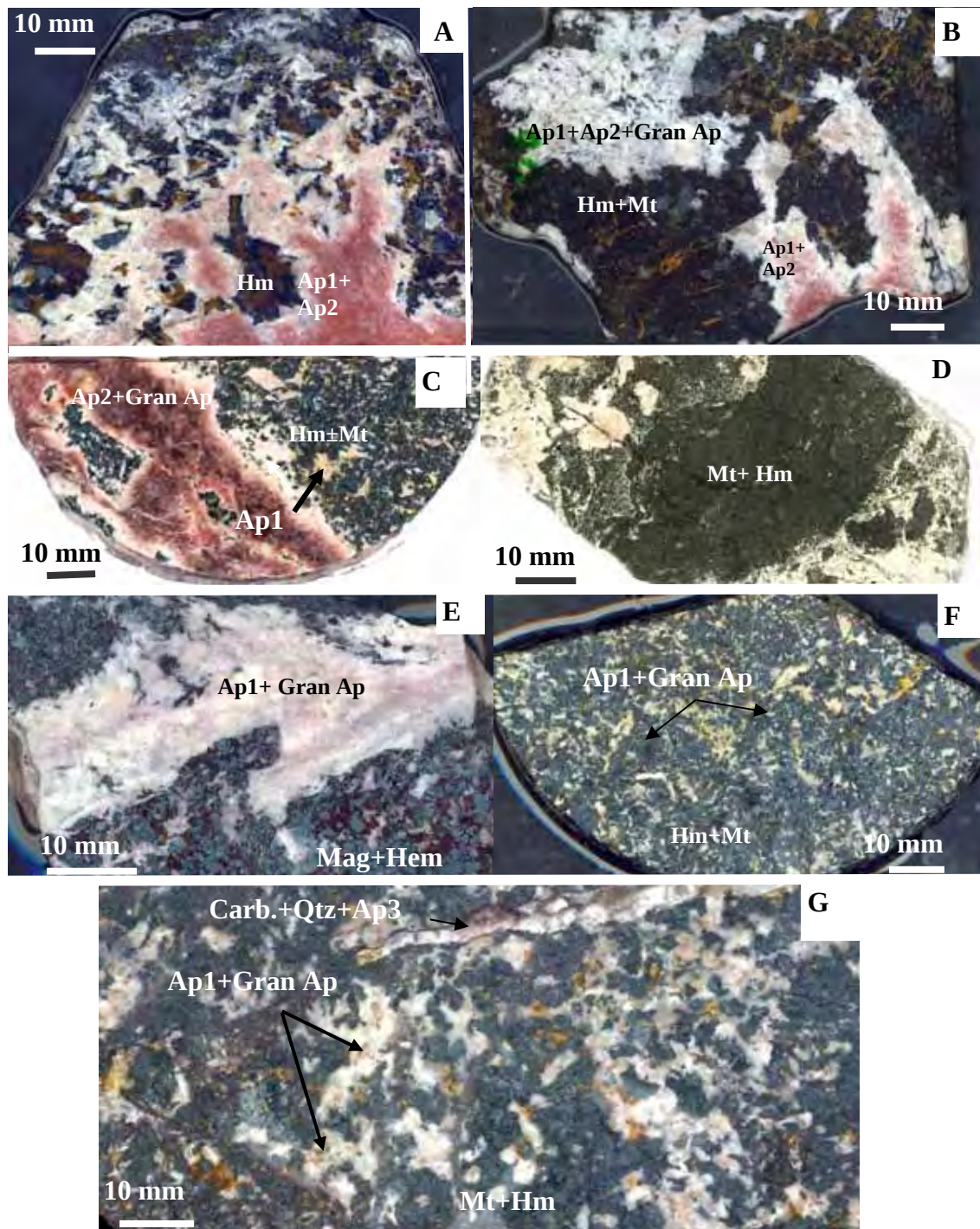
**Figure 4.9     Photomicrographs of brecciated marginal parts of main iron oxide core of the Esfordi system.**

- A:    Large crystals of hematite after magnetite with magnetite remnants as core outcrop close to B38.
- B – D:   Long and sieve shape hematite from N-W opening of Esfordi (close to B36).
- E:    Pseudomorphous hematite after primary magnetite. (Hole B1-2 m)
- F:    Blade shape hematite in an apatite 2-annealed apatite-carbonate matrix surface sample at the Fe-oxide rich core and apatite-rich zone boarder, close to B28.
- G:    Apatite and calcite veins cross-cutting brecciated Fe-oxide zone (same as F).



**Figure 4. 10 A-D: Magnetite 2 crystallization after hematite in brecciated Fe-oxide and apatite-rich ore. E and F: Pyrite and chalcopyrite occurrence in brecciated Fe-oxide ore (outcrop close to B41).**

Morphologically this form of apatite 1 is generally similar to apatite 2 patches, but more closely associated and mixed with magnetite crystals (Fig. 4.12). Magnetite crystals contain apatite 1 inclusions which are themselves inclusion-free and not associated with younger generations of apatite. These apatite 1 inclusions are typically 0.05-0.5 mm subhedral to euhedral crystals (Fig. 4.12).



**Figure 4. 11 Apatite 1 in the Fe-oxide core of Esfordi deposit.**

- A & B: Apatite rich patches of the massive Fe-oxide core associated with apatite 2 and granular apatite, from west quarry near hole B36.
- C: Remnants of Fe-oxide and apatite 1 in a vein of apatite 2 and granular apatite in Fe-oxide core (hole B38-12 m).
- D: Magnetite+hematite vein in the apatite 1-rich patches of the brecciated margin of Fe-oxide rich core (hole B21-43.5 m).
- E: A vein of apatite 1, 2 and granular apatite in the brecciated Fe-oxide core (surface sample close to hole B24),
- F & G: Disseminated apatite 1 and granular apatite in Fe-oxide rich core (hole B47-10 and 21 m).

Nearly all apatite 1 aggregates have been affected to some degree by subsequent brecciation. The majority of apatite 1 that is associated with the extensively brecciated margin of the Fe-oxide core is overgrown by other generations of apatite (e.g. apatite 2) and may be also locally replaced by calcite. In this zone and, to a lesser extent in the brecciated apatite-rich zone, a crude zonation may be observed in some apatite grains with abundant mineral (including monazite) and fluid inclusions in the apatite 1 cores but few inclusions in the apatite 2 rims (Fig 4.12 k, l and m).

The less brecciated, massive magnetite core is typically associated with apatite 1, but in the highly brecciated margin, hematite is spatially associated with apatite 1 and 2 as pervasive replacement of earlier magnetite and interstitial specularite.

Granular apatite, 10 to 100  $\mu\text{m}$  in size, occurs in trails and jigsaw-shaped corridors up to 1 mm wide and 100 mm long. The granular apatites are also present as matrix to apatite 1 and 2 crystals in P-dominant ore zones. This type of apatite is usually clear, anhedral to subhedral and replaces apatite 1 or apatite 2. The corridors of granular apatite usually surround apatite 1 crystals and contain very low REE contents. Based on crystal size and degree of brecciation, granular apatites may be further divided into fine and coarse types. Fine granular apatites are 10-50  $\mu\text{m}$  in size and sit in highly brecciated matrices or corridors. These crystals are always associated with larger (50-200  $\mu\text{m}$ ) granular apatite crystals within apatite 1 crystal remnants or close to apatite 2 fragments. A gradational change from apatite 1 to fine and coarse granular apatite is observed from apatite 1 remnants towards brecciated corridors. In the corridors the spaces between fine-grained granular apatite crystals are commonly filled by late carbonate and quartz (Fig 4.12 E and F). The apatite 1 within and adjacent to the granular apatite corridors show a sieve texture which suggests a dissolution of apatite 1 (Fig 4.12 O and P).

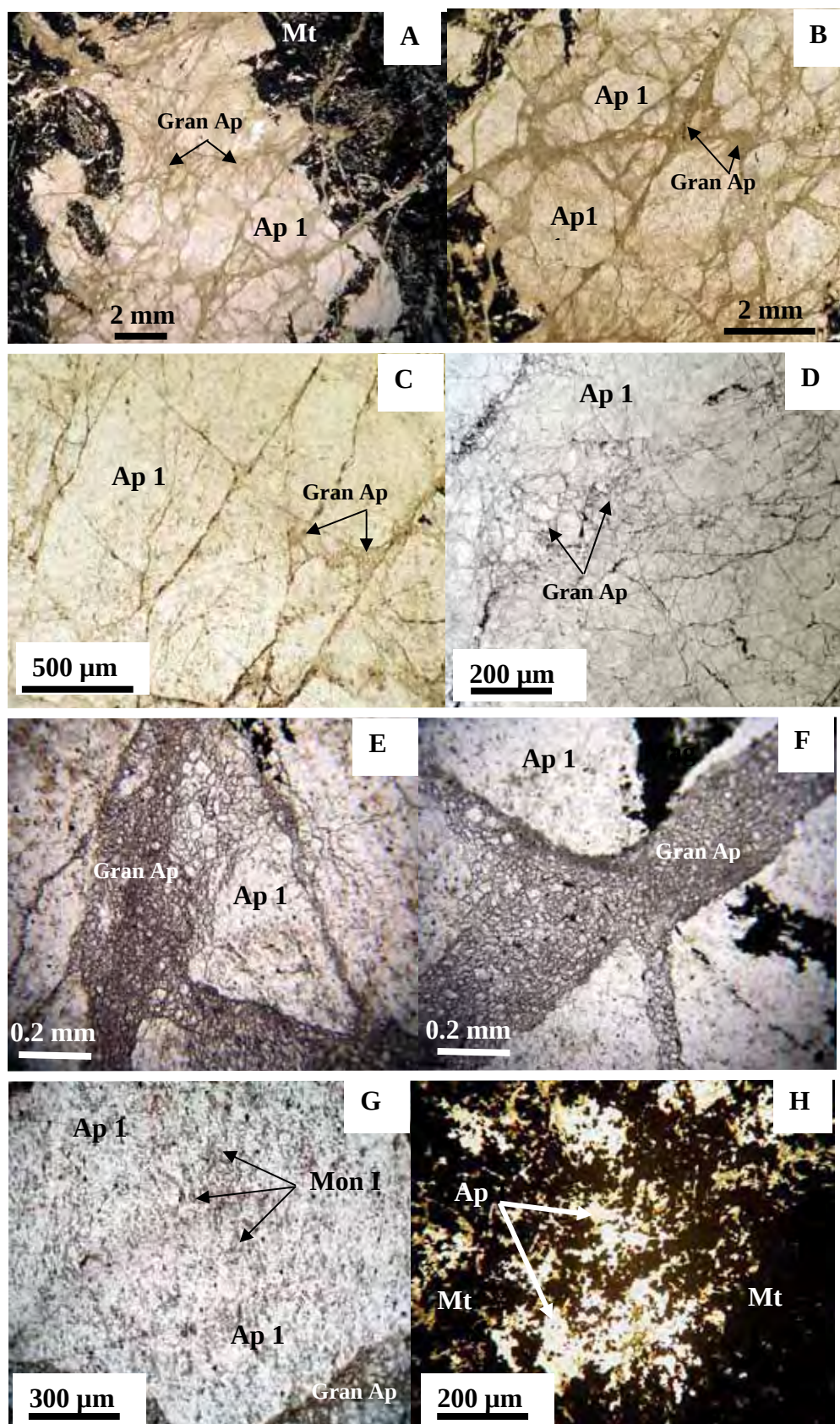


Figure 4. 12 (Caption on page 134.)

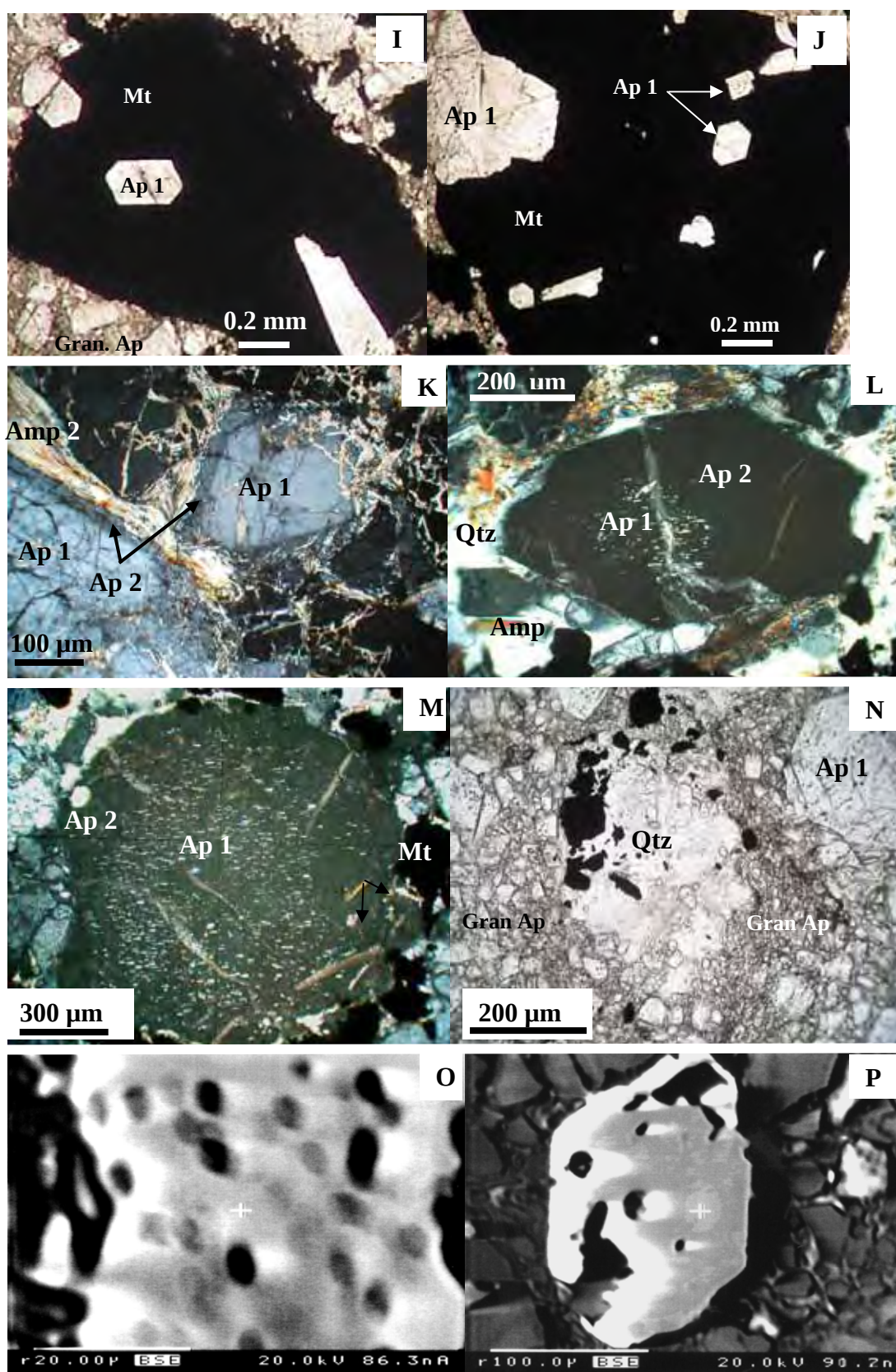


Figure 4.12 Continued (Caption on next page)

**Figure 4.12 Typical apatite 1 and granular apatite textural configurations at Esfordi.**

- A & B: Apatite 1 monomineralic patches in massive Fe-oxide core. Mozaic of remnant apatite 1 grains between corridors of fine granular apatite (PPL).
- C & D: Brecciated apatite 1 with early stages of granular apatite development in apatite rich patches of the magnetite rich core (PPL).
- E & F: Granular apatite corridors in apatite 1 patches in massive Fe-oxide core. The granular apatite are occurred as fine and coarse grained apatite(PPL).
- G: Apatite 1 in Fe-oxide core with monazite 1 inclusions (PPL).
- H: Apatite 1 as matrix to magnetite grains in massive Fe-oxide core (PPL).
- I & J: Apatite 1 inclusions in magnetite of the massive Fe-oxide core (PPL).
- K: Apatite 1 in brecciated Fe-oxide core. Mozaic of apatite 1 grain rimmed by apatite 2 with actinolite. Both apatite types are cut by late stage quartz veinlets and replacements (XPL).
- L & M: Apatite 1 and 2 in phosphate-rich zone. Apatite 1 with abundant inclusions rimmed by apatite 2, set in late stage quartz and actinolite (XPL).
- N: Apatite 1 with extensive development of granular apatite (PPL).
- O: Backscattered image of apatite 1 with sieve texture developed adjacent to granular apatite domains (B12-65).
- P: Backscattered image of partial dissolution of generally euhedral apatite 2 grain (B12-65)

### **4.3 APATITE-RICH MINERALISATION ZONE**

The apatite-rich zone ranges in thickness up to ~40 m. It is developed above the magnetite-rich core with which it displays both sharp and gradational contacts (Fig 4.3). The lower boundary of this zone is affected by brecciation and Fe enrichment. The upper contact of the apatite-rich zone is irregular with veins and veinlets extending into overlying volcanics and tuffs. The apatite-rich zone (Figs. 4.1 and 4.3) contains massive, brecciated and vein-type apatite variants, accompanied by minor actinolite and hematite. These variants show two main textural forms; (i) massive apatite with low proportion of amphibole (massive apatite-rich zone) and (ii) highly brecciated apatite ore with higher amphibole and Fe-oxide contents and brecciated remnants of massive apatite ore. Macroscopic and microscopic studies indicate weathering has not affected the apatite mineralisation.

#### **4.3.1 Massive apatite ore**

The massive, high grade apatite at Esfordi contains 20-30 %  $P_2O_5$ . This zone is developed over the Fe-oxide rich core as an stratigraphically conformable but irregular lens, which extend into the highly altered volcanoclastic rocks and grades to brecciated apatite and vein-type apatite mineralisation (Fig. 4.1 and 4. 3).

The massive apatite zone is poorly exposed at surface and has been destroyed by mining. Based on drill hole logging, the massive apatite-rich ore may be divided into massive remnant patches of apatite and zones within more extensive brecciated amphibole-rich P ore.

The thickness of the massive apatite blocks and lenses vary between 0.1 and 1m and is controlled by the intensity of brecciated corridors. These blocks are usually surrounded by highly brecciated apatite ore. The contacts with peripheral brecciated apatite ore is

normally gradational and rarely show direct contact with altered host rock or the brecciated Fe-oxide core.

In thin section, massive apatite is a monomineralic mosaic of fine (0.01-0.2 mm) anhedral to subhedral and coarse (0.2-10 mm) subhedral to euhedral grained apatite. In places 10-20  $\mu\text{m}$  interstitial hematite gives the apatite a distinctive pink to purple colour.

Massive apatite ore is dominated by a coarse grained apatite mosaics (0.2-20 mm) of apatite 2 containing distinctive secondary trails of fluid inclusions. Rims of apatite 2, 10-200  $\mu\text{m}$  thick, are also developed around apatite 1 grains (Fig. 4.12). Apatite 2 crystals are usually clear with very low solid inclusion content.

The majority of larger apatite 2 crystals have been broken to angular fragments ( $\sim$ 50-500  $\mu\text{m}$ ) due to subsequent brecciation. The resulting finely granular apatite and amphibole crystals are developed in the brecciated corridors.

The Fe-oxide content is variable through the massive apatite ore. The zones close to main Fe-oxide rich core with more brecciated channels show higher magnetite-hematite contents that gradually diminishes towards the overlying altered host rock. The Fe content of massive apatite is usually in the form of fine grained interstitial hematite that gives a pink to purple colour to the massive apatite. The pink massive apatite ore locally exhibit bleached patches and zones around coarse, hematite-free magnetite 2 -actinolite aggregates (Fig 4.13).

A late carbonate alteration overprints the massive apatite ore as matrix filling, veins and veinlets. The calcite veins contain considerable amount of rare earth carbonate such as synchysite and bastnaesite.

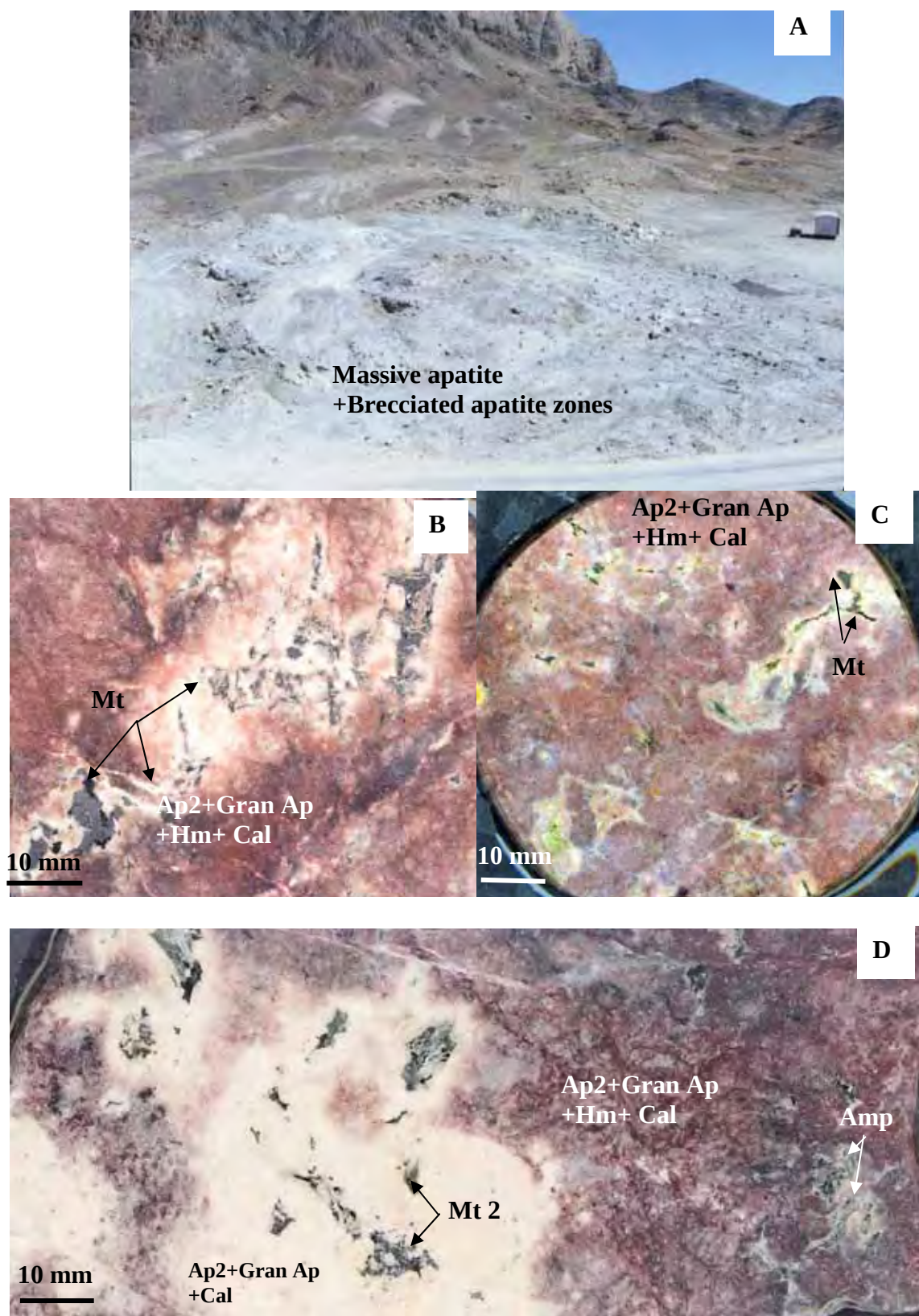
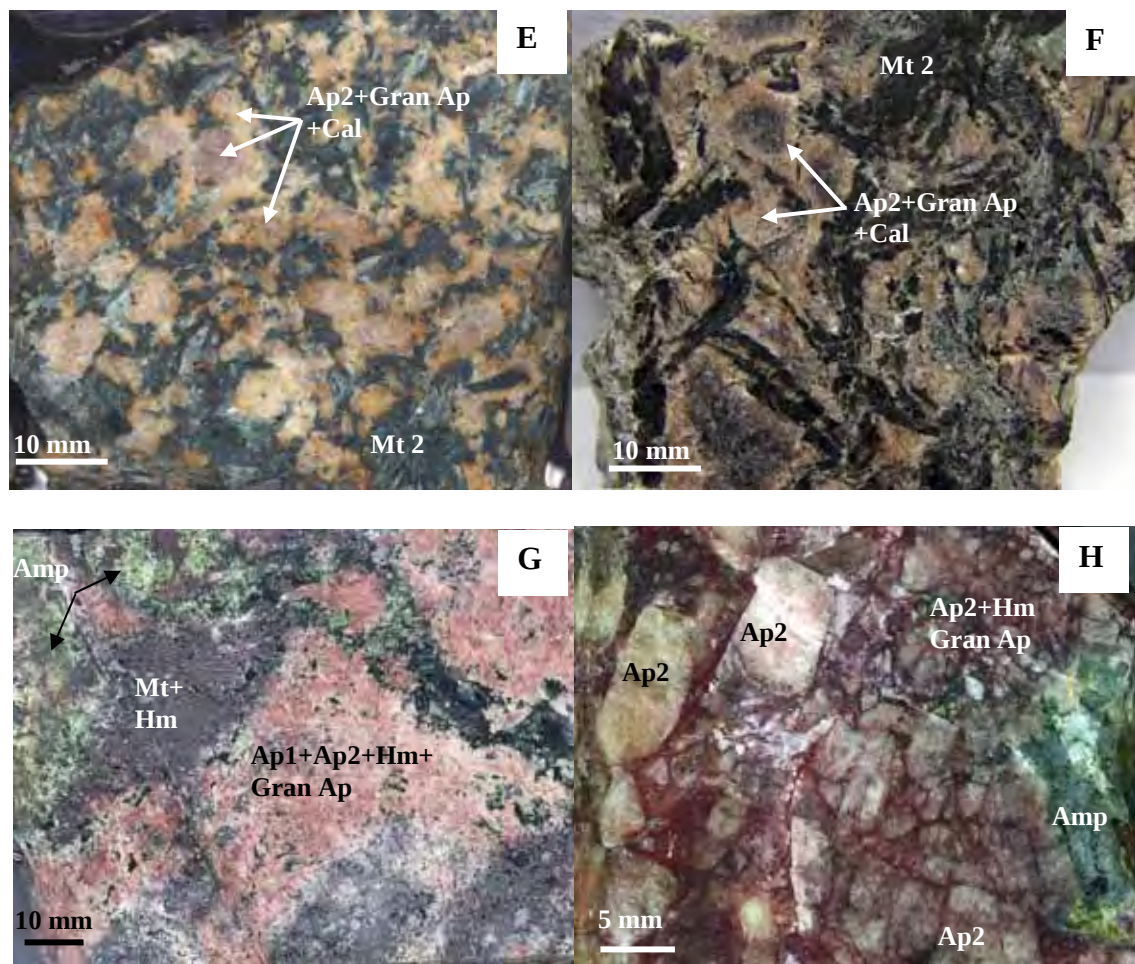


Figure 4. 13 (Caption on next page).



**Figure 4.13 Massive apatite ore with numerous brecciated apatite zones.**

- A: North western part of Esfordi massive and brecciated apatite-rich ore (the 3 m width of caravan can be used as scale).
- B – D: Purple massive apatite with bleached areas around magnetite 2 (holes B2-42 m, B9-1 m, B21-38 m).
- E & F: Brecciated apatite zone with large magnetite 2 crystals pseudomorphs after hematite (holes B9-53 m, B54-42 m).
- G: Brecciated jigsaw remnants of massive apatite in hematite-amphibole groundmass (hole B20-17 m).
- H: Large apatite 2 and amphibole crystals within brecciated apatite2-granular apatite-hematite matrix.

#### 4.3.2 Brecciated apatite zone

The brecciated apatite zone occurs peripheral to the massive apatite ore but also cut through the massive apatite as brecciated corridors. This zone also shows a distinctive occurrence of large green apatite crystals up to 20 cm long. The paragenetic stage most closely associated with the stratabound apatite-rich breccia zone is dominated by apatite – hematite with variable amounts of amphibole and calcite. The contact between the

brecciated apatite and Fe-oxide rich core may be sharp or gradational, whereas the contact between the brecciated apatite and the overlying altered host rock is mainly gradational with numerous apatite-rich veinlets.

Microscopically the brecciated apatite ore displays a range of angular apatite fragments (Fig 4.14). Apatite 2 is the dominant type of apatite in this zone and occurs as massive mosaics and linear arrays of 0.1 – 20 mm crystals, forming both clasts and matrix to widespread breccias and irregular vein-like masses. The other form of apatite 2 is large isolated crystals of euhedral apatite grains typically up to 150 mm with a distinctive green-yellow colour developed within brecciated apatite zone. These large apatites show gradational stage from euhedral to semi- and extensively brecciated crystals (Fig 4.14).

In brecciated apatite-rich zones, the fine granular apatite occurs in the brecciated matrix with apatite 2 fragments, hematite, monazite, allanite and pervasive calcite and quartz (Fig 4.14). The brecciated apatite ore contains large actinolite crystals (up to 15 mm), and Fe-oxide present as fine hematite films between brecciated apatite 2 grains (Fig 4.15) and large secondary magnetite grains with martitized rims. Locally magnetite has developed after hematite as pseudomorphous blades.

The final paragenetic stage is marked by a pervasive overprint of assemblages dominated by quartz and carbonate with minor actinolite and apatite together with a very late calcite veining episode. The carbonate overprinting is more widespread in highly brecciated ore, veins and tuffaceous sandstones. The massive Fe-oxide and apatite ore show a lower degree of carbonate overprinting. This suggests that the late pervasive carbonate alteration was strongly controlled by brecciation and resultant increase in permeability.

Stage apatite 3 is developed within late, pervasive quartz and carbonate matrix, as a minor phase in both Fe-oxide and phosphate bodies (usually accompanied by late

generation amphibole) (Fig 4.16). These apatites are commonly bipyramidal crystals, <100  $\mu\text{m}$  long, with low fluid inclusion contents and usually without any solid inclusions.

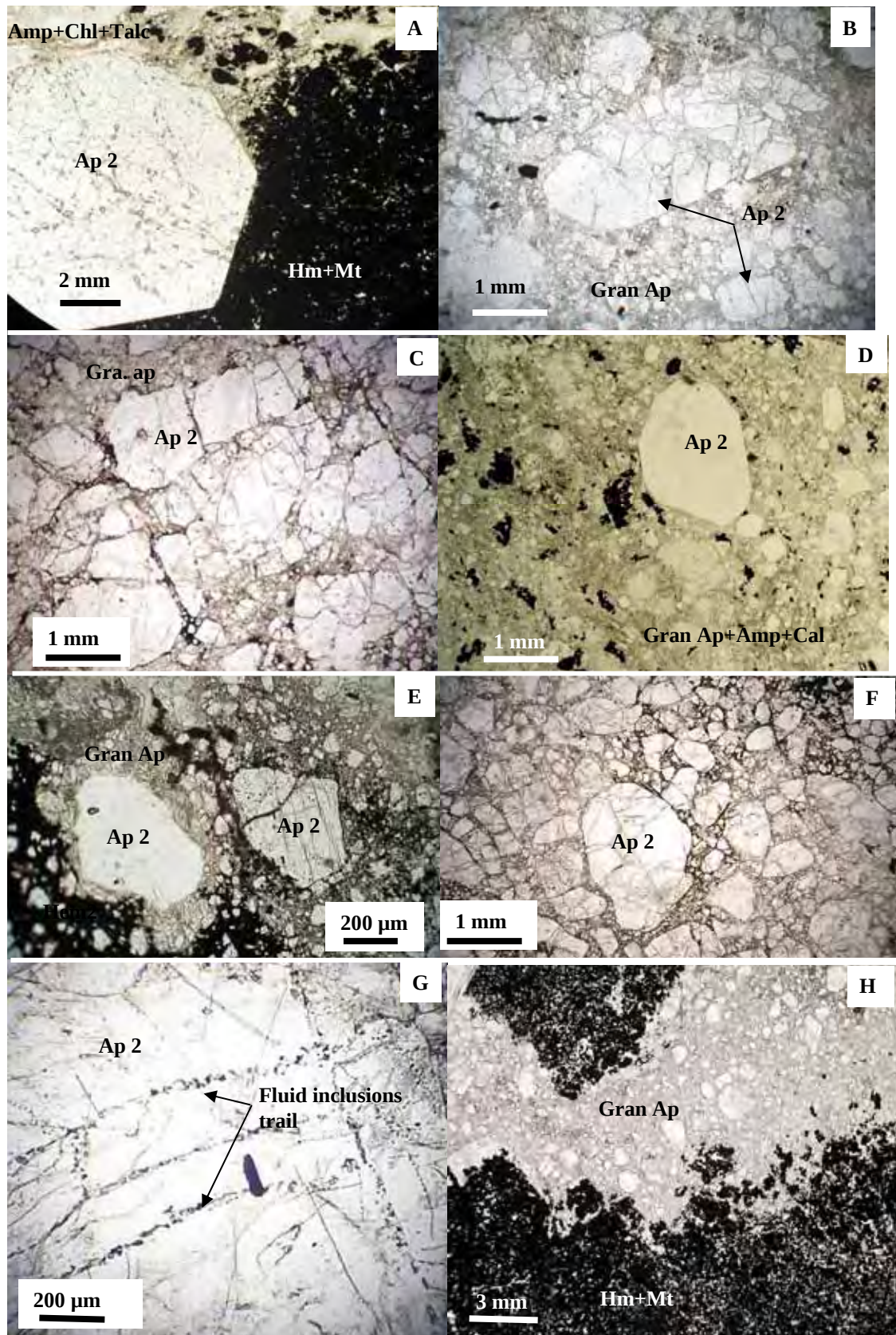
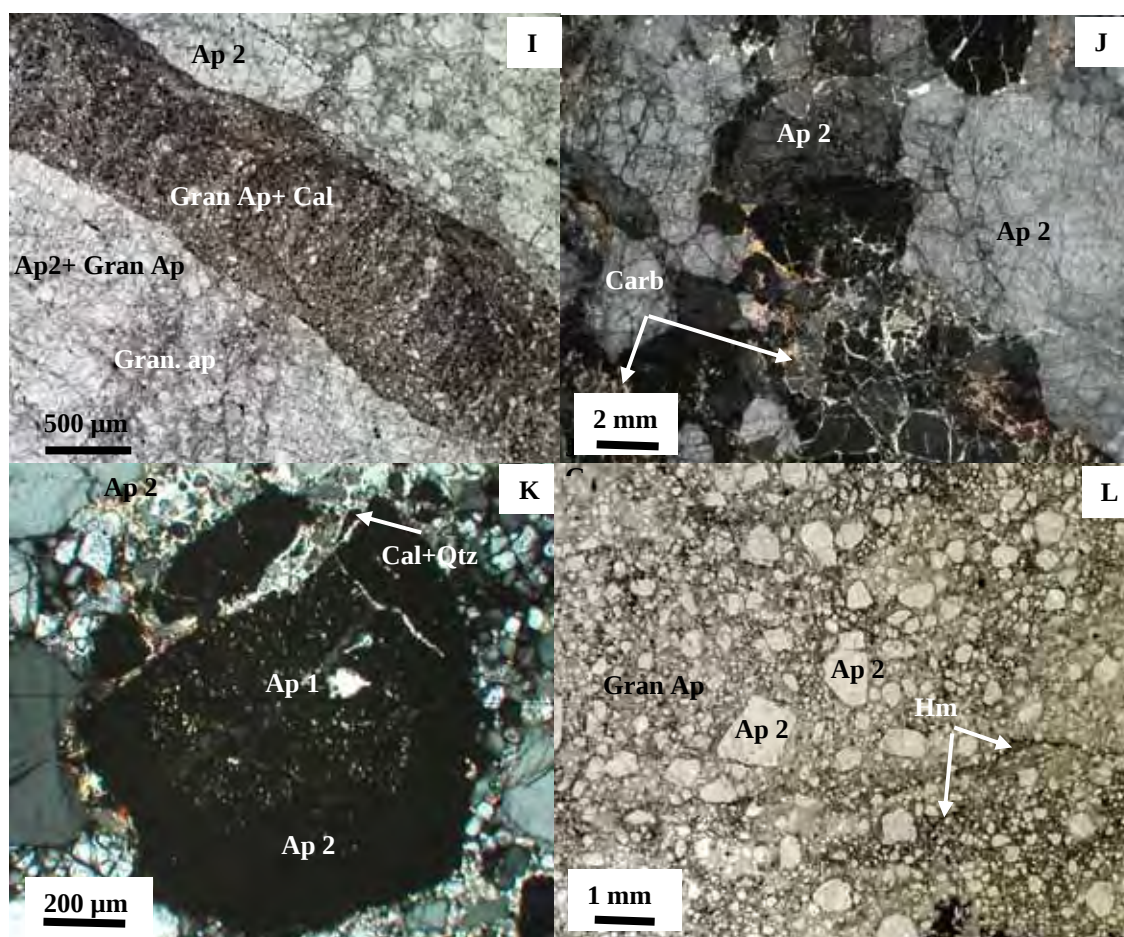


Figure 4. 14 (Caption on next page.)



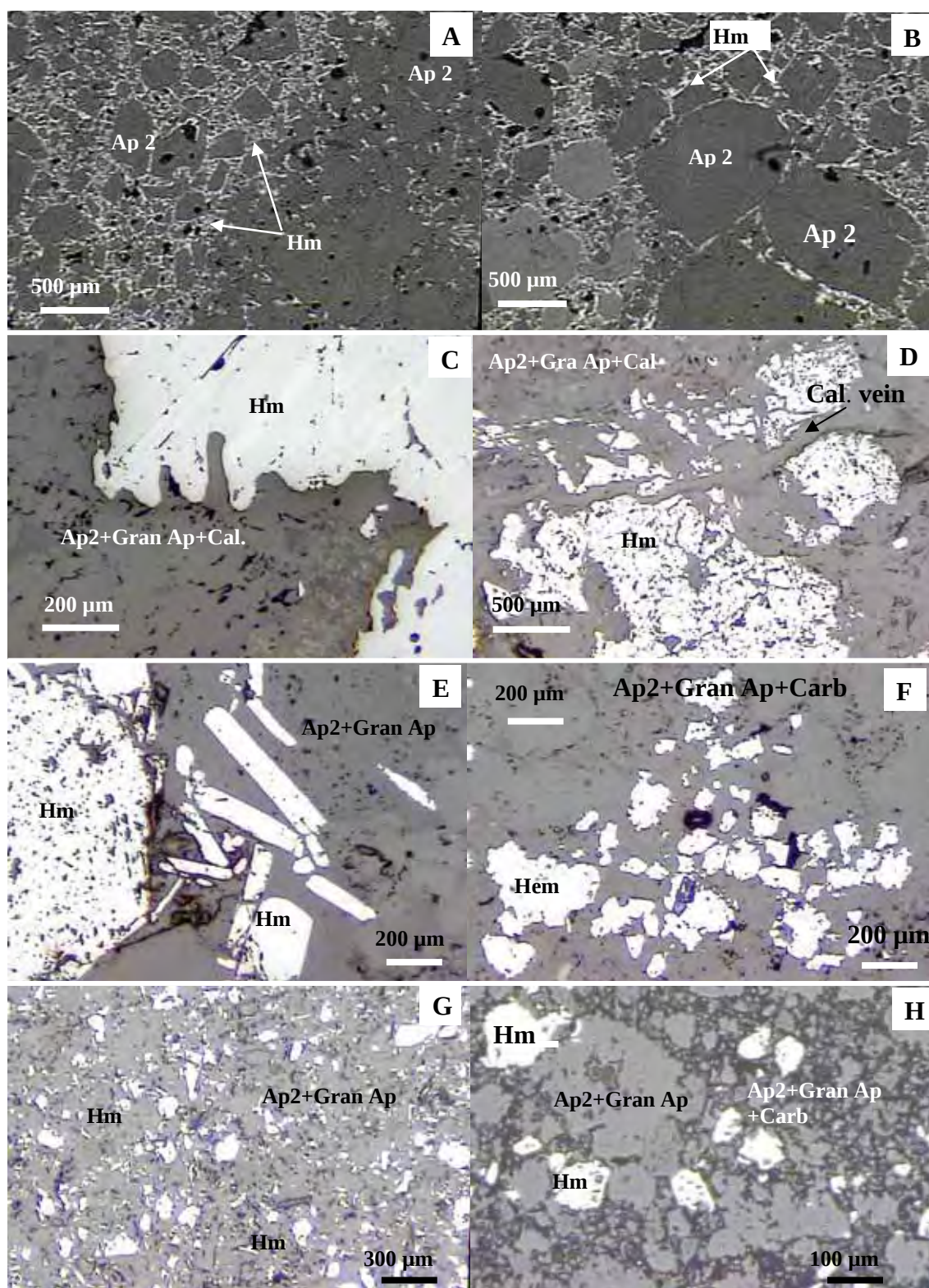
**Figure 4.14 Photomicrographs showing textures and mineral paragenetic association of the brecciated apatite zone at Esfordi.**

- A: Apatite 2 in brecciated margin of Fe-rich core. Euhedral apatite growth in a matrix of hematite and fine granular apatite 2 (101, PPL).
- B – D: Apatite 2 in apatite main zone. Brecciation of apatite 2 and development of granular apatite (hole B27-22 and B12-65, PPL).
- E: Apatite 2 and granular apatite in phosphate-rich zone. Apatite 1 grain rimmed by fine grained granular apatite (hole B12-60, PPL).
- F: Apatite 2 in highly brecciated zone of main apatite ore (hole Bb7-22, PPL).
- G: Trails of secondary fluid inclusions in Apatite 2(hole B7-14, PPL).
- H: Apatite 2 and granular apatite as a vein in the brecciated margin of the Fe-oxide rich core. Shattered apatite 2 grain set in finer granular apatite (hole B20-43, PPL).
- I: Apatite 2 and granular apatite in phosphate-rich zone. Fragmented large apatite 2 grain with trails of granular apatite, cross-cut by a carbonate vein (hole B9-5, PPL).
- J: Apatite 2 and granular apatite in massive apatite zone. Late carbonate and quartz filled the open spaces and locally replaced apatite 2 (hole B9-5, XPL).
- K: Apatite 1 rimmed by apatite 2 in a phosphate-rich zone. Euhedral apatite grain set in granular apatite, hematite, actinolite, carbonate and quartz (hole B12-65, XPL).
- L: Brecciated apatite 2 with intergranular fine hematite crystals and granular apatite (hole B7-14, PPL).

#### 4.4 LOW GRADE APATITE ORE

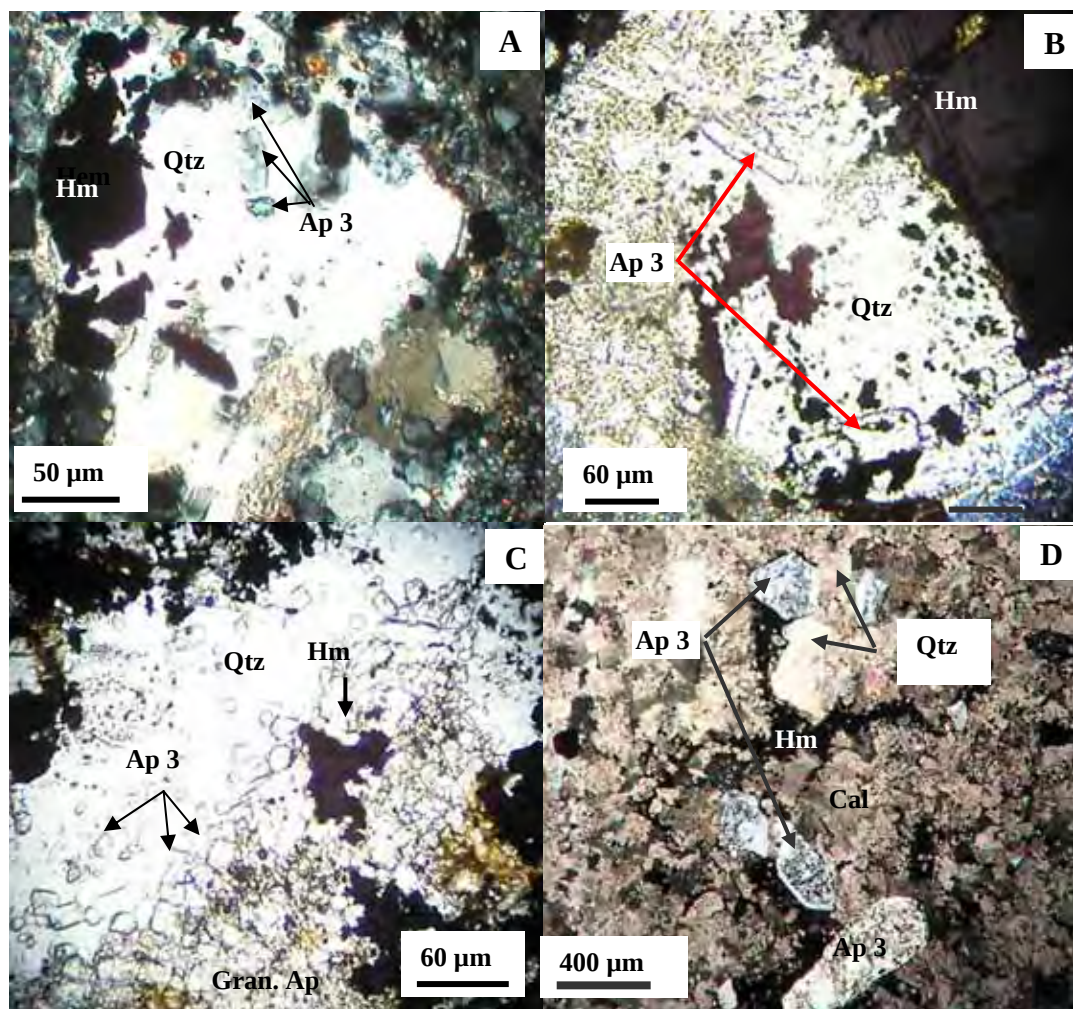
The Fe-rich core and overlying P-rich mineralisation are enveloped by a highly altered actinolite-rich suite of volcanic and volcanoclastic rocks (green rock). This package of rock contains numerous Fe–P veins and disseminated mineralisation. Due to the low total P content ( $\sim 1\text{--}6\%$   $\text{P}_2\text{O}_5$ ; Figure 4.4), the green rocks are classified as low grade ore except for locally thicker apatite veins.

The macroscopic similarity between brecciated corridors in the massive apatite zone and the apatite-rich veins raises a difficulty in separating these two categories in core logging, with clarification only possible based on spatial configuration and microscopic studies. The apatite-Fe-oxide veins range in thickness from a few mm to  $>2$  m (Fig 4.17). The contact of the veins and wall rock is usually sharp. The hematite content of apatite-rich veins varies from minor disseminated hematite to predominantly hematite with minor apatite. The hematite dominated veins are usually small ( $<0.1\text{--}10$  cm thick) and are widespread in peripheral amphibole-rich host rock, whereas the apatite dominated veins show various sizes from a few mm up to 2 m. Chlorite commonly overprints amphibole within a thin selvage to these veins (Fig 4.17 f). The thick apatite-rich veins show light colouration and have brecciated apatite, fragments of massive apatite, lithic fragments, actinolite-rich patches, calcite and quartz patches and veinlets. Fig 4.18 provides a schematic of the veins in Fig 4.17. The brecciated apatite grains are usually angular with sizes ranging up to a few cm. Pervasive overprinting by late stage carbonate and quartz is widespread. Fine grained interstitial hematite is also very common in apatite-rich veins and adjacent altered volcanics. The Fe-oxide occurred as either thin films of hematite in the matrix or between apatite and amphibole grains or as granular and fine lath-shaped crystals (specularite) in the late pervasive carbonate and quartz-rich matrix and veins. The apatite-rich veins are mainly apatite 2 in the form of green, brecciated and large euhedral crystals.



**Figure 4. 15 Hematite occurrences in brecciated apatite ore.**

- A & B: Hematite film between brecciated apatite 2 grains, this hematite gives a purple colour to brecciated apatite (hole B12-65 m).
- C: Large hematite crystal replaced by granular apatite and carbonate (EI3).
- D: Brecciated hematite grain, truncated by late carbonate veining (EI1).
- E: Late hematite crystals in the brecciated apatite ore (EI2).
- F: Patches of disseminated hematite grains in brecciated apatite ore (EI2).



**Figure 4. 16 Apatite 3 in phosphate-rich zone.**

- A & B: Apatite 3 in late stage quartz, which is interstitial to fragmented apatite 2 and brecciated hematite (XPL),
- C: Apatite 3 in a quartz vein in brecciated apatite zone.
- D: Apatite 3 in carbonate-rich patches in the immediate overlying altered volcanics.

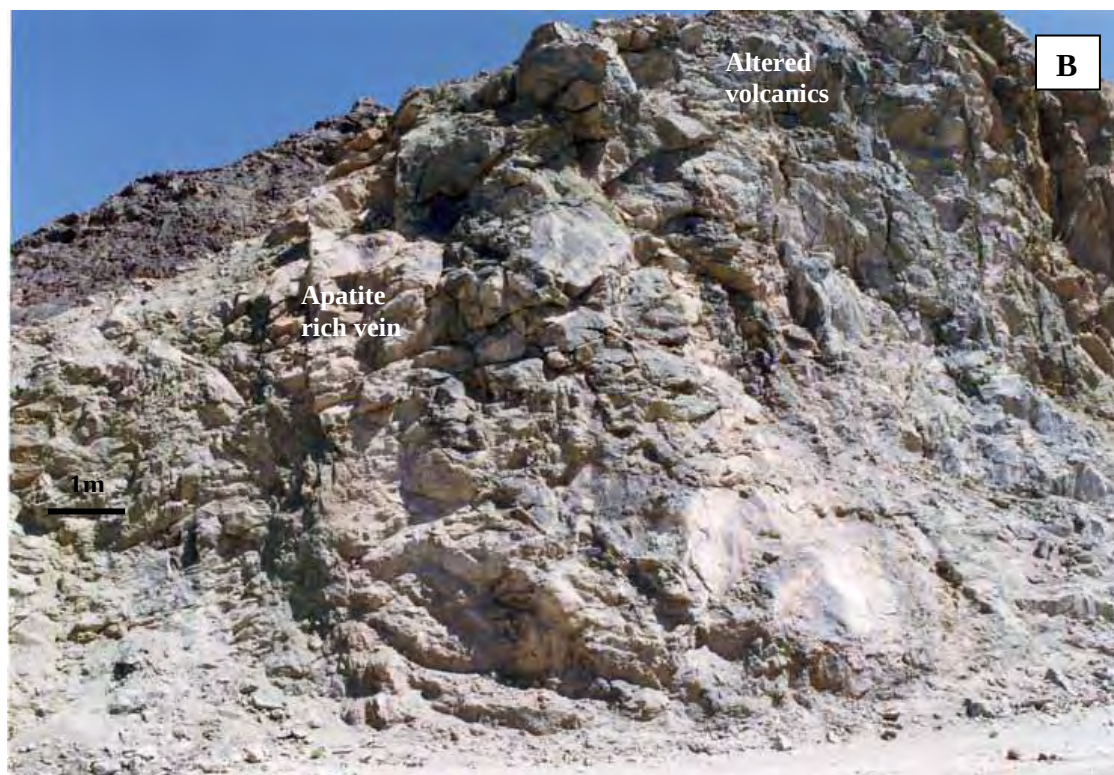
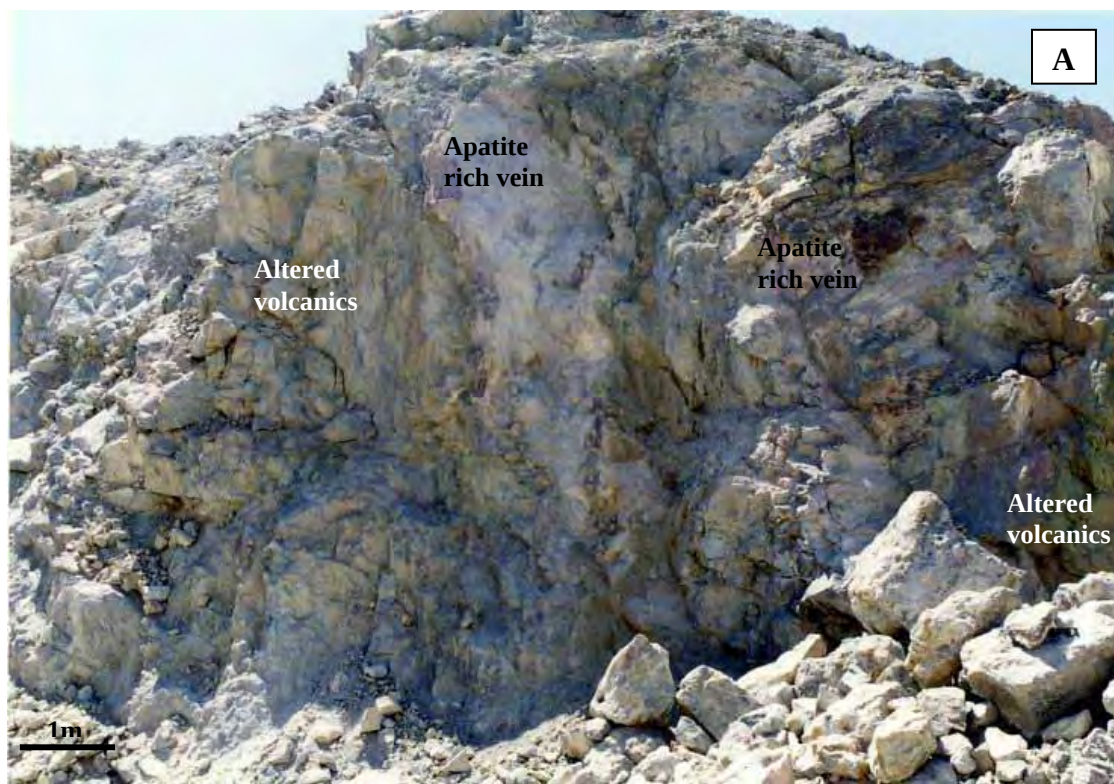
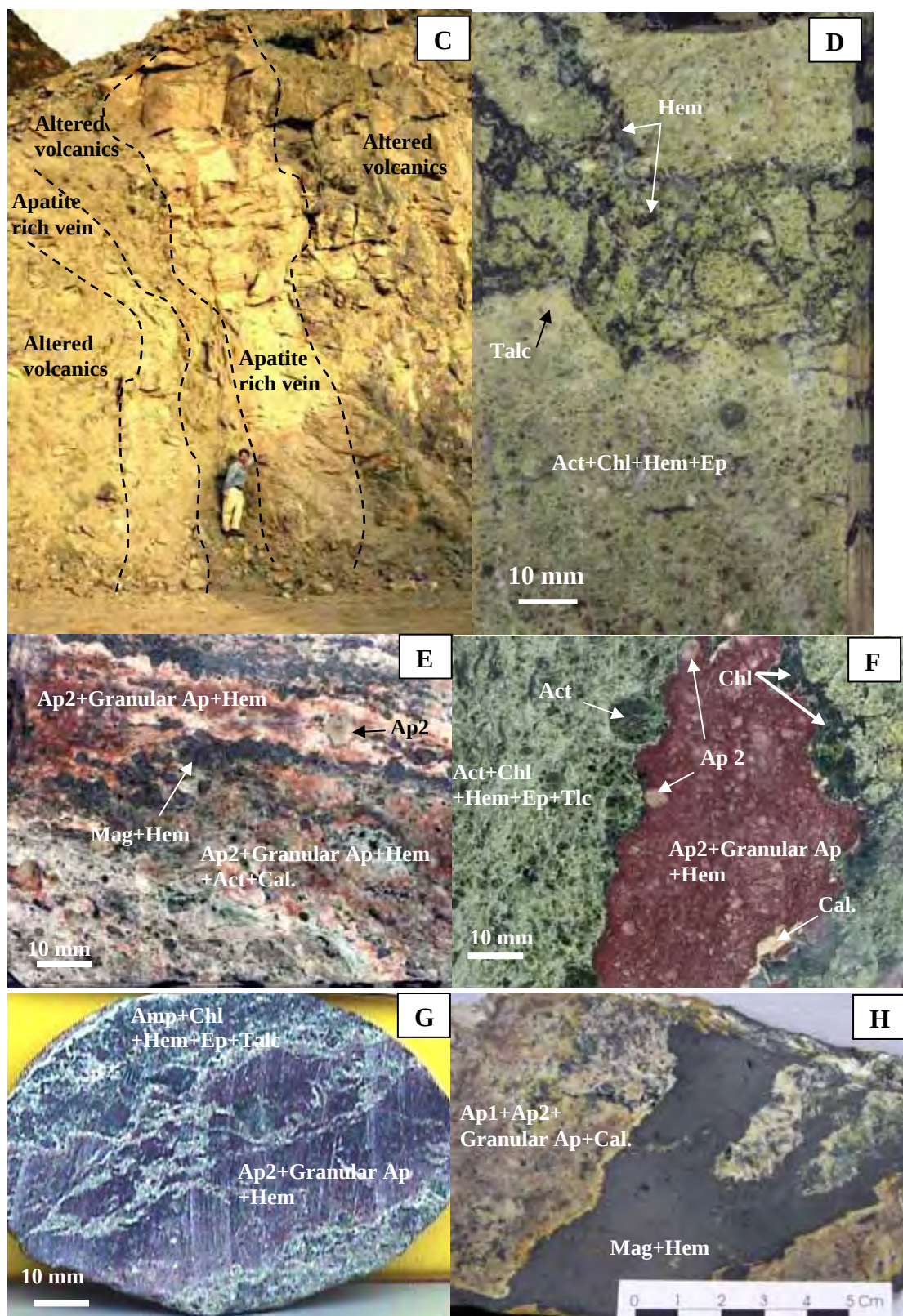


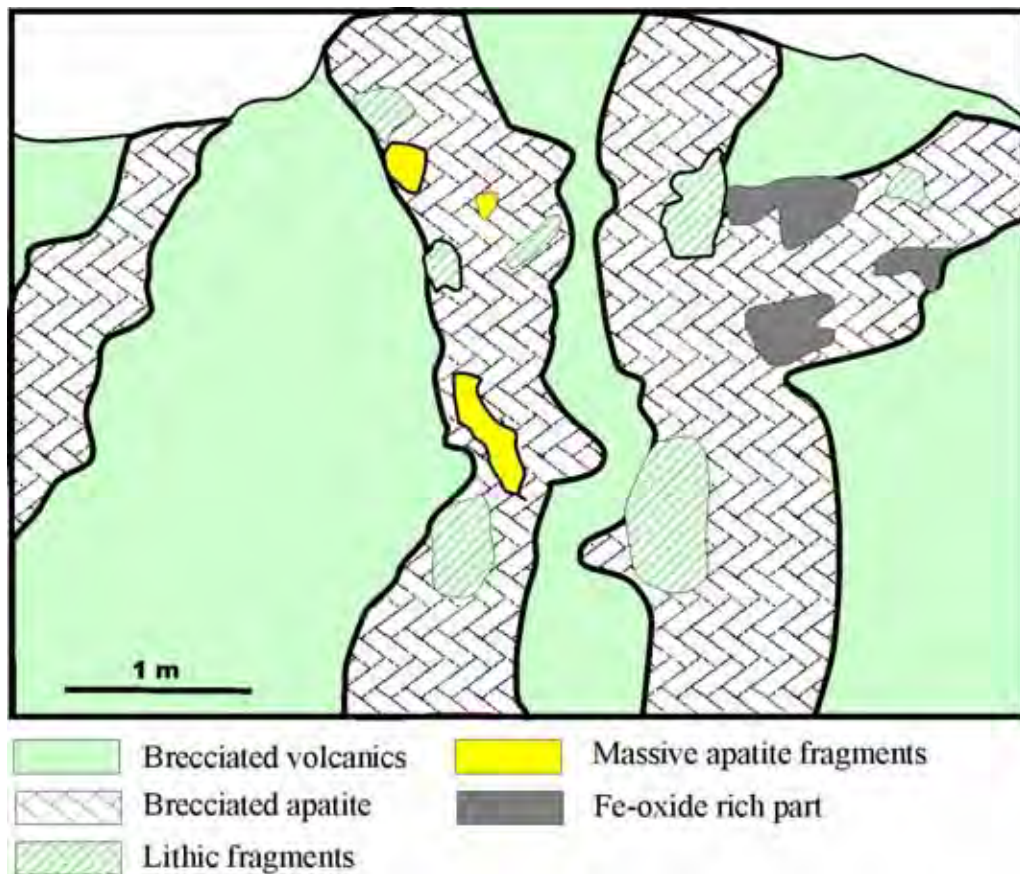
Figure 4. 17 (Caption on page 147.)



**Figure 4.17 Continued (Caption on next page).**

**Figure 4.17 Apatite and Fe-oxide vein mineralisation in Esfordi Fe–P deposit.**

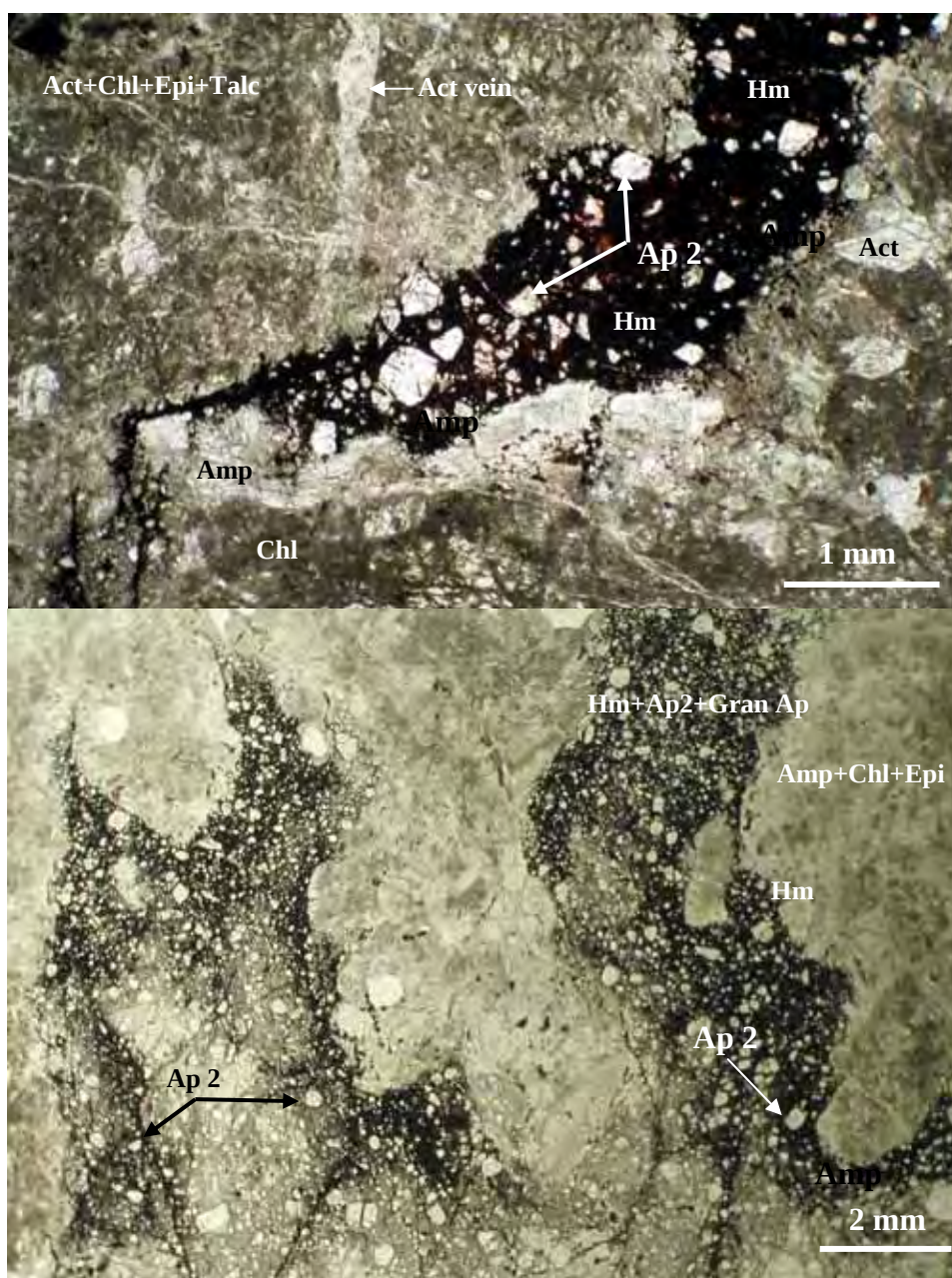
- A – C: Large apatite-rich veins in the hanging wall altered volcanics close to apatite-rich ore.
- D: Hematite vein in amphibole-rich altered rock, 20 m above the P-rich ore (Hole Bh1-4.5).
- E: Apatite-rich vein in brecciated altered volcanics, fine crystals of apatite associated with larger green apatite 2 crystals are sandwich between hematite-rich borders, NW of the P-rich zone (Hole B9-53).
- F & G: An apatite-rich vein with fine hematite crystals in extremely amphibole-rich altered rock of the hanging wall, chlorite crystallised after actinolite in the margin of the vein (Hole B61-5.5).
- H: Magnetite-hematite rich vein in the brecciated apatite-rich groundmass, sampled from the margin of the brecciated Fe-oxide and apatite ores. Fe-oxide core exposure (close to Hole B46).



**Figure 4. 18 Schematic illustration of the Fig 4.17a apatitic veins.**

The brecciated apatite 2 fragments are similar to those of the brecciated apatite ore. The matrix of veins consists of fine fragments of apatite 2, amphibole and Fe-oxide. Allanite and in lesser extent monazite are also associated with fine apatite 2 and minor granular apatite in the Fe-rich matrix (Fig 4.19).

The altered host volcanics and mineralisation are intruded by a series of doleritic bodies. Some dykes are strongly affected by amphibole-rich alteration and locally show Fe-oxide-apatite mineralisation whereas some are relatively fresh without any mineralisation.



**Figure 4. 19 Hematite-rich apatite veins in overlying amphibole-rich altered volcanics in the low grade ore zone, the apatites are apatite 2, granular apatite or apatite 3 (hole B70-15 m).**

## 4.5 APATITE CHEMISTRY

Apatite is the most abundant naturally occurring phosphate mineral and is a common accessory mineral in felsic and mafic rocks. The apatite structure allows many cations, such as  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{REE}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$  to substitute in the two VII-fold and IX-fold coordinated Ca sites. Anionic complexes, such as  $\text{AsO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{SiO}_4^{4-}$ , can substitute for the IV-fold coordinated  $\text{PO}_4^{3-}$ . The anion in the c-axis channel of the apatite structure is usually occupied by  $\text{F}^{-}$ ,  $\text{Cl}^{-}$  or  $\text{OH}^{-}$ .

The extensive substitution between  $\text{F}^{-}$ ,  $\text{Cl}^{-}$  and  $\text{OH}^{-}$  produces three major types of natural apatites. Among these three types,  $\text{F}^{-}$  apatites are the most common naturally occurring type. Additional substitutions for these anions are mono and divalent anions such as  $\text{Br}^{-}$ ,  $\text{I}^{-}$ ,  $\text{O}_2^{-}$ ,  $\text{O}_3^{-}$ ,  $\text{BO}_2^{-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{O}_2^{2-}$ ,  $\text{O}^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{O}_2^{2-}$  and  $\text{S}^{2-}$ .

Iron in natural apatites rarely exceeds 1 % (Pan and Fleet 2002).  $\text{Fe}^{2+}$  substitutes in both  $\text{Ca}^{2+}$  sites with a strong preference for the Ca1 site (Khudolozhkin *et al.* 1974). The late apatite 3 and granular apatite contain the highest and lowest Fe contents in the Esfordi system respectively. Apatite 1 and 2, the major constituent of the Esfordi apatite-rich ore, have similar average Fe content ( $\sim 0.1$  %).

The microprobe analyses indicate that the Esfordi apatites are F-rich with variable Cl content (Table 4.3). Apatite 1 has the highest Cl and Na (0.69 and 0.30 wt. %).

Apatite 2 also contains considerable amounts of Cl and Na, lower than apatite 1 but higher than apatite 3 and granular apatite. Apatite 3, associated with late carbonates and quartz has relatively low Cl and Na and high F contents. Granular apatites are depleted in Cl and Na and enriched in F. Further aspects of the apatite geochemistry are described in Chapter 6.

**Table 4. 3 Average electron microprobe analyses of different types of Esfordi apatites.**

|                                | Apatite 1<br>N=26 |           | Apatite 2<br>N=83 |           | Apatite 3<br>N=20 |           | Granular<br>apatite N=29 |           |
|--------------------------------|-------------------|-----------|-------------------|-----------|-------------------|-----------|--------------------------|-----------|
| Oxides<br>(wt %)               | Ave.              | Std. Dev. | Ave.              | Std. Dev. | Ave.              | Std. Dev. | Ave.                     | Std. Dev. |
| CaO                            | 52.53             | 0.70      | 53.67             | 0.91      | 54.66             | 0.75      | 54.94                    | 1.35      |
| P <sub>2</sub> O <sub>5</sub>  | 38.32             | 0.30      | 40.50             | 0.94      | 40.25             | 0.77      | 37.59                    | 5.95      |
| SiO <sub>2</sub>               | 0.32              | 0.07      | 0.24              | 0.06      | 0.07              | 0.06      | 0.11                     | 0.07      |
| La <sub>2</sub> O <sub>3</sub> | 0.37              | 0.11      | 0.30              | 0.20      | 0.03              | 0.05      | 0.06                     | 0.06      |
| Ce <sub>2</sub> O <sub>3</sub> | 0.90              | 0.12      | 0.78              | 0.26      | 0.06              | 0.11      | 0.11                     | 0.12      |
| Nd <sub>2</sub> O <sub>3</sub> | 0.39              | 0.09      | 0.31              | 0.17      | 0.04              | 0.05      | 0.08                     | 0.06      |
| Y <sub>2</sub> O <sub>3</sub>  | 0.20              | 0.04      | 0.20              | 0.11      | 0.02              | 0.05      | 0.02                     | 0.06      |
| SrO                            | 0.01              | 0.01      | 0.04              | 0.04      | 0.03              | 0.07      | 0.07                     | 0.06      |
| FeO                            | 0.10              | 0.04      | 0.11              | 0.07      | 0.25              | 0.41      | 0.06                     | 0.08      |
| Na <sub>2</sub> O              | 0.30              | 0.03      | 0.28              | 0.08      | 0.04              | 0.05      | 0.11                     | 0.09      |
| Cl                             | 0.70              | 0.08      | 0.39              | 0.16      | 0.11              | 0.07      | 0.06                     | 0.04      |
| F                              | 4.00              | 0.49      | 3.95              | 0.81      | 4.94              | 1.18      | 5.79                     | 1.07      |
| Total                          | 98.18             | 0.04      | 100.80            | 11.05     | 100.50            | 1.29      | 100.33                   | 3.61      |

BLD: Below level of Detection

#### 4.6 MAGNETITE-HEMATITE HORIZONS

The hanging wall of the Esfordi deposit contains several sedimentary units with sublayers of magnetite and minor hematite (Fig 4.21). These Fe-oxide sublayers are stratiform within the volcanoclastics and pebbly sandstones and siltstones. Their distribution is mainly restricted to the section between apatite-rich zone and the upper most jaspilite layer. Magnetite and hematite grains with grain sizes up to 30 mm are observed in these layers. The contacts between the poorly sorted altered volcanoclastic rocks and the sandstones are generally gradational, but somewhat masked by strong amphibole alteration.

The Fe-oxide rich sublayers are a few mm to 10 cm thick and locally occur in a green tuffaceous sandstone layers of 2 - 10 m thickness as indicated in one zone 20 m above the ore zone (Fig 4.21). The sandstone contains sedimentary structures such as graded bedding and cross-bedding but with some degree of hydrothermal overprinting.

Above the magnetite bearing sandstone, several horizons of pebbly sandstone contain 0.1 to 20 mm magnetite and hematite grains. These clastic units are up to 100 m thick and contain several trachyte and rhyolite intervals. This suite of rocks are the hanging wall amphibole-rich alteration zone (green rocks), the clastic rocks are the major part of the sequence and contain a wide range of clasts including lithic fragments. The lithic fragments are texturally unmodified and show original fabrics. These fragments are typically limestone, dolomite, jaspilite, siltstone and altered trachyte and rhyolite (Fig 4.21). The matrix is usually composed of finer clasts and authigenic minerals such as hematite, amphibole, chlorite, carbonate and quartz. The general rounded shape of the clasts, admixture of non-volcanic particles, association with limestone inter-bedding and partial diagenetic alteration suggests that these rocks are resedimented volcanoclastic deposits (McPhie *et al.* 1993).

The altered clastic and associated rhyolitic rocks also contain variable amount of Fe-oxide associated with apatite, actinolite and biotite, in veins, veinlets and open space fillings associated with apatite, actinolite and minor REE minerals, and also stockwork and films around mineral grains and clasts. The Fe-oxide clast size ranges from less than 0.1 to 20 mm are generally magnetite with various degrees of martitisation, whereas the open space fillings overgrowths are mainly hematitic. Some magnetite grains contain apatite inclusions and overgrowths of granular apatite and calcite (Fig 4.20 and 4.22).

The hematites are mainly in the form of specularite, laths shaped crystals and/or anhedral grains of size up to 2 mm. In a few cases the hematite crystals are pseudomorphous after magnetite. Fine grained, amorphous limonite and goethite also accompany hematite as secondary minerals on weathered surfaces.

Microscopically, Fe-oxide rich parts of the sandstones are mainly composed of magnetite with minor martite along cleavages, cracks and also narrow margins. The magnetite grains are either semi round or angular and up to 2 mm. Apatite crystals also

exist in close association with magnetite and, in some cases, are surrounded by magnetite which resembles the primary magnetite–apatite core of the system.

The groundmass of the magnetite clasts in Fe-oxide rich horizons is composed of sand and silt size quartz and lithic fragments composed of sericitised orthoclase and albite, amphibole, chlorite and epidote (Fig 4.22). The quartz grains are zoned and the matrix is filled by pervasive, late stage carbonate and quartz. The amphiboles show two textural forms including detrital grains and a younger generation of amphibole (amphibole 2) associated with quartz. The later occurred as small and elongate crystals (10-50  $\mu\text{m}$ ). Late stage calcite veins cross-cut the layering of the rock and contain small crystals of amphibole 2 (Fig 4.22).

#### **4.6.1 Fe-oxide – jaspilite -carbonate horizons**

A jaspilite layer of 2 to 6 m thickness is situated ~100 m stratigraphically above the Esfordi mineralizing zone. The jaspilite is conformable with the enclosing volcano-sedimentary layers, and is best exposed some 500 m NW of Esfordi (Fig 4.23). The jaspilite layer overlies the altered rhyolite, tuff and tuffaceous sandstone and is commonly associated with a 0.5-2 m carbonate horizon. It is overlain by volcaniclastic sandstone, shale and subsequently by a thick massive dolomite and limestone succession. This jaspilitic layer is the upper limit to extensive hanging wall amphibole-rich alteration (green rocks). The upper volcanic and volcaniclastic rocks show weak amphibole alteration.

Several patchy outcrops of jaspilite are also exposed in the hanging wall, close (~10-20 m) to the mineralisation but are disrupted by local faulting and penecontemporaneous erosion. All of these outcrops are associated with a thin bed of limestone (Fig 4.23).

The Fe-oxide rich horizons of these jaspilitic layers show a banding and layering with intervals of reddish jasper and chert. Microscopically, the rock is dominated by magnetite

and jasper. The magnetite grains are subhedral to euhedral (0.02 and 5 mm size) and martitized along the fractures. The rock matrix is composed of amorphous jasper, magnetite grains and fine hematite crystals. The hematites are generally fine (10-30  $\mu\text{m}$ ) and blade-shaped whereas the magnetite grains are larger (0.07- 0.5 mm), with euhedral or granular shape (Fig 4.24). The late stage pervasive calcite and quartz also overprints the textures.

#### **4.7 FE OXIDE CHEMISTRY AND COMPARISON WITH OTHER FE OXIDE ORES WORLDWIDE**

Based on field observations, and polished block and thin section examinations five type of magnetite and/or hematite occurrences were identified in Esfordi deposit, including massive Fe-oxide core, brecciated margin of Fe-oxide core and apatite-rich ore, hanging wall clastic Fe oxide horizons, Fe oxide associated with tuffs and doleritic dykes and the jaspilite layer.

The chemical composition of these magnetites and hematites has been investigated by electron microprobe analyses (Table 4.4, Table 7-Appendix 2). Among the elements analysed Ti and V show significant variation corresponding with different Fe oxide types. Core and breccia magnetite have a similar range of Ti values reflecting variable formation of associated ilmenite and rutile. They are significantly lower than the magnetites in the doleritic bodies. The V values overlap for core and brecciated margin magnetites but are slightly higher in clastic magnetite. The hematite associated with apatite-rich ore contains very low Ti and V. Magnetite 2, which crystallised after hematite has same range of Ti and V with specularites and magnetite associated with volcanoclastic rocks. The magnetite grains within jaspilite horizon are characterized by unmeasurably low V and variable  $\text{TiO}_2$  content with an average of 0.21 %. The content of other elements in all of these groups of

magnetites and hematites are negligible, however small Al and Mg concentrations in magnetites are due to spinel exsolution which are absent in hematite.

The Ti and V values of different types of Esfordi magnetites and hematites are plotted in Fig 4.20A. The magnetites within dolerites are well differentiated from the other groups, generally plot in the domain of Apatite-Iron ores (Kiruna type) or perhaps BIF in the case of jaspilites.

The Esfordi magnetite Ti and V compositions overlap with the range given for Kiruna-type in general although they are somewhat poorer in Ti than at the Mishdovan and Choghart deposits, but higher than at the Kirrunavarra deposit, which presented in Fig 4.20B.

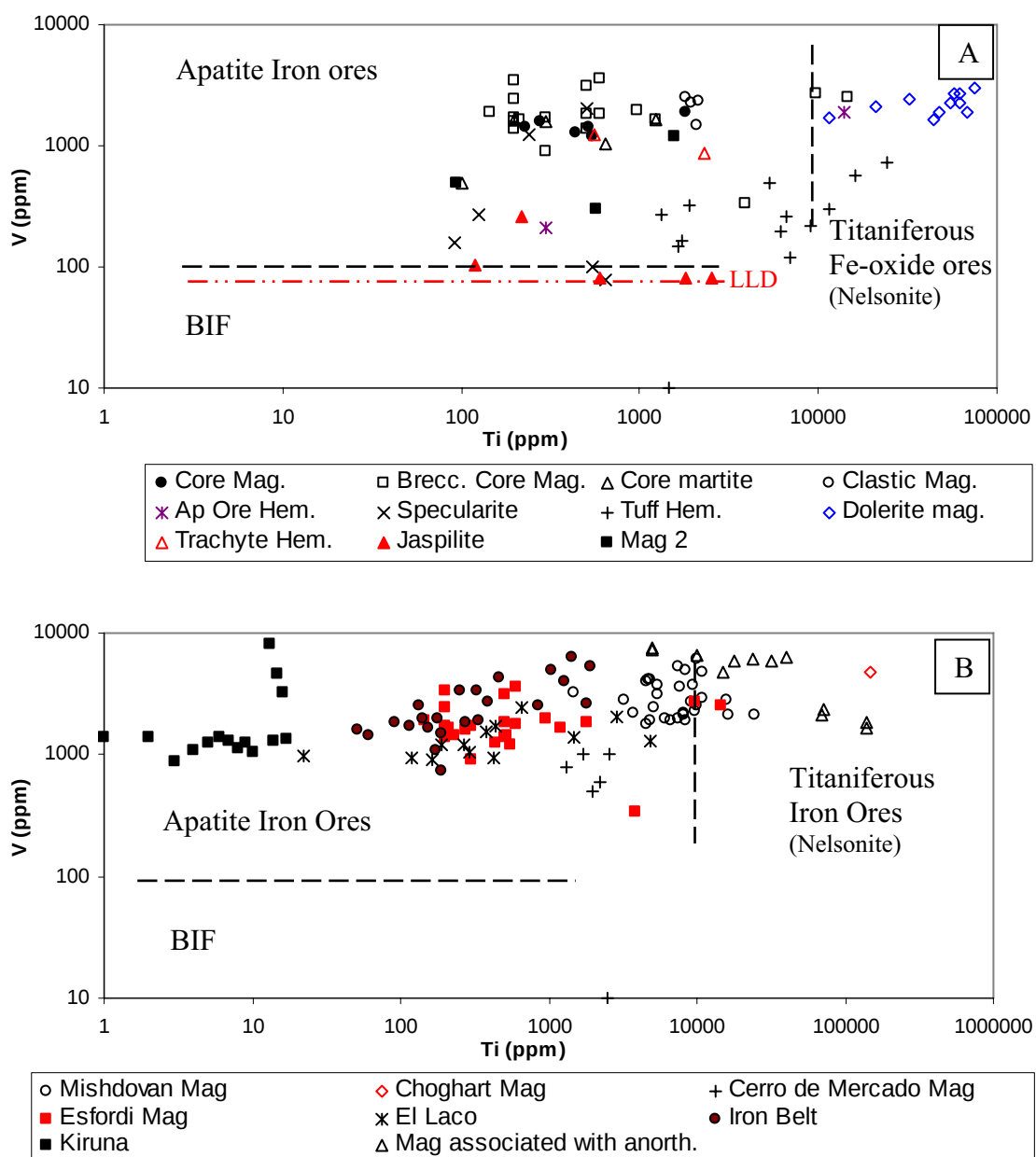
The magnetite associated with doleritic dykes plotted within the titaniferous Fe-oxide ores (Nelsonites) and the tuff hematite fields suggesting a composite origin, in part driven from both Esfordi apatite-Iron oxide and dolerites (Fig. 4.20).

**Table 4. 4 Average electron microprobe analyses of different types of Magnetite and hematite of Esfordi deposit.**

| Host                           | Magnetite-rich core |      | Brecciated core |       |       |       | Clastic Magnetite |       | Magnetite 2 |       | Specularite |       | Volcaniclastics |       | Jaspilite |       | Dolerite |       |
|--------------------------------|---------------------|------|-----------------|-------|-------|-------|-------------------|-------|-------------|-------|-------------|-------|-----------------|-------|-----------|-------|----------|-------|
|                                | N=7                 | N=14 | N=10            |       | N=5   |       | N=5               |       | N=5         |       | N=7         |       | N=12            |       | N=4       |       | N=5      |       |
|                                | Mt                  | Mt   | Mt              | Hm    | Ave.  | STDEV | Ave.              | STDEV | Ave.        | STDEV | Ave.        | STDEV | Ave.            | STDEV | Ave.      | STDEV | Ave.     | STDEV |
| Wt%                            | Mt                  | Mt   | Mt              | Hm    | Mt    |       | Mt                |       | Mt          |       | Hm          |       | Mt              |       | Mt        |       | Mt       |       |
| Label                          | Ave. %              | STDV | Ave.            | STDEV | Ave.  | STDV  | Ave.              | STDEV | Ave.        | STDEV | Ave.        | STDEV | Ave.            | STDEV | Ave.      | STDEV | Ave.     | STDEV |
| SiO <sub>2</sub>               | 0.21                | 0.37 | 0.08            | 0.10  | 0.06  | 0.05  | 0.04              | 0.00  | 0.03        | 0.02  | 0.12        | 0.10  | 0.02            | 0.02  | 0.02      | 0.01  | 0.07     | 0.04  |
| TiO <sub>2</sub>               | 0.20                | 0.27 | 0.12            | 0.17  | 0.24  | 0.51  | 0.29              | 0.10  | 0.11        | 0.11  | 0.06        | 0.04  | 0.93            | 0.79  | 0.21      | 0.18  | 8.67     | 2.39  |
| Al <sub>2</sub> O <sub>3</sub> | 0.06                | 0.03 | 0.04            | 0.03  | 0.03  | 0.01  | 0.16              | 0.03  | 0.01        | 0.00  | 0.30        | 0.23  | 0.41            | 0.28  | 0.28      | 0.15  | 0.79     | 1.09  |
| Cr <sub>2</sub> O <sub>3</sub> | 0.02                | 0.00 | 0.02            | 0.01  | 0.04  | -     | 0.04              | 0.01  | 0.03        | 0.01  | 0.03        | 0.01  | 0.04            | 0.01  | BLD       | -     | 0.29     | 0.04  |
| V <sub>2</sub> O <sub>5</sub>  | 0.28                | 0.05 | 0.29            | 0.13  | 0.32  | 0.18  | 0.32              | 0.15  | 0.16        | 0.10  | 0.10        | 0.13  | 0.05            | 0.03  | 0.05      | -     | 0.39     | 0.07  |
| MgO                            | 0.36                | -    | 0.03            | 0.04  | 0.03  | 0.02  | 0.05              | 0.00  | 0.30        | 0.28  | 0.24        | 0.36  | 0.14            | 0.10  | BLD       | -     | 0.03     | 0.02  |
| CaO                            | 0.05                | 0.07 | 0.07            | 0.13  | 0.08  | 0.12  | 0.08              | 0.10  | 0.10        | 0.05  | 0.15        | 0.13  | 0.03            | 0.01  | BLD       | -     | 0.05     | 0.03  |
| MnO                            | 0.03                | 0.01 | 0.03            | 0.02  | 0.04  | 0.02  | 0.01              | 0.01  | 0.02        | 0.00  | 0.04        | 0.04  | 0.05            | 0.02  | BLD       | -     | 0.99     | 0.45  |
| Fe <sub>2</sub> O <sub>3</sub> | 67.78               | 0.87 | 67.64           | 0.55  | 98.50 | 1.22  | 67.21             | 0.54  | 68.16       | 0.57  | 100.12      | 0.64  | 66.35           | 1.62  | 68.01     | 0.55  | 50.07    | 4.09  |
| FeO                            | 31.73               | 0.31 | 31.45           | 0.35  | 0.64  | 0.61  | 31.66             | 0.38  | 30.85       | 0.54  | 0.18        | 0.19  | 31.72           | 0.60  | 31.25     | 0.34  | 38.56    | 1.60  |
| NiO                            | 0.09                | 0.03 | 0.04            | 0.01  | 0.13  | -     | 0.03              | 0.01  | 0.04        | 0.02  | 0.60        | 0.00  | 0.04            | 0.02  | BLD       | -     | 0.04     | 0.04  |
| Na <sub>2</sub> O              | 0.06                | 0.04 | 0.03            | 0.01  | 0.03  | 0.01  | 0.02              | 0.01  | 0.04        | 0.03  | 0.07        | 0.10  | 0.01            | 0.01  | BLD       | -     | 0.02     | 0.01  |
| K <sub>2</sub> O               | BLD                 | -    | 0.02            | 0.01  | BLD   | -     | 0.00              | 0.00  | 0.03        | 0.02  | 0.02        | 0.01  | 0.04            | 0.02  | BLD       | -     | 0.03     | 0.02  |
| TOTAL                          | 100.37              | 0.45 | 99.70           | 0.56  | 99.85 | 0.48  | 99.77             | 0.21  | 99.51       | 0.63  | 101.17      | 1.04  | 99.56           | 0.64  | 99.78     | 0.73  | 99.44    | 0.48  |

**Note: The detailed analytical results are presented in Table 7, Appendix 2.**

BLD: Below level of Detection



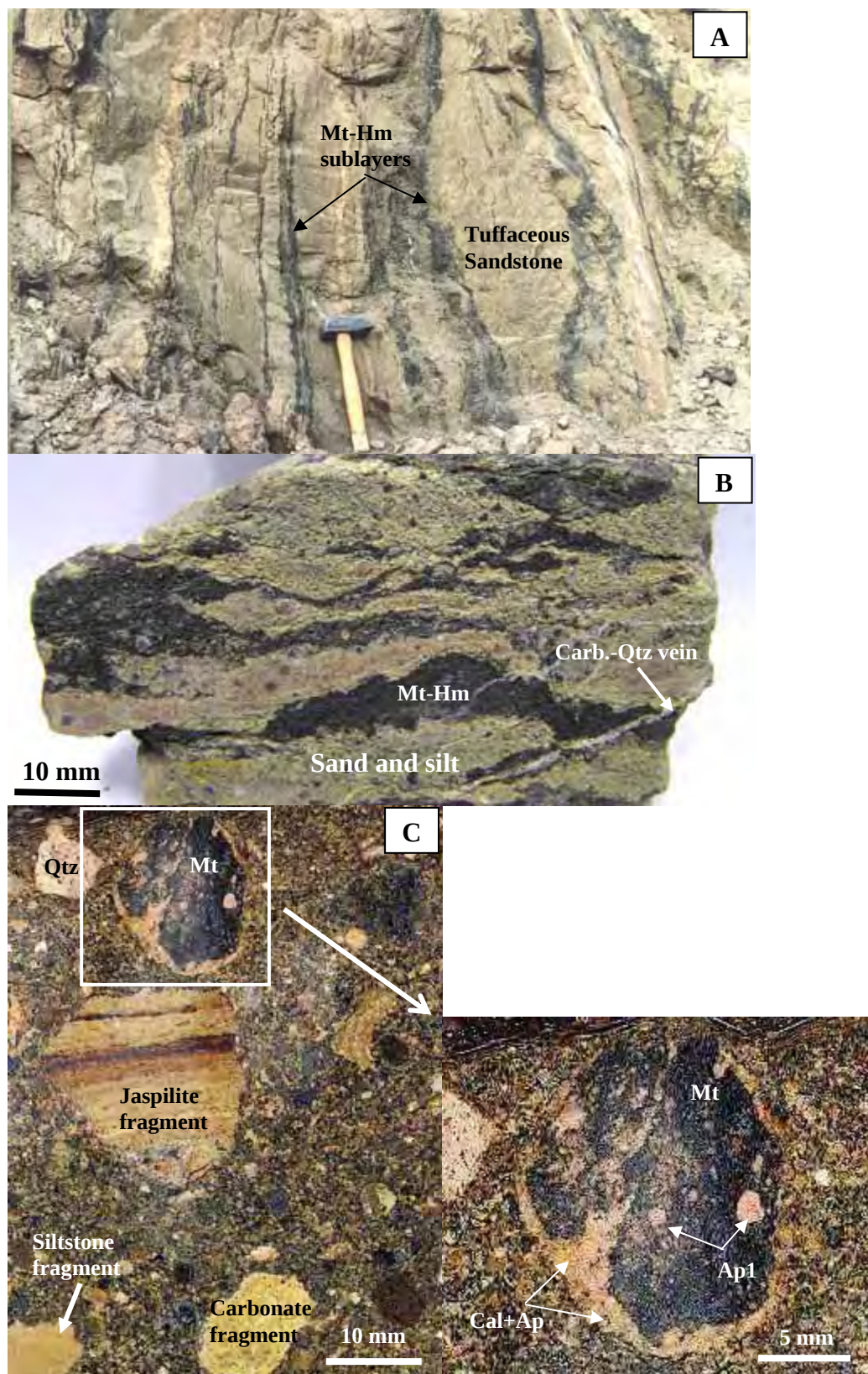
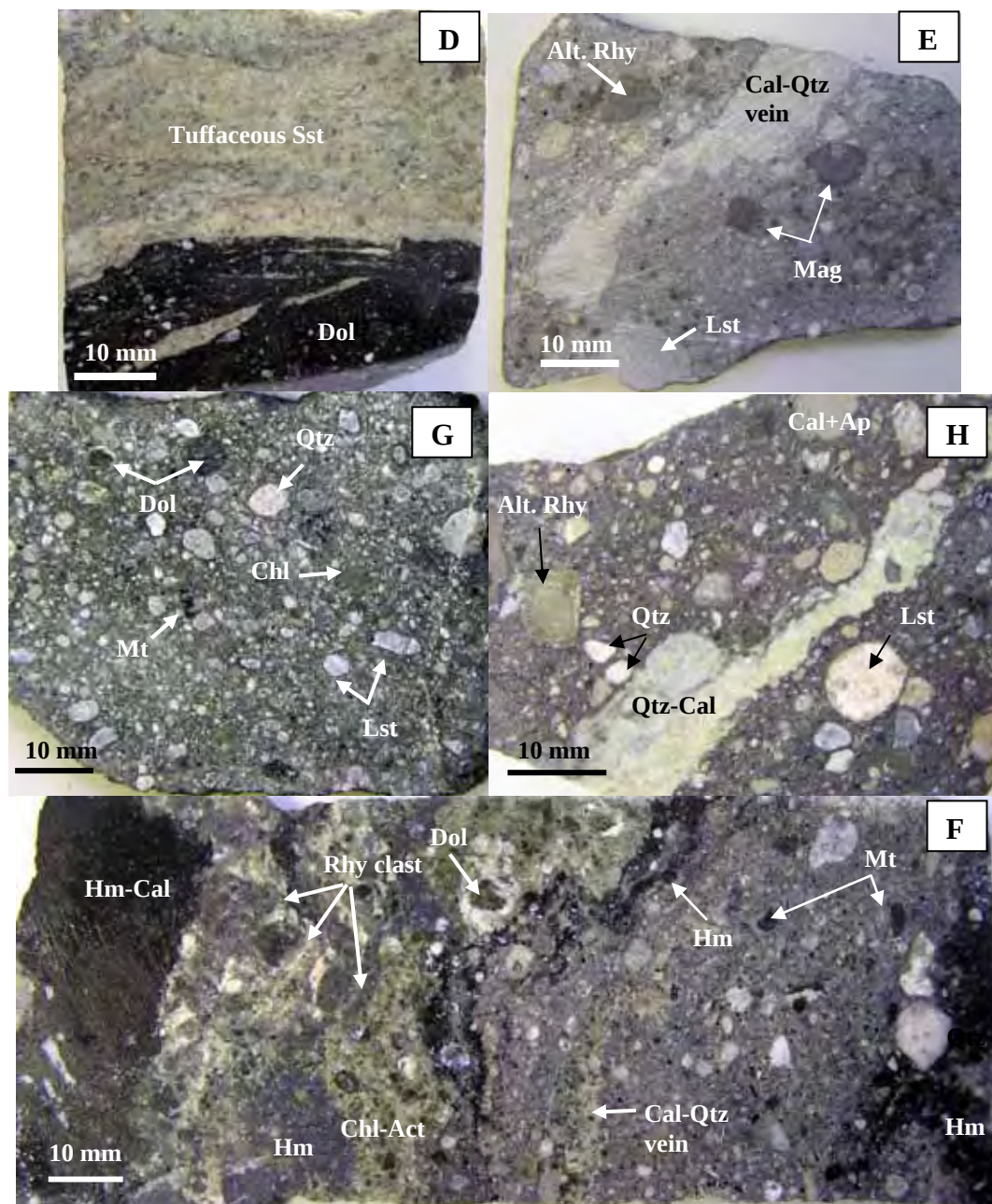
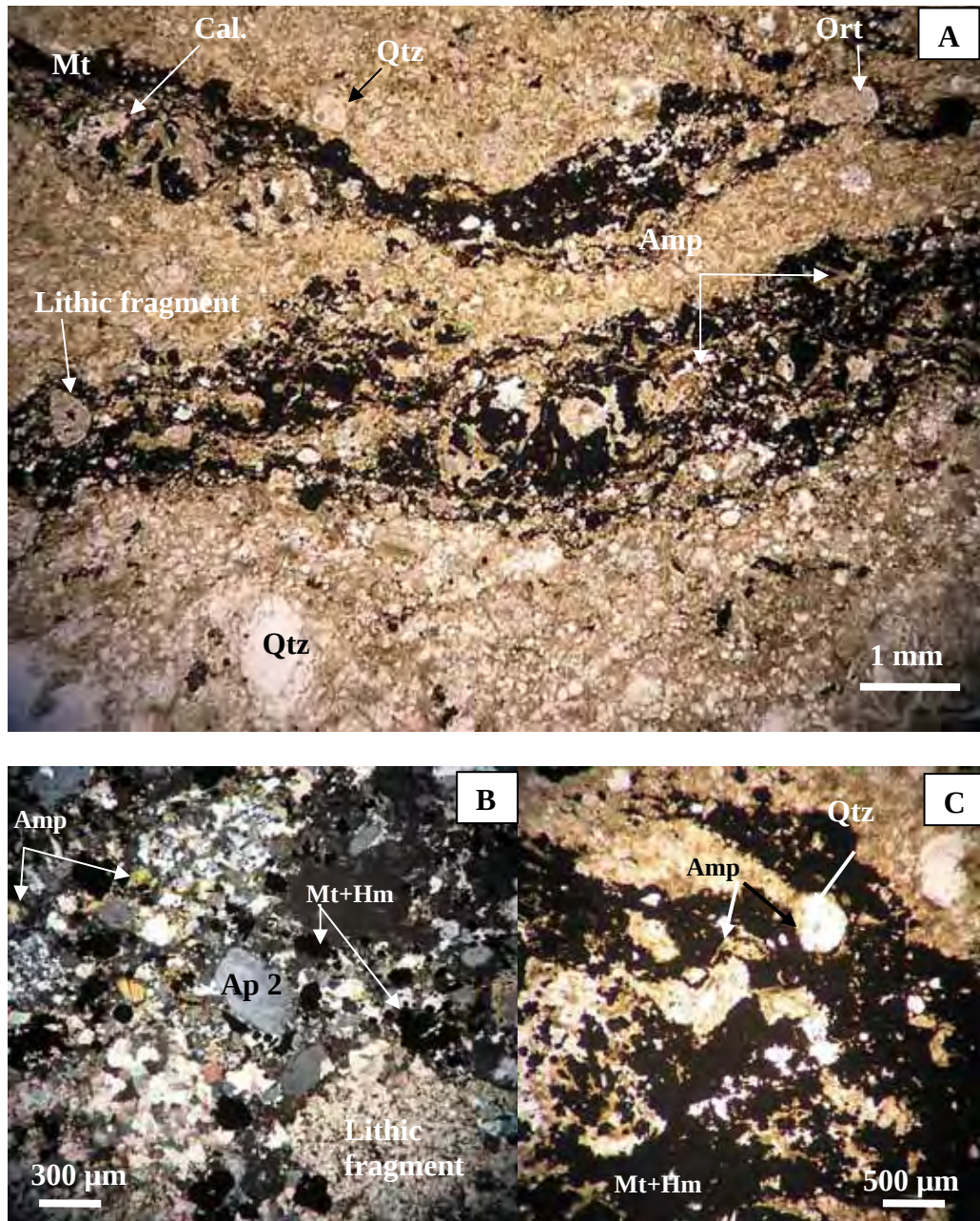


Figure 4. 21 (Caption on next page.)



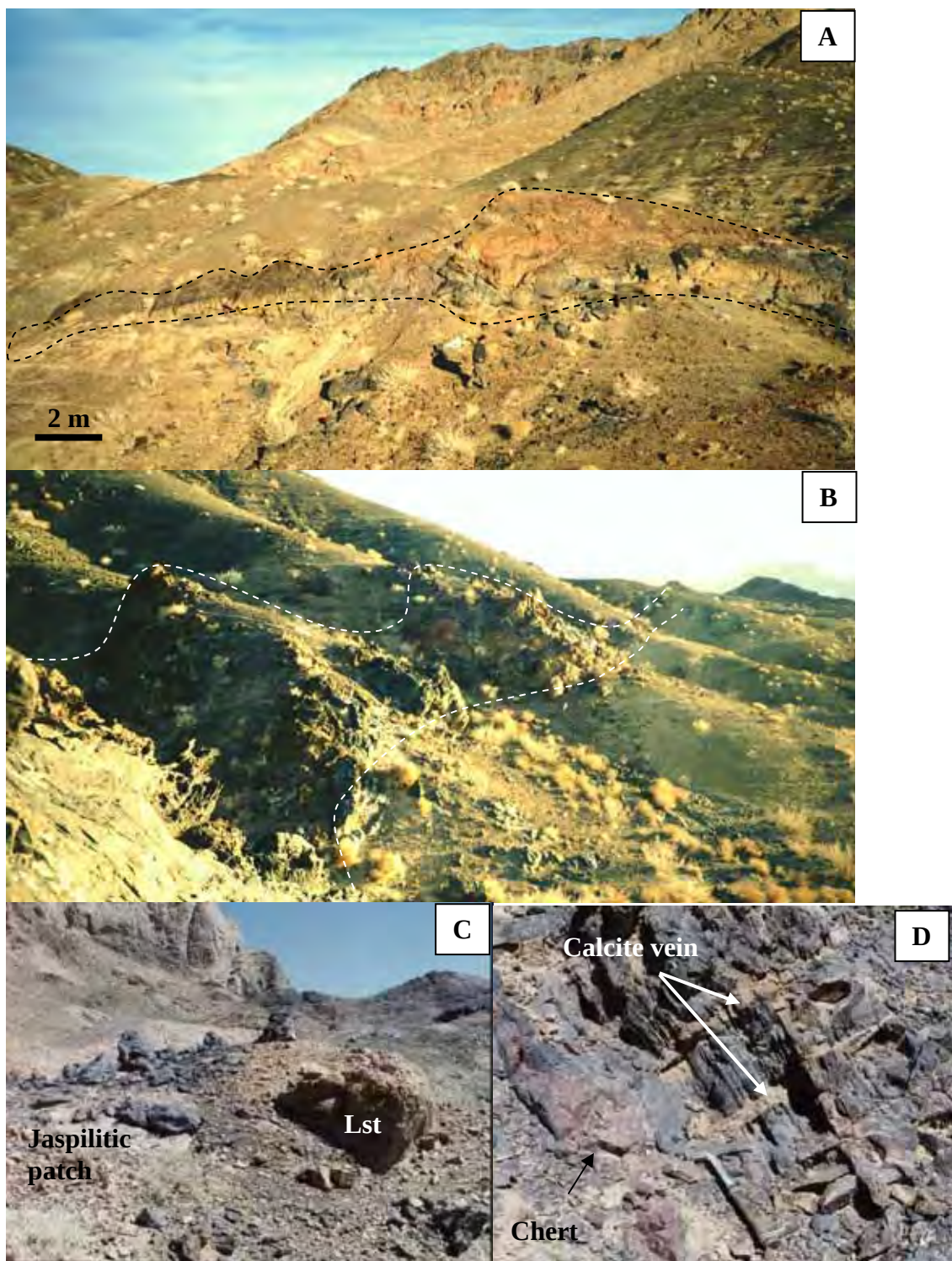
**Figure 4.21 Detrital Fe-oxide rich sedimentary rocks at Esfordi system.**

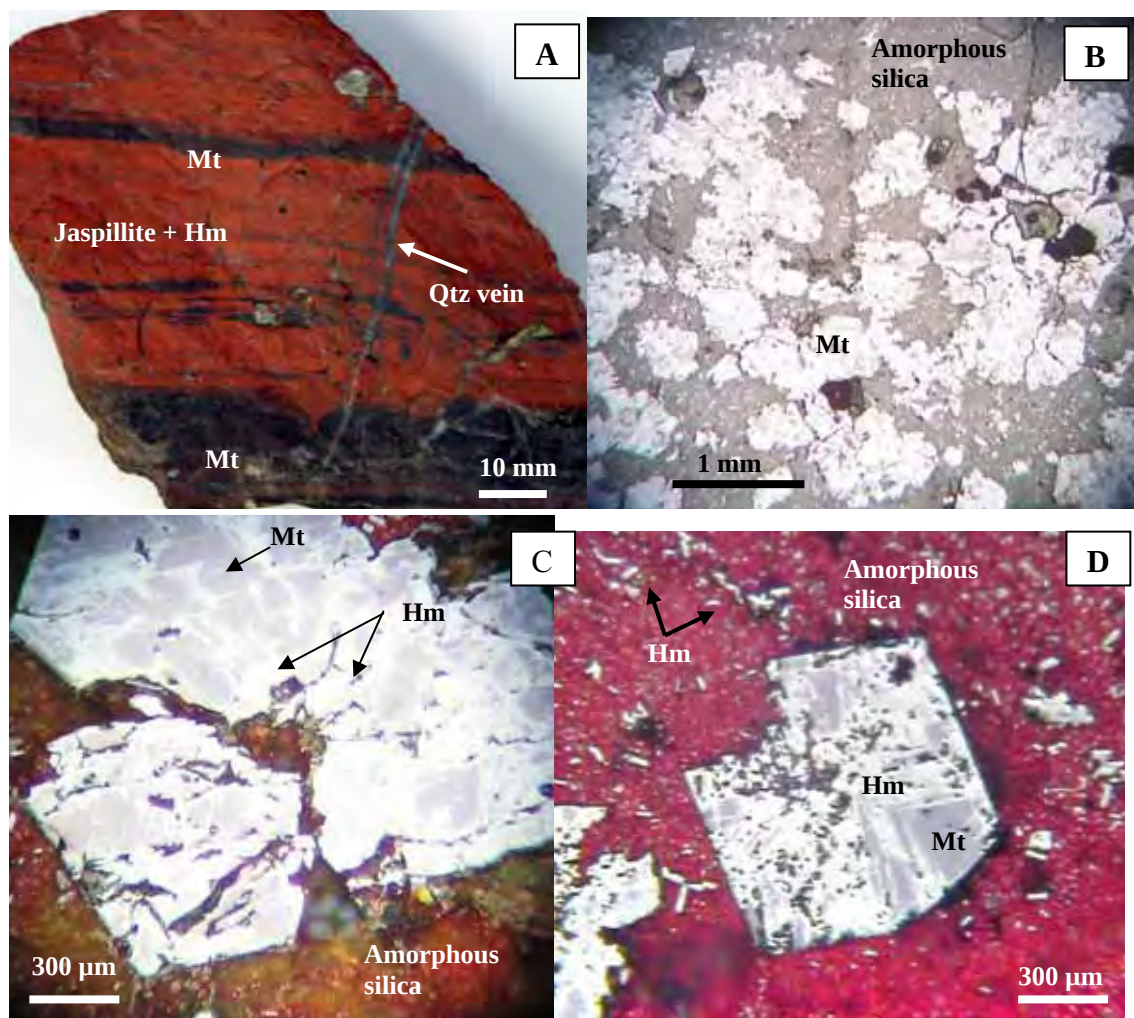
- A and B: Detrital magnetite-hematite sublayers in a sandstone horizon of the hanging wall altered volcanics. The sandstone layer is tilted by a local fault (50 m east of P ore).
- C: Polymictic pebbly sandstone with magnetite-apatite 1 detrital fragments in the altered overlying volcanics (hole B64-75 m).
- D: Tuffaceous sandstone with a dolomitic intercalation (hole B2-134.5 m).
- E – H: Typical pebbly sandstone of the Esfordi hanging wall. Rounded magnetite clasts and limestone, dolomite and altered rhyolite lithic fragments sit in a finer grained sand and silt size matrix, cut by a late quartz-calcite vein (hole B12-68 m, Bh1-13 m, Bh1-68 m).
- F: Extremely altered sandstone of the hanging wall. Several veins of actinolite-chlorite, hematite and calcite-quartz cut the rock. Actinolite, hematite and calcite are also present as pervasive open space filling. The dolomite and quartz clasts show an overgrowth of calcite and quartz (hole B4-4 m).



**Figure 4. 22 Microphotograph of detrital magnetite, hematite and apatite in the sandstone unit of the overlying altered volcanics (Green Rocks).**

A: Sublayers of detrital magnetite in tuffaceous sandstone; B: Lithic fragments and apatite within a magnetite-hematite rich matrix; C: Fe oxide rich horizon within highly altered tuffaceous sandstone.





**Figure 4. 24 Magnetite-rich jaspilitic layer**

- A: Hand specimen showing magnetite and chert intervals (an outcrop ~150 m NE of Esfordi mineralisation),
- B, C and D: Photomicrographs of euhedral to subhedral magnetite crystals in amorphous silica matrix showing late stage martitization along rim and fractures of magnetite grains (Same location as A).

## **CHAPTER 5      ALTERATION ZONES AND THEIR CHARACTERISTICS**

### **5.1    INTRODUCTION**

The Esfordi mineralizing system contains one of the most prominent alteration patterns among the Bafq Fe-oxide deposits. Besides the magnetite-rich ore body exposure, the greenish colour of the hydrothermal alteration envelope was the most important feature in assisting mine-scale exploration and targeting of mineralisation (NISCO 1971, 1979).

The Esfordi host volcanic sequence is composed of poorly stratified rhyolitic – dacitic lava, breccia and ash flows with volcanoclastic and sedimentary intercalations, intruded by a number of trachytic sills and doleritic dykes. Alteration of the Esfordi volcanic and volcanoclastic host rocks is chemically, mineralogically and texturally diverse, but can be classified into six groups including devitrification and diagenetic alteration, pervasive K-feldspar alteration, amphibole-rich alteration, exotic alteration, carbonate-rich and late epidote-chlorite-talc alteration.

Devitrification is mainly developed and preserved in glassy rhyolitic ash flows and unwelded tuffs of footwall sequence and rhyolitic flows and domes of hangingwall sequence. K-feldspar alteration is widespread throughout the Bafq district particularly Saghand Formation, which overprinted devitrification and diagenetic alteration in both Esfordi footwall and hangingwall. Amphibole alteration is well developed in the hangingwall porous volcanoclastic and clastic rocks with a prominent green color. Exotic alteration is characterized by three dominated amphibole, biotite, and sericite altered exotic

clasts within hangingwall volcanoclastic rocks. Late stage carbonate-quartz-epidote-chlorite alteration affected precursor rocks with both pervasive and vein-type overprints.

Due to the high intensity of alteration in the vicinity of mineralisation, recognition and classification of the precursor rocks is commonly difficult.

To investigate the alteration system, both outcrops and drill cores were closely examined and sampled. There are few outcrops in the footwall and hanging wall alteration envelope, hence, most attention was focused on 19 drill-holes logged to investigate the temporal and spatial pattern of hydrothermal alteration. More than 150 thin and polished-thin sections were examined and selected minerals were analysed by electron microprobe. Whole rock samples were analysed by XRD, XRF and ICP-MS. Alteration categories have been assessed on the basis of dominant mineral assemblages, chemical composition, texture and overprinting relationships.

The footwall and hanging wall sequences show somewhat similar alteration assemblages. The amphibole-rich alteration developed in the hanging wall sequence is the most extensive and masks the precursor least altered rocks and alteration assemblages. The footwall sequence contains weaker amphibole-rich alteration in which more widespread remnants of the earlier devitrification assemblages are preserved. In the following sections the different alteration assemblages and some of their chemical characteristics are described.

## **5.2 DEVITRIFICATION AND DIAGENETIC IMPRINTS**

The rhyolitic welded ash flows, unwelded tuffs of the footwall sequence were originally glassy or, at least, partly glassy. The glass-rich rocks in particular appear to have texturally evolved by subsequent processes such as devitrification, hydration and diagenesis which influenced subsequent hydrothermal alteration. Within strongly welded ash flows, containing widespread micropoikilitic and microgranular quartz attributed to

devitrification, subsequent alteration is weak (Fig 3.12) and limited to minor dusting of sericite and chlorite occur in a granular matrix and feldspar phenocrysts (Fig 5.1).

In domains containing glassy lithic fragments, such as flattened pumice, the glass has been transformed to sericite, quartz±chlorite±carbonate and Fe-oxide (Fig 5.1b). Where mixtures of fine pumice, other lithic and crystal fragments occur, the glass has been transformed to sericite, quartz, Fe-oxide±chlorite+carbonate assemblage. This produced a crude compaction foliation (S1) around more competent lithic and mineral clasts (Fig 5.1 a and b). Uncompacted lithic grains containing micropoikilitic quartz rims may contain cores of quartz and sericite (Fig 5.1 d).

The original glassy welded ash flows and coherent rhyolite flows and domes show remnant devitrification and diagenetic alteration in the hanging wall sequence. Reticulated quartz veinlets and patches of coarser crystal aggregates are common features of hanging wall coherent rhyolite lava and dome. The characteristics are similar to those in the footwall sequence, but many devitrification and diagenetic features are only preserved as remnants because of strong K and Ca alteration overprints. Early matrix textures and mineralogies in the pebbly sandstone and unwelded tuff units are similarly poorly preserved, however some fragments with vitric textures of rhyolitic lavas or ash flows are preserved. These lithic clasts generally consist of fine granular quartzose to quartzo-feldspathic assemblages with minor dusty sericite-chlorite-carbonate overprint. For the purpose of comparison these remnant domains in the lavas and welded ash flows are treated as least altered rocks. Chemical analyses of these rocks are presented in Table 8, Appendix 2.

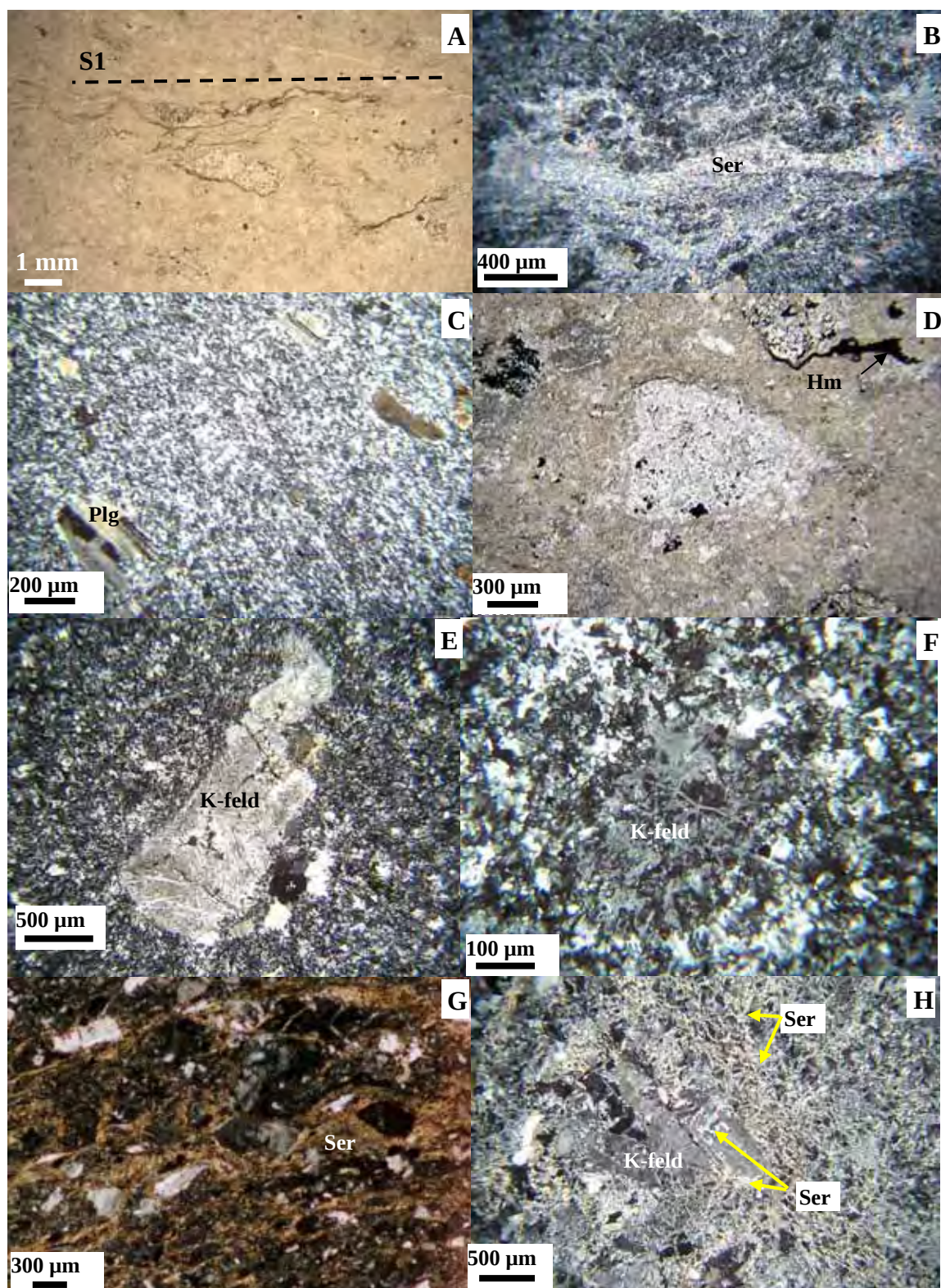


Figure 5. 1 (Caption on next page).

**Figure 5.1 Photomicrographs of altered volcanics of the Esfordi footwall succession.**

- A: Devitrified welded tuff rich in pumice. S1 is a compaction foliation defined by Fe-oxide-sericite rich horizon and flattened pumice (fiamme). The groundmass composed of a fine grained quartz-feldspar-sericite assemblage (PPL).
- B: Flattened pumice (fiamme) filled by sericite, chlorite and quartz (Hole Bh 20-75, XPL).
- C: Fine grained quartzo-feldspathic matrix dusted with sericite and plagioclase phenocrysts in the coherent rhyodacite of the Esfordi hangingwall dome (XPL).
- D: Relatively non-deformed pumice filled by quartz-feldspar and sericite enclosed in a welded ash flow of the Esfordi footwall (Hole Bh3-60, XPL).
- E: K-feldspar overgrowth in devitrified cryptocrystalline matrix of footwall welded ash flow. The matrix has extensive sericite-chlorite overgrowth (Hole B9-99, XPL)
- F: K-feldspar altered welded ash flow with micropoikilitic K-feldspar engulfing quartz (RT3, rhyolitic dome, XPL).
- G: Devitrified matrix of a rhyolitic flow. The glass dominated matrix is extensively altered to sericite and chlorite (Hangingwall rhyolitic dome, XPL).
- H: Sericite rich devitrified ash flow with K-feldspar overgrowth. Sericite partially replaced K-feldspar (B2-53, XPL).

### 5.3 K-FELDSPAR ALTERATION

Both K-feldspar and albite-rich alteration assemblages have been reported in the Bafq district by Förster and Jafazadeh (1994) and NISCO (1971, *et seq.*). At Esfordi, K-feldspar alteration is wide-spread and surrounds both amphibole-rich alteration zones and P-Fe-oxide mineralisation. Its distribution, however, does not appear to be related to proximity to P-Fe-oxide mineralisation. Daliran (2002) reported extensive K-alteration throughout the Bafq district.

In the footwall sequence welded ash flows are mesoscopically characterised by grey colouration, but K-feldspar rich assemblages may give a pink hue to the rock. This alteration assemblage is not texturally destructive and is characterised by pervasive replacement of vesicles and pumice fragments as well as granular quartz-feldspar matrices. Volcaniclastic and clastic rocks of the footwall sequence also show some degree of K-feldspar alteration, with overgrowths on feldspars and lithic fragments (Fig 5.2). The boundaries between remnant domains of devitrification and K-feldspar alteration are not well defined and appear gradational. In places the K-feldspar assemblage also develops as narrow selvages on devitrified lithic clasts, quartz aggregates and as veinlets. These K-feldspar grains may be lightly dusted with sericite.

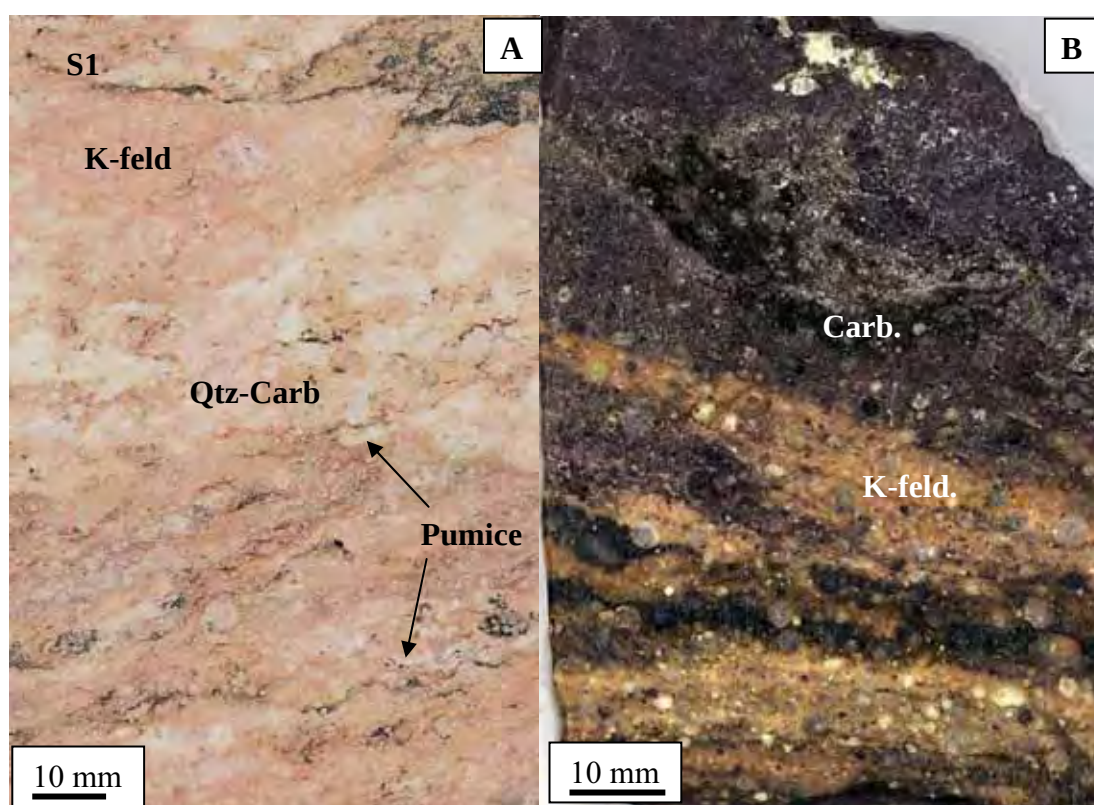
In the hanging wall sequence the majority of volcanic and volcaniclastic rocks have a pinkish colour which is mainly due to K-feldspar with fine hematite inclusions. As in the footwall remnants of least altered of rhyolitic volcanics locally have a grey to cream colour. These rocks exhibit development of devitrification features such as micropoikilitic quartz. The coherent rhyolites and welded ash flows generally show weaker development of secondary K-feldspar than more porous non welded zones. Overgrowths on K-feldspar phenocrysts (Fig 3.13 p), growth of coarse grained K-feldspar aggregates overprinting earlier granular quartz- feldspar domains are observed in rhyolite flows and the matrices

of volcanoclastic units (Fig 5.3 e, f and h), particularly the polymictic sandstones and non-welded ash flows. Where plagioclase occurs as phenocrysts in a granular groundmass of quartz and feldspar, the cores to the grains are dusted by sericite and largely replaced by K-feldspar. Adjacent to the amphibole-rich alteration zone the K-feldspar is partially replaced by sericite together with chlorite  $\pm$  biotite  $\pm$  carbonate  $\pm$  hematite. At the contact the K-feldspar is dusted by fine actinolite. These features are illustrated at a mesoscopic and microscopic scale in Fig 5.2 and Fig 5.3.

A preliminary evaluation of the chemical changes associated with the development of K-feldspar alteration has been undertaken. This has involved the selection of several samples for whole rock analysis, that appear to be least altered by secondary K-feldspar development. For comparison, several samples containing secondary K-feldspar development or adjacent to the amphibole-rich alteration zone showing sericite $\pm$ chlorite $\pm$ biotite $\pm$ carbonate overprint have also been analysed (Table 8, Appendix 2). As in all such exercises, assumptions are made that the least altered rocks are the precursors of the more altered rocks, although SiO<sub>2</sub> to Zr/Ti ratios (Fig 5.4) suggest a reasonable degree of coherence.

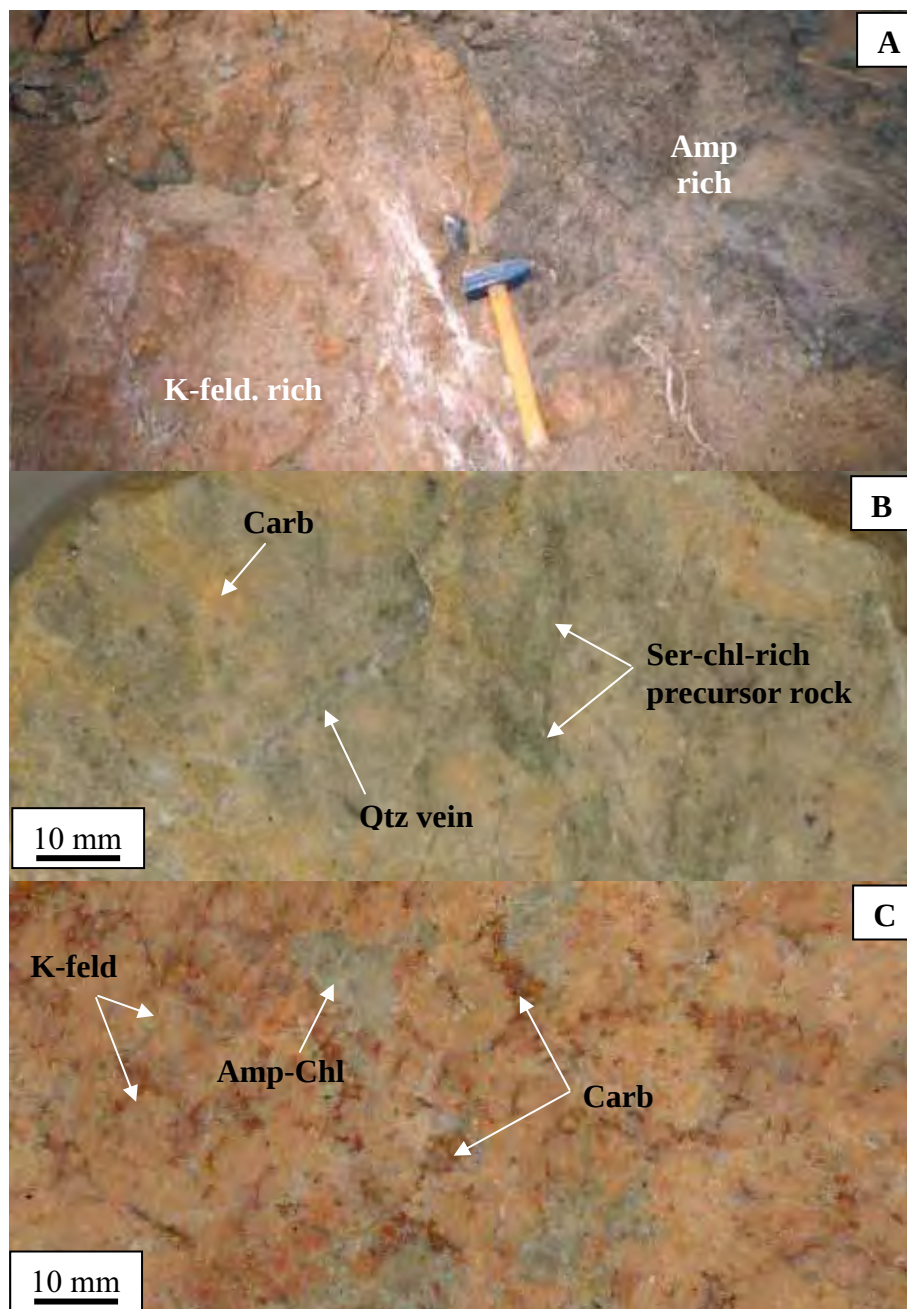
To estimate relative changes in bulk chemical composition associated with K-feldspar alteration, the isocon scheme of Grant (1986) as adapted by Huston (1993) has been used. On the diagrams the scaled analyses of the altered rocks was plotted against their least altered equivalents. The more immobile elements plot along an isocon, which is the basis for estimating gain and loss in the altered rocks. In this set Zr, Ti, Al, Nb and Ga were considered as immobile elements. The isocon diagram for both K-feldspar and K-feldspar – sericite type alteration are shown in Fig 5.5 and the relative mass changes in Fig 5.6. The most significant depletion in both subtypes is that of Na which can be attributed to the disappearance of albite or albitic compound of plagioclase. In the K-feldspar type the most significant enhancements are of K and Rb reflecting the development of secondary K-

feldspar, in which Rb is likely to substitute for K. In the K-feldspar-sericite type the most significant enrichments compared to the least altered equivalent are again K and Rb, reflecting both K-feldspar and sericite development, and Mg, Fe, Mn, and Zn, reflecting the development of chlorite and biotite. An enhancement for P may also be significant reflecting the introduction from the adjacent P- Fe-oxide mineralising system.



**Figure 5. 2 Polished slabs of Esfordi footwall rocks showing pervasive K-feldspar alteration.**

- A: Pink K-feldspar rich altered tuff with paler colour quartz-carbonate overprint. Darker laminae containing more abundant sericite and hematite defined S1 (hole B64-108 m).
- B: K-feldspar-carbonate rich horizons in a polymictic sandstone. The more porous horizons are generally more affected by potassic and subsequent late stage carbonate alterations (hole B9-99 m).



**Figure 5. 3 Pervasive K-feldspar alteration of Esfordi hanging wall volcanic and volcanoclastic rocks.**

- A: Outcrop of the sharp contact between K-feld rich volcanic rock and chlorite-amphibole altered vein of Esfordi hanging wall.
- B: Polished slab of felsic volcanic rock with mild K-feldspar alteration. Note the patches of pink orthoclase and late quartz-carbonate veins (hole Bh4-71m, Esfordi hanging wall).
- C: Polished slab of K-feldspar rich altered rhyolite with overprinted chlorite-amphibole and carbonate alteration (rhyolitic dome, Esfordi hanging wall).

Plots of alteration indices have been used by Large *et al.* (2001) to clarify bulk chemical changes associated with alteration patterns in felsic volcanic rocks associated with volcanic hosted massive sulphide mineralisation. The alteration indices have been used to illustrate the relative positions of least altered, K-feldspar and K-feldspar–sericite altered rocks in the Esfordi mineralising system. The alteration index (AI) of Ishikawa *et al.* (1976) is estimated as follows:

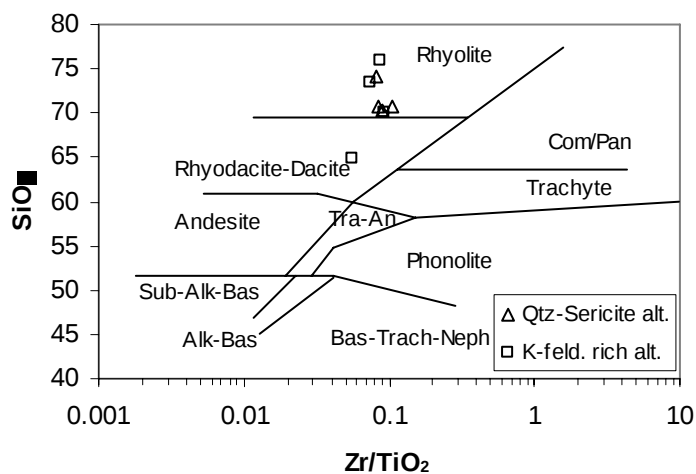
$$AI = 100 (MgO + K_2O) / (MgO + K_2O + CaO + Na_2O)$$

This has been used to illustrate the replacement of plagioclase and volcanic glass by sericite and chlorite during hydrothermal alteration. The chlorite–carbonate–pyrite index (CCPI) of Large *et al.* (2001) is estimated as follows:

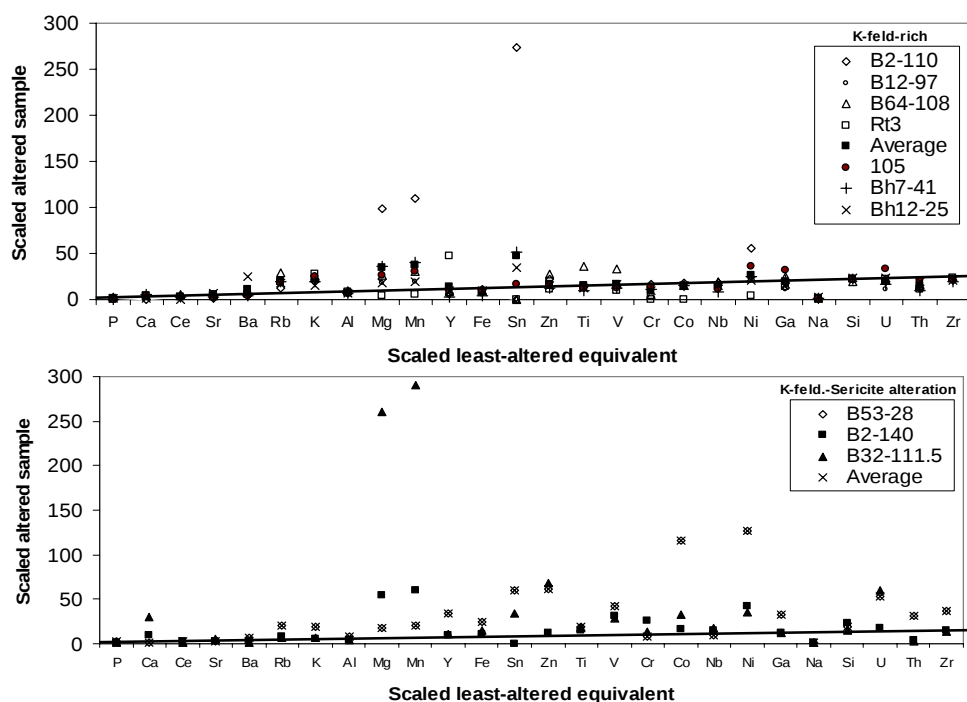
$$CCPI = 100 (MgO + FeO) / (MgO + FeO + K_2O + Na_2O)$$

This has been used to illustrate the replacement of feldspar and volcanic glass by chlorite, dolomite-ankerite and pyrite - Fe-oxide. The alteration box plot is a simple graphical method of combining the AI and CCPI to characterise diagenic or hydrothermal (early propylitic) alteration in primarily felsic volcanic rocks. Within the box plot, fields may be arbitrarily drawn to represent least altered compositions. The AI–CCPI plot of the Esfordi samples representing least altered, and varying degrees of K-feldspar and K-feldspar - sericite alteration is shown in Fig 5.7. Based on the literature, petrographic and chemical criteria, a AI of 20–65 and CCPI of 15–45 encompass the least altered samples at Esfordi. Samples showing increasing K-feldspar development plot towards the position of K-feldspar on the box plot. Samples with an increasing degree of sericite±chlorite±biotite±carbonate development plot toward sericite. The sample closest to the amphibole-rich alteration and the P–Fe-oxide mineralisation, plots near to the sericite-chlorite line. Similar chemical trends can be seen in the data reported by Daliran

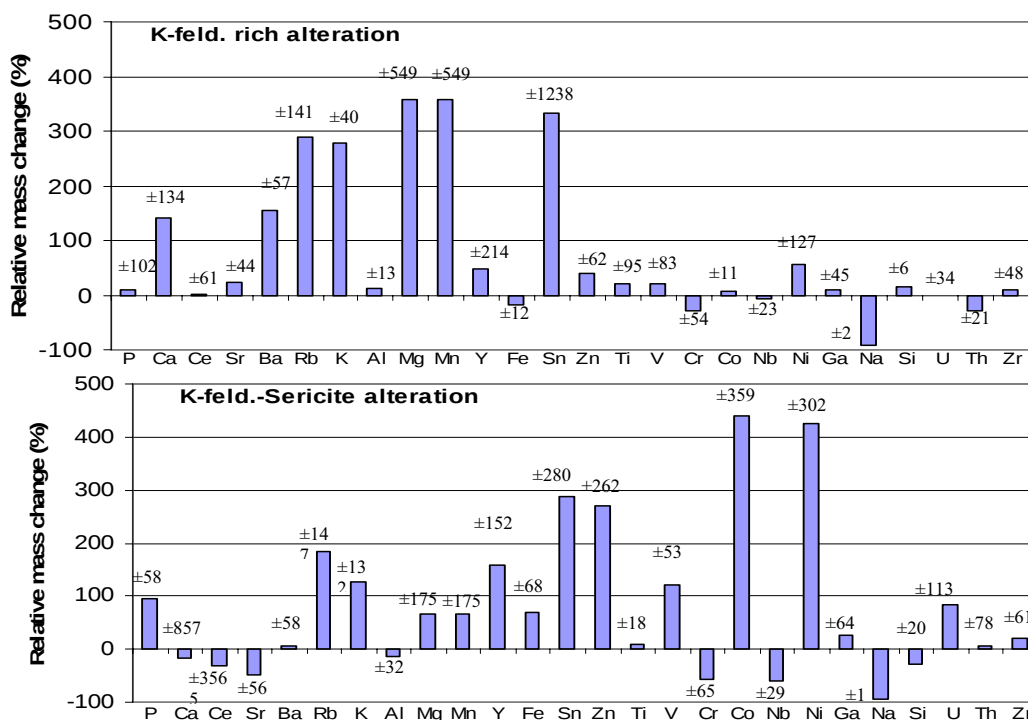
(1990) from rhyolitic volcanic rocks hosting Fe-oxide-P mineralisation at Mishdovan (Fig 5.7 b).



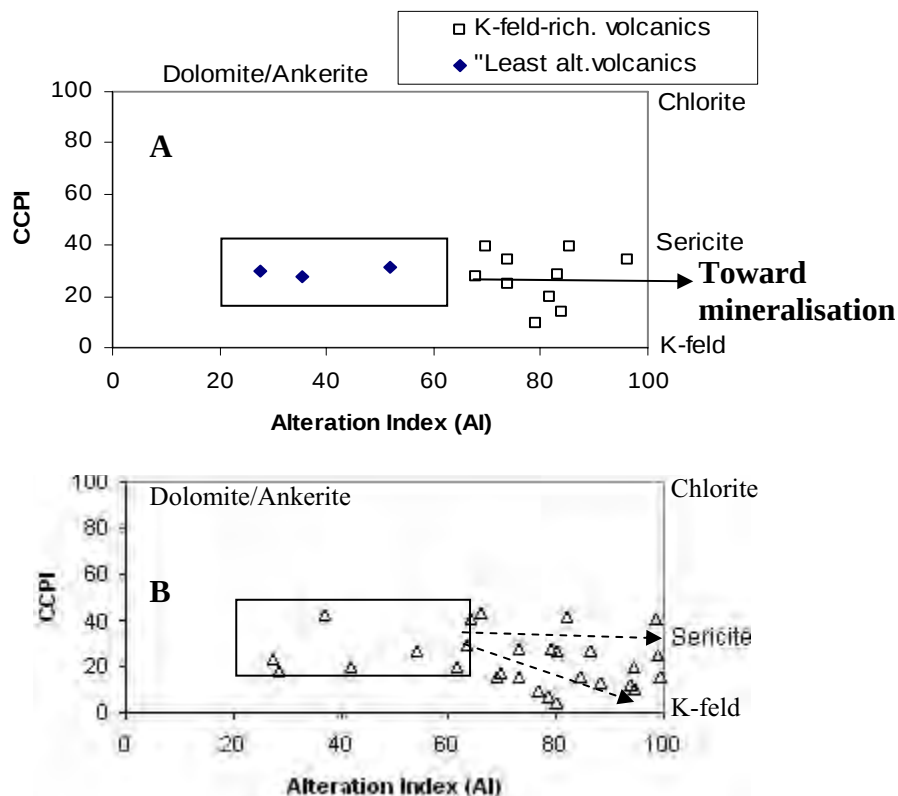
**Figure 5. 4** Immobility element plot for quartz-sericite and K-feldspar rich altered rocks.



**Figure 5. 5** Isocon diagram for Esfordi K-feldspar-rich altered rocks (solid line is the best fit isocon calculated based on the least altered rhyolite).



**Figure 5.6** Histograms illustrating relative mass changes for K-feldspar and K-feldspar-sericite rich altered rocks of the Esfordi mineralising system.



**Figure 5.7** Alteration box plot showing the least altered volcanics and K-feldspar altered rocks. A: Esfordi volcanic and volcanoclastic rocks, B: Mishdovan volcanic rocks (compositions from Daliran, 1990).

## 5.4 AMPHIBOLE ALTERATION

The prominent green colouration and the coarse grain size (up to 20 mm) of the minerals in the amphibole-rich assemblages resulted in their early recognition by geologists (NISCO, 1969 *et seq.*). These assemblages are characterised by actinolite amphibole together with a range of other minerals including pyroxene, garnet, scapolite, biotite, hematite, chlorite and carbonate.

Overlying the P-Fe-oxide zone is an extensive well-developed zone of amphibole-rich alteration extending along the entire length of the mineralisation in a 500 by 200 m elliptical shape. It gradually weakens 50 m laterally away from the ore body but extends up to 150 m into the overlying sequence (Figs. 4.2 and 4.3).

Surface observations and drill core data suggest that the amphibole alteration in the footwall is typically weak and restricted to a narrow zone up to 5 m thick in immediate proximity to the Esfordi mineralisation. The lateral intensity, continuity and thickness, are controlled by the distribution of more porous unwelded or poorly welded sections of the ash flows and local joints and fracture in welded ash flows.

Amphibole forms fine crystal aggregates in veins, veinlets and fractures. Unwelded tuffs and associated pebbly sandstones also contain actinolite in both matrix and clasts. The footwall amphibole alteration is texturally and mineralogically similar to the distal variant of the amphibole-rich alteration of the hanging wall sequence.

The amphibole-rich alteration shows variable intensity, mineralogy and textural character in different parts of the alteration system. Significant controlling factors seem to be precursor chemical composition, porosity and proximity to the mineralisation.

Macroscopically three variants of amphibole-rich alteration have been observed. These variants are (i) intense, texturally destructive and amphibole alteration with subordinate pyroxene, garnet, scapolite, chlorite and sericite situated within 10 m of mineralisation (ii) texturally non-destructive amphibole-rich alteration with subordinate K-

feldspar, green biotite, chlorite and sericite, pervasively developed peripheral to the magnetite-rich core and (iii) a system of irregular amphibole-rich veins cutting through pervasive K-feldspar-rich altered rocks and least altered volcanics of the outer border of the green rock alteration zone (Figs. 5.8 and 5.9). The contact of green rocks with precursor K-feldspar-rich altered rocks may be either gradational or sharp. Large veins are generally developed along faults, brecciated zones and lithological discontinuities. The overlying and peripheral volcanics may also exhibit minor incipient amphibole alteration in the form of dissemination and veinlets (Fig 5.10). Within the amphibole-rich alteration zone there are relict domains of light coloured rocks, rich in quartz and K-feldspar, and retaining their porphyritic texture.

Similar amphiboles occur as an accessory mineral in the P mineralisation, where it comprises medium to coarse grained intergrowths of quartz, chlorite, talc, epidote  $\pm$  garnet, within apatite-hematite rich veins and veinlets. The amphibole-rich alteration strongly overprinted precursor rock and usually mask original textures and structures, whereas in the original textures in the overlying weakly altered rocks are preserved (Fig 5.10 and Fig 5.1 a and b).

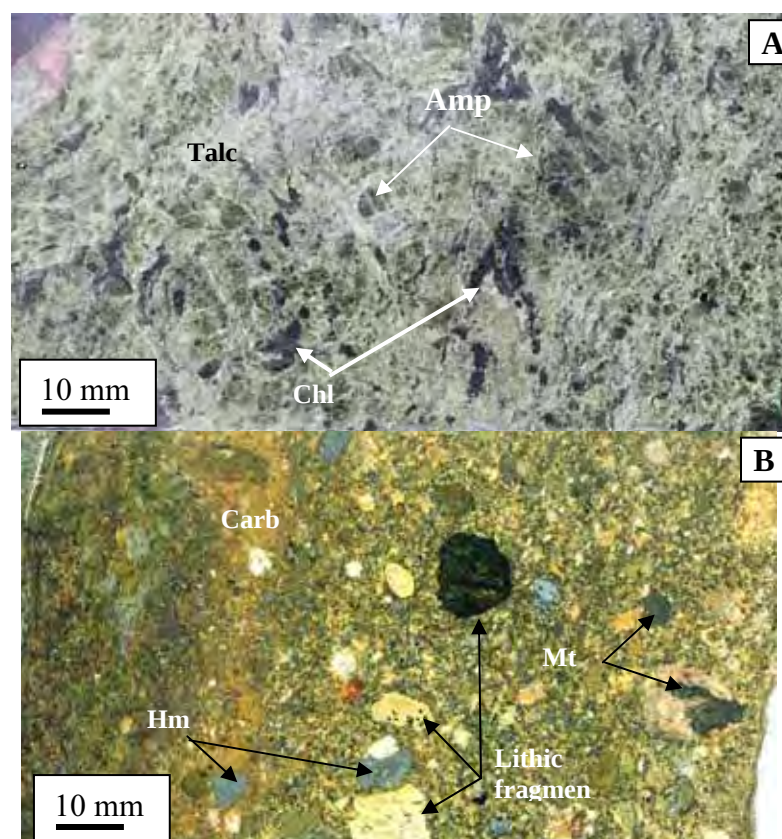
The distribution of amphibole within the mineralised zone is variable compared with the adjacent altered host rocks. The massive apatite style of ore shows lower total amphibole content than the brecciate style. The mineral assemblage for this zone is apatite-Fe-oxide-actinolite-calcite-quartz-allanite-monazite. The amphiboles mainly occurs as anhedral to elongate crystals in veins, veinlets and local patches with of sizes  $\sim 0.01$  to  $> 30$  mm. Fe-oxide and calcite are usually associated with these green amphibole veins and patches. The apatite-rich domains generally show lower contents of amphibole. The large actinolite crystals usually show bending and contain allanite and locally surrounded by carbonate and fine elongate actinolite crystals. The massive magnetite core generally contains very low amphibole levels, but the apatite-rich patches within massive

magnetite core contain amphiboles with generally similar characteristics to the amphiboles associated with apatite-rich ore.

The brecciated P-rich ore show green amphibole aggregates within a brecciated apatite–Fe-oxide–carbonate matrix, as well as veins, veinlets and patches. The mineral assemblage is similar to massive P-rich ore but with a higher proportion of amphibole and calcite. The amphibole crystals are generally anhedral but display strong cleavage.



**Figure 5. 8 Amphibole-chlorite rich veins in the K-feldspar altered host rock of Esfordi, hanging wall sequence, ~150 m northeast of the mineralisation.**



**Figure 5.9 A: Amphibole-rich alteration without any preservation of precursor textures (hole B61-5.5). B: Amphibole-rich alteration of a volcanoclastic rock in which texture is largely preserved (hole B64-75).**

Calcite veins cross cutting massive amphibole-rich alteration also contain fine fibrous actinolite (10-50  $\mu\text{m}$ ), suggesting a younger generation of amphibole associated with later stage carbonate-rich alteration (Fig 5.10).

Based on various appearance, textures and paragenesis, the Esfordi amphiboles may be classified into two main groups. The first generation of amphiboles (amphibole 1) occurs as core to the second generation (amphibole 2) and also remnants of heavily altered crystals. This generation of amphibole is closely associated with pyroxene in texturally destructive, amphibole-rich alteration. The precursor lithology is uncertain but the Nb/Y versus  $\text{Zr}/\text{TiO}_2$  suggests andesite, dacite or a volcanoclastic rock with a significant proportion of mafic volcanic clasts. Amphibole 1 is usually shows darker green colour and extensively replaced by paler amphibole 2, quartz, carbonate, chlorite, talc and sericite (Fig 5.10).

Amphibole 2 is the most widespread type in the amphibole-rich altered zone. Microscopically, amphibole occurs as either coarse euhedral to subhedral blades or fine grained subhedral crystals in quartz, K-feldspar and carbonate groundmass. The coarsest crystals of actinolite occurred as laths up to 3 cm long in brecciated zones in the vicinity of the P mineralisation. Here all precursor primary volcanic and sedimentary textures and minerals have been destroyed (Fig 5.10 A-H).

The second variant of amphibole 2 occurs as light coloured, fine (10-500  $\mu\text{m}$ ) elongate crystals, associated with carbonate and quartz, filled open spaces and replaced amphibole 1, pyroxene and K-feldspar (Fig 5.10 and 5.11). These amphiboles can be contrasted with the brown coloured amphiboles in relatively fresh mafic igneous bodies such as doleritic dykes and trachytic sills (Fig. 3.19 G-I).

The biotite is generally green in colour and occur as individual crystals or aggregates in the matrix or dense population inside the mafic lithic fragments (Figs. 5.10 and 5.19). Within trachyte bodies the biotite replaces mafic minerals, fills vesicles and forms veinlet with quartz and calcite. Biotite is partially replaced by chlorite in most samples.

In and adjacent to trachytic bodies in both the footwall and hanging wall sequences secondary biotite is developed. Some parts of the volcanoclastic units with a significant proportion of mafic clasts also contain biotite+K-feldspar-quartz-carbonate assemblages. The spatial distribution of these biotite bearing assemblages imply it is a marginal part of the amphibole alteration system.

The chemical composition of the Esfordi amphiboles has been investigated in different zones of the mineralizing system, using a Cameca SX50 electron microprobe. The chemical analyses are presented in Appendix 3. Cations in amphiboles were normalised to 23 oxygens as described by Triboulet (1992).  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  have been estimated based on Papike *et al.* (1974).

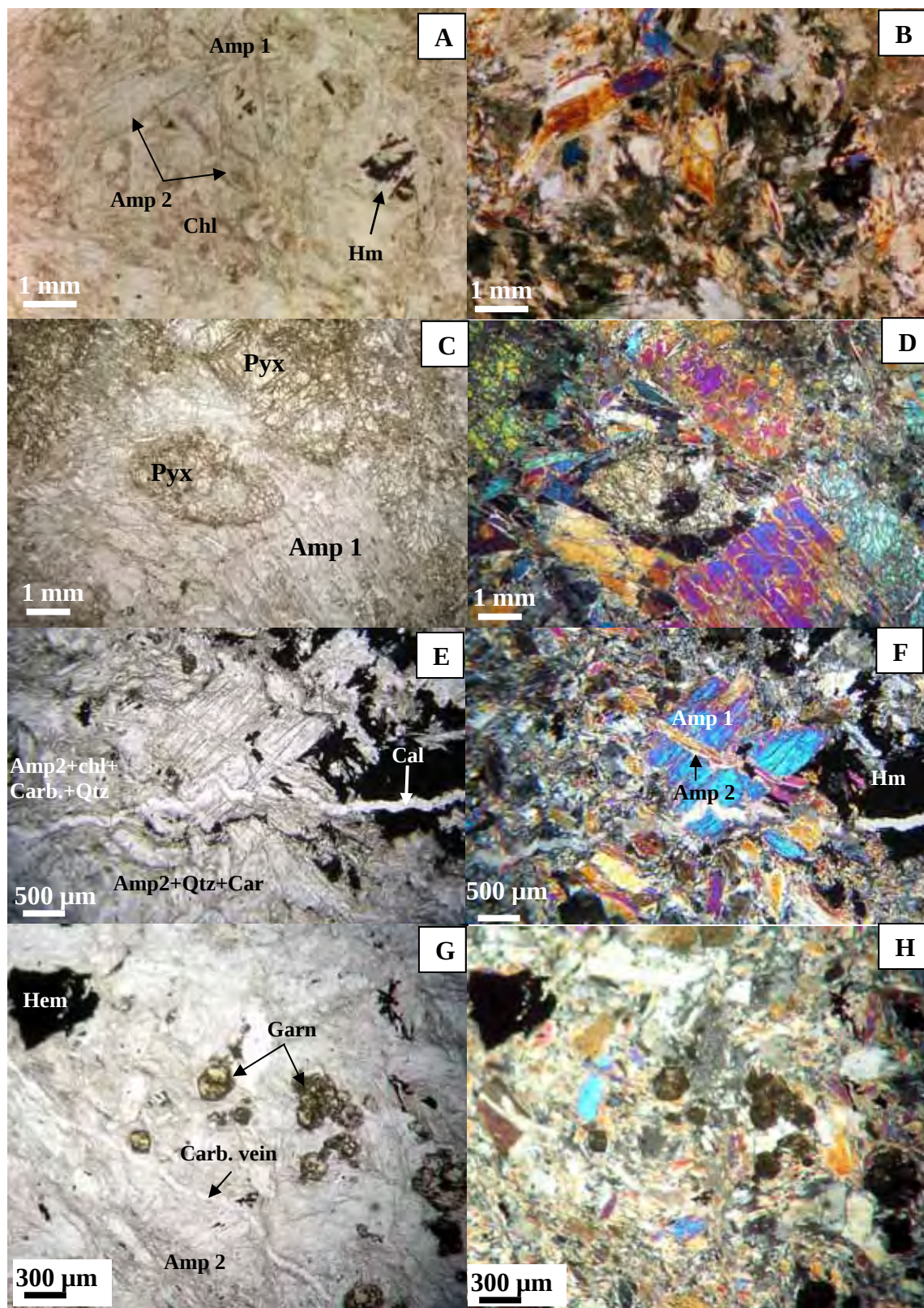


Figure 5. 10 (Caption on page 182 and 183).

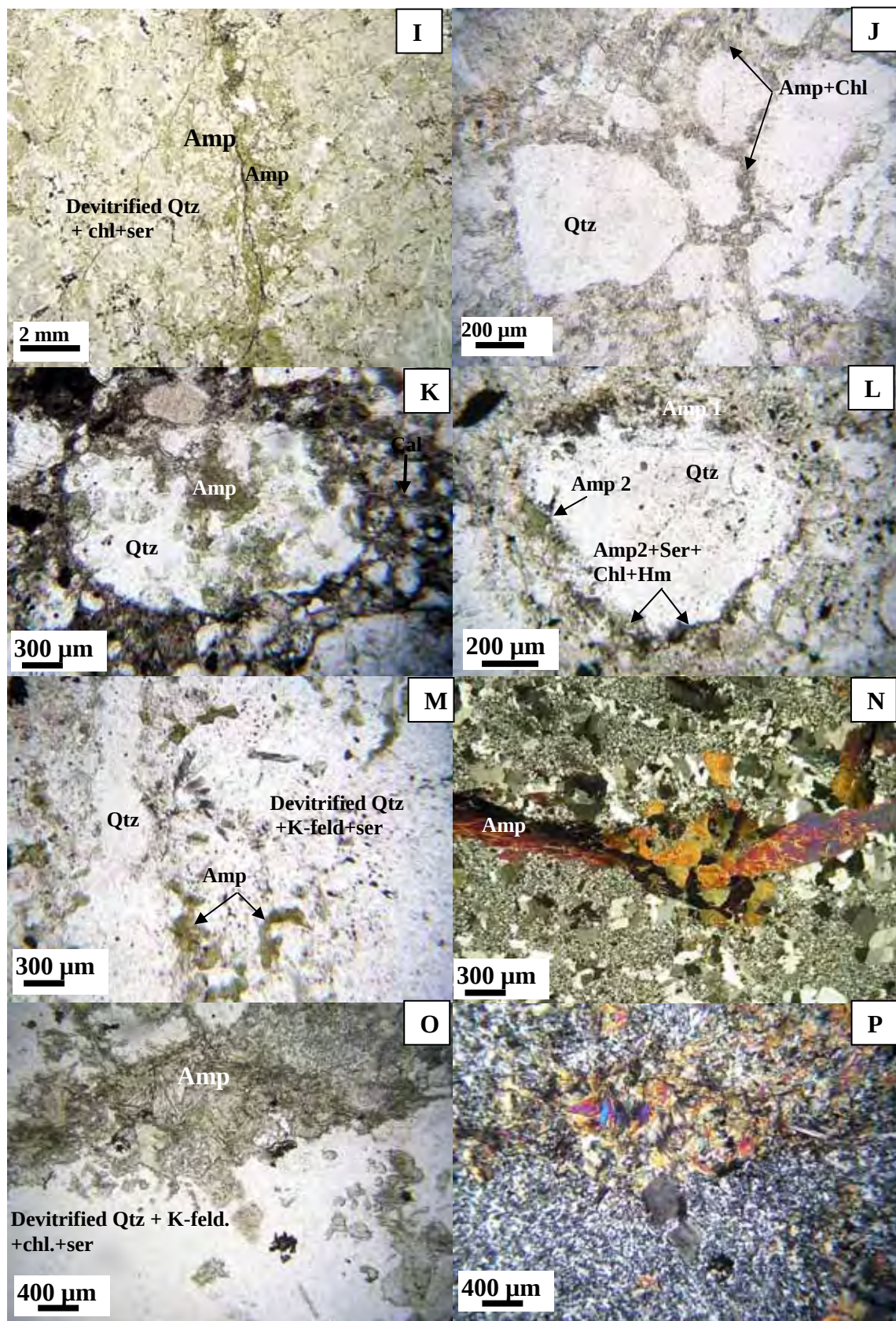
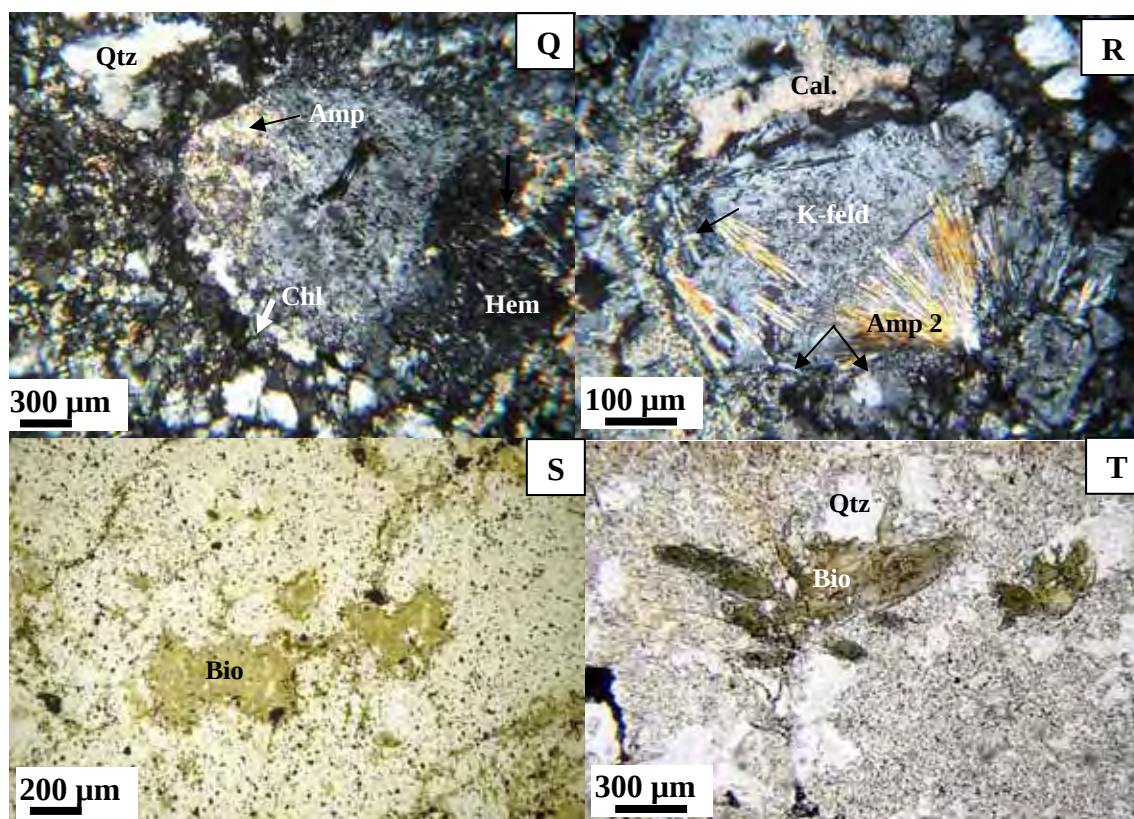


Figure 5.10 Continued (Caption on page 182 and 183).



**Figure 5.10 Photomicrograph of various styles of amphibole-rich alteration in the volcanic and volcanoclastic rocks of Esfordi mineralizing system.**

- A (PPL) & B (XPL) Strong amphibole alteration without textural preservation at the margin of breccia style P mineralisation.
- C (PPL) & D (XPL) Amphibole 1, pyroxene, scapolite and plagioclase. Amphibole 2 overprinted and replaced the amphibole 1, pyroxene and plagioclase.
- E (PPL) & F (XPL) Amphibole-rich altered rock without textural preservation. Two generation of amphibole overprinted by late stage carbonate vein.
- G (PPL) & H (XPL): An amphibole-garnet rich altered rock without textural preservation. The carbonate vein overprinted the amphibole-garnet assemblage.
- I (PPL): Amphibole-rich vein in a felsic ash flow tuff with subordinate amphibole-chlorite alteration, immediate footwall of Esfordi mineralisation. The groundmass is mainly quartzo-feldspathic with minor sericite and chlorite (hole B53-28 m).

**Figure 5.10 Continue.**

- J – L (PPL): Pebbly sandstone with considerable fragments of welded tuff with well developed amphibole-chlorite alteration replacing quartz grains (hole B2-140 and Bh4-65).
- M (PPL): Ash flow with quartzo-feldspathic matrix overprinted by amphibole (hole Bh11-45)
- N (XPL): An amphibole 2 vein cutting through a rhyolite with reticulated quartz veining (105).
- O (PPL) & P (XPL) Amphibole 2 overprinting in a poikilitic devitrification texture in a rhyolite ash flow with K-feldspar phenocrysts. The amphibole crystals developed along the original compaction (S1).
- Q (XPL): K-feldspar aggregate developed in a quartzo-feldspathic matrix and all overprinted by amphibole and chlorite (hole B12-14).
- R (XPL): K-feldspar overprinted by amphibole 2 needle shape crystal overgrowth (hole B12-14).
- S (PPL): Biotite in trachyte of the footwall sequence replacing earlier ferromagnesian mineral (hole Bh10-82 m) and cross-cut by veinlets of quartz, biotite and carbonate. Biotite is pervasively partially replaced by chlorite.
- T (PPL): Well shaped greenish biotite associated with quartz and calcite in welded ash flows of footwall sequence (hole B64-108 m, PPL).

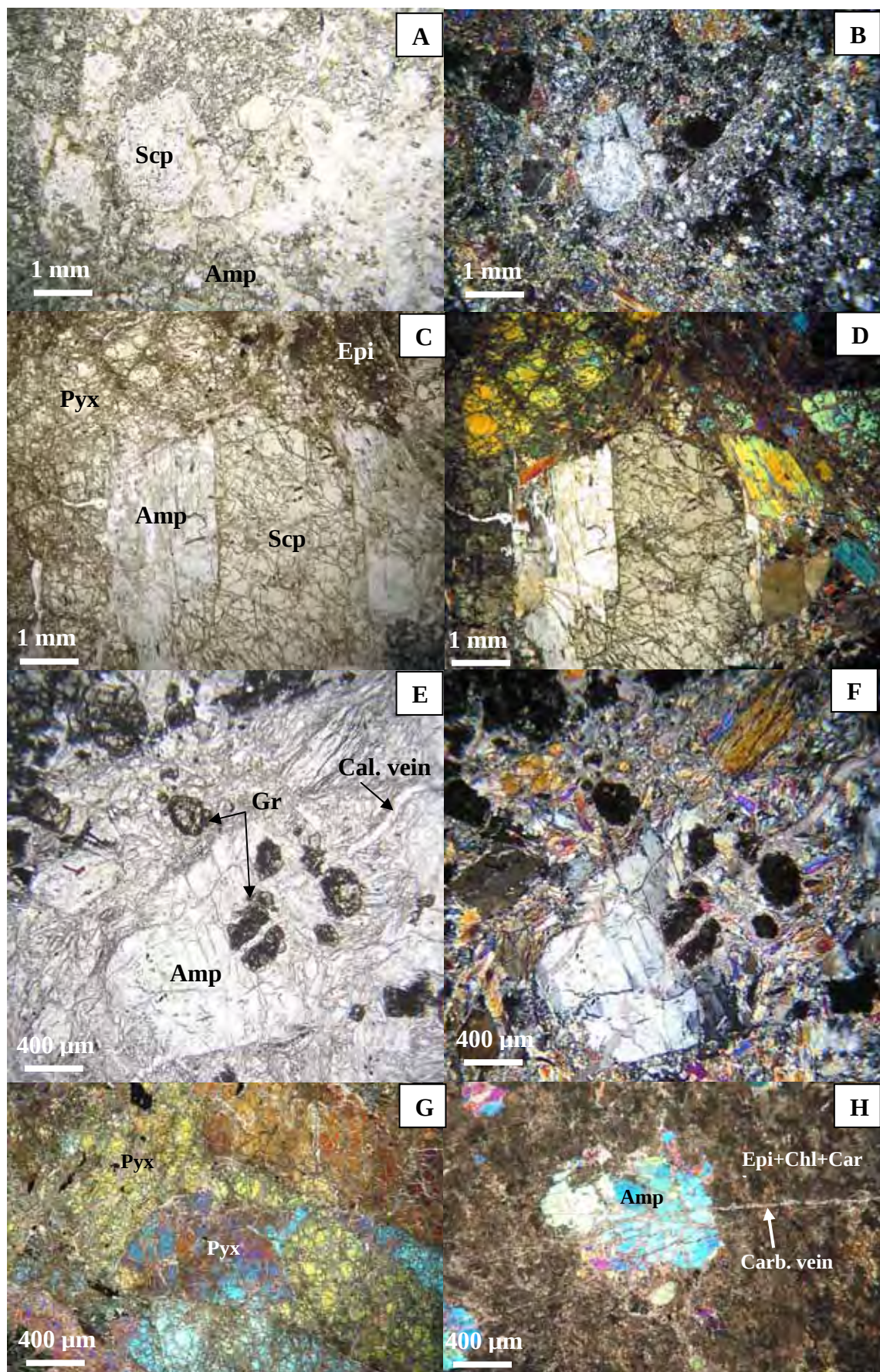


Figure 5. 11 (Caption on next page).

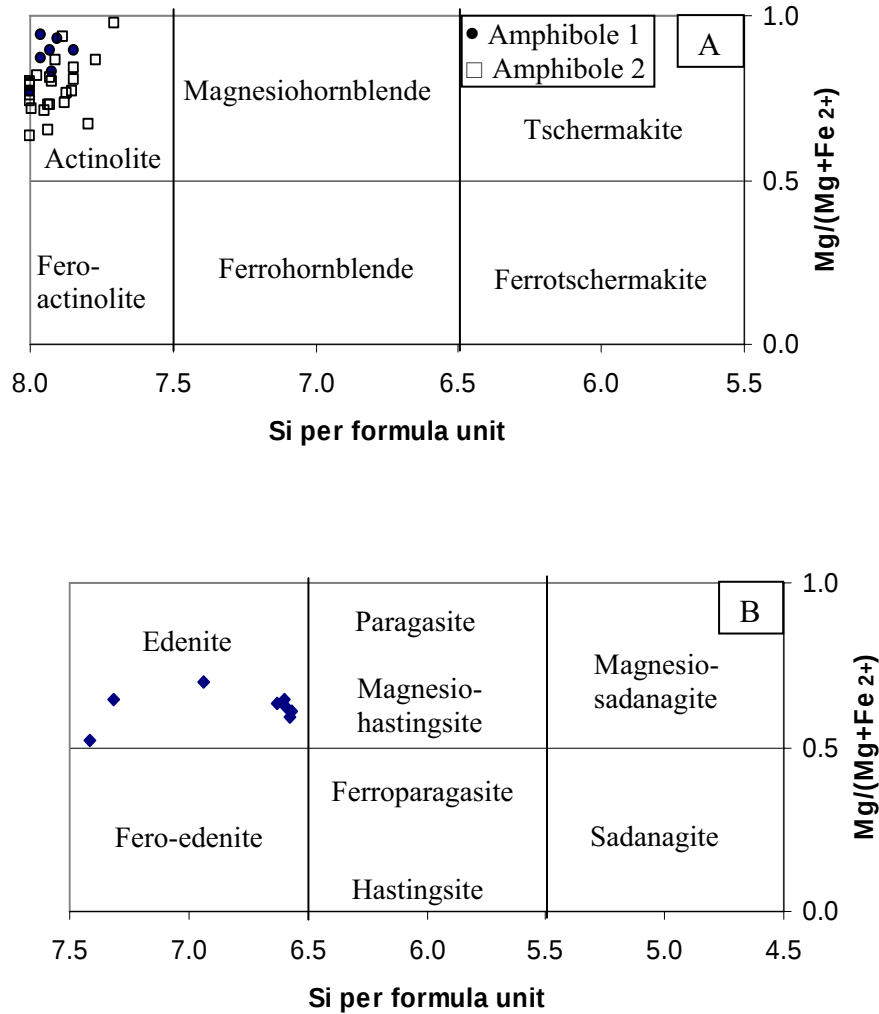
**Figure 5.11 Photomicrographs of pyroxene-scapolite-garnet-amphibole assemblages.**

- A (PPL) & B (XPL): Scapolite associated with feldspar remnants in an extensively amphibole overprinted fabric. The relicts of the fine devitrified quartzo-feldspathic matrix are still preserved. Carbonate and quartz are also overprinted the facies (hole B53-41 m).
- C (PPL) & D (XPL): An altered mafic rock with relatively large pyroxene and amphibole 1 crystals overprinted by scapolite and amphibole 2. The whole facies is overprinted by chlorite and epidote (Gr-ac1).
- E (PPL) & F (XPL): An extensively altered rock with several assemblages overprinted original rock. Pyroxene, garnet and scapolite overprinted by amphibole-chlorite and epidote-talc-calcite overprinted previous assemblages. Note the calcite vein, which cuts the amphibole and trapped garnet (Gr-ac1).
- G: Large crystals of pyroxene in an altered mafic rock Gr; XPL).
- H: An altered mafic rock with pyroxene strongly overprinted by epidote-chlorite and carbonate. The amphibole is partially overprinted. A carbonate vein cuts all these assemblage Gr; XPL).

Amphiboles exhibit an extremely wide range of chemical compositions Leake *et al.* (1997, 2003) classified amphiboles into four major groups, Mg-Fe-Mn-Li, calcic, calcic-sodic and sodic, based on the calculated cation occupancy of the B-site in the amphibole structure. The characteristic double chain structure of the amphibole fundamentally consists of talc-like strips made up by five cations (such as Fe and Mg) octahedrally coordinated in sites M1, M2, and M3 and sandwiched between two inward pointing bands of tetrahedra and bound to adjacent strips by the larger M4 cations (Ca, Na, K) and sometimes by additional large A site cation (Deer *et al.*, 1967).

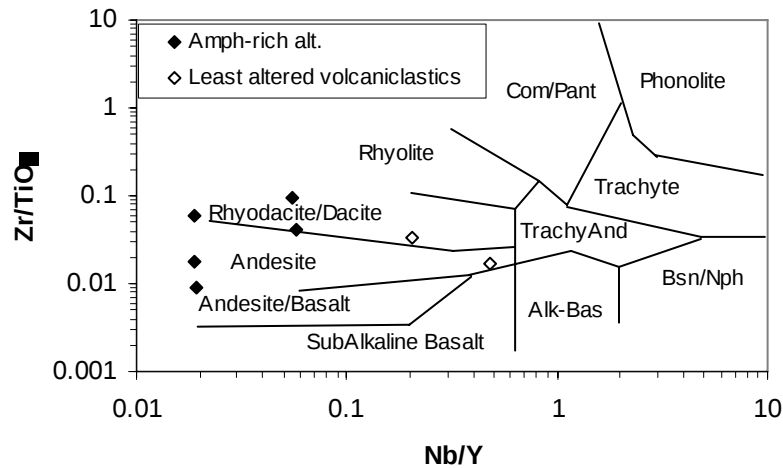
According to the IMA nomenclature (Leake *et al.*, 1997) nearly all analysed amphibole 1 and 2 can be classified calcic amphiboles and plot in the actinolite field (Fig 5.12). The igneous amphiboles associated with variably altered doleritic bodies have  $\text{Na}+\text{K} > 0.5 \%$ , and plot in the edenite field. The distribution of Si, Al and Na in the amphibole structure depends on the P-T-X conditions. Elevated temperature can decrease  $\text{Si}^{4+}$  and increase Ti,  $^{\text{VI}}\text{Al}$  and  $\text{Na}_A$  cations in amphiboles. The  $^{\text{IV}}\text{Al}$  and  $\text{Na}_{M4}$  content also can increase with increasing pressure (Raase, 1974; Brown, 1977a,b,c). Among the Esfordi amphiboles, igneous edenite of the doleritic dykes show the highest Ti,  $^{\text{VI}}\text{Al}$  and  $\text{Na}_A$  values. Amphibole 1 show relatively higher Ti,  $^{\text{VI}}\text{Al}$  and  $\text{Na}_A$  in respect to amphibole 2, which would be consistent with a slightly higher formation temperature for first generation amphibole.

Although the majority of the hanging wall green rocks show amphibole-rich overprint, some altered rocks at the vicinity of the mineralisation show the amphibole-pyroxene-scapolite-albite-garnet assemblage. This Na-Ca-rich assemblage is generally observed within rocks without any remnant textures. Scapolite occurs with pyroxene, amphibole, garnet, and albite and generally replaced by amphibole 2, chlorite and epidote (Fig 5.15).



**Figure 5. 12 Classification of Esfordi calcic amphiboles A: Amphibole 1 and 2 associated with alteration zone, B: Amphibole associated with doleritic dykes (Leake *et al.*, 1997)**

The occurrence of scapolite with an amphibole -pyroxene dominated matrix and the later overprint of amphibole 2, epidote and carbonate suggests that this Na-Ca-rich assemblage is a variant of amphibole-rich alteration probably controlled by the precursor lithology. Due to destructive alteration, the precursor rock fabric has been destroyed and the precursor rock type masked, but an immobile element plot suggests a rhyodacite/dacite to andesite volcanoclastic of similar bulk chemical composition as the precursor rock (Fig 5.13). A slight shift of the amphibole-rich altered samples to the left in Fig. 5.13 is probably due to Y enrichment.

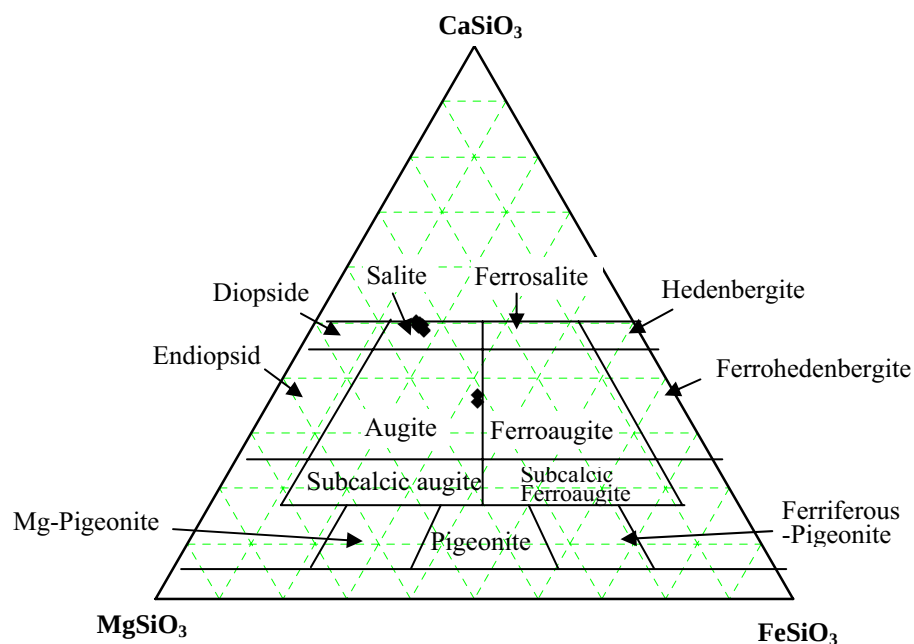


**Figure 5. 13 Immobile element plot of selected amphibole-rich altered rocks without textural preservation and least altered volcaniclastic rocks.**

Pyroxene generally exists as remnants in an amphibole-rich matrix and is generally replaced by chlorite, sericite, epidote and carbonate. Table 5.2 presents the pyroxenes composition formulas, based on 6 oxygens. The pyroxenes compositions are mainly plotted in the salite and at the boundary of the augite and ferroaugite fields (Fig 5.14).

Garnet occurs as remnants of euhedral crystals enclosed by amphibole 2 and talc. The garnet associated with amphibole, pyroxene and scapolite. Most of the garnets are extensively altered and overprinted by epidote (Fig 5.15). Representative electron microprobe analyses and formula calculation of garnets are presented in Table 5.3. As the table shows the garnets are mainly andradite  $[Ca_3Fe_2(SiO_4)_3]$  with a minor grossular component (Fig 5.13).

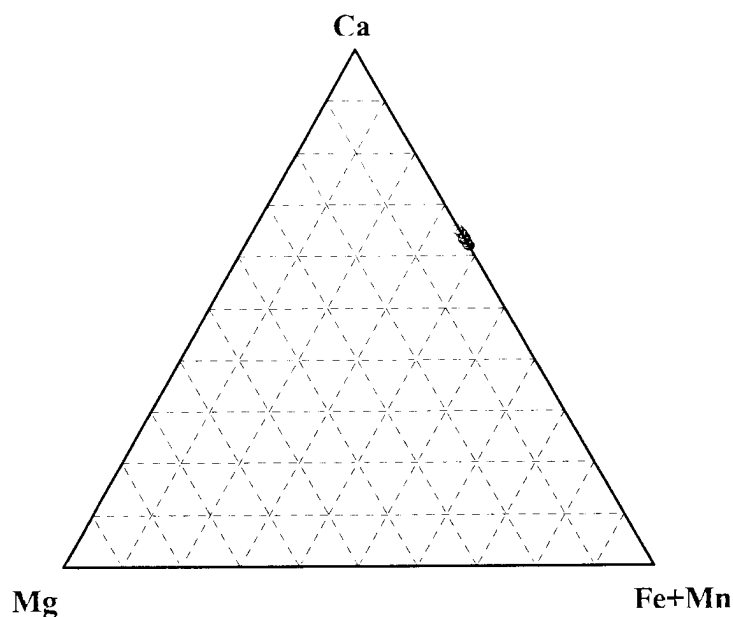
EMP analyses of pyroxene and green biotite are presented in Tables 5.2 and 5.4. Minor amounts of albite (20-300  $\mu m$  in size) developed in the matrix of some volcaniclastics in close association with K-feldspar in the weaker amphibole alteration zones.



**Figure 5. 14 Pyroxene classification based on the clinopyroxene nomenclature after Poldervaart and Hess (1951).**

**Table 5. 1 Representative probe analyses, cation per formula unit and mineral proportion of pyroxenes of Esfordi altered volcanics.**

| Label                                                   | B9-3  | B9-4  | B9-5  | B9-6  | B9-8  | B9-9  | B9-10 | B9-11 | B9-14 |
|---------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>                                        | 54.00 | 54.47 | 53.67 | 53.80 | 54.65 | 54.21 | 54.21 | 54.08 | 53.86 |
| Al <sub>2</sub> O <sub>3</sub>                          | 0.23  | 0.36  | 0.31  | 0.32  | 0.38  | 0.65  | 0.65  | 0.11  | 0.23  |
| FeO                                                     | 7.15  | 7.25  | 7.61  | 7.63  | 7.08  | 14.12 | 14.12 | 6.84  | 7.01  |
| MgO                                                     | 14.79 | 14.20 | 14.49 | 14.70 | 14.40 | 13.75 | 13.75 | 15.05 | 15.00 |
| CaO                                                     | 21.38 | 21.37 | 21.00 | 21.43 | 21.49 | 16.54 | 15.54 | 22.33 | 21.91 |
| Na <sub>2</sub> O                                       | 1.09  | 1.18  | 1.23  | 1.19  | 1.30  | 0.18  | 0.18  | 0.76  | 0.77  |
| K <sub>2</sub> O                                        | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.02  | 0.02  | 0.02  | 0.01  |
| Total                                                   | 98.64 | 98.91 | 98.33 | 99.07 | 99.29 | 99.47 | 98.47 | 99.20 | 98.80 |
| Si                                                      | 2.02  | 2.03  | 2.02  | 2.01  | 2.03  | 2.04  | 2.05  | 2.01  | 2.01  |
| Al                                                      | -0.02 | -0.03 | -0.02 | -0.01 | -0.03 | -0.04 | -0.05 | -0.01 | -0.01 |
| Al                                                      | 0.03  | 0.05  | 0.03  | 0.02  | 0.05  | 0.06  | 0.08  | 0.02  | 0.02  |
| Fe(iii)                                                 | 0.04  | 0.01  | 0.06  | 0.08  | 0.03  | 0.00  | 0.00  | 0.04  | 0.03  |
| Fe(ii)                                                  | 0.18  | 0.22  | 0.18  | 0.16  | 0.19  | 0.45  | 0.45  | 0.17  | 0.19  |
| Mg                                                      | 0.82  | 0.79  | 0.81  | 0.82  | 0.80  | 0.77  | 0.77  | 0.84  | 0.84  |
| Ca                                                      | 0.86  | 0.85  | 0.85  | 0.86  | 0.85  | 0.67  | 0.63  | 0.89  | 0.88  |
| Na                                                      | 0.08  | 0.09  | 0.09  | 0.09  | 0.09  | 0.01  | 0.01  | 0.05  | 0.06  |
| Total                                                   | 4.01  | 4.00  | 4.02  | 4.02  | 4.01  | 3.96  | 3.95  | 4.01  | 4.01  |
| Fe <sup>2+</sup> /(Fe <sup>2+</sup> +Fe <sup>3+</sup> ) | 0.81  | 0.96  | 0.75  | 0.67  | 0.87  | 1.29  | 1.38  | 0.82  | 0.86  |
| Fe <sup>3+</sup> /(Fe <sup>3+</sup> +Fe <sup>2+</sup> ) | 0.19  | 0.04  | 0.25  | 0.33  | 0.13  | -0.29 | -0.38 | 0.18  | 0.14  |
| Wo                                                      | 43.19 | 43.68 | 42.59 | 42.90 | 43.52 | 35.08 | 33.65 | 44.68 | 44.15 |
| En                                                      | 41.58 | 40.39 | 40.90 | 40.94 | 40.57 | 40.58 | 41.42 | 41.91 | 42.05 |
| Fs                                                      | 11.24 | 11.55 | 11.98 | 11.84 | 11.16 | 23.64 | 24.21 | 10.65 | 10.99 |
| Ac                                                      | 3.99  | 4.38  | 4.52  | 4.32  | 4.75  | 0.70  | 0.71  | 2.76  | 2.80  |



**Figure 5. 15 Garnet composition plot based on EMP analyses and atom per formula unit.**

**Table 5. 2 Representative probe analyses of andradite garnets of Esfordi altered volcanics.**

|                                                                     | Gr-1  | Gr-2  | Gr-3  | Gr-4  | Gr-5  | Gr-6  | Gr-7  | Gr-8  | Gr-9  |
|---------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>                                                    | 35.08 | 35.25 | 33.01 | 36.11 | 35.08 | 35.12 | 34.99 | 35.57 | 35.15 |
| TiO <sub>2</sub>                                                    | --    | --    | --    | --    | --    | --    | --    | --    | --    |
| Al <sub>2</sub> O <sub>3</sub>                                      | 0.31  | 0.16  | 0.14  | 0.65  | 0.89  | 0.23  | 0.54  | 2.25  | 0.52  |
| Fe <sub>2</sub> O <sub>3</sub> T                                    | 26.82 | 27.51 | 27.88 | 27.15 | 25.77 | 27.04 | 26.94 | 24.28 | 27.26 |
| MgO                                                                 | 0.00  | 0.05  | 0.00  | 0.00  | 0.00  | 0.06  | 0.00  | 0.13  | 0.00  |
| CaO                                                                 | 33.24 | 32.52 | 32.46 | 32.52 | 33.15 | 33.21 | 33.21 | 32.61 | 33.57 |
| Na <sub>2</sub> O                                                   | 0.01  | BLD   | BLD   | BLD   | 0.01  | BLD   | 0.01  | 0.03  | BLD   |
| K <sub>2</sub> O                                                    | 0.01  | 0.01  | BLD   | BLD   | BLD   | BLD   | 0.01  | 0.01  | BLD   |
| P <sub>2</sub> O <sub>5</sub>                                       | 0.01  | 0.03  | BLD   | BLD   | 0.01  | 0.01  | BLD   | 0.01  | 0.03  |
| Total                                                               | 95.48 | 95.53 | 93.49 | 96.43 | 94.91 | 95.67 | 95.70 | 94.88 | 96.53 |
| Formula based on 12 oxygens inc. Fe <sup>2+</sup> /Fe <sup>3+</sup> |       |       |       |       |       |       |       |       |       |
| Si                                                                  | 2.796 | 2.813 | 2.711 | 2.841 | 2.801 | 2.796 | 2.783 | 2.822 | 2.774 |
| Ti                                                                  | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Al                                                                  | 0.029 | 0.015 | 0.013 | 0.060 | 0.084 | 0.022 | 0.051 | 0.210 | 0.048 |
| Cr                                                                  | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Fe <sup>3+</sup>                                                    | 1.609 | 1.653 | 1.723 | 1.608 | 1.549 | 1.620 | 1.613 | 1.450 | 1.620 |
| Fe <sup>2+</sup>                                                    | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mn                                                                  | 0.000 | 0.003 | 0.000 | 0.000 | 0.000 | 0.004 | 0.000 | 0.008 | 0.000 |
| Mg                                                                  | 3.949 | 3.868 | 3.973 | 3.814 | 3.946 | 3.941 | 3.938 | 3.857 | 3.949 |
| Ni                                                                  | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Zn                                                                  | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ca                                                                  | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.001 | 0.002 | 0.000 |
| Total                                                               | 8.385 | 8.353 | 8.421 | 8.324 | 8.382 | 8.383 | 8.385 | 8.349 | 8.392 |
| Andradite                                                           | 97.92 | 98.89 | 99.10 | 95.62 | 94.08 | 98.44 | 96.42 | 85.28 | 96.63 |
| Grossular                                                           | 2.08  | 0.84  | 0.89  | 4.38  | 5.92  | 1.24  | 3.56  | 14.02 | 3.37  |

**Table 5.3 EMP analyses of green biotite associated with amphibole-chlorite alteration and igneous brown biotite associated with doleritic dykes.**

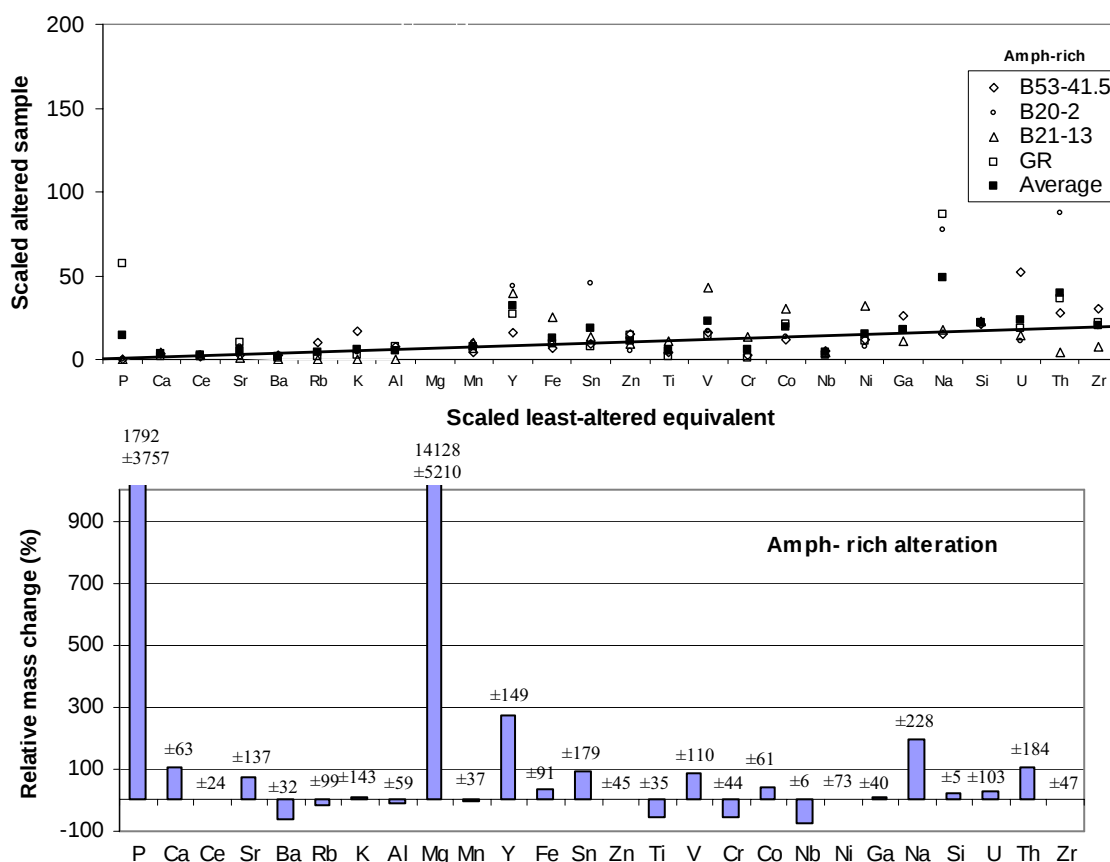
|                                | Green biotite associated with altered volcanics (N=20) |      | Brown biotite associated with dolerite (N=36) |      |
|--------------------------------|--------------------------------------------------------|------|-----------------------------------------------|------|
| Label                          | Ave                                                    | STDV | Ave                                           | STDV |
| SiO <sub>2</sub>               | 38.02                                                  | 1.65 | 35.31                                         | 2.03 |
| TiO <sub>2</sub>               | --                                                     | --   | --                                            | --   |
| Al <sub>2</sub> O <sub>3</sub> | 14.85                                                  | 0.95 | 13.57                                         | 1.56 |
| FeO T                          | 14.54                                                  | 2.94 | 20.62                                         | 3.10 |
| MnO                            | 0.00                                                   | 0.00 | 0.00                                          | 0.00 |
| MgO                            | 15.40                                                  | 2.00 | 9.58                                          | 2.88 |
| CaO                            | 0.10                                                   | 0.09 | 0.65                                          | 2.59 |
| Na <sub>2</sub> O              | 0.05                                                   | 0.03 | 1.53                                          | 3.08 |
| K <sub>2</sub> O               | 8.20                                                   | 1.10 | 8.02                                          | 2.16 |
| P <sub>2</sub> O <sub>5</sub>  | 0.02                                                   | 0.03 | 0.03                                          | 0.02 |
| SrO                            | 0.00                                                   | 0.00 | 0.00                                          | 0.00 |
| Cl                             | 0.35                                                   | 0.17 | 0.07                                          | 0.11 |
| F                              | 1.03                                                   | 0.89 | 0.01                                          | 0.01 |
| Total                          | 92.56                                                  | 1.82 | 89.38                                         | 2.61 |

The amphibole-rich alteration is most strongly developed in volcanoclastic such as polymictic pebbly sandstones. These sandstones have a contrasting provenance and hence contrasting chemical compositions. They are intercalated with lenticular limestone and dolomite.

Sandstone samples (hole Bh11-45 and Bh1-13) have been considered as least altered equivalents of some of the more intensely altered amphibole-rich rocks. They are derived from the fringes of the amphibole alteration and contain significant sericite, chlorite and carbonate. A further 2 samples (hole B53-41.5 and B20-2) contain pervasive amphibole development, but retain some elements of the original sandstone texture. Samples B53-41.5 also contains remnant domains of coarse K-feldspar but the amphibole is to a large extent pseudomorphed by carbonate (Fig 3.19 e). The higher Fe, Ni and Cr in the least altered lithologies suggest a higher proportion of mafic than felsic volcanic lithic clasts in the precursor of the more of the amphibole-rich samples, with the relict sandstone textures. This is confirmed in the immobile element plot (Fig 5.13). The other three

samples (hole B21-13, Gr-ac-1 and GR) contain large amounts of coarse amphibole, pyroxene and garnet (Fig 5.10) but give no indication of precursor lithology.

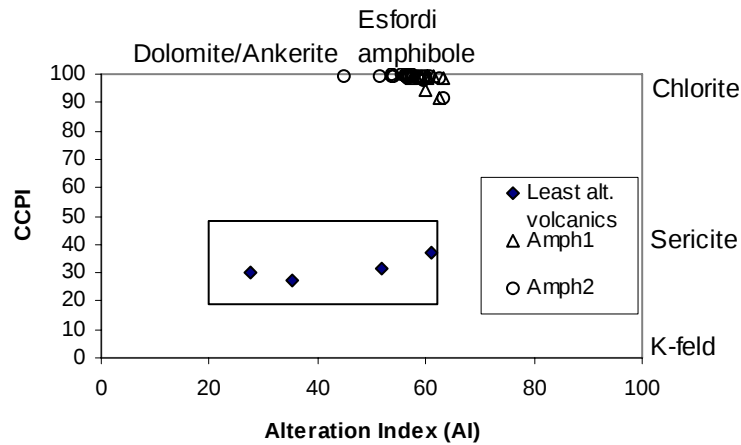
These samples contain very low  $\text{Al}_2\text{O}_3$  contents. Given the low mobility of Al in most regimes, it could appear likely that the precursor lithology was not the polymict sandstone, but rather a carbonate or carbonate-rich lens. Data from the analysis are plotted on an isocon diagram using the approach of Huston (1993) (Fig 5.16). This is for comparative purposes only and there is no implication of introduction or depletion of most components. For this purpose Al, Ga, and Zr have been considered as approaching immobility. However for the original sandstones the difference in Ca almost certainly indicates introduction of Ca with increasing intensity of alteration.



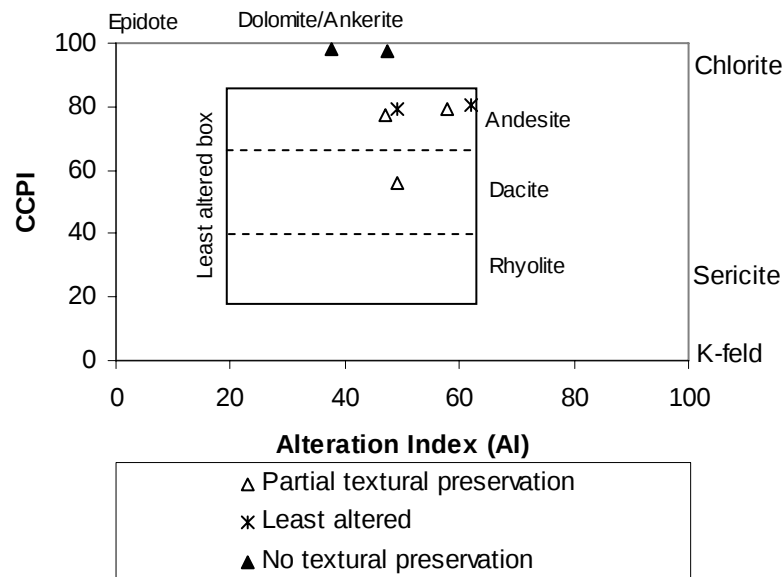
**Figure 5. 16 Isocon diagram (the solid line is the best fit isocon calculated based on the average of two least altered volcaniclastic sample, Bh11-45 and Bh1-13), and relative gain and loss charts of the Esfordi amphibole-rich altered volcanics and tuffs.**

The AI and CCPI of host rocks of amphibole-rich alteration at Esfordi range between 37.6–57.7 and 55.9–97.8. The plot of amphibole compositions from Esfordi on the CCPI – AI plot is shown in Fig 5.17. The low AI range in the amphibole-rich alteration is mainly because this technique measures the intensity of plagioclase and glass destruction to form non Ca and Na phases, sericite and chlorite and thus does not discriminate the formation of Ca-rich amphibole. In Fig 5.18 the least alteration boxes are defined on the basis of those developed by Large *et al.* (2001). Although Large *et al.* (2001) indicated that caution is required in plotting data from volcanic derived sediments on CCPI – AI diagrams to clarify trends of increasing intensity of hydrothermal alteration, particularly in terms of the issues precursor heterogeneity. The relative position of the amphibole-rich rocks and the least altered box should provide an indication of relative degree of chemical alteration. However sensitivity of CCPI to chlorite or amphibole development may result from differences in the original Fe and Mg levels in the more mafic rocks.

Using immobile element plot (Fig 5.12) a average basalt, andesite to rhyodacite composition is suggested for the volcanoclastic derived rocks, which would be expected to have a spread of original Fe and Mg contents. There is some doubt about this classification, given the Y levels (Table 5.1, amphibole altered rocks), which suggest a degree of mobility during alteration in this zone. The texturally least altered samples have CCPI values (~ 80) above their texturally more altered equivalents (55, 77). The amphibole-rich samples with no relict textures have very high CCPI values (~ 97). These samples are within 10 m of the P – Fe-oxide mineralisation. However as previously noted the precursor of these rocks is almost certainly not volcanoclastic, but the CCPI still indicates significant introduction of Fe and Mg. The CCPI however may be useful for defining intense amphibole-rich alteration as it separates the zones proximal to the P-Fe-oxide mineralisation from the more distal more K-rich sericite bearing zones.



**Figure 5. 17 Plot of Esfordi amphibole 1 and 2 in the CCPI-AI alteration box.**



**Figure 5. 18 AI and CCPI box plot for amphibole-chlorite rich altered rocks and their least equivalents.**

#### 5.4.1 Exotic alteration

The volcanoclastic unit, which overlaps and hosts the P-Fe-oxide mineralisation contains abundant clasts of magnetite often with hematite overgrowths, which contain disseminations or small patches of apatite 2. Although amphibole-rich alteration is developed within the matrix of the pebbly sandstones with greater intensity close to the Fe-P mineralised zones, within the peripheries of amphibole-rich zone where the alteration intensity is weak, clasts of exotic hydrothermal alteration can be clearly

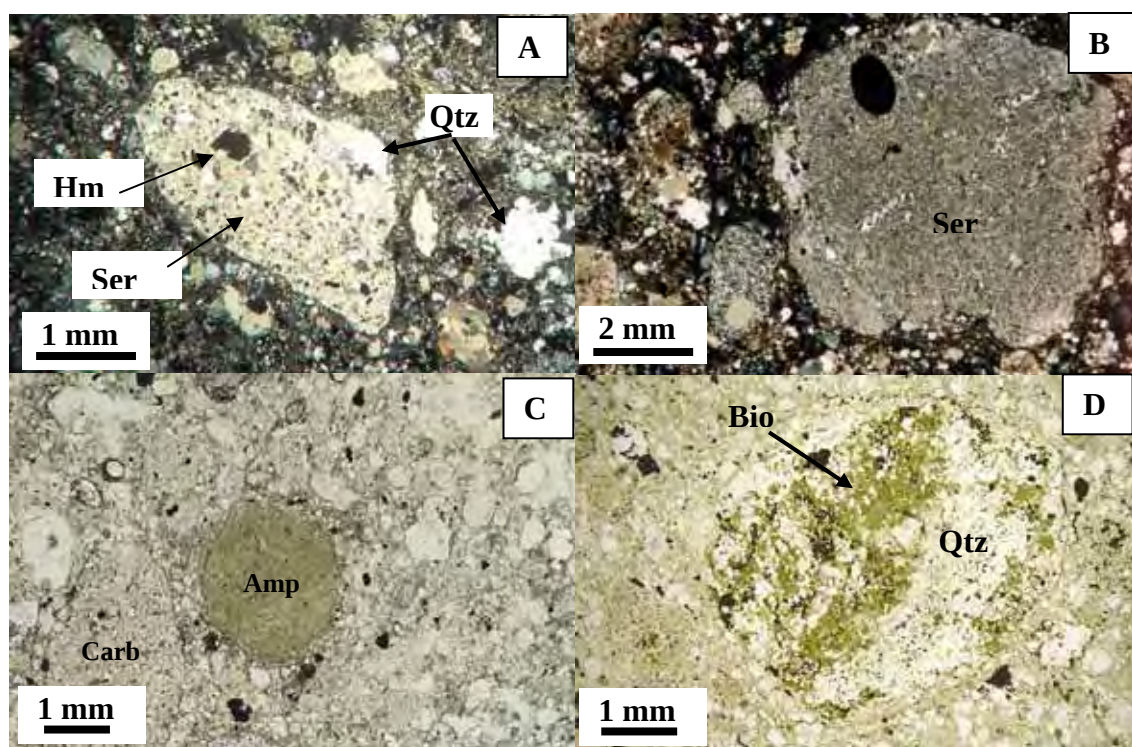
discerned (Fig 5.19), some of which may have thin overgrown rims of actinolite. Three main types of altered well rounded clasts can be recognised.

The most common are clasts with a high intensity of actinolite replacement. The clasts are up to 30 mm and typically rounded. Some are monomineralic actinolite with no preservation of original textures (Fig 3.17 i). Others contain actinolite disseminations and patches within felsic volcanic clasts (Fig 3.17 j). These clasts could represent selective alteration of particularly susceptible lithologies, but the low level of alteration in the supporting sandstone matrix suggest that the alteration was prior to sedimentation. Also relatively common are clasts made up of quartz and patchy sericite. The sericite ranges up to 100  $\mu\text{m}$  in size (Fig 5.19) but does not have any preferred orientation and is typically of intensive hydrothermal alteration rather than that from the high metamorphic rocks of the high grade Boneh-Shurow Complex. These clasts are markedly different from the sericite bearing assemblages on the margin of the K-feldspar rich and amphibole-rich alteration zones. No clasts of granitic intrusions are present.

A third group of exotic alteration clasts are those containing quartz-biotite-carbonate (Fig 5.19). These have remnant embayed quartz grains clearly indicating the precursor felsic volcanics. The biotite is forming irregular patches, disseminations and veinlets and is clearly not of metamorphic type. Similar biotite also replaces the adjacent sandstone matrix, so that selective replacement of a particularly susceptible clast cannot be ruled out. However the diversity of nearby clast characteristics tends to suggest otherwise.

## **5.5 CARBONATE-QUARTZ-(EPIDOTE-CHLORITE-SERICITE) ALTERATION**

A carbonate-rich assemblage typically overprints the mineralisation and wall rocks. This includes the felsic volcanics, volcanoclastics and also intrusive bodies and takes the form of widespread carbonate  $\pm$  quartz veins (Fig 5.20 b and c), many of which have peripheral zones where the wall rocks are transformed to carbonate +chlorite+epidote



**Figure 5. 19 Exotic, altered clasts in the Esfordi hanging wall pebbly sandstone.**

A and B: Sericite-rich lithic fragments (hole Bh1-13, XPL), C: A round amphibole-rich clast without textural preservation (hole Bh3-48, PPL), D: Biotite-rich clast in an altered pebbly sandstone (hole Bh3-48, PPL).

dominated assemblages (Fig 5.20 b). Zone of pervasive carbonate development not related to fracture systems are also prominent (Fig 5.20 d). The intensity of pervasive carbonate overprinting spatially increases toward the mineralisation and in many cases masks primary volcanic or volcanoclastic textures resulting a spotty, veined pale coloured rock. Pervasive vein and patchy carbonate alteration generally overprint K-feldspar and amphibole-rich alteration. The carbonate veins locally contain fine lath-shape amphibole 2 and sericite and cut the quartz-rich veins.

Carbonate minerals are generally calcite, however siderite, ankerite and dolomite are locally observed.

There is some degree of similarities between carbonate alteration in VMS systems and Esfordi. Herrmann and Hill (2001), suggest that the carbonate infill and replacement resulted from the mixing of hydrothermal fluids and seawater below the palaeosea floor in

permeable volcanic units. Based on isotopic studies at the Henty gold deposit, western Tasmania, Callaghan (2001) suggested that carbonate influx was the result of a district-wide magmatic CO<sub>2</sub> devolatilization event, which commenced during early hydrothermal activity and continued for a period beyond ore formation. The distinct textural differences between pervasive carbonate infills and replacements and veining and the cross-cut relation of these two carbonate alteration facies in Esfordi suggests at least two episode of carbonate development. The isotopic studies (Chapter 7) also suggest two distinct groups of carbonates, which probably resulted from mixing of magmatic CO<sub>2</sub>-rich fluids with sea water below the palaeosea floor.

A local late stage chlorite-epidote-talc-carbonate alteration overprinted the amphibole-rich zone (Figs. 5.15 and 5.19 h). The distribution of this assemblage is not uniform and seems to have been controlled by the precursor rocks and the density of fractures and joints. Typically the mafic volcanoclastic with destructive amphibole alteration show well developed overprint of chlorite-epidote and talc. Chlorite and, to a lesser extent, talc are generally observed as an envelope to brecciated apatite ore and apatite-Fe-oxide veins in the amphibole-rich altered zone. Chlorite generally replaced the margins of amphibole-rich zone along the wall rock.

The intensity of epidote-chlorite alteration spatially decreases away from intense amphibole-rich altered rocks at the vicinity of mineralisation towards the pervasive K-feldspar-rich alteration. Chlorite replaced both types of amphiboles and in extensively altered zones locally forms up to 80 modal percent of the rock. Epidote is locally dominant and replaced feldspar, amphibole, garnet and pyroxene (Figs. 5.15 and 5.19). Talc shows variable distribution and usually replaced pyroxene and amphibole and fills the matrix as feathery crystals.

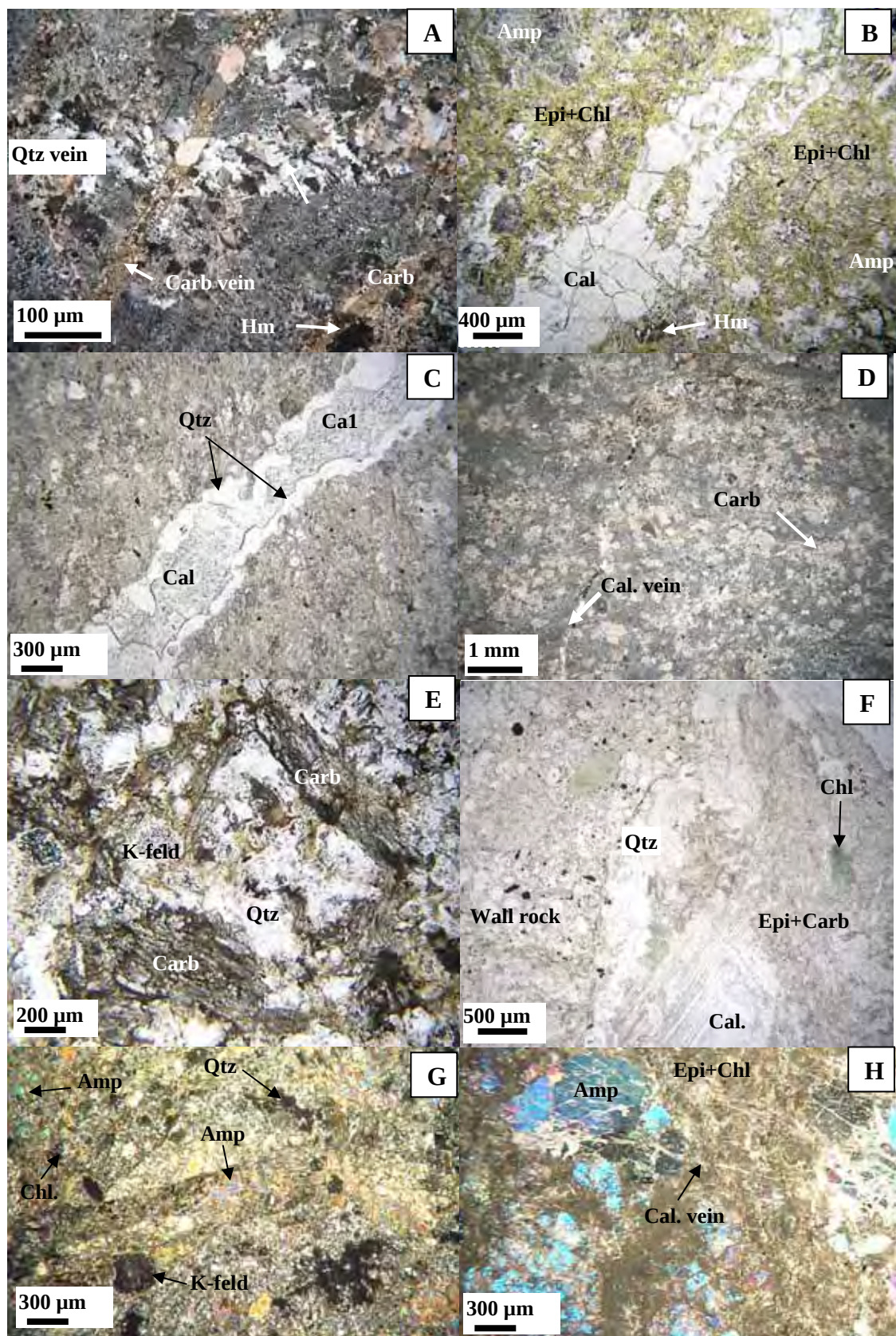


Figure 5. 20 (Caption on next page.)

**Figure 5.20 Photomicrograph of carbonate alteration facies in Esfordi volcanic sequence.**

- A: Extensive veining in a welded tuff with pervasive quartz-carbonate alteration. Note the calcite vein cut the quartz vein and pervasive carbonate alteration. (Hole B2-52; XPL).
- B: Calcite vein cut the amphibole-rich alteration assemblage. The calcite vein has a well developed pervasive and halo of epidote-chlorite overprinting the amphibole-rich alteration hole B9-110, footwall; PPL).
- C: A quartz-carbonate vein in a semi welded tuff, which quartz crystallised first at the borders of vein and calcite occupy the middle part. (Hole B12-94; PPL).
- D: Pervasive carbonate alteration of a vitric welded ash tuff with a spotty texture. (Hole B3-60; XPL).
- E: Pseudomorphous carbonate after amphibole in amphibole-rich altered ash flow. The remnant K-feldspar grains have been replaced by precursor amphibole and sericite. (Hole B53-41; PPL).
- F: Chlorite overprinted the quartz-feldspathic matrix associated with late carbonate vein. A rhombic calcite developed in the carbonate-quartz vein. (Hole B11-54 m; PPL)
- G: Chlorite overprinted amphibole in an amphibole-rich altered rock without textural preservation at the margin of breccia style P mineralisation Gr, (XPL).
- H: An amphibole-rich alteration strongly overprinted by carbonate-epidote-chlorite alteration, Gr, (XPL).

**Table 5. 4    Electron micro probe analyses of some carbonates of the Esfordi system. Calcite, dolomite, ankerite and siderite generally occurred as veins and pervasive patches and replacements associated with quartz.**

| Calcite                        |        |        |        |        |        |        |        |        |        |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| (wt %)                         | B12-41 | 101-4  | 101-6  | B9-12  | B9-16  | B9-20  | 101-20 | B9-12  | B9-16  |
| SiO <sub>2</sub>               | 0.08   | 0.04   | 0.02   | 0.01   | 0.05   | 0.03   | BLD    | 0.01   | 0.05   |
| Al <sub>2</sub> O <sub>3</sub> | 0.02   | BLD    | BLD    | BLD    | BLD    | 0.03   | 0.02   | BLD    | BLD    |
| P <sub>2</sub> O <sub>5</sub>  | 0.12   | 0.21   | 2.21   | BLD    | 0.25   | 0.03   | 0.17   | BLD    | 0.25   |
| CaO                            | 55.99  | 52.63  | 53.87  | 55.63  | 55.44  | 55.95  | 55.82  | 55.63  | 55.44  |
| MgO                            | 0.20   | 0.57   | 0.20   | 0.04   | 0.07   | 0.12   | 0.13   | 0.04   | 0.07   |
| FeO                            | 0.16   | 3.23   | 1.21   | 0.16   | 0.17   | 0.17   | 0.54   | 0.16   | 0.17   |
| Na <sub>2</sub> O              | 0.04   | BLD    | 0.04   | 0.04   | 0.02   | BLD    | 0.03   | 0.04   | 0.02   |
| K <sub>2</sub> O               | 0.01   | BLD    | 0.01   | 0.01   | 0.01   | BLD    | BLD    | 0.01   | 0.01   |
| CO <sub>2</sub> *              | 44.16  | 43.81  | 43.15  | 43.71  | 43.60  | 44.06  | 44.19  | 43.71  | 43.60  |
| Total                          | 100.78 | 100.49 | 100.72 | 99.61  | 99.60  | 100.39 | 100.90 | 99.61  | 99.60  |
| Dolomite, Ankerite, Siderite   |        |        |        |        |        |        |        |        |        |
| (Wt %)                         | Bh1-1  | Bh1-2  | Bh1-3  | Bh1-4  | B4-1   | B4-2   | B4-3   | B4-4   | 108-22 |
| SiO <sub>2</sub>               | 8.82   | 0.07   | 0.04   | 0.00   | 0.06   | 0.03   | 0.06   | 0.03   | 1.57   |
| Al <sub>2</sub> O <sub>3</sub> | 3.72   | 0.03   | BLD    | 0.02   | 0.01   | BLD    | 0.01   | BLD    | 0.05   |
| P <sub>2</sub> O <sub>5</sub>  | 0.00   | 0.00   | 0.05   | 0.03   | 0.02   | 0.04   | 0.02   | 0.04   | 0.17   |
| CaO                            | 24.63  | 41.04  | 29.33  | 29.12  | 28.16  | 30.81  | 28.16  | 30.81  | 28.05  |
| MgO                            | 12.23  | 9.74   | 20.54  | 20.88  | 17.03  | 16.40  | 17.03  | 16.40  | 0.64   |
| FeO                            | 10.32  | 4.20   | 3.10   | 3.27   | 9.31   | 6.89   | 9.31   | 6.89   | 29.54  |
| Na <sub>2</sub> O              | 0.01   | 0.01   | BLD    | BLD    | BLD    | 0.01   | BLD    | 0.01   | 0.04   |
| K <sub>2</sub> O               | 1.07   | 0.12   | BLD    | BLD    | 0.01   | BLD    | 0.01   | BLD    | 0.03   |
| CO <sub>2</sub> *              | 38.95  | 45.35  | 47.29  | 47.59  | 46.34  | 46.25  | 46.34  | 46.25  | 40.76  |
| Total                          | 99.76  | 100.57 | 100.35 | 100.91 | 100.93 | 100.43 | 100.93 | 100.43 | 100.85 |

\* CO<sub>2</sub> has been calculated

## **CHAPTER 6      RARE EARTH ELEMENT MINERALOGY AND GEOCHEMISTRY**

### **6.1      INTRODUCTION**

The Esfordi P-Fe mineralisation system is enriched in REE (~ 0.2 – 1.5 %) with an associated array of accessory REE minerals and distinctive REE geochemical patterns within the different paragenetic stages and host rocks. Studies on the distribution of REE have provided valuable insight into linkages between associated igneous rocks and the evolution of mineralizing systems (Fleischer 1983; Giere and Sorensen 2004; Harlov *et al.* 2002; Henderson 1984; Naslund *et al.* 2002). REE can partially fractionated by a range of geological processes and, coupled with a degree of immobility in many environments, has provided a significant geochemical tool for investigating a range of geological processes (Heinrich *et al.* 1999; Henderson 1984; Lipin and McKay 1989; Shmulovich *et al.* 2002).

Routine, high quality REE assay data were not available from the mine operation, but semiquantitative emission spectrographic data from isolated drill holes, together with ICPMS data in the current investigation indicates that total REE contents broadly follows P levels.

More than 39 samples from the different ore types, host rocks and igneous bodies were analysed for REE by ICPMS following microwave bomb HF/HClO<sub>4</sub>/HNO<sub>3</sub> digestion and the major elements determined by X-ray fluorescence (Philips PW1400 XRF sequential spectrometer (Appendix 2). The REE composition of various mineral phases from 24 polished thin sections has been investigated by electron microprobe (Appendix 2).

This chapter summarises the characteristics of REE mineralogy at Esfordi, in a textural and paragenetic context, with the main focus on REE geochemical patterns in the

Esfordi mineralisation, particularly the apatites and associated host rocks. The minerals with significant REE contents at Esfordi which show systematic relationships in the paragenetic stages of Fe-oxide-P mineralisation are considered in three groups; phosphates, carbonates and silicates.

## **6.2 REE PHOSPHATE AND CARBONATE MINERALS**

Six different non-silicate REE minerals have been identified by electron microprobe analyses supported by optical methods and limited XRD. The most abundant mineral is monazite. Xenotime, britholite, synchysis and bastnasite are also present as minor phases.

### **6.2.1 Monazite**

Monazite is one of the most abundant REE mineral at Esfordi and has a close relationship with apatite. Monazite occurs as inclusions in the first generation of apatite (apatite 1), associated with the main magnetite-rich core of the mineralizing system, as well as inclusions and individual mineral grains in the brecciated apatite ore body and in late quartz-carbonate-apatite veins and pervasive replacements. The highest concentration of monazite is associated with the brecciated apatite-rich ore.

Based on texture, chemistry and associated mineral assemblage, two subgroups have been identified. Type 1 monazite is associated with primary apatite 1, which largely occurs as 5-100  $\mu\text{m}$  inclusions within patches in massive magnetite in the main magnetite core of the Esfordi system. It is also present as larger (20-200  $\mu\text{m}$ ) grains among granular apatite in the P-rich zone. Mosaics of primary apatite 1 commonly contain domains of subsequent brecciation and granulation. Apatites in such zones show very low contents of monazite inclusions (Fig 6.1 a). Monazite 1 is predominantly fine grained and surrounded by apatite 1 and occur as small groups of transparent and green coloured crystals. Type 2 monazite generally occurs as 20-400  $\mu\text{m}$  grains in brecciated matrix of apatite 1, apatite 2, granular apatite, amphibole 1, hematite and allanite 1. Large crystals of monazite 2 were found in the heavily brecciated domains of apatite-rich ore with allanite 1 and 2 as crystal

aggregates especially in a close association with actinolite aggregates and veins (Fig 6.1 g-k). Textural evidence suggests monazite 1 formed prior to monazite 2. Ayers *et al.* (1999) and Townsend *et al.* (2000) have suggested that recrystallisation during hydrothermal alteration of pre-existing monazite can result a patch zoning. Some monazite 1 grains in the brecciated apatite ore show a colour zonation that is interpreted as younger generation of monazite 2 growing during the subsequent brecciation and alteration episodes (Fig 6.1).

Monazite 2 is usually subhedral to euhedral shape crystals of various colours, from green to brown, within brecciated matrix and tracks of apatite 2. Monazite 2 is also often associated with allanite 1 and 2, xenotime and, to lesser extent, synchysite and bastnaesite. Monazite 2 is also present as small (20-100  $\mu\text{m}$ ) crystals in hematite-rich veins within altered rhyolite volcanics closely associated with apatite 2 (Fig. 6.1 m).

Monazite is an anhydrous light rare earth orthophosphate  $[(\text{Ce},\text{La})\text{PO}_4]$ , of monoclinic structure (space group  $\text{P2}_1/\text{n}$ ,  $Z=4$ ) (Anthony *et al.* 2000). From experimental studies it has been found that orthophosphates of La, Ce, Pr, Nd, Sm and Eu crystallize in a monazite monoclinic structure whereas orthophosphates of Ho, Er, Tm, Yb, Lu and Y form a tetragonal xenotime structure (Rappaz *et al.* 1981). In the monazite structure, LREE are located in a polyhedron coordinated to nine oxygen ions, whereas in the xenotime structure, HREE, Y and Sc are located in a polyhedron coordinated to eight oxygen ions (Boatner 2002). Natural monazites show a diverse composition and complete miscibility with brabanite  $[\text{Ca},\text{Th},\text{U}(\text{PO}_4)_2]$  (Bea 1996; Förster 1998a).

Quantitative electron microprobe analysis was conducted on 51 monazite grains (Table 6.1). The composition of monazite 1 in respect to type 2 show higher La and La/Ce

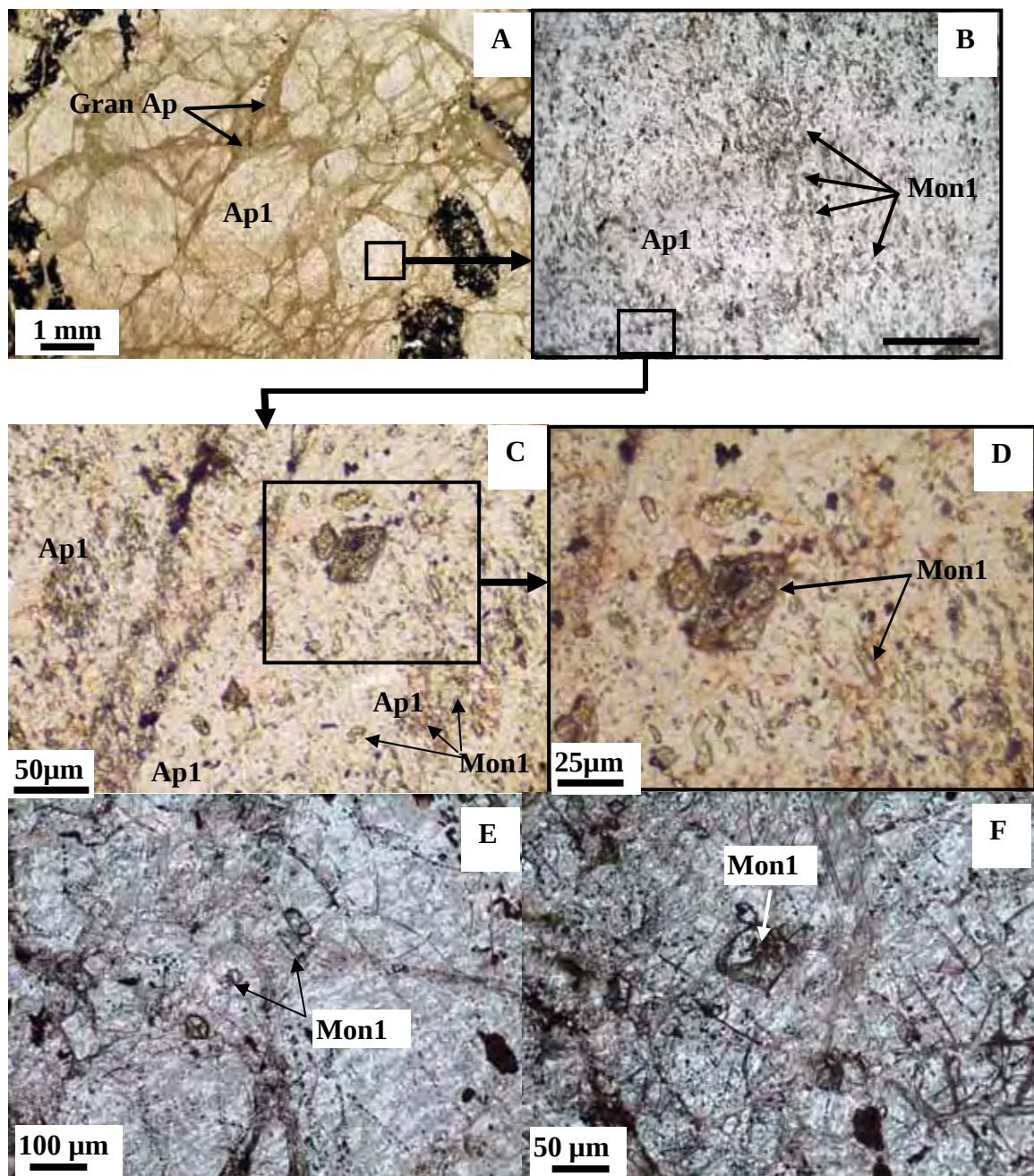


Figure 6. 1 (Caption on page 206).

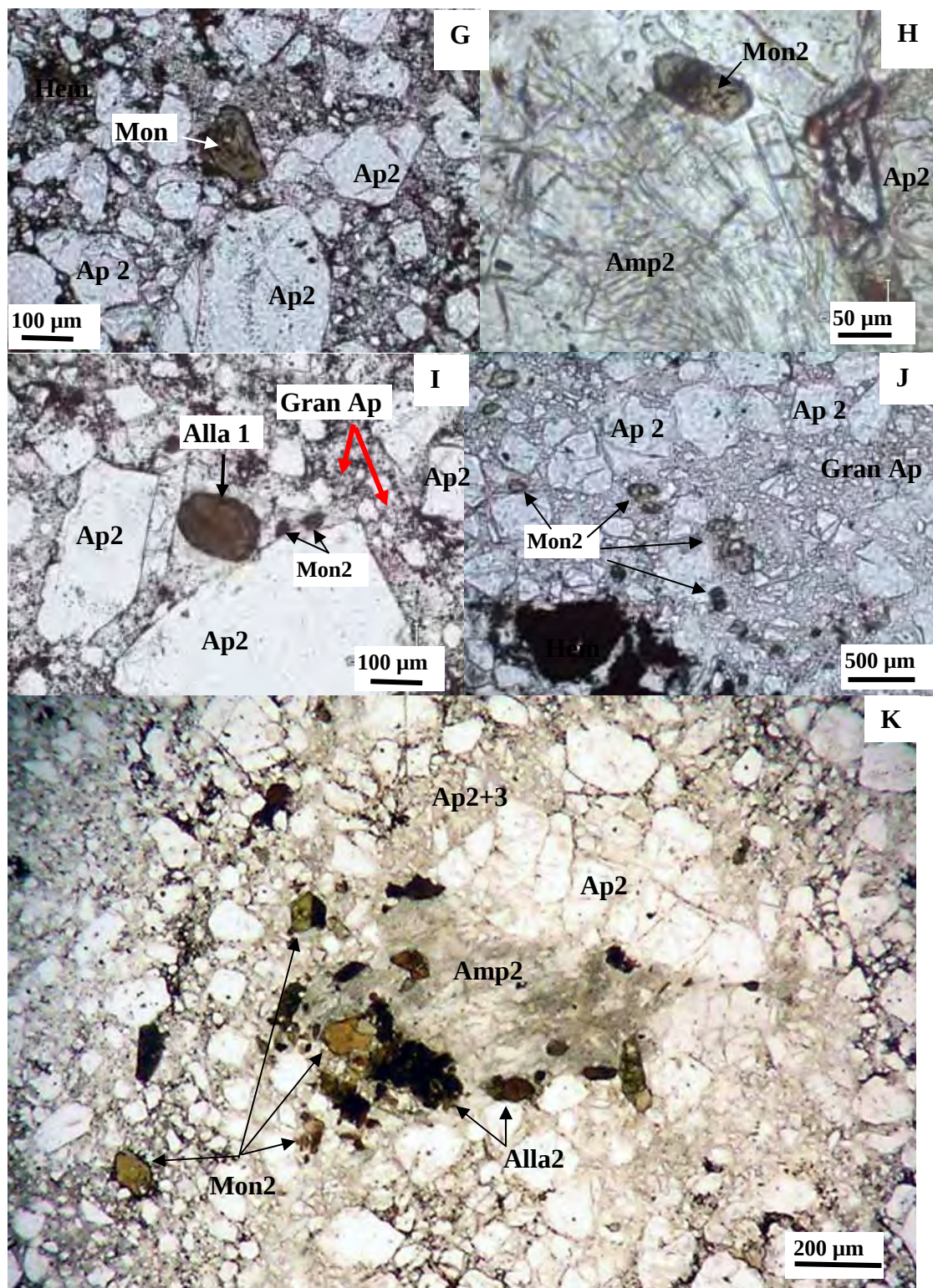
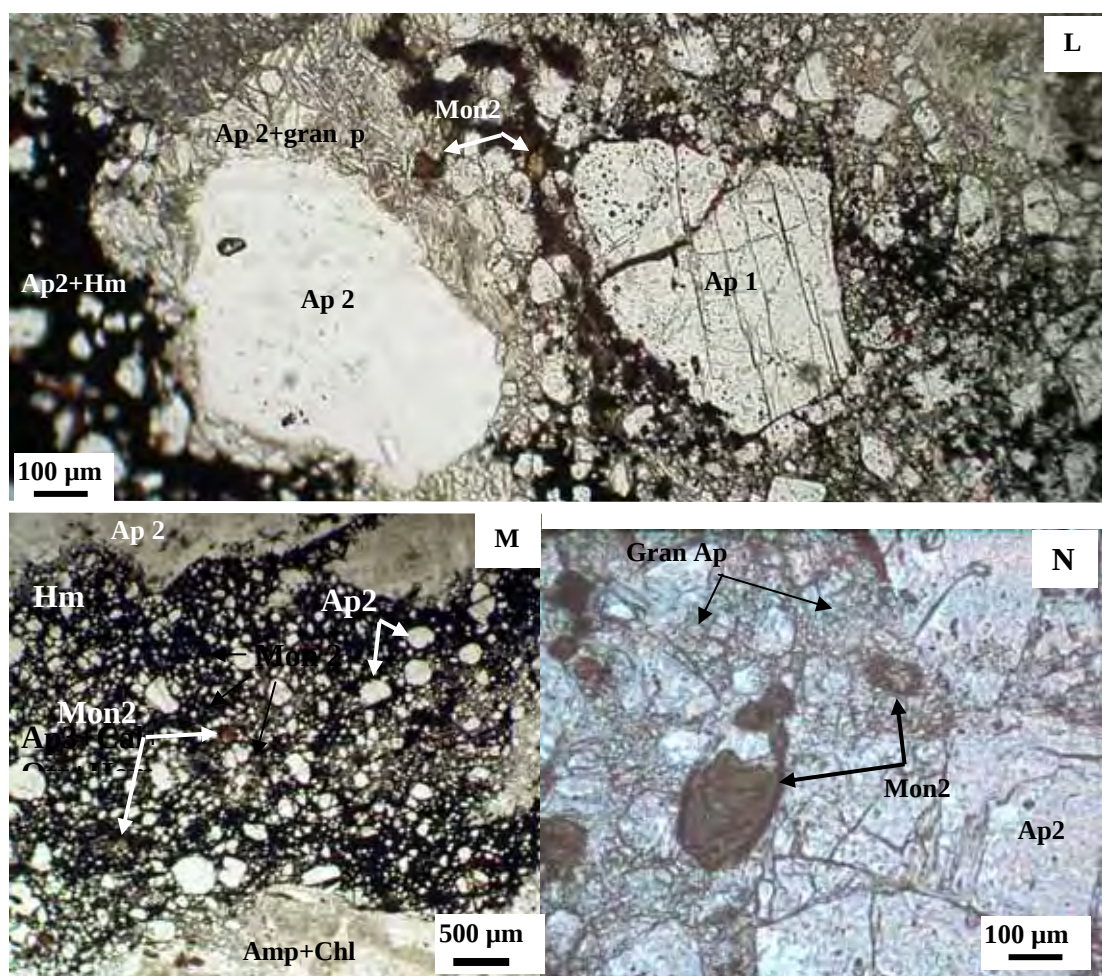


Figure 6.1 Continued (Caption on next page).



**Figure 6.1 Monazites in Esfordi mineralizing system.**

- A - D: Monazite 1 inclusions within apatite1 in Fe-rich core. (sample 108, PPL).
- E & F: Monazite 1 in apatite 1 core of zoned apatite in apatite-rich zone. (Hole B20-43 m; PPL).
- G, H & J: Monazite 2 in apatite-rich zone. Monazite 2 set in finer grained brecciated matrix of apatite 2, granular apatite, hematite and carbonate and associated with amphibole 2 and allanite 2 in a brecciated matrix of apatite 2 and granular apatite. (Hole B12-65; PPL).
- I: Allanite 1 associated with apatite 2, granular apatite and monazite 2 in brecciated P-rich zone. (Hole B9-5; PPL).
- K: Monazite 2 in apatite-rich zone. Monazite 2 associated with allanite 2, amphibole 2 and granular apatite in a brecciated matrix of apatite 2. (Hole B12-60; PPL).
- L: Monazite 2 in brecciated apatite-rich zone. Monazite 2 associated with the overgrowth of apatite 2 and granular apatite on an apatite 2 grain. An older apatite1 with monazite 1 inclusions is in the right hand side of the image (hole B12-38. PPL).
- M: Monazite 2 in altered rhyolitic host. Monazite 2 occurred within a hematite-rich vein associated with apatite2 and late stage pervasive carbonate (hole B70-16, PPL).
- N: Monazite 2 in apatite-rich zone. Monazite 2 grain showing a colour zonation (Cx, PPL).

ratio but lower Ce, Nd, Pr, Sm, and  $\Sigma\text{REE}+\text{Y}$ . Type 1 monazite is generally characterised by higher La/Nd, La/Y, and La/Ce ratios (Table 6.1 and Figs. 6.2 and 6.3). The higher average La/Y ratio in monazite 1 suggests that the LREE are more fractionated in this group than monazite 2. Monazites often contain significant U and Th in their structure (Förster 1998a; Harlov *et al.* 2002; Henderson 1984), however, the majority of Esfordi monazites are poor in Th and U (Table 6.1).

The chondrite normalised (cn) patterns (Wakita *et al.* 1971; Taylor and McLennan 1985) of monazite 1 and 2 are illustrated in Fig 6.2. Both types of monazite are LREE enriched with La enrichment in monazite 1 and Ce enrichment in monazite 2. Higher  $(\text{La}/\text{Ce})_{\text{cn}}$ ,  $(\text{La}/\text{Nd})_{\text{cn}}$  and  $(\text{La}/\text{Sm})_{\text{cn}}$  ratios in monazite 1 demonstrating higher degree of fractionation of the LREE whereas the lower slope reflects enrichment of the heavier LREE, Pr, Nd and Sm.

### 6.2.2 Xenotime

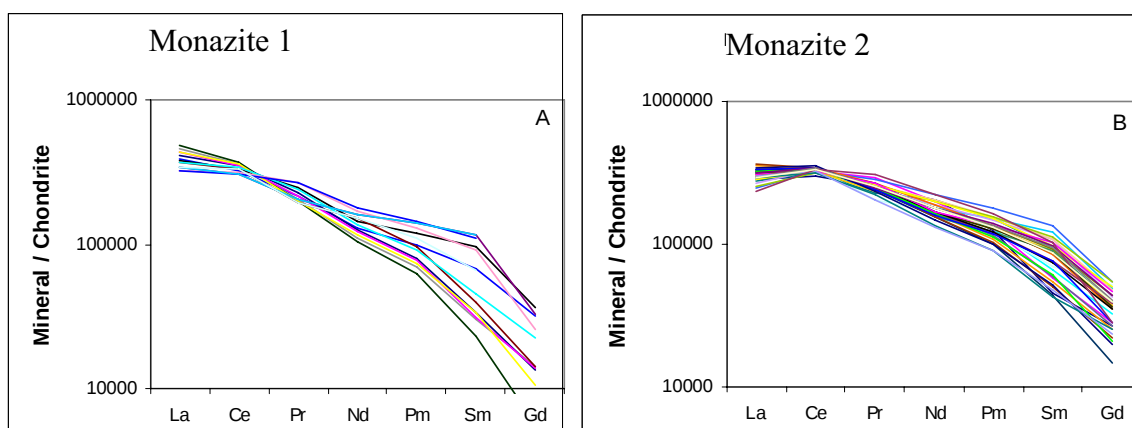
Xenotime occurs as a minor phase, mainly in the brecciated apatite-rich ore as individual grains in the matrix. It is typically associated in aggregates with monazite 2 and allanite 1. The xenotime grains ranging in size from 10 to 50  $\mu\text{m}$  and typically form subhedral, short prisms. Xenotime grains are usually transparent to translucent with a greenish to greenish brown colour. Textural varieties of xenotime are presented in Fig 6.4. The grains are predominantly intergrown or associated with monazite in the matrix of granular apatite, hematite, carbonates and quartz. Xenotime and monazite grains may be also embedded in a matrix of quartz.

Xenotime  $[(\text{Y},\text{HREE})\text{PO}_4]$  is a Y-rich orthophosphate with REE maxima generally at Yb or Dy, and is isostructural with zircon. Xenotime has a tetragonal structure (space group:  $I4_1/\text{amd}$ ,  $Z=4$ ). In the xenotime structure, the heavier rare earths, Y or Sc are located in a polyhedron in which they are coordinated to eight oxygen ions.

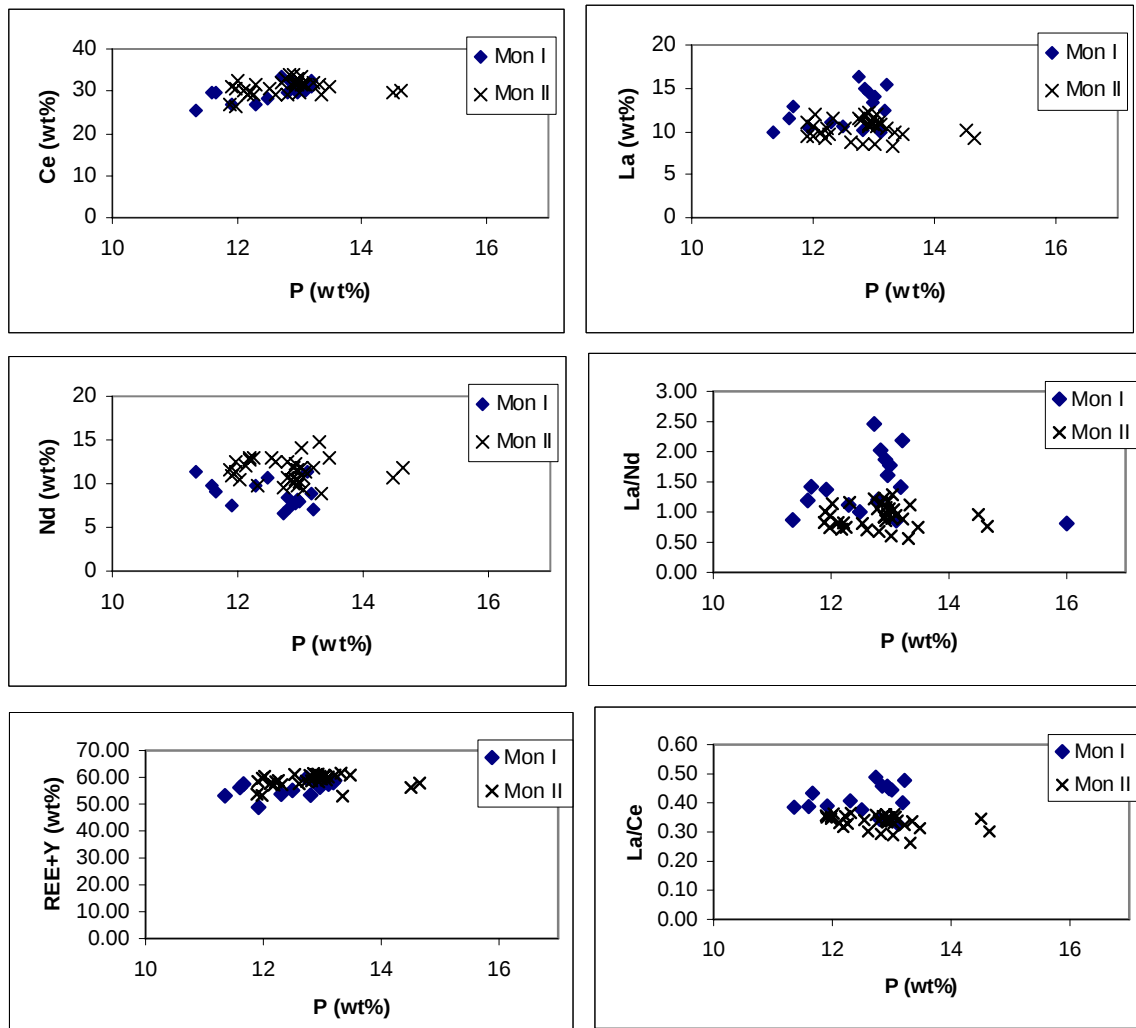
**Table 6. 1 Electron Microprobe analyses of Esfordi monazites.**

|                                | Monazite 1 (n=16) |         | Monazite 2 (n=35) |         |
|--------------------------------|-------------------|---------|-------------------|---------|
| Oxides (wt %)                  | Ave               | Std Dev | Average           | Std Dev |
| SiO <sub>2</sub>               | 0.31              | 0.24    | 0.20              | 0.32    |
| Al <sub>2</sub> O <sub>3</sub> | 0.02              | 0.04    | 0.02              | 0.02    |
| La <sub>2</sub> O <sub>3</sub> | 14.78             | 2.37    | 12.14             | 1.20    |
| Ce <sub>2</sub> O <sub>3</sub> | 35.41             | 2.12    | 35.48             | 1.51    |
| Pr <sub>2</sub> O <sub>3</sub> | 3.19              | 0.39    | 3.55              | 0.30    |
| Nd <sub>2</sub> O <sub>3</sub> | 10.76             | 2.05    | 13.14             | 1.60    |
| Sm <sub>2</sub> O <sub>3</sub> | 1.39              | 0.70    | 1.84              | 0.55    |
| Gd <sub>2</sub> O <sub>3</sub> | 0.75              | 0.37    | 1.07              | 0.32    |
| Tb <sub>2</sub> O <sub>3</sub> | BLD               | --      | BLD               | --      |
| Dy <sub>2</sub> O <sub>3</sub> | 0.12              | 0.09    | 0.17              | 0.09    |
| Ho <sub>2</sub> O <sub>3</sub> | BLD               | --      | BLD               | --      |
| Er <sub>2</sub> O <sub>3</sub> | 0.06              | 0.07    | 0.06              | 0.06    |
| Yb <sub>2</sub> O <sub>3</sub> | BLD               | --      | 0.01              | 0.02    |
| Y <sub>2</sub> O <sub>3</sub>  | 0.51              | 0.30    | 0.53              | 0.32    |
| CaO                            | 1.18              | 0.83    | 0.99              | 1.06    |
| MgO                            | BLD               | --      | BLD               | --      |
| FeO                            | BLD               | --      | 0.06              | 0.26    |
| ThO <sub>2</sub>               | 0.42              | 0.34    | 0.37              | 0.72    |
| UO <sub>2</sub>                | BLD               | --      | BLD               | --      |
| P <sub>2</sub> O <sub>5</sub>  | 29.27             | 0.85    | 29.04             | 1.09    |
| SO <sub>3</sub>                | 0.30              | 0.25    | 0.13              | 0.19    |
| F                              | 0.98              | 0.17    | 0.90              | 0.13    |
| Total                          | 99.16             | 2.43    | 99.69             | 1.78    |
| ΣREE +Y                        | 57.16             | 1.56    | 58.09             | 1.65    |
| La/Ce                          | 0.42              | 0.05    | 0.34              | 0.03    |
| La/Y                           | 39.12             | 16.73   | 31.00             | 13.62   |
| La/Nd                          | 1.45              | 0.49    | 0.94              | 0.19    |
| (La/Ce)cn                      | 1.11              | 0.12    | 0.91              | 0.08    |
| (La/Sm)cn                      | 8.20              | 5.41    | 4.19              | 1.61    |
| (La/Nd)cn                      | 2.73              | 0.93    | 1.77              | 0.35    |
| (La/Y)cn                       | 241.64            | 103.31  | 191.45            | 84.15   |

BLD: Below level of detection; cn: Chondrite normalised



**Figure 6. 2 Chondrite normalised patterns of A: monazite 1 and B: monazite 2 (Pm is calculated as the average of Nd and Sm, chondrite values from McDonough et al 1992).**



**Figure 6.3 LREE contents of monazites from Esfordi apatite ore.**

Amlı (1975) described REE zoned xenotime inclusions with LREE enrichment towards the rims of the grains, exsolved from apatite crystals in the Glosersheia Granite Pegmatite of southern Norway. Some larger grains of xenotime in close association with apatite 2 crystals show a faint zonation in backscattered images (Fig 6.5).

The Esfordi xenotime have traces of  $\text{SiO}_4^{4-}$  replacing  $\text{PO}_4^{3-}$  (Table 6.2). Minor substitution of  $\text{U}^{4+}$ ,  $\text{Th}^{4+}$  and  $\text{Si}^{4+}$  for  $\text{Y}^{3+}$  and  $\text{Ca}^{2+}$  for  $\text{P}^{3+}$  is indicated. The main mechanisms for the replacement of Y and REE by U and Th are charge balancing coupled substitutions involving Si and Ca (Förster 1998b; van Emden *et al.* 1997). The chondrite normalised REE distribution show a typical HREE enrichment with a very low  $(\text{La}/\text{Y})_{\text{cn}}$  ratio (Fig 6.6).

### 6.2.3 Synchysite and Bastnaesite

The fluorocarbonates synchysite and bastnaesite at Esfordi are mainly observed in the brecciated apatite-rich ore and apatite-rich veins in altered host rocks. Synchysite and bastnaesite occur as 20 - 400  $\mu\text{m}$  crystals closely associated with monazite 2 and allanite 1 grains between apatite 2 grains, within the apatite-rich zone. They are always observed in close relationship to the late pervasive carbonate alteration and almost always occur in carbonate-rich matrix, replacements and veins (Fig 6.7). The synchysite grains are usually transparent to translucent and show a prismatic shape with rhombohedral outline. They range from colourless or pale yellow to yellowish brown. Bastnaesite grains are very similar in appearance to synchysite but less abundant.

Synchysite  $[\text{Ca}(\text{Ce},\text{La},\text{Nd},\text{Y})(\text{CO}_3)_2\text{F}]$  and bastnaesite  $[(\text{Ce},\text{La})(\text{CO}_3)\text{F}]$  are hexagonal fluorocarbonates. Based on the respective predominant rare earth element previous workers have recognised synchysite-(Ce), synchysite-(Nd) and very rare synchysite-(Y) (Anthony *et al.* 2000). Synchysite is closely related to three other distinct minerals, parasite, bastnaesite and rontgenite-(Ce). Synchysite-(Ce) and bastnaesite-(Ce) are the end members of a Ca-REE fluorocarbonate mineral series. This series of minerals are composed of ratios of  $(\text{CeF}):(\text{CO}_3):[\text{Ca}(\text{CO}_3)]$  layers of 1:1:0, 2:2:1, 3:3:2 and 1:1:1 for bastnaesite-(Ce), parasite-(Ce), rontgenite-(Ce) and synchysite-(Ce) respectively (Meng *et al.* 2002; Ni *et al.* 1993; Wang *et al.* 1994).

The Esfordi synchysites are synchysite-(Ce) with high La and Nd. The Esfordi bastnaesites are bastnaesite-(Ce) which is the most common form of bastnaesite. The result of electron microprobe analyses of selected grains presented in Table 6.2. Fig 6.8 illustrates chondrite normalised REE distribution pattern of synchysite and bastnaesite grains, which show LREE enrichment.

**Table 6. 2 Selected Electron Microprobe analyses of Esfordi xenotime, synchysite and bastnaesite.**

| Mineral                        | Xenotime    |         | Synchysite  |         | Bastnaesite |         |
|--------------------------------|-------------|---------|-------------|---------|-------------|---------|
| Oxides (wt %)                  | Average N=5 | Std Dev | Average N=4 | Std Dev | Average N=2 | Std Dev |
| SiO <sub>2</sub>               | 0.82        | 1.37    | BLD         | --      | BLD         | --      |
| La <sub>2</sub> O <sub>3</sub> | BLD         | BLD     | 10.12       | 0.79    | 13.96       | 0.39    |
| Ce <sub>2</sub> O <sub>3</sub> | 0.13        | 0.04    | 26.57       | 1.01    | 39.97       | 0.47    |
| Pr <sub>2</sub> O <sub>3</sub> | BLD         | 0.03    | 2.50        | 0.14    | 2.83        | 0.16    |
| Nd <sub>2</sub> O <sub>3</sub> | 0.06        | 0.09    | 9.54        | 0.81    | 10.15       | 1.07    |
| Gd <sub>2</sub> O <sub>3</sub> | 5.16        | 0.69    | 1.28        | 0.20    | 1.75        | 0.40    |
| Tb <sub>2</sub> O <sub>3</sub> | 0.68        | 0.11    | BLD         | --      | BLD         | --      |
| Dy <sub>2</sub> O <sub>3</sub> | 5.66        | 0.59    | 0.47        | 0.13    | 0.58        | 0.24    |
| Ho <sub>2</sub> O <sub>3</sub> | 1.07        | 0.15    | 0.08        | 0.03    | --          | --      |
| Er <sub>2</sub> O <sub>3</sub> | 4.01        | 0.18    | 0.12        | 0.04    | 0.18        | 0.08    |
| Yb <sub>2</sub> O <sub>3</sub> | 2.82        | 0.12    | 0.06        | 0.02    | 0.06        | 0.02    |
| Y <sub>2</sub> O <sub>3</sub>  | 43.82       | 0.16    | 2.06        | 0.11    | 1.79        | 0.25    |
| ThO <sub>2</sub>               | 0.34        | 0.33    | BLD         | --      | BLD         | --      |
| UO <sub>2</sub>                | 0.23        | 0.11    | 0.03        | 0.02    | 0.03        | 0.01    |
| CaO                            | 0.01        | 0.13    | 18.14       | 2.16    | 0.28        | 0.12    |
| FeO                            | 0.25        | 1.16    | 0.18        | 0.19    | 0.01        | 0.02    |
| P <sub>2</sub> O <sub>5</sub>  | 34.12       | 1.94    | 0.43        | 0.49    | 0.07        | 0.03    |
| CO <sub>2</sub>                | --          | --      | 25.11       | 0.25    | 24.70       | 0.45    |
| F                              | BLD         | 0.03    | 6.09        | 0.65    | 8.12        | 0.48    |
| -O=F <sub>2</sub>              | --          | --      | -2.26       | 0.23    | -3.89       | 0.04    |
| Total                          | 99.96       | 1.65    | 100.49      | 0.43    | 100.59      | 0.17    |
| ΣREE +Y                        | 51.65       | 1.34    | 46.70       | 2.41    | 62.39       | 0.25    |
| La/Ce                          | 0.49        | 0.50    | 0.37        | 0.03    | 0.35        | 0.01    |
| La/Y                           | 0.00        | 0.00    | 5.32        | 0.18    | 8.54        | 1.44    |
| (La/Sm)cn                      | --          | --      | 4.06        | 0.25    | 4.54        | 0.30    |
| (La/Y)cn                       | 0.00        | 0.00    | 4.07        | 52.80   | 6.53        | 49.87   |

BLD: Below level of detection Limit; cn: Chondrite normalised (Chondrite values from McDonough et al 1992).

## 6.3 RARE EARTH ELEMENT SILICATES

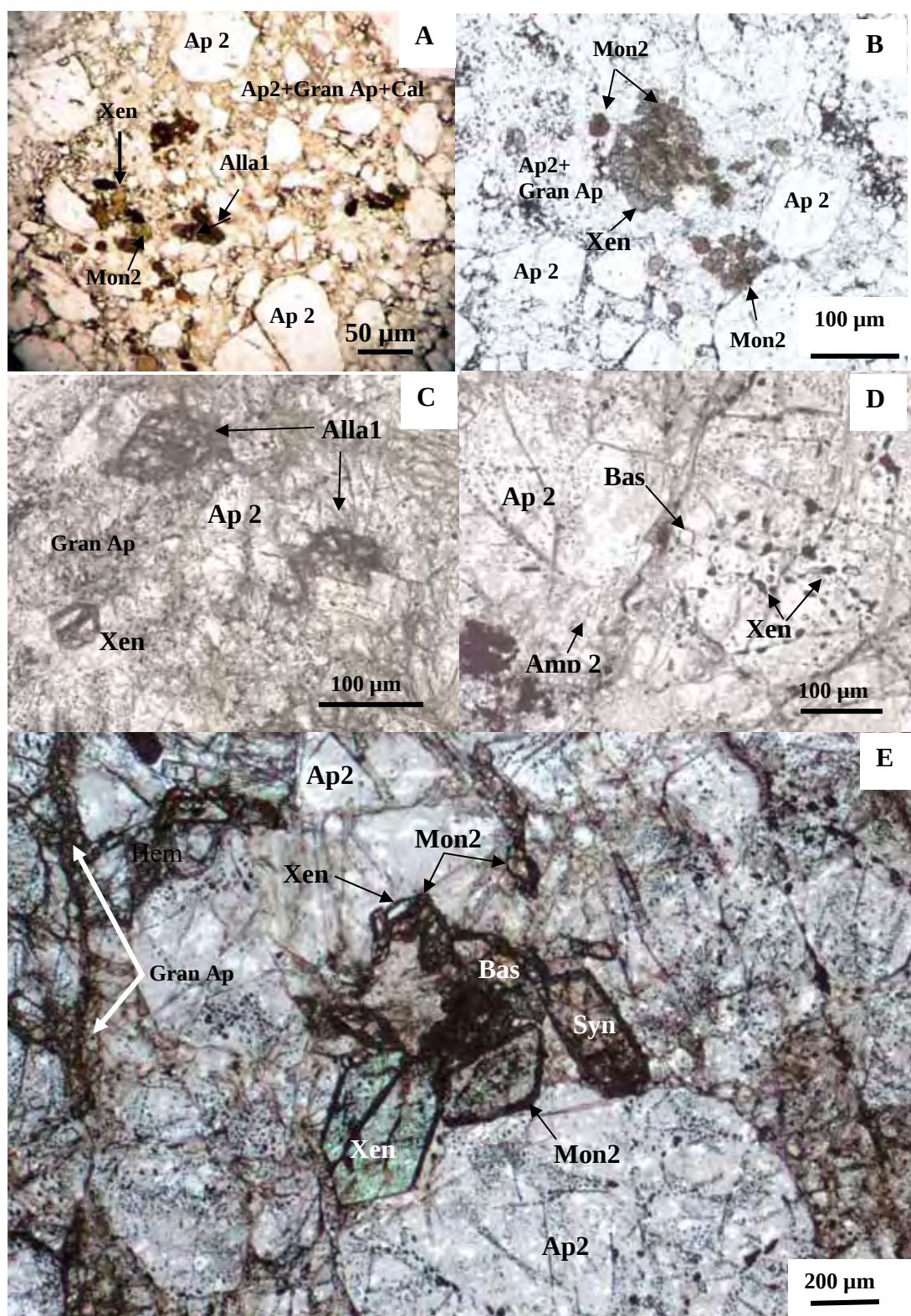
### 6.3.1 Allanite

Allanite is the most abundant REE mineral in the Esfordi deposit and occurs in two paragenetic associations. Allanite 1 includes individual grains in the brecciated apatite-rich ore and is closely associated with brecciated apatite 2, granular apatite and monazite 1. This type of allanite usually occurs as euhedral to subhedral crystals within the size range 10 - 300 µm. Some grains show a faint twinning and optical zonation. The zonation colour varies from dark brown and brown to yellowish brown. The apatite-rich patches in the magnetite-rich core show a very low allanite content, whereas the brecciated apatite-

rich zone in the hanging wall of the magnetite core has the highest concentration of allanite 1. Allanite 1 is often accompanied by monazite 2 (Figs. 6.1, 6.3 and 6.9).

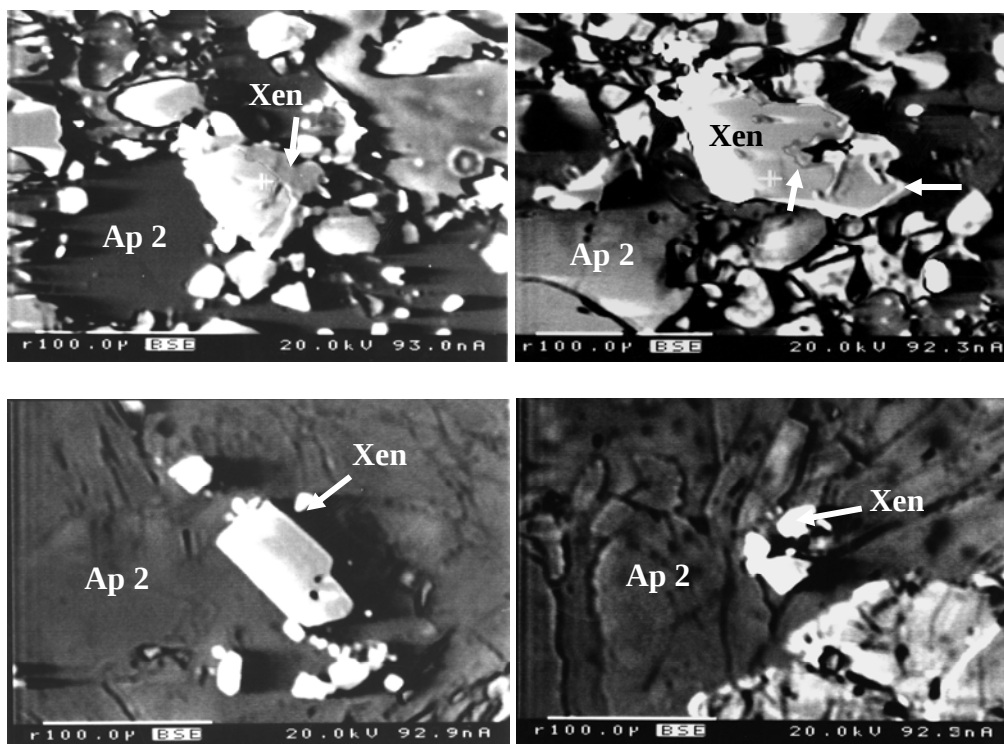
Allanite 1 occurs in two different assemblages; brecciated apatite matrix of the apatite-rich zone and hematite-apatite veins in the extensively altered volcanic rocks host to the apatite-rich zone. The second group of allanites is usually closely associated with amphibole-rich assemblage in the brecciated apatite-rich zone and apatite-Fe-oxide veins in the altered host rocks. It occurs as anhedral to subhedral 0.01 to 1 mm crystals. Elongate allanite 2 pseudomorphs of actinolite clearly show the replacement of the younger generation of Ca-rich amphiboles by allanite 2 (Fig 6.9). Allanite 2 is rarely associated with amphibole 1 in the system. Large patches of allanite 2-britholite-amphibole 2-hematite aggregates, within highly brecciated matrix, are one of the significant textural features in brecciated apatite-rich ore (Fig 6.9).

Allanite is a member of the epidote group  $[A_2M_3Si_3O_{12}(OH)]$ . The A-sites (A1 and A2) typically contain large, highly coordinated cations, such as  $Ca^{2+}$ ,  $Sr^{2+}$  or  $REE^{3+}$ , whereas the M-sites (M1, M2, and M3) admit octahedrally coordinated cations, including  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{3+}$ ,  $Fe^{2+}$  and  $Mg^{2+}$ . Large amounts of additional elements ( $Th^{4+}$ ,  $U^{4+}$ ,  $Zr^{4+}$ ,  $P^{5+}$ ,  $Ba^{2+}$ ,  $Cr^{3+}$  and others) may also be present in the mineral (Deer *et al.* 1986; Dollase 1971; Gieré and Sørensen 2004). Allanite has a monoclinic structure (space group  $P2_1/m$ ,  $Z=2$ ) with a light brown to black colour in hand specimen and brownish yellow to brown with strong pleochroism under the microscope (Anthony *et al.* 2000). The REE ions are located in the polyhedron coordinated to nine oxygen ions. LREE zoning in allanite has been attributed to a complex interplay between coupled substitutions, mineral-structure constraints and geochemical environment. According to Deer *et al.* (1986) the coupled replacement of  $Ca^{2+} + Fe^{3+} \leftrightarrow REE^{3+} + Fe^{2+}$  express the relationship between common [Fe,Al]-epidotes and allanite. Another possible substitution is  $Ca^{2+} + Al^{3+} \leftrightarrow REE^{3+} + Fe^{2+}$ .

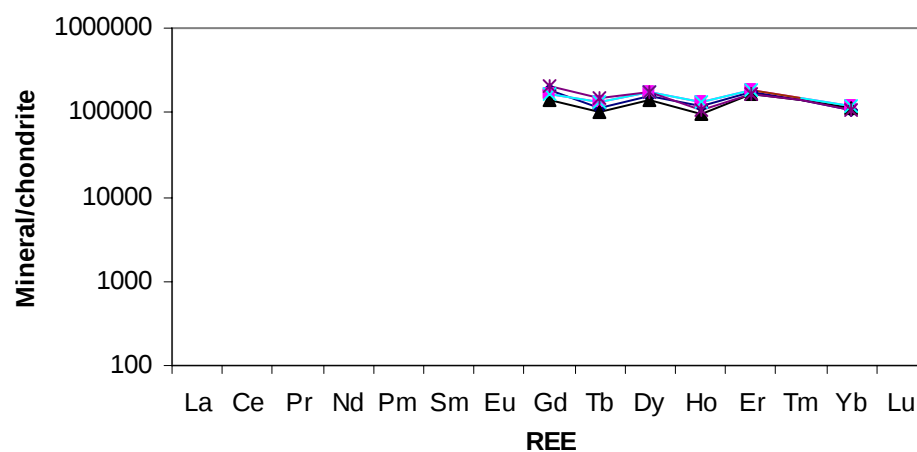


**Figure 6.4 Xenotime bearing mineralization at Esfordi.**

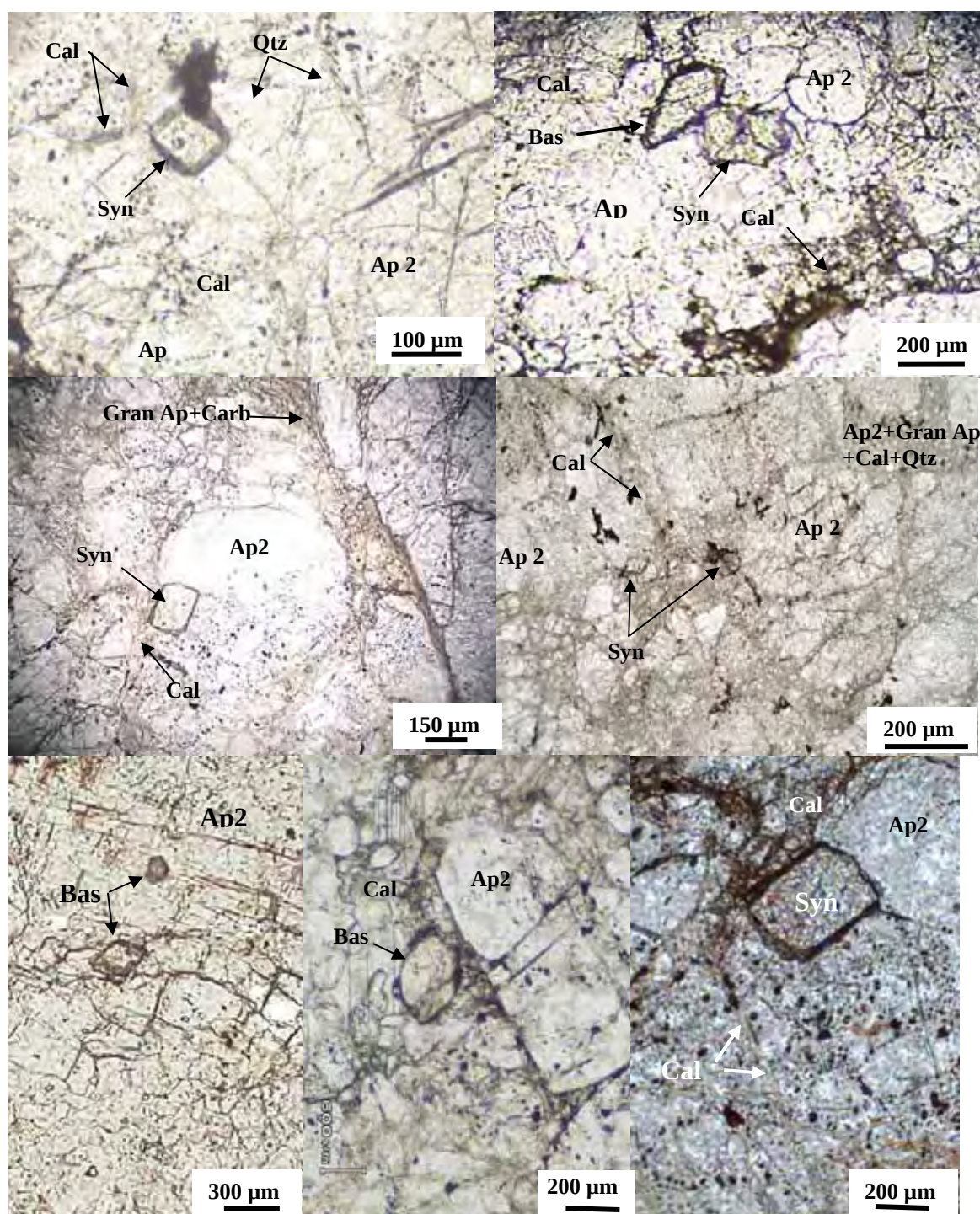
- A and B: Xenotime in apatite rich zone. Xenotime associated with monazite2 set in brecciated apatite2, granular apatite and carbonate matrix (Hole B9-53, PPL).
- C: Xenotime associated with allanite 2 in apatite rich zone (Cx, PPL).
- D: Xenotime inclusions in apatite 2 in brecciated apatite rich zone with high pervasive carbonate alteration (126, PPL).
- E: Xenotime, monazite and REE carbonates in phosphate-rich zone. Euhedral xenotime set between apatite2 grains. Corridors of granular apatite cut the apatite 2 (Cx, PPL).



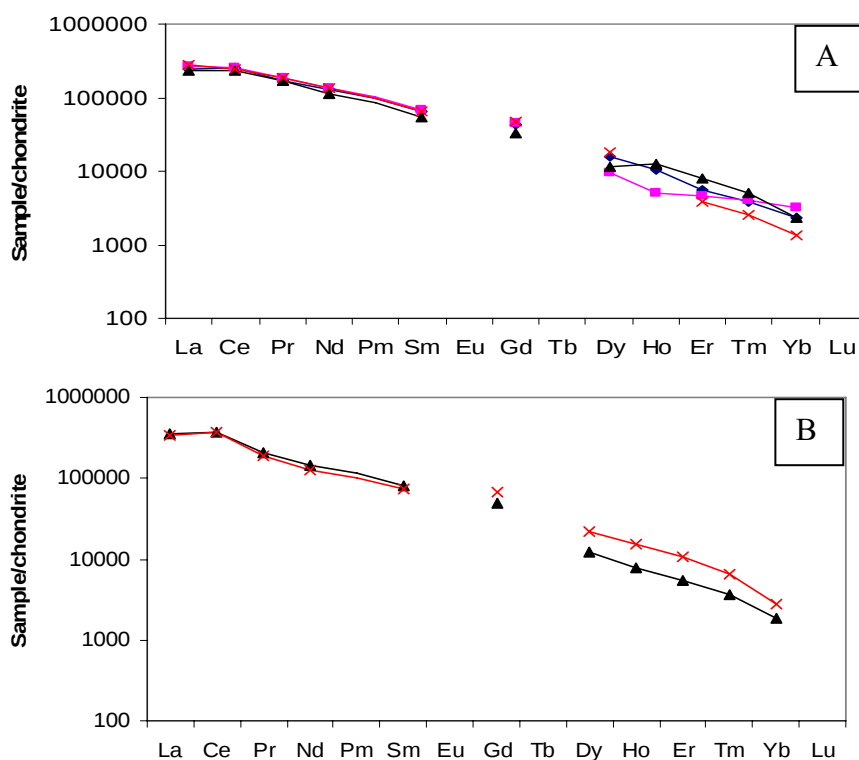
**Figure 6. 5** Backscattered images of Esfordi xenotime with patchy zoning in brecciated apatite 2.



**Figure 6. 6** Chondrite normalised REE distribution of Esfordi xenotime (Chondrite values from McDonough 1992).



**Figure 6.7** Microphotographs Synchysite and bastnaesite in Esfordi mineralizing system. Synchysite and bastnaesite occurred within or with close relation to carbonate veins and replacement in the brecciated apatite-rich ore, associated with apatite2 and granular apatite (samples R3, A11 and A6, PPL).

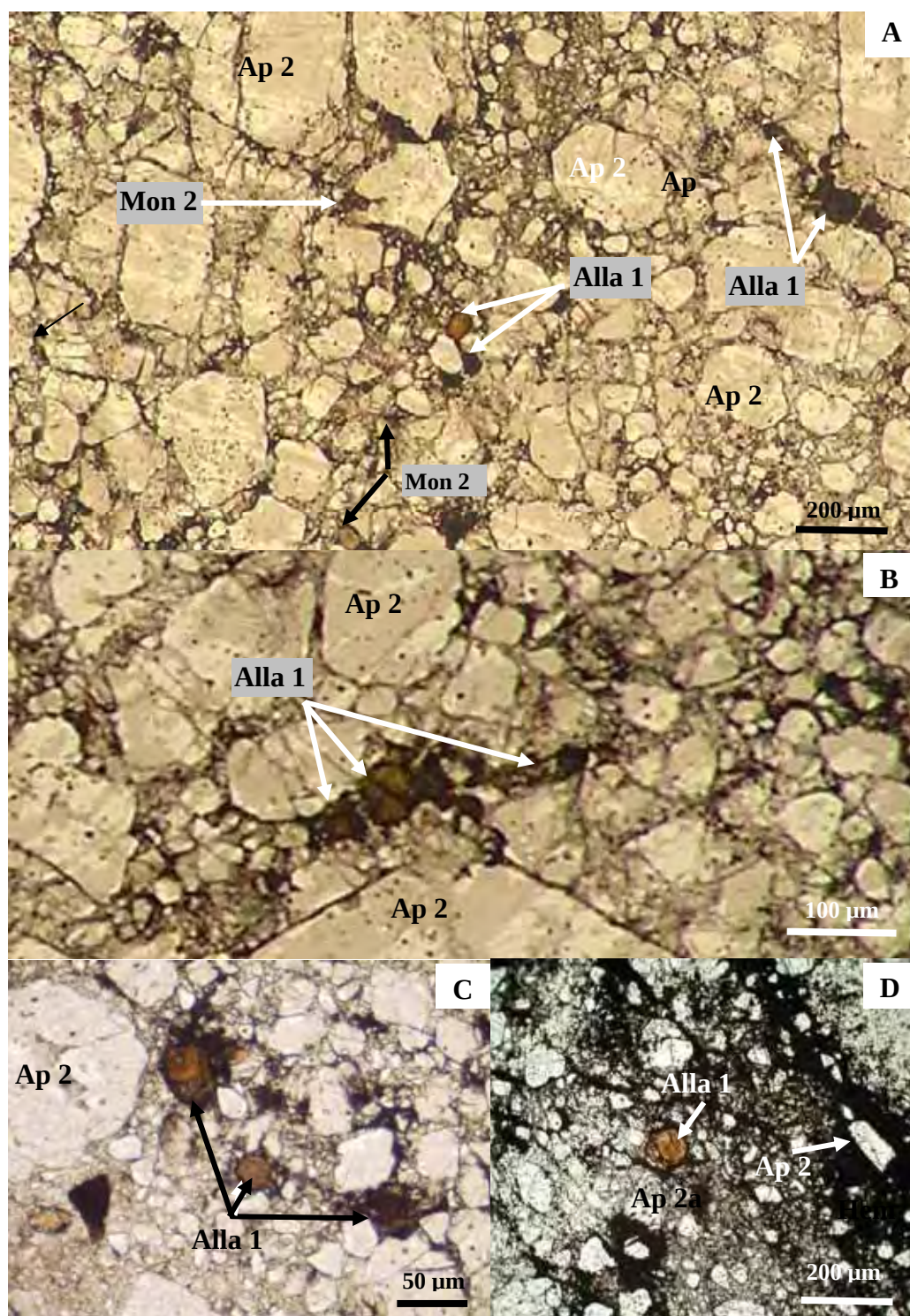


**Figure 6.8 Chondrite normalised REE distribution pattern of Esfordi synchysite (A) and bastnaesite (B).**

Thus, allanites are characterised as the only member of the epidote group in which REE and  $\text{Fe}^{2+}$  iron are essential constituents (Kartashov *et al.* 2002). Numerous analyses of allanite from various environments showed that Ce is always greater than La with the Ce:La ratio generally between 2/1 and 3/1 (Deer *et al.* 1986; Frondel 1964).

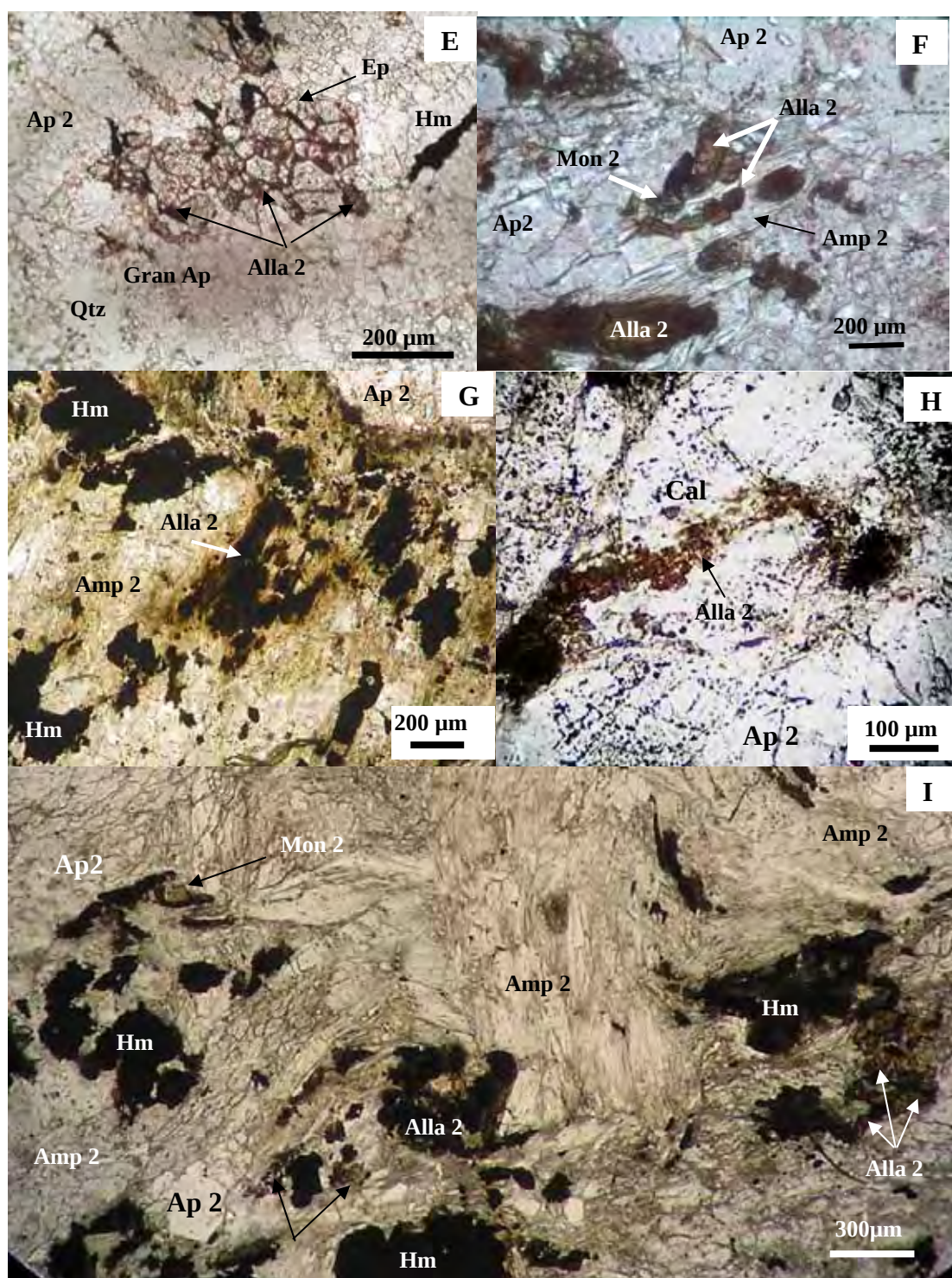
Allanite grains from a variety of mineralisation types and host rocks at Esfordi were analyzed. Some back scattered electron (BSE) images show cryptically altered areas within single grains, which were avoided during microprobe analysis.

Two varieties of allanite are known, allanite-(Ce),  $[(\text{Ce}, \text{Ca}, \text{Y})_2(\text{Al}, \text{Fe}^{2+}, \text{Fe}^{3+})_3(\text{SiO}_4)_3(\text{OH})]$ , and allanite-(Y),  $[(\text{Y}, \text{Ca}, \text{Ce})_2(\text{Al}, \text{Fe}^{2+}, \text{Fe}^{3+})_3(\text{SiO}_4)_3(\text{OH})]$ . The majority of allanites in this study are allanite-(Ce), characterised by higher La/Nd and La/Y ratios and also  $(\text{La}/\text{Sm})_{\text{cn}}$  and  $(\text{La}/\text{Y})_{\text{cn}}$  ratios than allanite 1, which suggests stronger REE differentiation in allanite 2 (Table 6.3).



**Figure 6. 9 Microphotograph of Esfordi allanite mineralisation.**

A-D: Allanite 1 associated with monazite 2 in brecciated apatite-rich ore (hole B9-1, B12-65, PPL).



**Figure 6.9. Continued.**

- E: Allantite 2 associated with epidote and hematite in highly brecciated ore (sampl 106, PPL).
- F & H: Allantite 2, monazite 2 and hematite associated with amphibole 2 as patches and veins in brecciated ore (hole B21-29, PPL),
- G & I: Allantite 2 in a carbonate vein in brecciated apatite ore (sample Cx, PPL).

Representative results of quantitative electron-microprobe analyses are presented in Table 6.3. Allanite 2 is slightly richer in REE, Fe and F than allanite 1. Allanite 2 was Fig 6.10 illustrates  $\Sigma$ REE versus Ca+Al and Si, and Si versus Ca and Fe for allanite 1 and 2. The trend suggests the coupled substitution of REE for Ca+Al in allanite 1 and 2.

The allanite 1 crystals belong to hematite-apatite veins in altered volcanic host rocks which are a distinct group with lower  $\Sigma$ REE and higher Si and Ca+Al in respect to the allanite 1 crystals within brecciated apatite matrix of apatite-rich zone. Substitution of Si and Ca+Al for REE in the vein type allanite 1 suggests higher Si, Ca and Al contents of the solutions. This could be related to influence of late pervasive quartz and carbonate alteration of older allanite 1 crystals. Thus the trends in Fig 6.10 suggest a progressive evolution from poor Si -Ca and rich in Fe and REE fluids to solutions rich in Si and Ca.

Uranium in the majority of Esfordi allanite 1 and 2 is below detection limit. Allanite 1 contains up to 1.2 wt % Th, whereas type 2 has no detectable Th. Exley (1980) found that hydrothermal allanites exhibit a REE zoning in which the core has a greater LREE content and higher Ce/Y ratio compared with the rim. Microscopic studies and BSE images of Esfordi allanites show a zonation in some grains of allanite 1 (Fig 6.11). Electron microprobe analyses show that the core is more enriched in LREE than the rim (Fig 6.12).

The REE chondrite normalised plot of Esfordi allanites (Taylor and McLennan 1985; Wakita *et al.* 1971) indicate a LREE enrichment in both types of allanite, with higher La enrichment in allanite 2 (Fig 6.13).

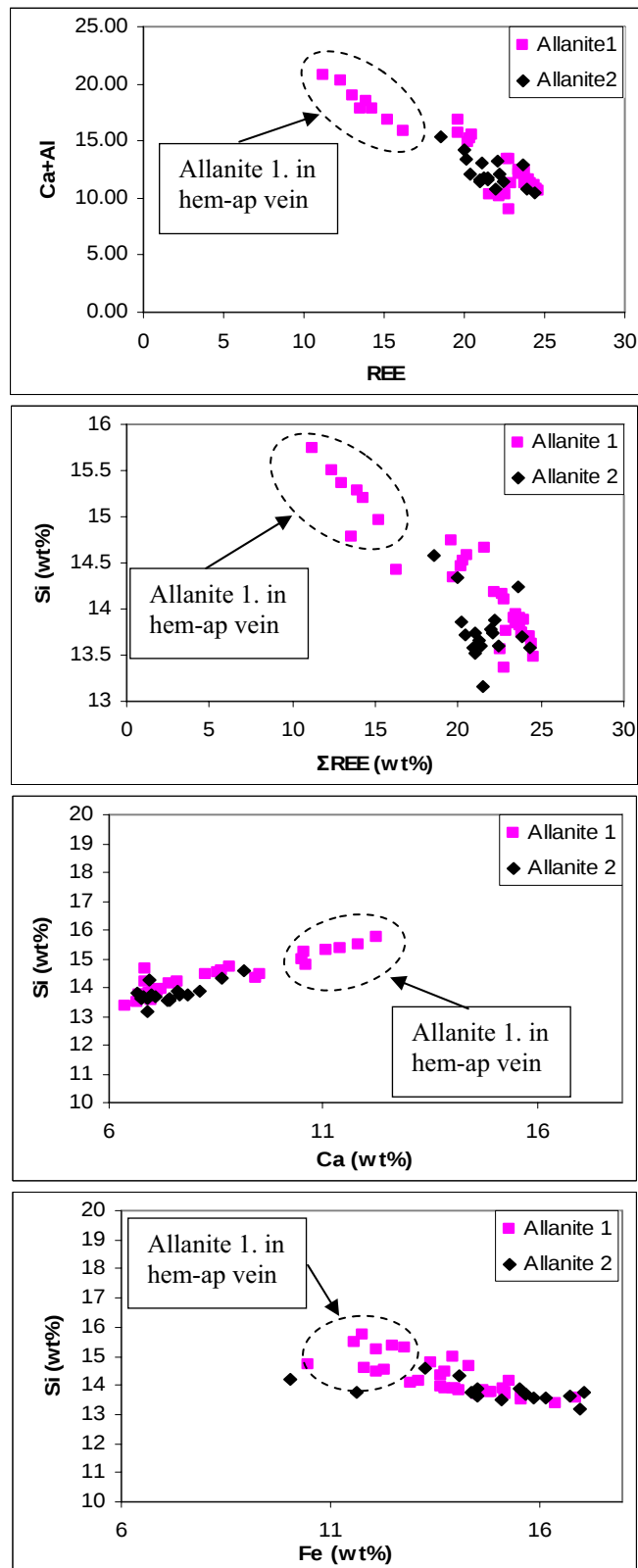
**Table 6. 3 Electron microprobe analyses of Esfordi allanites.**

| Oxide (wt %)                   | Allanite 1<br>n=35 |         | Allanite 2<br>n=17 |         |
|--------------------------------|--------------------|---------|--------------------|---------|
|                                | Average            | Std Dev | Average            | Std Dev |
| SiO <sub>2</sub>               | 30.49              | 1.36    | 29.48              | 0.71    |
| Al <sub>2</sub> O <sub>3</sub> | 10.39              | 2.97    | 9.10               | 1.64    |
| La <sub>2</sub> O <sub>3</sub> | 4.46               | 1.19    | 5.79               | 1.24    |
| Ce <sub>2</sub> O <sub>3</sub> | 14.12              | 3.41    | 14.26              | 1.54    |
| Pr <sub>2</sub> O <sub>3</sub> | 1.26               | 0.21    | 1.24               | 0.13    |
| Nd <sub>2</sub> O <sub>3</sub> | 3.87               | 0.61    | 3.70               | 0.73    |
| Sm <sub>2</sub> O <sub>3</sub> | 0.30               | 0.14    | 0.21               | 0.10    |
| Gd <sub>2</sub> O <sub>3</sub> | 0.09               | 0.08    | 0.02               | 0.04    |
| Y <sub>2</sub> O <sub>3</sub>  | 0.07               | 0.05    | 0.07               | 0.06    |
| ThO <sub>2</sub>               | 0.06               | 0.23    | 0.00               | 0.00    |
| UO <sub>2</sub>                | 0.04               | 0.03    | 0.02               | 0.03    |
| CaO                            | 11.44              | 2.46    | 10.38              | 0.96    |
| MgO                            | 0.13               | 0.12    | 0.33               | 0.43    |
| FeO <sup>Total</sup>           | 17.85              | 1.90    | 19.07              | 2.38    |
| P <sub>2</sub> O <sub>5</sub>  | 0.05               | 0.07    | 0.03               | 0.03    |
| F                              | 0.11               | 0.11    | 0.33               | 0.20    |
| H <sub>2</sub> O               | 1.60               | 0.07    | 1.59               | 0.04    |
| Total                          | 96.35              | 0.93    | 97.73              | 1.11    |
| ΣREE                           | 20.67              | 4.19    | 21.27              | 1.53    |
| La/Nd                          | 1.2                | 0.4     | 1.7                | 0.7     |
| La/Ce                          | 0.3                | 0.0     | 0.4                | 0.1     |
| La/Y                           | 1559.7             | 5487.2  | 4396.1             | 9552.7  |
| Ce/Y                           | 4762.5             | 16476.8 | 12415.7            | 27188.9 |
| (La/Sm) <sup>cn</sup>          | 9.8                | 6.2     | 14.6               | 5.3     |
| (La/Y) <sup>cn</sup>           | 1192.7             | 4196    | 3361.8             | 7305    |

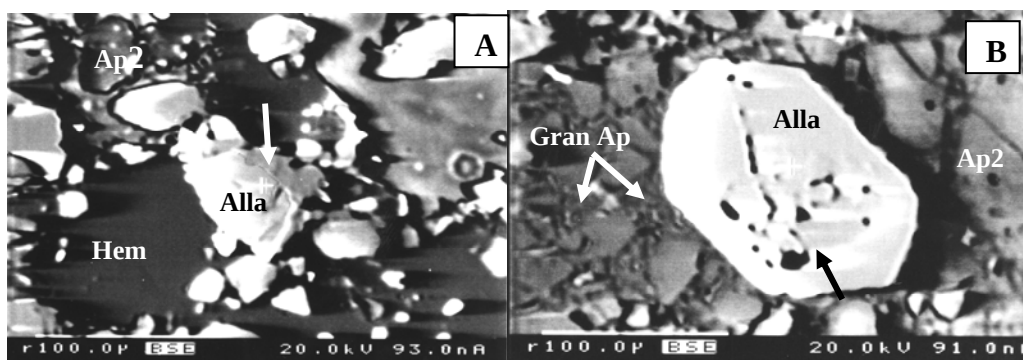
<sup>1</sup>MnO, TiO<sub>2</sub>, Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu were not determined.

<sup>2</sup>Total Fe measured as FeO.

<sup>3</sup>cn: Chondrite normalised

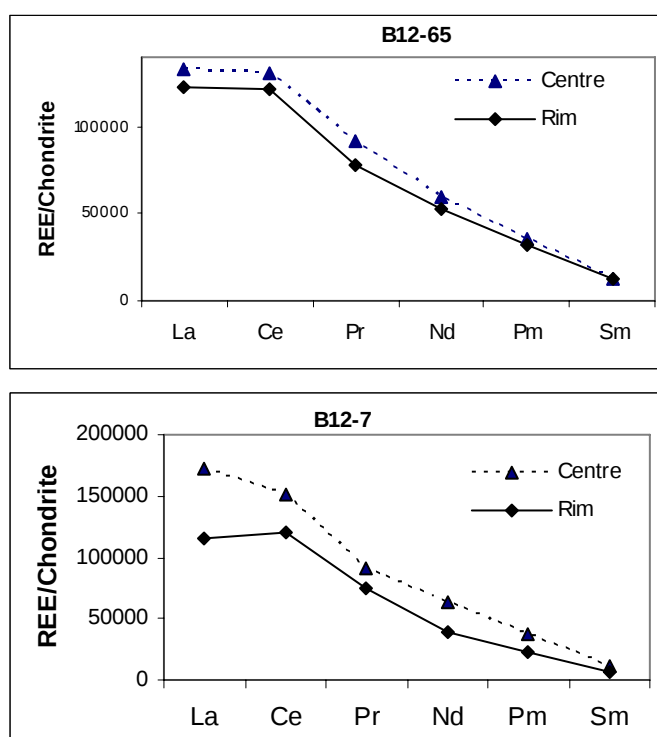


**Figure 6. 10** Plot of allanite 1 and 2 microprobe analyses and their substitution patterns.

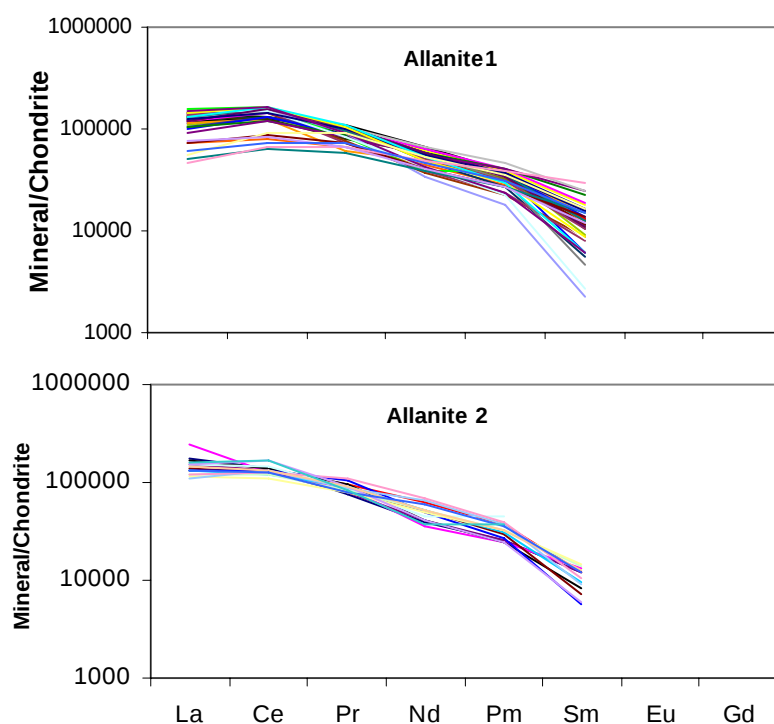


**Figure 6. 11 Backscattered image of Esfordi allanite 1 grains.**

- A: Zoned irregular shape allanite 2 in brecciated apatite-rich zone (Sample 107).
- B: Euhedral allanite with irregular zoning in brecciated apatite 2 matrix of apatite-rich zone (Hole B12-65m).



**Figure 6. 12 Chondrite normalised REE distribution of Esfordi zoned allanite 1.**  
**Both samples are from brecciated apatite-rich zone with close association to monazite 2 (Pm is calculated as the average of Nd and Sm, Chondrite normalized values from McDonough 1992).**



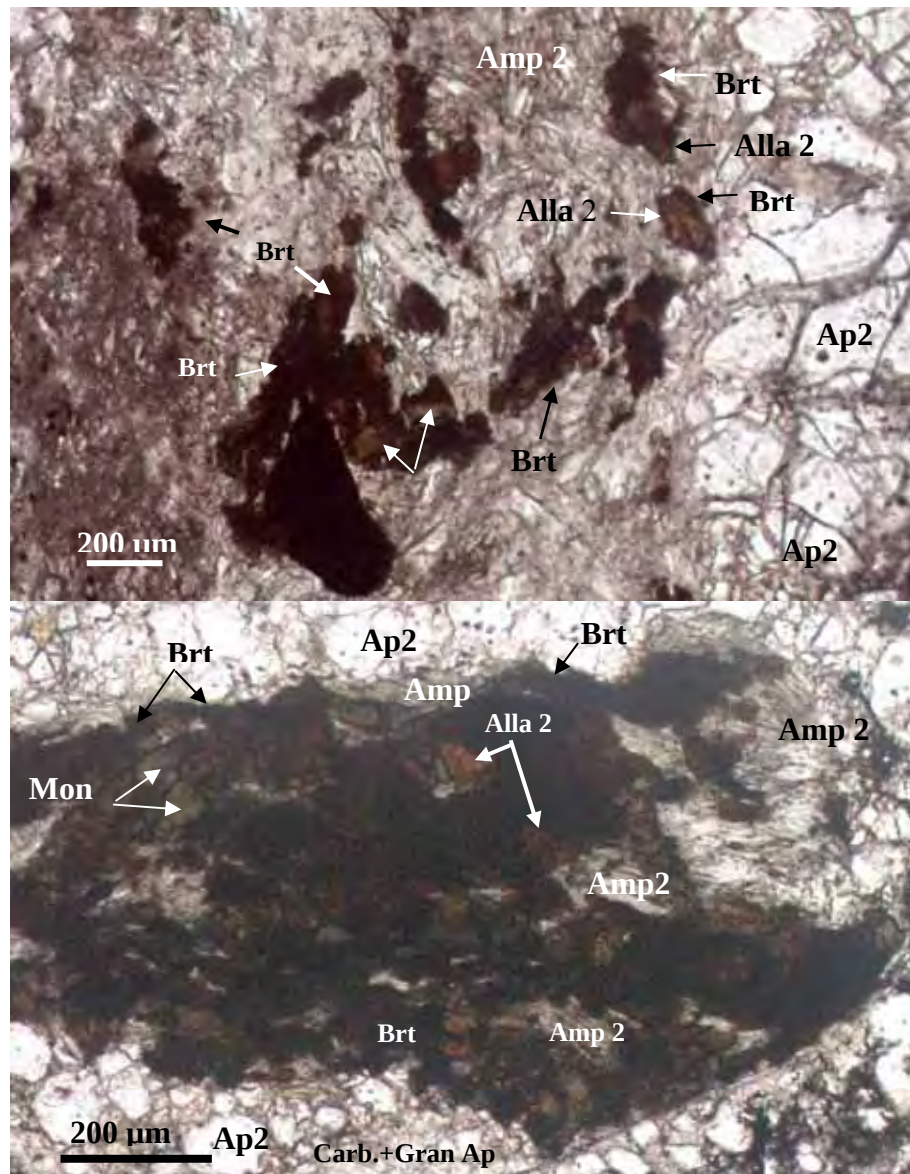
**Figure 6. 13 Chondrite normalised pattern of allanite 1 and 2 (Pm is calculated as the average of Nd and Sm; Chondrite normalized values from McDonough 1992).**

### 6.3.2 Britholite

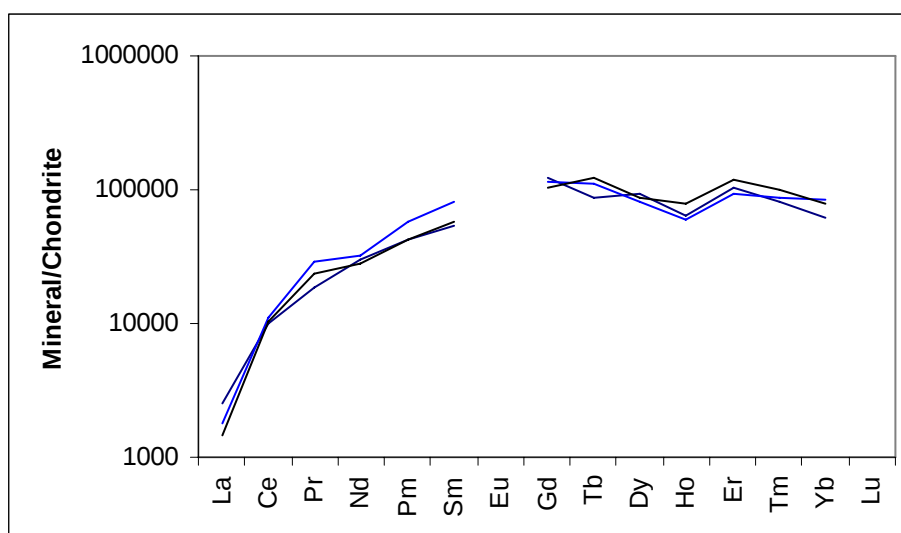
In Esfordi, britholite always occurs in brecciated apatite-rich zone associated with allanite 2 and monazite 2 as discrete grains or concentrated along the margins of allanite 2-rich patches (Fig 6.14). Britholite shows brown, greenish brown, and dark colour with distinctive pleochroism. Due to similarities between britholite and allanite, recognition of britholite by optical techniques was cross-checked by electron microprobe point analyses. The britholites are enriched in HREE and Y (Fig 6.15). The REE are dominated by Y with a flat normalised HREE pattern and low  $(La/Sm)_{cn}$  and  $(La/Y)_{cn}$  ratios.

Britholite, a rare-earth (REE) mineral isostructural with apatite (hexagonal nesosilicate mineral with the space group of  $P6_3/m\ 3/m$ ), has the general formula  $[(Ce,REE,Ca,Na)_5((Si,P)O_4)_3(OH,F)]$  with  $Si > P$ . It is one of the most abundant REE-bearing mineral phases, typically found in nepheline syenites and in contact metasomatic rocks related to alkali syenites and granites. Two natural end-members are known,

britholite-(Ce) (formerly lessingite) and britholite-(Y) (Anthony *et al.* 2000; Deer *et al.* 1986; Oberti *et al.* 2001). The Esfordi britholites are britholite-(Y)  $[(Y,Ca)_5(SiO_4; PO_4)_3(OH; F)]$ .



**Figure 6. 14** Britholite crystals associated with allanite 2 and monazite 2 in P-rich ore (Hole B9-2 m and sample CX, PPL).



**Figure 6. 15 Chondrite normalised pattern of Esfordi britholites (Chondrite normalized values from McDonough 1992).**

#### 6.4 REE CONTENT OF APATITE

Apatite is an important host for REE and Y in various geological environments (Fleet and Pan 1995, 1997; Fleet *et al.*, 2000; Pan and Fleet 2002). As described in Chapter 4, based on field observations, petrographic and geothermometric studies, three different types of apatite were identified. The first two generation of apatites have been affected (dissolved, leached and replaced) by subsequent brecciation and late stage carbonate and quartz veining.

One of the diagnostic characteristics of apatite 1 is the presence of monazite 1 within crystals as 5 to 50  $\mu\text{m}$  inclusions (Fig 6.1). A crude zonation may be observed in some apatite grains with mineral (including monazite 1) and fluid inclusions more abundant in the grain cores as compared the rims of apatite 2 (see Figs 4.12 K, L, M and 4.14 K). Apatite 1 contains  $\Sigma(\text{La,Ce,Nd})$  up to 1.74 wt % with an average of 1.43 wt % (Table 6.4).

Rare earth mineral inclusions within apatite 2 are rare, however intergranular monazite 2, xenotime, and allanite 1 are common. Apatite 2 shows an average of 1.19 wt %  $\Sigma(\text{La, Ce, Nd})$ . Apatite 2 is richer in Cl than apatite 1, averaging 0.43 wt %. Granular apatites contain  $\Sigma(\text{La, Ce, Nd})$  up to 0.51 wt % with an average of 0.22 wt %. Apatites 3

crystals are without any solid inclusions and low  $\Sigma(\text{La,Ce,Nd})$  content (averaging 0.11 wt %). Apatites associated with the dolerite dykes contain an average of 0.55 wt %,  $\Sigma(\text{La,Ce,Nd})$ . This type of apatite shows an average of 2.25 and 0.36 wt % F and Cl respectively. The composition of these apatites is presented in Table 6.4.

Apatite has the general formula  $A_5(\text{XO}_4)_3\text{Z}$ . The A site accepts cations such as  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{REE}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ , and comprise two sites that exhibit VII-fold and IX-fold coordination. The X site is generally the  $\text{P}^{5+}$  position with IV-fold coordination. Sometimes low amount of  $\text{Si}^{4+}$ ,  $\text{S}^{6+}$ ,  $\text{As}^{5+}$ , and  $\text{V}^{5+}$  occupy the X-site. The Z-site is always occupied by  $\text{F}^-$ ,  $\text{Cl}^-$  or  $\text{OH}^-$ .

The REE abundances in minerals are largely controlled by substituting for Ca positions (McKay 1989). The selectivity of Ca-bearing minerals for REE is largely depends on the size of the Ca positions in mineral structure relative to the REE. The  $\text{REE}^{3+}$  and  $\text{Y}^{3+}$  ions substitute for  $\text{Ca}^{2+}$  with electrostatic balance provided by substitution of  $\text{Si}^{4+}$  for  $\text{P}^{5+}$  or  $\text{Na}^+$  for additional  $\text{Ca}^{2+}$  (Rakovan and Hughes 2000; Roeder *et al.* 1987; Ronsbo 1989; Pan and Fleet 2002);



Esfordi apatites are generally dominant in the LREE similar to that of many Kiruna-type magnetite apatite systems. Generally, Esfordi apatites are F-rich and relatively low in Cl (< 0.91 wt %) and OH content. The LREE content of apatites is strongly correlated with corresponding content of both Na and Si (Fig 6.16, Table. 6.4).

The patterns of coupled REE substitution in textural categories of Esfordi apatites can be seen in the scattered plots in Fig 6.17. Fig 6.16a shows a significant group of apatite 1 and 2 with monazite 1 inclusions. The apatite 1 and 2 crystals without monazite 1 inclusions tend to be more enriched in LREE than those with inclusions. The granular, fine grained apatite crystals associated with apatite 1 are texturally divisible to less granular

and highly granular types. The degree of granularity shows a direct relation to Ce+La+Nd depletion. This suggests that the monazite 1 inclusions and part of the monazite 2 grains, formed from REE derived from the apatite 1 and 2.

Six almost pure apatite samples, without solid inclusions from brecciated apatite-rich ore, contained 0.2–0.45 wt % SO<sub>3</sub>.

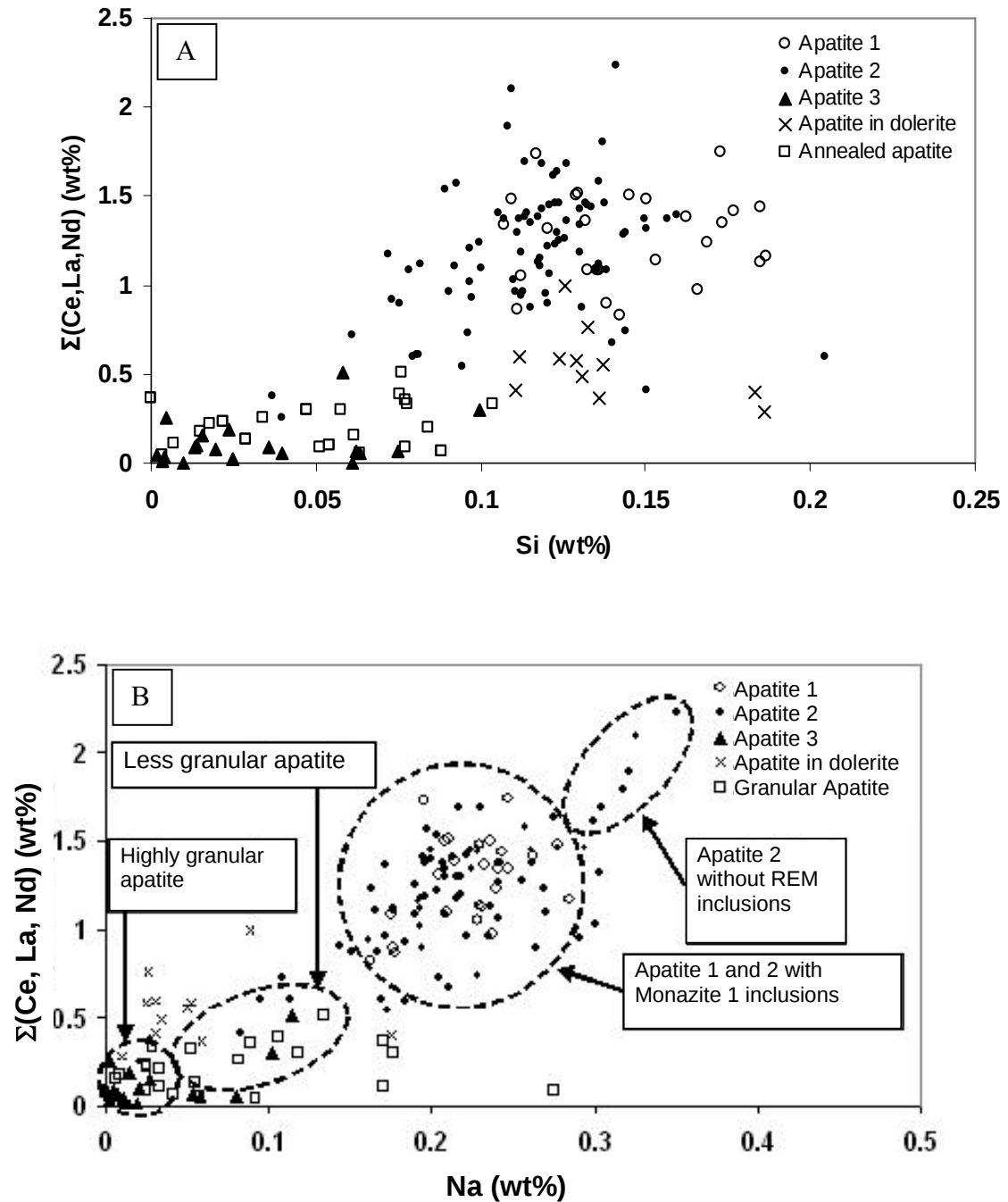
Several analytical traverses have been performed on apatite 2 grains. Figs 6.19 and 6.20 show the concentration of Cl, F, Y, La, Ce, and Nd. The core to the apatite grains is slightly enriched in La, Ce, and Nd (Fig 6.18). In samples 102-2 and B20-34 the crystals show at least two generations of apatite exits - the core, which may represent apatite 1 or 2 with high REE contents, and the rim with relatively low REE contents.

The zonation with consistent depletion in REE toward the rims of the apatite grains parallels the paragenetic trend from stage 1 and 2 to later granular and stage 3 apatites.

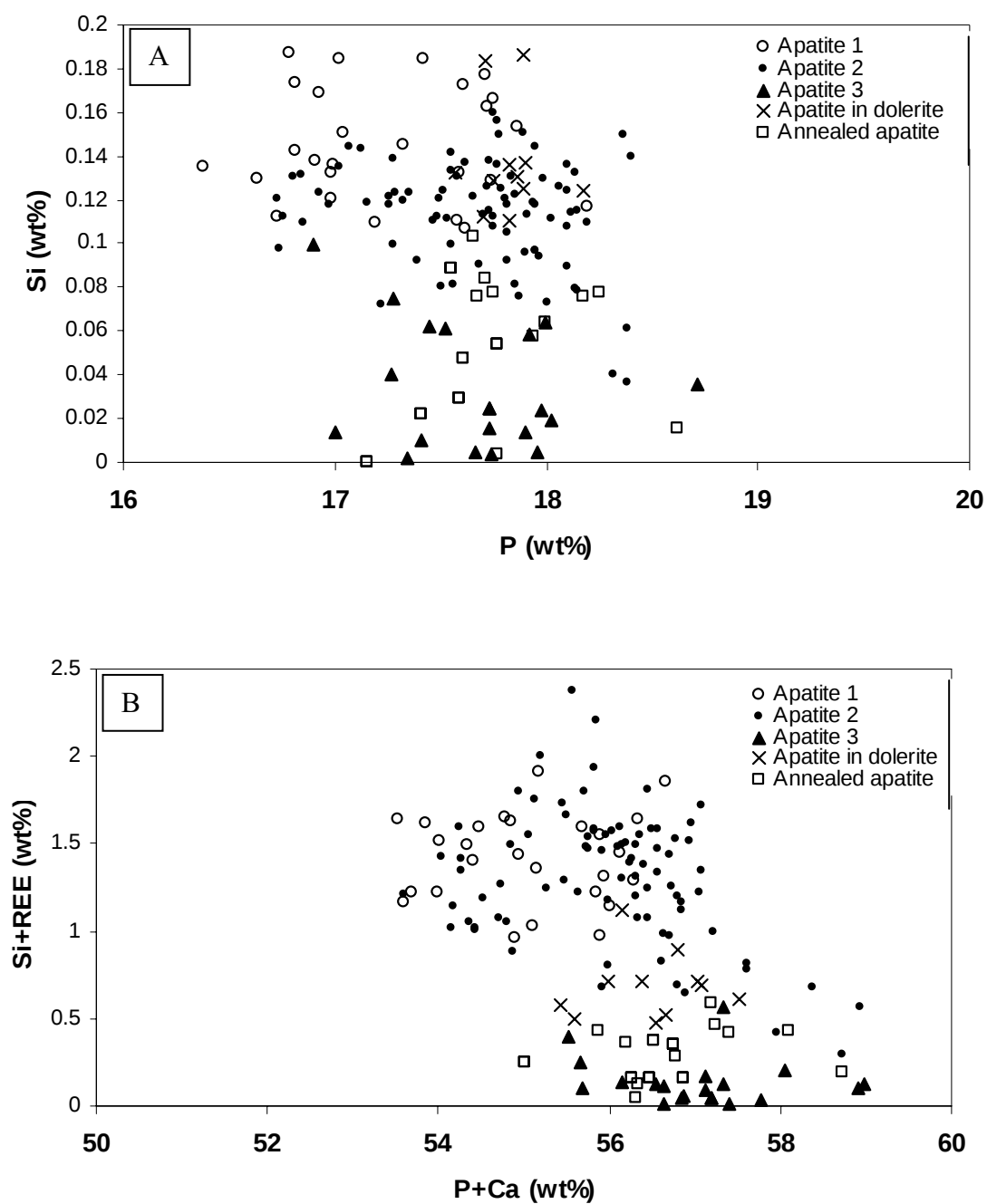
## **6.5 WHOLE ROCK RARE EARTH ELEMENT DISTRIBUTIONS**

The REE contents of selected rocks were determined to allow comparison between least altered and various hydrothermally altered rocks. This allows assessing the REE patterns of the different facies of the Esfordi Fe–P mineralizing system, rather than providing rigorous constraints to the petrogenesis of the various igneous rock groups.

Some 39 samples, representing a range of rocks from Esfordi regime together with adjacent intrusives, have been analysed for REE by ICP-MS. The results are presented as summary statistics for major lithological groups in Table 6.5. A complete set of analytical results is given in Appendix 2. Individual samples from the lithological groups are presented as a series of chondritic ratios in Figs 6.21 to 6.23.



**Figure 6. 16 Si, Na, ΣREE compositions of Esfordi apatites. A: Scatter plot of REE content versus Si in different types of Esfordi apatites, B: Well differentiated scattered plot of Esfordi apatites.**

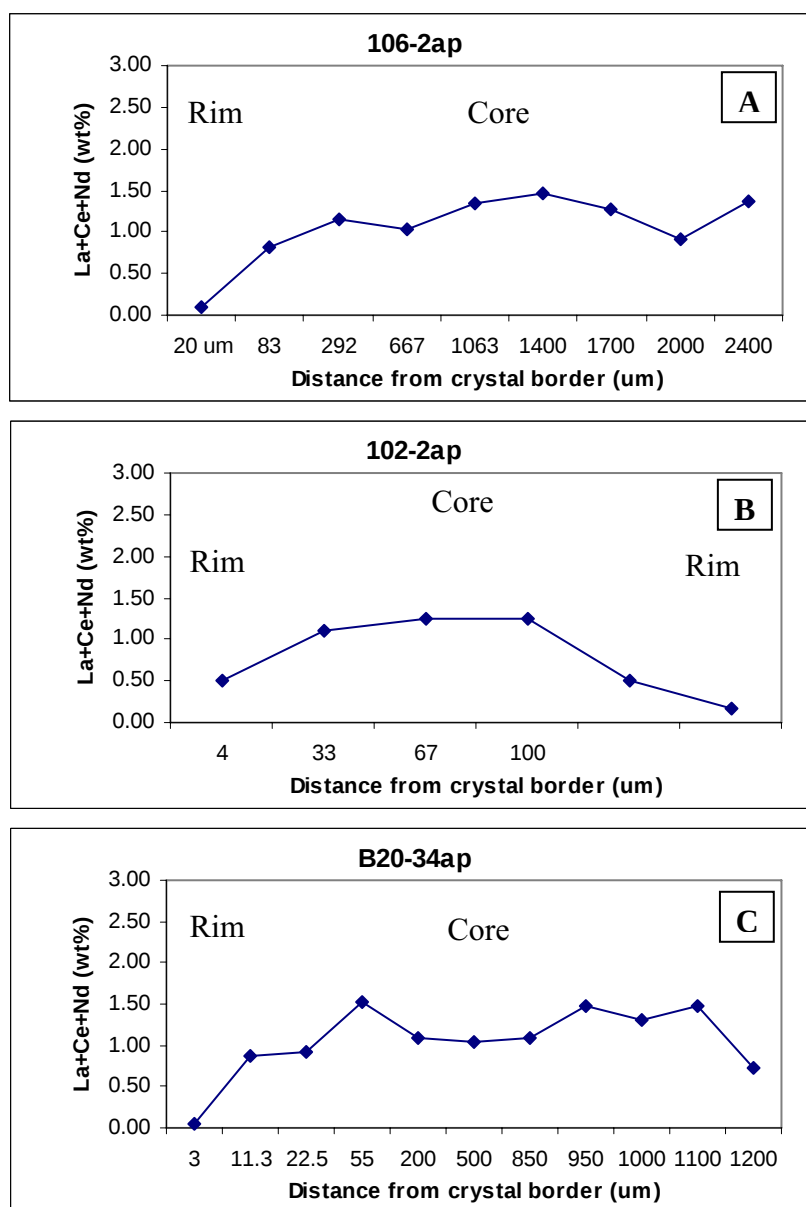


**Figure 6. 17 Plot of Si versus P (A), and REE+Si versus P+Ca coupled substitution of Esfordi apatites (B).**

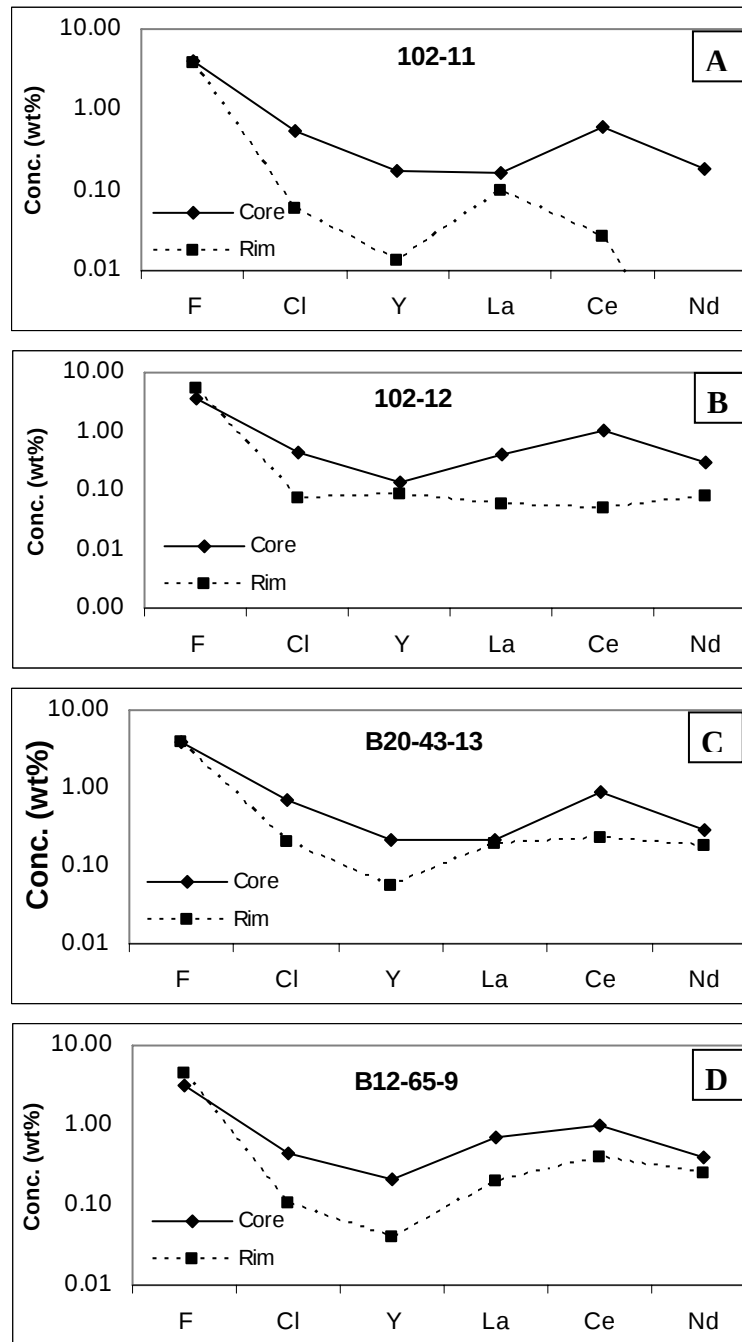
**Table 6. 4 Chemical characteristics of the different Esfordi apatites.**

| Oxide<br>(wt %)                   | Apatite 1<br>N=26 |              | Apatite 2<br>N=83 |                | Apatites 3<br>N=20 |            | Apatite in Dolerite<br>N=11 |                 | Granular apatite<br>N=29 |            |
|-----------------------------------|-------------------|--------------|-------------------|----------------|--------------------|------------|-----------------------------|-----------------|--------------------------|------------|
|                                   | Average           | Std Dev      | Average           | Std Dev        | Average            | Std Dev    | Average                     | Std Dev         | Average                  | Std Dev    |
| SiO <sub>2</sub>                  | 0.32              | 0.07         | 0.24              | 0.06           | 0.07               | 0.06       | 0.29                        | 0.05            | 0.10                     | 0.06       |
| La <sub>2</sub> O <sub>3</sub>    | 0.38              | 0.11         | 0.30              | 0.17           | 0.03               | 0.05       | 0.17                        | 0.13            | 0.06                     | 0.06       |
| Ce <sub>2</sub> O <sub>3</sub>    | 0.90              | 0.12         | 0.78              | 0.26           | 0.06               | 0.11       | 0.30                        | 0.15            | 0.11                     | 0.12       |
| Nd <sub>2</sub> O <sub>3</sub>    | 0.39              | 0.09         | 0.31              | 0.17           | 0.04               | 0.05       | 0.18                        | 0.10            | 0.08                     | 0.06       |
| Y <sub>2</sub> O <sub>3</sub>     | 0.09              | 0.12         | 0.20              | 0.11           | 0.02               | 0.05       | 0.08                        | 0.06            | 0.02                     | 0.06       |
| CaO                               | 52.53             | 0.69         | 53.67             | 0.91           | 54.66              | 0.74       | 54.32                       | 0.58            | 54.94                    | 1.35       |
| SrO                               | BLD               | --           | 0.04              | 0.04           | 0.03               | 0.07       | 0.18                        | 0.08            | 0.07                     | 0.06       |
| FeO                               | 0.10              | 0.04         | 0.11              | 0.07           | 0.25               | 0.41       | 0.53                        | 0.21            | 0.06                     | 0.08       |
| Na <sub>2</sub> O                 | 0.30              | 0.03         | 0.28              | 0.08           | 0.04               | 0.05       | 0.07                        | 0.06            | 0.11                     | 0.09       |
| P <sub>2</sub> O <sub>5</sub>     | 38.32             | 0.28         | 40.50             | 0.94           | 40.25              | 0.77       | 40.85                       | 0.35            | 37.59                    | 5.95       |
| Cl                                | 0.69              | 0.08         | 0.39              | 0.15           | 0.11               | 0.07       | 0.36                        | 0.11            | 0.06                     | 0.03       |
| F                                 | 4.00              | 0.49         | 3.95              | 0.81           | 4.94               | 1.18       | 2.25                        | 0.29            | 5.79                     | 1.07       |
| Total                             | 98.06             | 0.12         | 100.77            | 11.05          | 100.50             | 1.29       | 99.59                       | 0.62            | 100.33                   | 3.61       |
| ΣLa,Ce,Nd<br>(La/Y) <sub>cn</sub> | 1.43<br>9.87      | 0.12<br>4.73 | 1.19<br>121.79    | 0.37<br>936.56 | 0.11<br>--         | 0.12<br>-- | 0.55<br>1072.61             | 0.20<br>2635.17 | 0.22<br>--               | 0.13<br>-- |

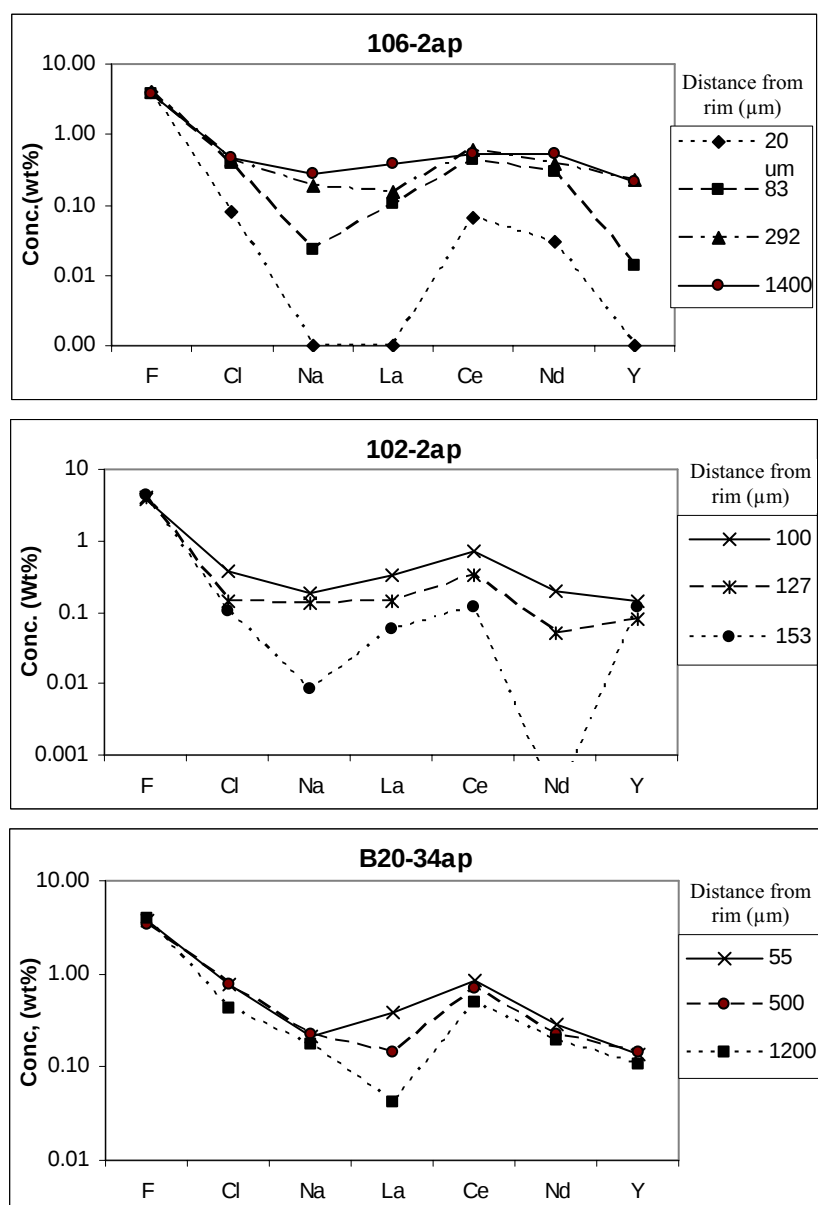
BLD: Below level of detection ; cn: Chondrite normalised



**Figure 6. 18 Chemically zoned apatite 1, A: detrital apatite 2 as core and apatite 3 as rim in overlying detrital magnetite–apatite sublayers; B and C: apatite 1 without optical zoning in apatite-rich patches of magnetite-rich core of the Esfordi system.**



**Figure 6. 19 Chemical profiles from apatite 1 and 2 grains: A and B: Apatite 1 with monazite inclusions associated with granular apatite from the magnetite-rich core; C and D: Clear large crystals of apatite 2 in a brecciated matrix brecciated apatite-rich zone of the system.**



**Figure 6. 20** Chemical profiles from apatite 1 and 2 grains: **A:** detrital grain of apatite 2 from detrital magnetite–apatite sublayers, **B:** apatite 1 from magnetite-rich core of the system.

**Table 6.5 ICP-MS analyses of REEs of the Esfordi host rocks and adjacent intrusives.**

|                                | Narigan<br>Granite<br>N=3 | Dolerite<br>N=4 | Least alt.<br>volcanics<br>N=4 | Least altered<br>volcaniclastics<br>N=2 | K-feld.<br>rich alt.<br>N=3 | Amph.<br>rich alt.<br>N=5 |
|--------------------------------|---------------------------|-----------------|--------------------------------|-----------------------------------------|-----------------------------|---------------------------|
| La <sub>2</sub> O <sub>3</sub> | 377.54                    | 98.46           | 50.48                          | 43.91                                   | 303.33                      | 57.90                     |
| Ce <sub>2</sub> O <sub>3</sub> | 38.62                     | 159.68          | 71.57                          | 180.72                                  | 66.32                       | 195.48                    |
| Pr <sub>2</sub> O <sub>3</sub> | 3.98                      | 16.47           | 7.05                           | 19.37                                   | 6.42                        | 23.37                     |
| Nd <sub>2</sub> O <sub>3</sub> | 15.77                     | 63.52           | 23.41                          | 68.49                                   | 23.27                       | 101.23                    |
| Sm <sub>2</sub> O <sub>3</sub> | 3.24                      | 11.37           | 4.30                           | 11.58                                   | 3.95                        | 23.42                     |
| Eu <sub>2</sub> O <sub>3</sub> | 0.77                      | 3.65            | 1.24                           | 2.48                                    | 0.80                        | 2.97                      |
| Gd <sub>2</sub> O <sub>3</sub> | 3.46                      | 10.97           | 3.80                           | 11.39                                   | 3.64                        | 25.18                     |
| Tb <sub>2</sub> O <sub>3</sub> | 0.64                      | 1.66            | 0.55                           | 1.75                                    | 0.57                        | 3.67                      |
| Dy <sub>2</sub> O <sub>3</sub> | 3.80                      | 8.10            | 3.11                           | 8.88                                    | 2.97                        | 23.70                     |
| Ho <sub>2</sub> O <sub>3</sub> | 0.85                      | 1.58            | 0.62                           | 1.90                                    | 0.66                        | 4.45                      |
| Er <sub>2</sub> O <sub>3</sub> | 2.43                      | 3.90            | 2.08                           | 4.93                                    | 2.09                        | 13.98                     |
| Tm <sub>2</sub> O <sub>3</sub> | 0.39                      | 0.52            | 0.33                           | 0.73                                    | 0.36                        | 1.95                      |
| Yb <sub>2</sub> O <sub>3</sub> | 2.55                      | 3.02            | 9.25                           | 4.48                                    | 2.62                        | 13.54                     |
| Lu <sub>2</sub> O <sub>3</sub> | 0.41                      | 0.46            | 0.39                           | 0.72                                    | 0.51                        | 1.77                      |
| Y <sub>2</sub> O <sub>3</sub>  | 23.26                     | 39.18           | 18.84                          | 53.44                                   | 17.32                       | 137.11                    |
| Σ LREE                         | 374.62                    | 98.46           | 50.48                          | 43.91                                   | 344.11                      | 343.22                    |
| ΣHREE+Y                        | 31.00                     | 57.16           | 32.43                          | 72.39                                   | 25.33                       | 184.92                    |
| ΣREE+Y                         | 406.28                    | 358.94          | 167.44                         | 351.53                                  | 370.13                      | 530.71                    |
| (La/Lu) <sub>cn</sub>          | 141.69                    | 18.58           | 16.14                          | 5.81                                    | 49.79                       | 3.58                      |
| (La/Sm) <sub>cn</sub>          | 114.68                    | 4.41            | 11.98                          | 2.14                                    | 36.68                       | 1.36                      |
| (La/Yb) <sub>cn</sub>          | 194.00                    | 18.86           | 16.08                          | 6.11                                    | 65.23                       | 3.07                      |
| (Gd/Yb) <sub>cn</sub>          | 1.16                      | 2.96            | 1.21                           | 2.27                                    | 1.14                        | 1.78                      |
| (Ce/Ce*)                       | 0.08                      | 0.55            | 0.53                           | 0.97                                    | 0.12                        | 0.84                      |
| (Eu/Eu*)                       | 0.64                      | 0.99            | 0.89                           | 0.66                                    | 0.63                        | 0.42                      |
| (LREE/HREE) <sub>cn</sub>      | 58.00                     | 10.47           | 11.02                          | 9.16                                    | 26.86                       | 4.65                      |

cn: Chondrite normalized; (Chondrite normalized values from McDonough 1992).

The Narigan Granite shows a wide range of REE content with La relative enrichment. The Esfordi syenite shows higher REE content with Ce enrichment and significantly higher Sm and Eu than the Narigan Granite, but both bodies show similar (La/Lu)<sub>cn</sub> ratios, which suggests similar LREE fractionation (Table 6.5). The high bulk REE+Y contents of the Narigan Granite (average = 274.0 ppm) is strongly enriched in La with very weak Ce anomaly (average(Ce/Ce\*)=0.06) and negative Eu anomaly (average(Eu/Eu\*)=0.63). The least altered Esfordi rhyolites show similar bulk REE+Y content to the Narigan Granite.

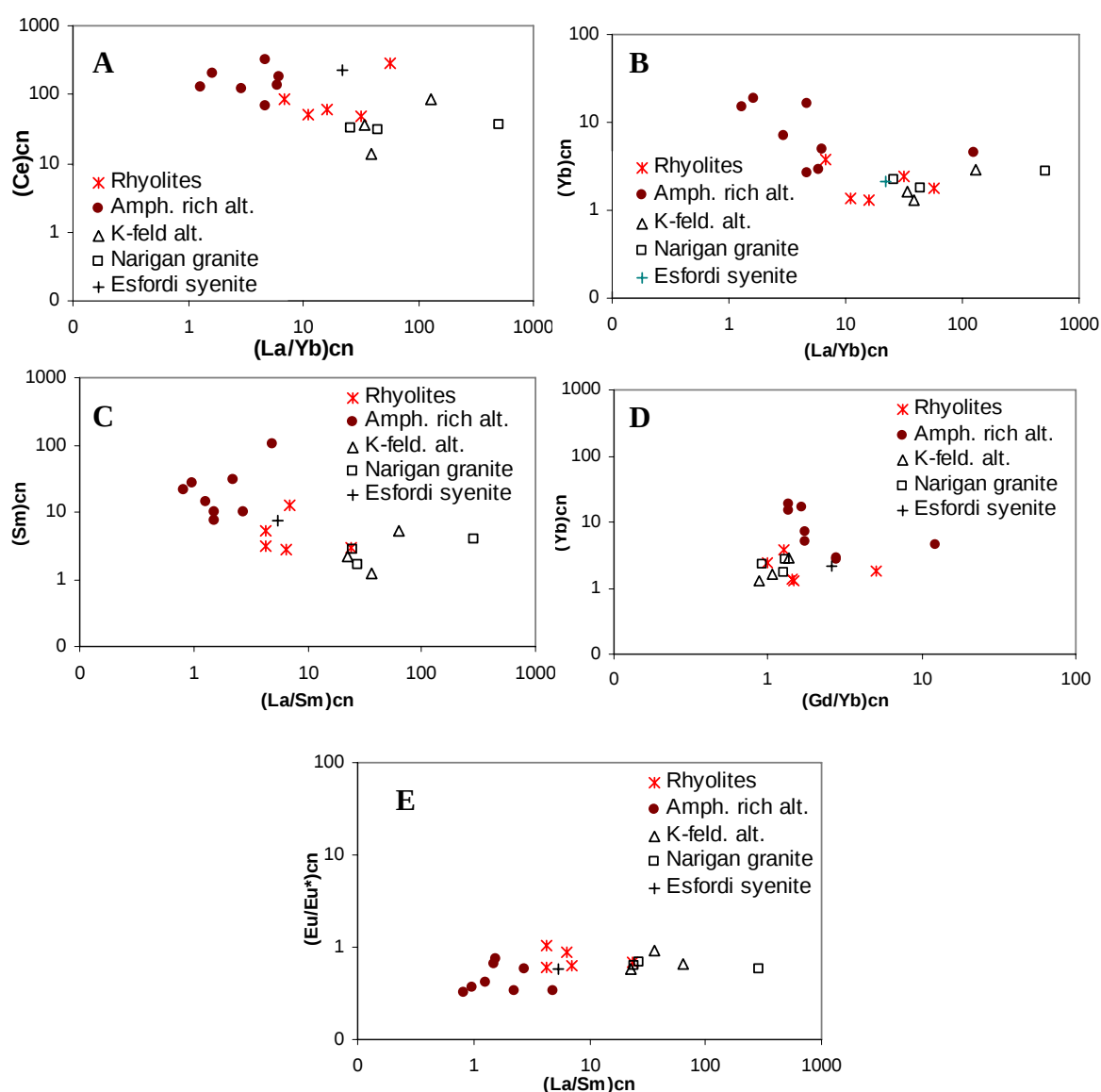
**Table 6.6 ICP-MS analyses of REE content of magnetite-rich core, apatite-rich zone and jaspilite layer of the Esfordi mineralizing system (P analysed by XRF).**

| Average (ppm)                        | Magnetite rich Core<br>N=3 | Mag. Core Margin<br>N=3 | Ap. rich zone<br>N=8 | Ap2 crystals<br>N=2 | Jaspilite layer<br>N=1 |
|--------------------------------------|----------------------------|-------------------------|----------------------|---------------------|------------------------|
| P <sub>2</sub> O <sub>5</sub> (wt %) | 10.04                      | 17.37                   | 26.73                | NA                  | 0.08                   |
| La <sub>2</sub> O <sub>3</sub>       | 315.42                     | 1669.53                 | 2967.63              | 3049.23             | 26.55                  |
| Ce <sub>2</sub> O <sub>3</sub>       | 1119.31                    | 4034.58                 | 6631.34              | 7162.47             | 39.22                  |
| Pr <sub>2</sub> O <sub>3</sub>       | 134.66                     | 425.08                  | 732.43               | 876.00              | 1.65                   |
| Nd <sub>2</sub> O <sub>3</sub>       | 461.02                     | 1552.05                 | 2608.38              | 3030.99             | 4.14                   |
| Sm <sub>2</sub> O <sub>3</sub>       | 94.29                      | 278.28                  | 400.45               | 524.35              | 0.59                   |
| Eu <sub>2</sub> O <sub>3</sub>       | 10.44                      | 31.00                   | 36.93                | 47.91               | 0.51                   |
| Gd <sub>2</sub> O <sub>3</sub>       | 106.26                     | 299.61                  | 402.24               | 545.58              | 0.51                   |
| Tb <sub>2</sub> O <sub>3</sub>       | 16.48                      | 48.50                   | 50.41                | 68.40               | 0.08                   |
| Dy <sub>2</sub> O <sub>3</sub>       | 84.49                      | 223.40                  | 252.19               | 367.12              | 0.46                   |
| Ho <sub>2</sub> O <sub>3</sub>       | 18.61                      | 50.37                   | 48.26                | 70.62               | 0.08                   |
| Er <sub>2</sub> O <sub>3</sub>       | 45.91                      | 124.80                  | 130.46               | 191.36              | 0.26                   |
| Tm <sub>2</sub> O <sub>3</sub>       | 6.06                       | 17.00                   | 15.86                | 23.38               | 0.03                   |
| Yb <sub>2</sub> O <sub>3</sub>       | 31.67                      | 93.37                   | 84.72                | 123.49              | 0.21                   |
| Lu <sub>2</sub> O <sub>3</sub>       | 4.31                       | 12.17                   | 10.58                | 15.46               | 0.02                   |
| Y <sub>2</sub> O <sub>3</sub>        | 466.35                     | 1391.99                 | 1462.39              | 1987.36             | 1.72                   |
| Σ LREE                               | 1816.23                    | 6802.03                 | 11399.56             | 12514.45            | 61.59                  |
| ΣHREE+Y                              | 640.65                     | 1853.52                 | 2017.88              | 2789.09             | 2.79                   |
| ΣREE+Y                               | 2465.89                    | 8682.33                 | 13449.35             | 15344.92            | 64.82                  |
| (La/Lu) <sub>cn</sub>                | 8.157                      | 14.25                   | 28.50                | 19.10               | 116.60                 |
| (La/Sm) <sub>cn</sub>                | 1.78                       | 3.35                    | 4.26                 | 3.29                | 25.52                  |
| (La/Yb) <sub>cn</sub>                | 7.28                       | 11.41                   | 23.05                | 15.49               | 78.18                  |
| (Gd/Yb) <sub>cn</sub>                | 3.20                       | 2.70                    | 4.02                 | 3.69                | 2.00                   |
| (Ce/Ce*)                             | 0.89                       | 0.67                    | 0.62                 | 0.63                | 0.51                   |
| (Eu/Eu*)                             | 0.32                       | 0.32                    | 0.28                 | 0.27                | 2.79                   |

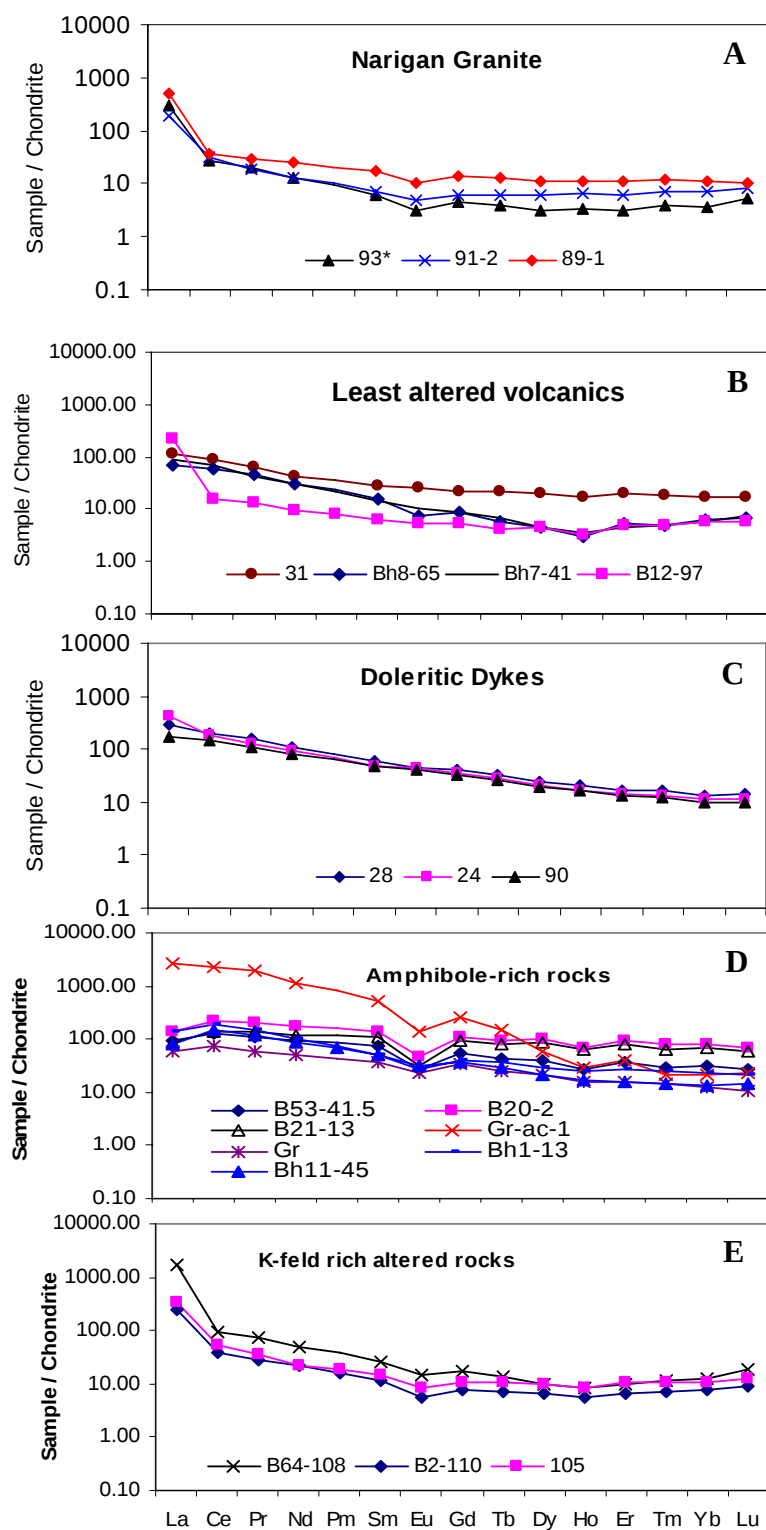
cn: Chondrite normalised; NA: Not Analysed

Various degrees of REE fractionation and Eu anomaly occur in the granites and rhyolites, including the least altered and highly altered samples (Fig 6.21). The plots show higher REE and specially LREE fractionation in granites and rhyolites than highly altered amphibole-rich rocks (Fig 6.21 a–c). The amphibole-rich altered samples generally exhibit a flat pattern with strong negative Eu anomaly (Fig 6.22 d). The sample Gr-ac-1 is an amphibole-rich altered rock without textural preservation. The occurrence of small veinlets of hematite and apatite produced significant LREE enrichment whereas the samples Bh1-13 and Bh11-45 are the least altered volcanoclastic rocks with considerable mafic lithic components.

The dolerites display low LREE enrichment (Fig 6.22 and Table 6.15), placing them in the range of typical alkali basalts (3.6–34) (Henderson, 1984). The slight variations in La contents of the doleritic bodies (Fig 6.22c) are probably controlled by different degrees of alteration overprints in these rocks. Similar patterns of La enrichment in the Narigan Granite, K-feldspar rich alteration zones and least altered rhyolite (sample B12-97) is consistent with widespread circulation of low temperature solutions that have produced weak sericite alteration (similar to that reported by Iida *et al.*, 1998).



**Figure 6. 21 REE ratio plots of least altered and altered Esfordi host rocks and adjacent intrusives.**



**Figure 6. 22 Chondrite normalised pattern of Narigan Granite and a range of rock from the Esfordi system (Chondrite normalized values from McDonough 1992).**

As described in Chapter 4, based on borehole data and macroscopic and microscopic evidence, the Esfordi mineralizing system consists of a magnetite–apatite core surrounded by brecciated hematite-apatite and apatite-rich bodies, associated with a range of mineral assemblage and, finally, an overlying stratiform hematite-jaspillite horizon.

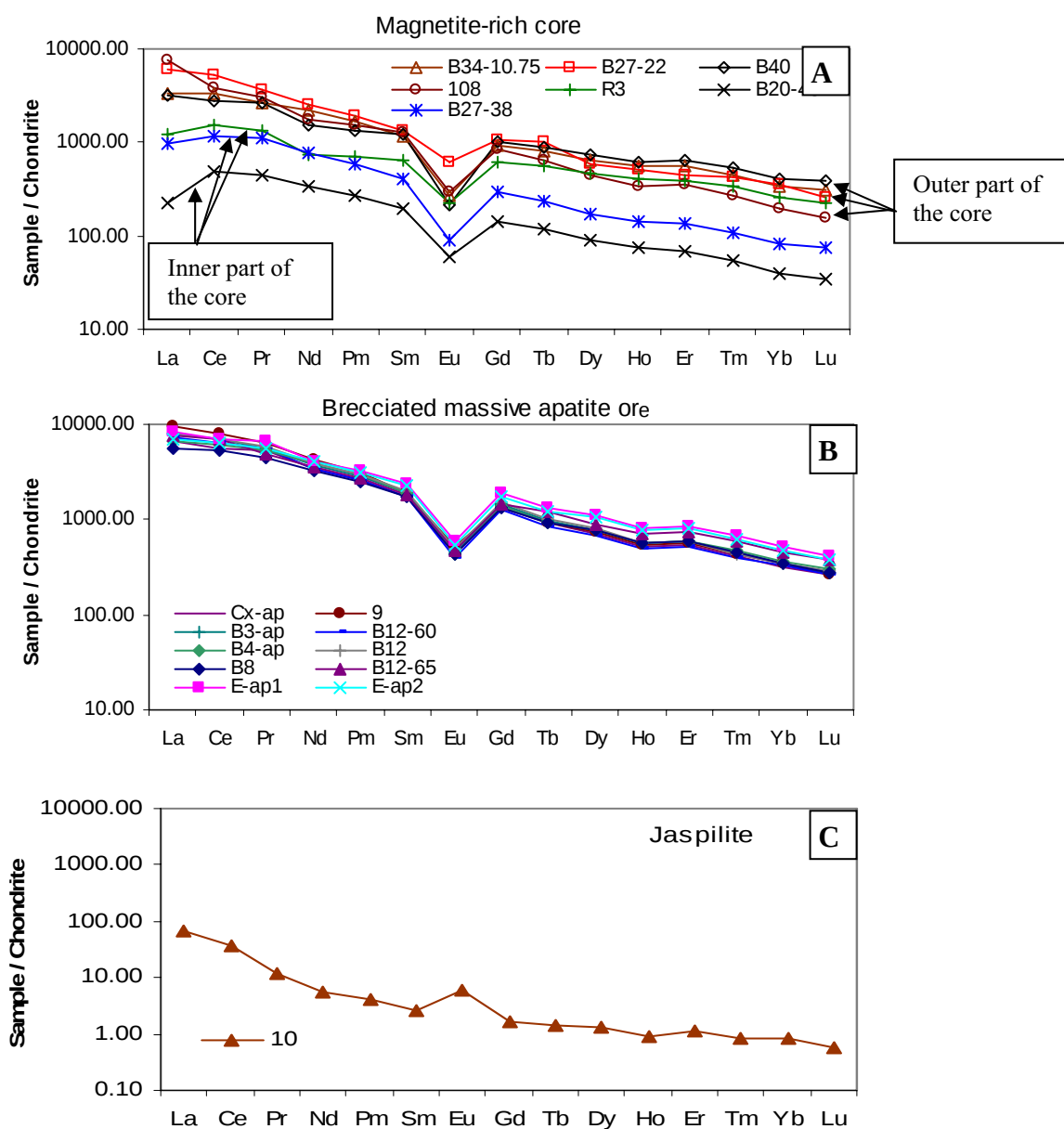
The magnetite-rich core of the system contains an average of 3271.6 ppm, REE+Y. The massive magnetite–apatite core has average HREE+Y and LREE values of 1913.29 and 5637.82 ppm respectively. Two samples from the magnetite-rich marginal zone of the Fe-oxide core show lower REE values (LREE of 2090.8 and 826.8 ppm; HREE of 464.9 and 231.1 ppm). The massive magnetite-rich core has higher values of HREE and a lower degree of REE fractionation, whereas the brecciated margin is more differentiated and depleted in REE (Fig 6.23).

The magnetite core, with its high proportion of apatite 1 remnants and granular apatite patches, contains an average 8300 ppm  $\Sigma$  REE+Y, whereas the brecciated apatite from the main P ore body averages 14007 ppm and the associated large apatite 2 crystals 15344 ppm. Depletion of LREE from the core could have caused enrichment in HREE and reduction of the  $(\text{La/Lu})_{\text{cn}}$ ,  $(\text{La/Yb})_{\text{cn}}$  and  $(\text{La/Sm})_{\text{cn}}$  ratios. The massive magnetite–apatite core has a lower degree of REE and LREE fractionation, whereas the apatite-rich brecciated margin has higher  $\Sigma$ REE content and LREE fractionation due to the higher apatite 2 content (Table 6.6). The  $\Sigma$ REE+Y contents and  $(\text{La/Lu})_{\text{cn}}$ ,  $(\text{La/Sm})_{\text{cn}}$  and  $(\text{La/Yb})_{\text{cn}}$  ratios in the brecciated apatite ore and large green apatite crystals (apatite 2), are greater than the apatites associated with magnetite-rich core. This suggests concentration of REE and more LREE fractionation in the brecciated apatite ore (Fig 6.23 and 6.24). The REE fractionation within the P-rich zone that might have been expected for the massive apatite-rich ore and its abundant REE enriched apatite, compared with the REE depleted granular apatite, has probably been disturbed by the development of monazite, allanite and xenotime. The Eu/Eu\* value of the magnetite-rich core and apatite-rich zones are very

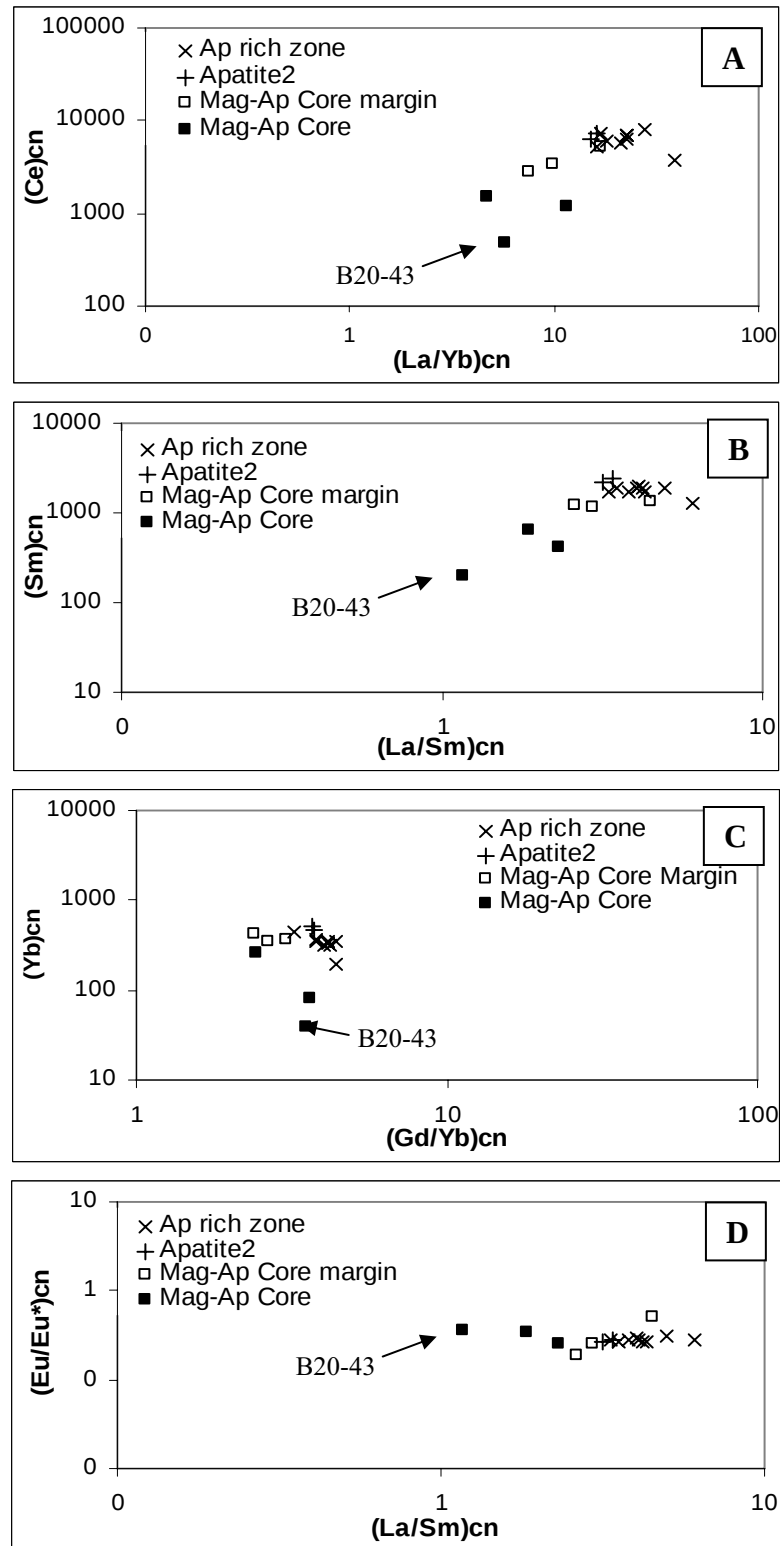
close and showing a negative Eu anomaly (Table 6.6). The close ( $\text{Eu}/\text{Eu}^*$ ) and ( $\text{Ce}/\text{Ce}^*$ ) values suggest oxidizing conditions and probably similar hydrothermal solution.

The magnetite-rich core is generally richer in granular apatite and shows lower LREE contents compare with the brecciated core margin and apatite rich zone. Sample B20-43 is an outlier in this group but contains abundant granular apatite (Fig 6.24). The REE ratio and chondrite normalised pattern show the brecciated margin of the magnetite-rich core is half-way between the LREE depleted core and the LREE enriched apatite-rich zone (in particular sample R3 which is strongly depleted in LREE compared with the HREE). Sample R3 also contains a strong overprint of carbonate that may have caused LREE mobilization in this late stage process, as well as dissolution of apatite 1 and 2.

The jaspilite layer contains very low amounts of REE+Y but with a very high ( $\text{La}/\text{Lu}$ )<sub>cn</sub>, ( $\text{La}/\text{Sm}$ )<sub>cn</sub> and ( $\text{La}/\text{Yb}$ )<sub>cn</sub> ratios. The Esfordi jaspilite does not show the negative Ce anomaly typical of sea water (Fig 6.23). Mills and Elderfield (1995) identified strong LREE enrichment with a positive Eu anomaly in a modern, high temperature (250°C) VHMS system associated with an active TAG mound within the Mid-Atlantic Ridge. This indicates the dominant influence of hydrothermal solutions in jaspilite formation.



**Figure 6. 23 Chondrite normalised pattern of magnetite-rich core (A), apatite-rich rocks (B) and jaspilite layer (C) of the Esfordi system (Chondrite normalized values from McDonough 1992).**



**Figure 6. 24 Chondrite normalised REE plot of samples from different magnetite-rich core and mineralised zones of the Esfordi system.**

## **CHAPTER 7      FLUID INCLUSION AND STABLE ISOTOPE STUDIES**

### **7.1      INTRODUCTION**

Fluid inclusion and stable isotope studies were conducted on various ore and host samples of Esfordi mineralizing system to investigate the evolution of the P-T-X conditions of the mineralizing fluids. The physical and chemical characteristics of fluid inclusions has also been analysed to assist in understanding the role of fluids in alteration and mineralisation processes at Esfordi.

In the following section the morphology and thermal characteristics of fluid inclusions hosted in various types of apatite and quartz of Esfordi deposit is documented. The O and S stable isotope analyses of various mineral phases and bulk samples and related interpretations in regard to fluid inclusion data is presented in the next section of this chapter.

### **7.2      FLUID INCLUSION STUDIES**

Fluid inclusions from different generations of apatite and the late stage quartz crystals were studied. The samples examined were selected from drill cores and fresh exposures of the apatite and Fe-oxide dominant zones. Based on field relationships, textural, mineralogical and geochemical criteria (Chapter 4 and 5), a paragenesis of apatite deposition, deformation and dissolution can be recognised. This essentially involves an early stage dominated by magnetite  $\pm$  apatite followed by a stage dominated by apatite  $\pm$  hematite  $\pm$  actinolite. Subsequent overprints are dominated by carbonate  $\pm$  quartz  $\pm$  chlorite  $\pm$  epidote. Three types of primary fluid inclusions have been identified in the first and second generations of apatite mineralisation on the basis of their textural context and microthermometric properties. A number of liquid-dominated inclusions in apatite 1 and 2

contain trapped crystals of magnetite and/or hematite determined by their morphology and magnetic properties.

The primary inclusions selection was based on the criteria of Roedder (1984) such as isolation, occurrence within well developed crystals, and free inclusion domains, inclusions with daughter and trapped phases, and occurrence along crystal growth surfaces. Microthermometric measurements were carried out at CSIRO Division of Exploration and Mining, Sydney, using a Linkam TMS 91 temperature control unit and a THMS 600 heating–freezing stage mounted on a Nikon Optiphot microscope equipped with FX-35DX camera. The samples were prepared as free-standing doubly polished apatite and quartz slices with ~0.3 mm thickness. Stage calibration was carried out using synthetic fluid inclusion standards and pure substances (Roedder, 1984). Accuracy is estimated at  $\pm 0.3$  °C in the range  $-90$  to  $+30$  °C and  $0.5$  °C at higher temperatures. Estimated accuracies for the different measurements are given in Table 7.1. Salinities were calculated from final ice melting temperature using the equation of Potter and Clynne (1978) and are expressed as equivalent wt. % NaCl.

**Table 7.1 Measurements and accuracy of fluid inclusions geothermometry.**

| Measurements                                                             | Abbreviation    | Accuracy (°C) |
|--------------------------------------------------------------------------|-----------------|---------------|
| First melting of aqueous ice                                             | T <sub>mi</sub> | $\pm 0.3$     |
| Last melting of aqueous ice                                              | T <sub>mf</sub> | $\pm 0.3$     |
| Total homogenization of inclusion contents (excepting daughter crystals) | T <sub>h</sub>  | $\pm 0.5$     |
| Final dissolution of daughter phases                                     | T <sub>dx</sub> | $\pm 0.5$     |

### 7.2.1 Apatite 1

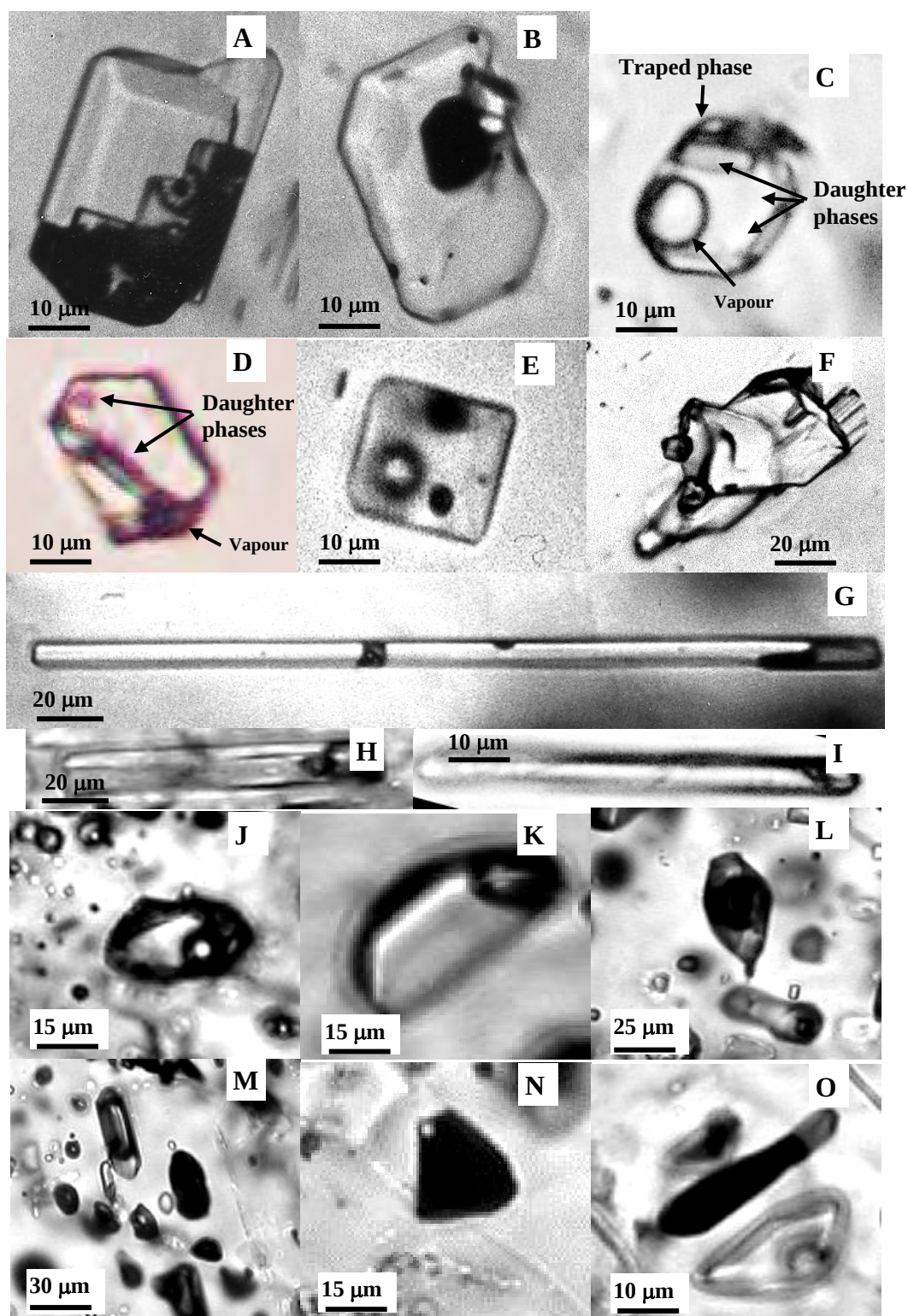
Apatite 1 is mainly present in white, monomineralic patches and intergrowths with magnetite in the Fe-oxide core of the Esfordi mineralised system and as remnant cores to massive apatite breccia blocks within the main phosphate zone (Figs 4.11 and 4.12).

The remnant apatite 1 is a mosaic of subrounded grains, typically 0.1-2 mm in size, cut by corridors of fine, granular apatite. Monazite is common as 5 to 50  $\mu\text{m}$  inclusions. A

crude zonation may be observed in some grains with fluid and other inclusions more abundant in the cores than the rims of apatite 2. Magnetite grains, 0.1-1 mm in size, are closely associated with apatite 1 but hematite is also spatially associated with those apatites as pervasive replacement of magnetite and as interstitial specularite.

Among the primary inclusions, three types of inclusions have been observed; three phase (L+V+S), two phase (L+V) and monophasic vapour inclusions (Fig 7.1). The apatite crystals generally show a central zone of systematically developed fluid inclusions and several generations of irregular trails of secondary inclusions associated with later brecciation and apatite deposition. The systematic elongate inclusions (typically 50-100  $\mu\text{m}$  but up to 500  $\mu\text{m}$ ) commonly occur along the c-axis of the apatite crystals and associated with various solid inclusions. The three phase inclusions are abundant and usually liquid-rich. They contain up to three different daughter phases and rare trapped magnetite or hematite. The daughter phases have been tentatively identified as halite, sylvite and possibly Ca and Fe-chlorides, based on their morphology, optical properties and behaviour on heating.

Most of the inclusions studied required a high degree of supercooling to induce freezing, usually between -70 and -120 °C. Upon warming to about -60 °C the ice displayed a granular texture with brown color. The first ice melting temperature ( $T_{\text{mi}}$ ) ranged from -44 to -52 °C suggesting  $\text{CaCl}_2$  as the major solute present along with  $\text{Mg}^{2+}$  and  $\text{Na}^+$  (Shepherd *et al.*, 1985; Davis *et al.*, 1990). The final ice melting temperature ( $T_{\text{mf}}$ ) for the ice phase was between -3 and -21 °C (Fig 7.6) indicating a fluid salinity between 5.0 and 23.0 wt % NaCl equivalent (Potter and Clynne, 1978; Bodnar, 1993). The typical  $T_{\text{mf}}$  values of -10 to -14 °C correspond to the salinity between 13.9 and 17.8 wt % NaCl equivalent. The homogenization temperature ( $T_{\text{h}}$ ) of the liquid and vapour was between 235 and 505 °C with most values in the range 375-425 °C (Fig 7.5).



**Figure 7.1 Photomicrographs of inclusions in apatite 1.**

- A – E: Regular shaped multi-daughter phase inclusions and Fe-oxide trapped phase,
- F: Irregular three phase (L+S+V) inclusion.
- G – I: Rod-shape three phase (L+S+V) inclusion
- J & K: Two phase (L+V) fluid dominated inclusions
- L & M: Two phase (L+V) gas dominated inclusions,
- N & O: Gas inclusions.

Sylvite dissolves between 125-250 °C and halite dissolves in a wide range of temperature from 340 to 500 °C. The opaque solid phases persisted to 600 °C without any sign of dissolution. No pressure correction was applied to these values as the deposition appears to have occurred in either shallow water or a sub-aerial regime penecontemporaneous with felsic volcanism and the salinity of inclusions demonstrate a pressure of entrapment <150 bars (Hass, 1976; Roedder and Bodnar, 1980).

### **7.2.2 Apatite 2**

Apatite 2 is the dominant type in the main phosphate zone and takes two forms (i) massive mosaics and linear arrays of 0.1–20 mm apatite that is commonly purple due to interstitial hematite and which occurs as both clasts and matrix in the widespread breccias and (ii) irregular, vein-like masses of green-yellow, euhedral grains up to 150 mm in size (Figs. 4.11-4.14). Apatite 2 rims, up to 200 µm thick, are also developed around apatite 1 grains.

In this generation of apatite, two groups of inclusions have been studied; the primary inclusions in petrographically classified apatite 2 and trails of presumably secondary inclusions in the apatite 1. These inclusions are typically 20-150 µm in size and show various morphologies including negative crystals, elongate, semi-oval and irregular. Three, two and mono-phase gas inclusions have been observed, but two-phase (L+V) inclusions are most common with liquid-rich and vapour-rich end members. The vapour phase typically occupies 5-20 % and 40-80 % of the inclusions volumes of these variants respectively (Fig 7.2). In some inclusions the vapor bubble displays a narrow darker rim, which could be interpreted as CO<sub>2</sub> vapour phase. Because of the small size of inclusions and the darker vapour rim, measuring the CO<sub>2</sub> freezing and melting temperature was not possible.

The first ice melting temperature ( $T_{mi}$ ) was between -30 and -40 °C and the last between -3 and -19 °C (Fig 7.6), with most values between -9 and -5 °C corresponding to 12.8–18.6

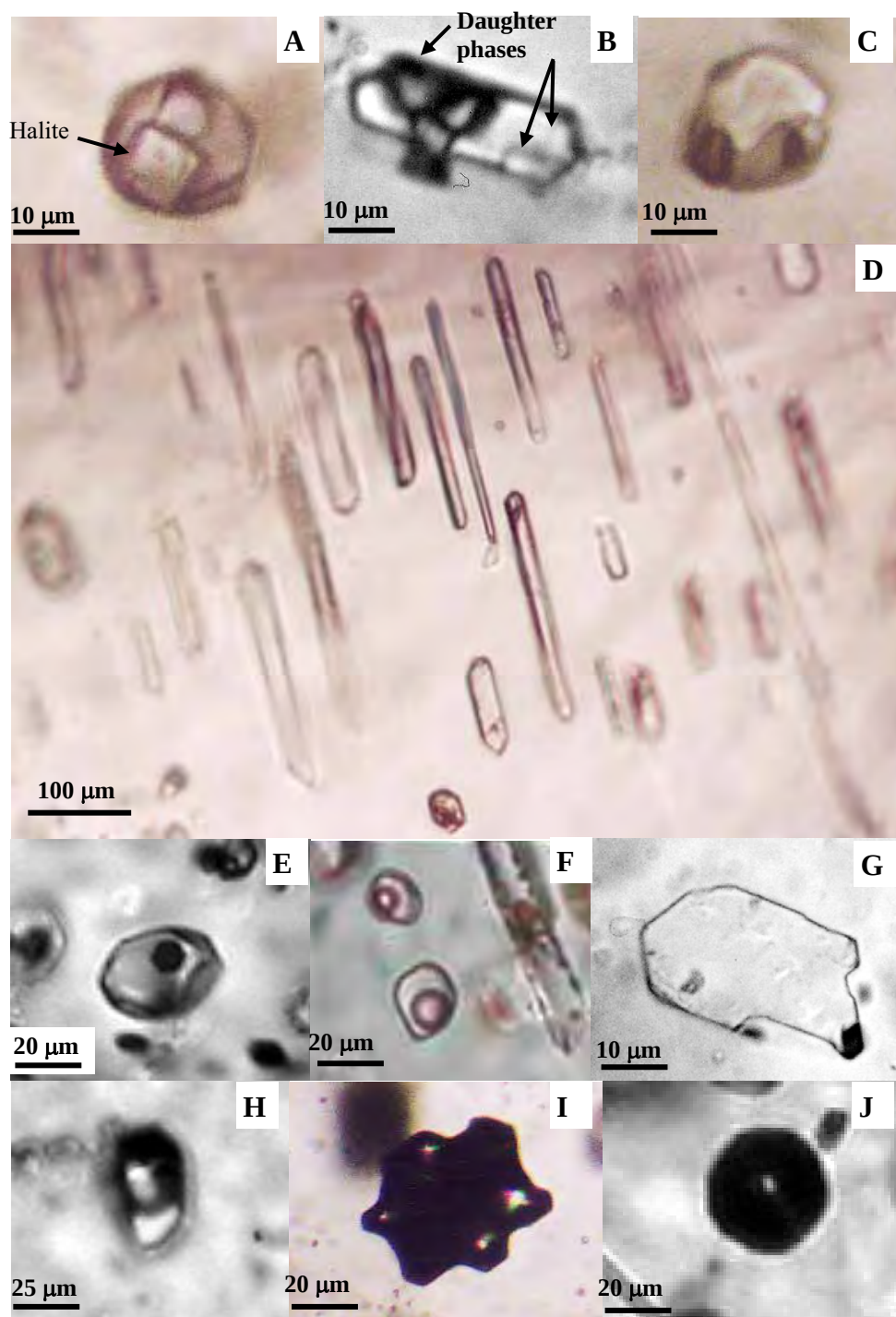
wt percent NaCl equivalent. On heating, apatite 2 inclusions showed a wide range of homogenization temperatures (145 to 495 °C) though the majorities were between 195 and 295 °C (Fig 7.5).

### **7.2.3 Apatite 3**

Apatite 3 is a minor phase in a pervasive late stage overprint in both Fe-oxide and phosphate bodies, where it is accompanied by carbonate and quartz (Fig 4.16). These apatites are often bipyramidal, <100 µm long and display a very low concentration of fluid inclusions and few solid inclusions. Most of the fluid inclusions are <20 µm and liquid-rich two-phase with small vapor bubble (approximately 5 vol. %) or mono-phase liquid inclusions. As a result of the size of inclusions, last ice melting points and salinity estimates could not be reliably determined. Homogenization temperature ( $T_h$ ) ranges between 105–225 °C with most values between 135 and 185 °C (Fig 7.5).

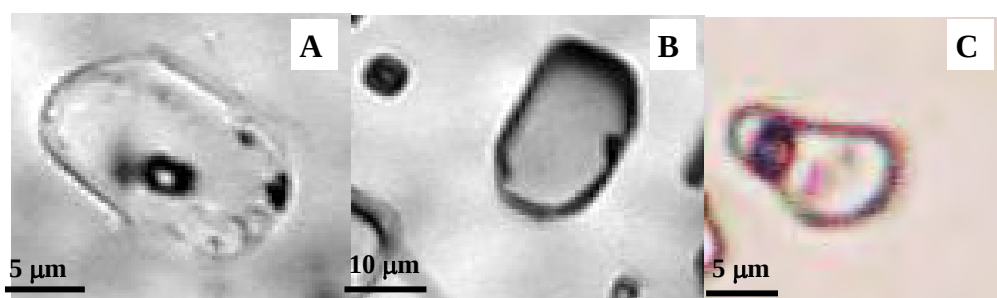
### **7.2.4 Quartz inclusions**

Quartz is widespread as a minor phase through the Esfordi mineralizing system, occurring as veins, cavity fillings and interstitial phases (Figs. 4.16 a-c). Although its temporal relation to apatite 2 and 3 is ambiguous, the quartz is most commonly associated with the late apatite 3, but also the apatite 2. Most of the crystals are clear with a low number of fluid inclusions. The majority of inclusions are 30-100 µm and are two phase (L+V) inclusions but three and mono phase inclusions are also present (Fig 7.4). In the three phase inclusions the solid phase is halite, which is readily distinguishable from its morphology and optical properties. The last ice melting temperature ( $T_{mf}$ ) of quartz inclusions lay between -11 and -3 °C with a mode of -6 °C corresponds to 9.2 wt percent NaCl. The homogenization temperature ( $T_h$ ) was between 115 –195 °C with a mode around 150 °C (Fig 7.5).

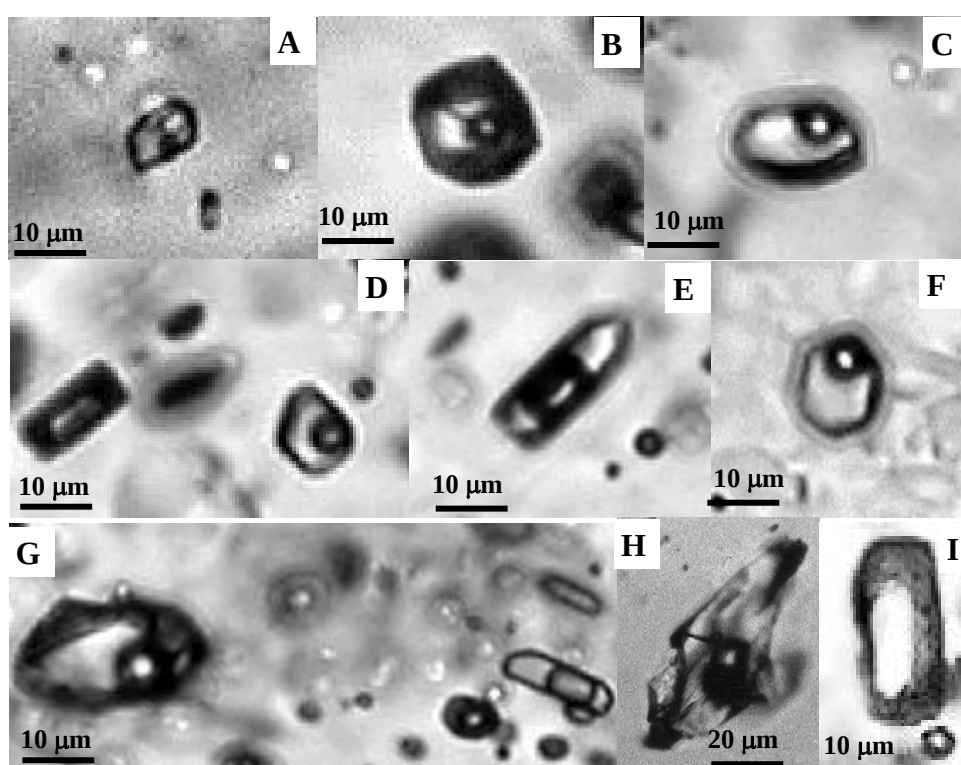


**Figure 7.2 Photomicrographs of inclusions in apatite 2 from brecciated P-rich ore.**

- A – C: Three-phase fluid inclusions with at least two daughter phase. Note the cubic shape of halite in A.
- D: A group of rod-shape three (V+L+S) and two (V+L) phase fluid inclusions,
- E & F: Two-phase oval shape inclusion,
- G: Two phase fluid dominated inclusion,
- H: Two phase gas dominated inclusion,
- I & J: Irregular and oval shaped gas inclusions.



**Figure 7.3** Photomicrographs of two (V+L) phase liquid dominated fluid inclusions in apatite 3.

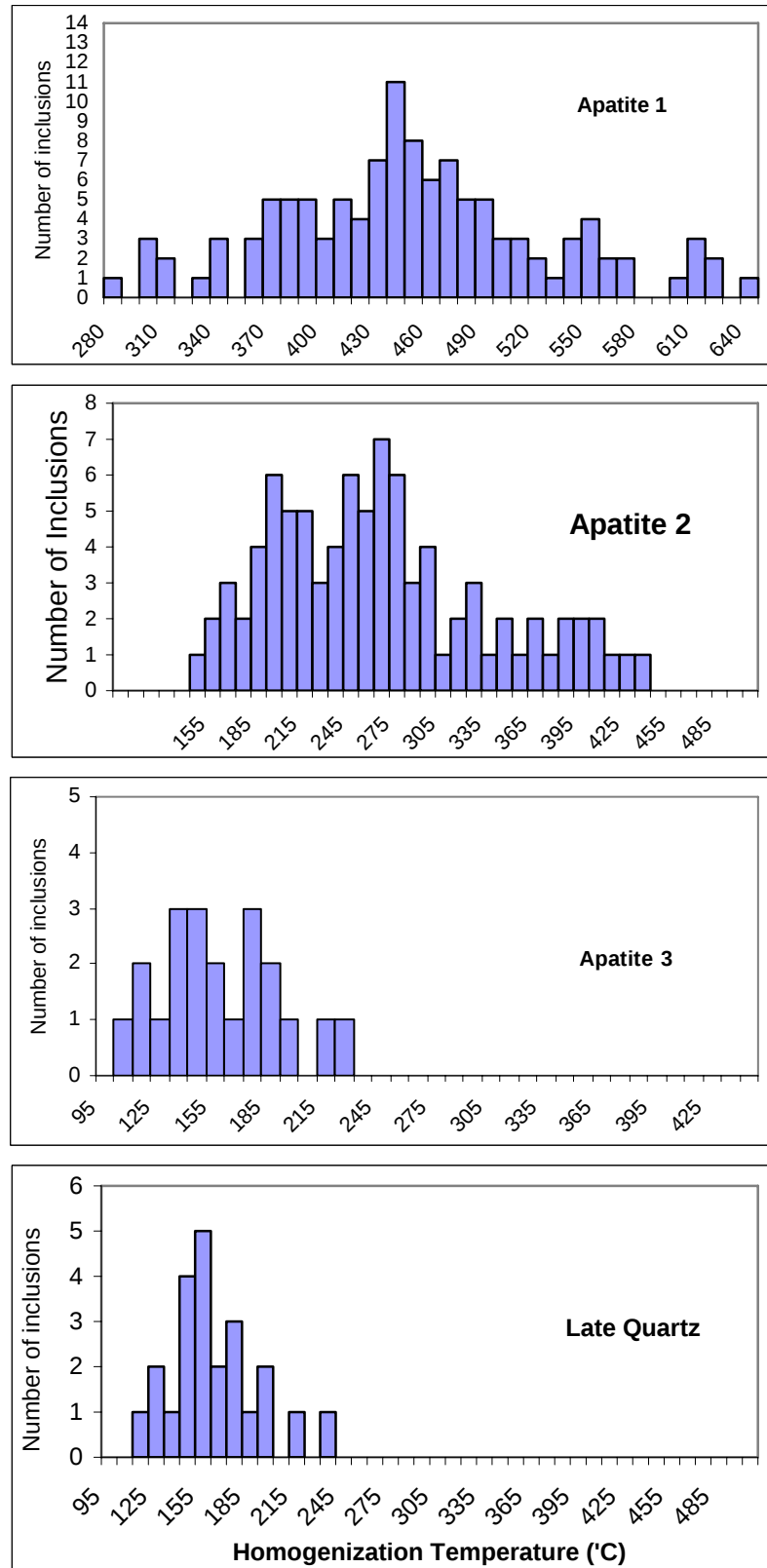


**Figure 7.4** Photomicrographs of fluid inclusions in quartz.

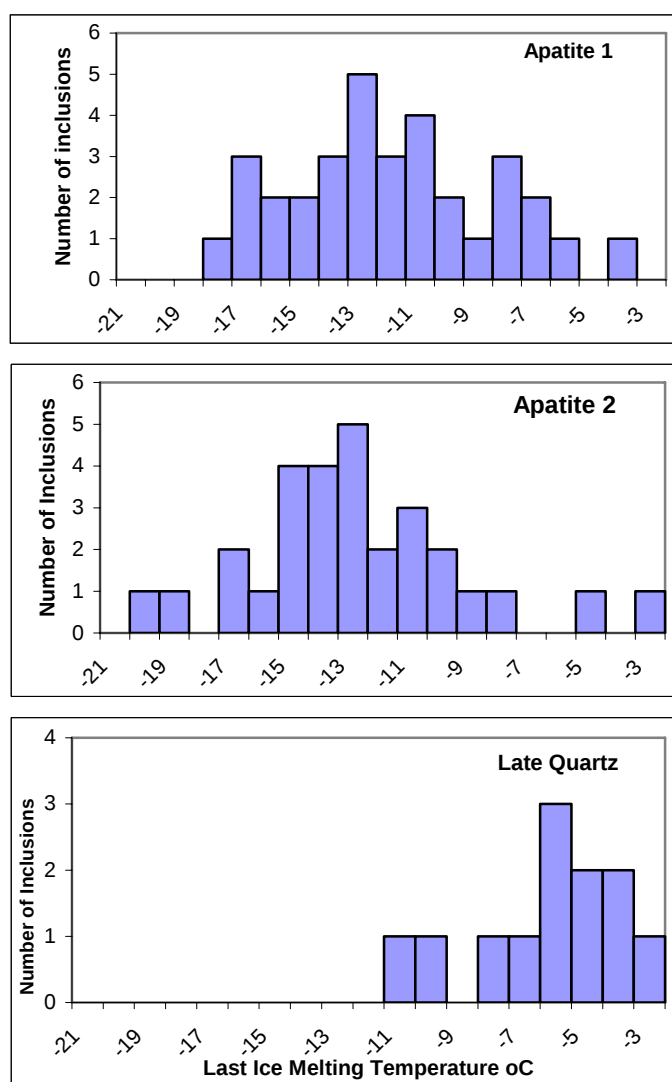
A to G: Two (V+L) phase liquid dominated fluid inclusions.

H: Irregular liquid dominated inclusion.

I: Monophasic fluid inclusion.



**Figure 7.5** Histograms illustrating fluid inclusion homogenisation temperatures for inclusions in three types of apatite and quartz



**Figure 7.6** Histograms illustrating last ice melting temperature for inclusions in apatite 1 and 2 and late quartz.

### 7.3 OXYGEN STABLE ISOTOPE STUDIES

Drill hole and fresh mine exposure samples were chosen from the main magnetite–apatite and apatite-hematite ore bodies to characterize the solutions associated with early magnetite–apatite, apatite-hematite-actinolite and late stage carbonate-quartz assemblages. The magnetite, hematite, quartz, actinolite and carbonates were separated by combination of handpicking and conventional magnetic separation. The magnetite samples were derived from the brecciated magnetite–apatite ore zone in the Fe-rich core of the Esfordi system and jaspilite layers in the hanging wall. The hematite and actinolite samples were

obtained from the main apatite-hematite-actinolite assemblage in the phosphate ore zone and quartz and carbonates from the pervasive alteration assemblages. Whole rock samples were also selected from lowest intensity altered rhyolite wallrock, dolerite dykes and different alteration zones including amphibole-rich, K-feldspar-rich variants at Esfordi to provide some indication of the isotopic composition of the host rock.

The whole rock samples inevitably include a proportion of cavity fillings and alteration minerals such as late carbonate quartz and actinolite. Whole rock and mineral samples were, therefore, treated with 10 % nitric acid to remove carbonates, and quantitative mineralogical compositions of the residues determined from X-ray diffraction (Phillips PW 1830) patterns using SIROQUANT™. Oxygen was extracted from the minerals and whole rock powders using BrF<sub>5</sub> at 600 °C and a CO<sub>2</sub> conversion technique (Baertschi and Silverman, 1951). Isotopic analyses were performed using a Finnigan Mat Delta E mass spectrometer at CSIRO Exploration and Mining, Sydney. The PDB-1 and Vienna SMOW standards were used for C and O isotopes respectively. All values measured are reported as ‰ deviation from SMOW standard and the data are summarised in Table 7.2.

Massive magnetite that is texturally associated with the apatite 1 displays relatively low  $\delta^{18}\text{O}$  values (-0.1 to 1.3 ‰). Whereas the magnetite associated with the brecciated apatite- rich, hematite and actinolite zone show higher values (1.2-2.2 ‰), magnetite separates from breccia style mineralisation most typically situated along the margins of the main Fe-rich core to the Esfordi system are only slightly enriched in  $^{18}\text{O}$ . Hematites from the main phosphate ore body, containing predominantly stage 2 mineralisation, occur in two texturally distinct forms; (i) thick rims about magnetite cored grains and (ii) veins and breccias of coarse bladed or feathery hematite. Both forms of hematite have similar  $\delta^{18}\text{O}$  values of 0.4 to 1.4 ‰. The  $\delta^{18}\text{O}$  for magnetite from the exhalative jaspilite layer is 1.7 ‰ more enriched than the stage 1 magnetite mineralisation but is similar to the magnetite-bearing breccias.

Secondary magnetites after hematite and specularite from brecciated apatite ore and altered hanging wall tuff have  $\delta^{18}\text{O}$  values of 4.73-6.84 ‰. Magnetite and hematite from the ferruginous fragments within the tuffaceous sandstone overlying and peripheral to the phosphate ore body show a  $\delta^{18}\text{O}$  range of -1.0 to 2.0 ‰. The magnetite bearing grains range from monomineralic massive types through to lithic grains with disseminated magnetite, overgrowths are common on both types, which may be variably martitized.

**Table 7.2 Carbon and oxygen isotope data in bulk host rocks and mineral separates.**

| Sample No | Rock/mineral type | $\delta^{18}\text{O}$ ‰<br>SMOW | $\delta^{13}\text{C}$ ‰<br>PDB | Remarks                                                                         |
|-----------|-------------------|---------------------------------|--------------------------------|---------------------------------------------------------------------------------|
| B8        | Carbonate         | 16.9                            | -6.1                           | Pervasive in main massive apatite ore                                           |
| 101       | Carbonate         | 18                              | -5.7                           | Pervasive in brecciated apatite-magnetite ore                                   |
| B4        | Carbonate         | 17.9                            | -7.3                           | Pervasive in massive apatite-hematite ore                                       |
| 102       | Carbonate         | 19.4                            | -7.0                           | Carbonate as vein in main magnetite ore                                         |
| Bh12-86   | Carbonate         | 18.8                            | -4.9                           | Carbonate as vein in main phosphate ore?                                        |
| B12-94    | Carbonate         | 18.1                            | -4.5                           | Carbonate as vein in main phosphate ore                                         |
| E-Ap1     | Carbonate         | 23.9                            | -4.7                           | Carbonate replacing apatite crystal                                             |
| E-Ap2     | Carbonate         | 21.5                            | -6.1                           | Carbonate replacing apatite crystal                                             |
| B8        | Quartz            | 17.1                            | -                              | Cavity filling in brecciated apatite-actinolite                                 |
| B12-65    | Quartz            | 16.5                            | -                              | Cavity filling in brecciated apatite-magnetite                                  |
| 104       | Quartz            | 16.0                            | -                              | Cavity filling in main phosphate ore                                            |
| 107       | Quartz            | 16.4                            | -                              | Cavity filling in altered tuff                                                  |
| B12-9     | Quartz            | 17.6                            | -                              | Interbeds of Qtz-rich sandstone within altered tuff                             |
| B1-13     | Quartz            | 14.8                            | -                              | Detrital Qtz sandstone within altered tuff                                      |
| B12-65    | Actinolite        | 7.1                             | -                              | Brecciated apatite, rim of Fe-oxide core                                        |
| B9        | Actinolite        | 9.2                             | -                              | Brecciated apatite-rich zone                                                    |
| B20-17    | Actinolite        | 10.7                            | -                              | Highly altered tuff top of apatite-rich zone                                    |
| B54-42    | Actinolite        | 8.2                             | -                              | Brecciated apatite                                                              |
| Gr-ac-1   | Actinolite        | 9.5                             | -                              | Highly altered tuff with garnet                                                 |
| B12-38    | Chlorite          | 9.7                             | -                              | Highly altered tuff                                                             |
| 104       | Magnetite         | 1.7                             | -                              | Massive magnetite                                                               |
| 102       | Magnetite         | 2.2                             | -                              | Magnetite in brecciated type apatite                                            |
| B1-2      | Magnetite         | 1.3                             | -                              | Massive brecciated magnetite-apatite                                            |
| B12-9     | Magnetite         | 1.2                             | -                              | Main apatite ore                                                                |
| B40       | Magnetite         | -0.1                            | -                              | Massive magnetite                                                               |
| B54-42    | Magnetite         | 0.31                            | -                              | Massive magnetite                                                               |
| B20-43    | Magnetite         | 0.1                             | -                              | Massive brecciated magnetite                                                    |
| B12-65    | Magnetite         | 1.6                             | -                              | Brecciated apatite, rim of Fe-oxide core                                        |
| B20-17    | Magnetite         | 6.84                            | -                              | Secondary magnetite in brecciated altered tuff of the apatite-ore hanging wall. |
| B2-42     | Magnetite         | 4.73                            | -                              | Secondary magnetite in brecciated apatite ore                                   |

**Table 7.2 Continued**

| Sample No | Rock/mineral type | $\delta^{18}\text{O}$ ‰<br>SMOW | $\delta^{13}\text{C}$ ‰<br>PDB | Remarks                                            |
|-----------|-------------------|---------------------------------|--------------------------------|----------------------------------------------------|
| 32-1      | Magnetite         | 0.0                             | -                              | Disseminated magnetite in rhyolite                 |
| 32-2      | Magnetite         | -0.1                            | -                              | Detrital magnetite                                 |
| 106       | Magnetite         | 2.0                             | -                              | Magnetite sublayers in tuffaceous sandstone        |
| 10        | Magnetite         | 1.7                             | -                              | Fe-oxide-jaspilite layer                           |
| 107       | Hematite          | 9.8                             | -                              | Hematite after early magnetite                     |
| 52        | Hematite          | 11.1                            | -                              | Specularite in main phosphate zone                 |
| Bh1-13    | Hematite          | 3.2                             | -                              | Detrital hematite in sandstone                     |
| 101       | Hematite          | 5.2                             | -                              | Specularite after magnetite                        |
| B52-42    | Hematite          | 1.36                            | -                              | Altered tuff                                       |
| 120       | Hematite          | 2.33                            | -                              | Vein-type hematite in altered tuff                 |
| B20-2     | Alt. rhyolite*    | 11.8                            | -                              | Amphibole-rich alteration zone                     |
| B53-41    | Alt. rhyolite*    | 12.8                            | -                              | Amphibole-rich alteration zone                     |
| B64-108   | Alt. rhyolite*    | 12.8                            | -                              | K-feldspar rich alteration zone                    |
| Bh7-41    | Alt. rhyolite*    | 10.9                            | -                              | K-feldspar rich alteration zone                    |
| B10-82    | Rhyolite*         | 12.7                            | -                              | Porphyry rhyolite, 30 m below the apatite rich ore |
| 31        | Rhyolite*         | 9.8                             | -                              | Rhyolite, 500 m E of Esfordi Fe-oxide core         |
| 85        | Rhyolite*         | 9.4                             | -                              | Rhyolitic tuff, 3 km NW of Esfordi Fe-oxide core   |
| 105       | Rhyolite*         | 9.5                             | -                              | Rhyolite, 100 m SE of Esfordi Fe-oxide core        |
| Bh8-65    | Rhyolite*         | 10.8                            | -                              | Volcanic rhyolite, interbedded with alt. tuff      |
| Bh12-25   | Tuff*             | 12.4                            | -                              | Rhyolitic tuff, interbedded with sandstone         |
| 23        | Granite*          | 8.7                             | -                              | Esfordi granite, 2 Km North of Esfordi             |
| NG1       | Granite*          | 10.0                            | -                              | Narigan Granite, 10 km South of Esfordi            |
| 93        | Granite*          | 10.5                            | -                              | Narigan Granite, 15 km South of Esfordi            |
| 24        | Dolerite*         | 6.9                             | -                              | dyke 50 m SE of Fe-oxide core                      |
| 28-2      | Dolerite*         | 5.5                             | -                              | dyke 100 m East of Fe-oxide core                   |
| 89-1      | Dolerite*         | 7.6                             | -                              | dyke in Narigan Granite, 10 km South of Esfordi    |
| 90        | Dolerite*         | 5.9                             | -                              | dyke in Narigan Granite, 15 km South of Esfordi    |
| B2-140    | Sandstone*        | 15.4                            | -                              | Sandstone interbedded with footwall rhyolite       |
| B2-110    | Sandstone*        | 8.6                             | -                              | Sandstone interbedded with footwall rhyolite       |

\* Whole rock analysis

The O isotopic composition range from values similar to those in stage 1 magnetite mineralisation through those of stage 2 hematite bearing mineralisation. These could be interpreted as representing eroded fragments of mineralisation and preserving their original isotopic composition or interacting with fluid continuing to circulate through the sandy detritus as indicated by the magnetite overgrowths. Interacting fluids may have enriched stage 2 composition with varying contribution from seawater depending on the prevailing temperature.

Whole rock rhyolite  $\delta^{18}\text{O}$  values range from 8.6 to 10.8 ‰ and fall within the range of values typical for granites and felsic volcanics (Taylor, 1968; Sheppard, 1981). Three samples collected from the Narigan Granite and two exposures north of Esfordi show

whole rock  $\delta^{18}\text{O}$  values range from 8.7 to 10.5 ‰. Whole rock Esfordi dolerite  $\delta^{18}\text{O}$  values range from 5.5 to 6.9 ‰ and the Narigan doleritic dykes vary from 5.9 to 7.6 ‰. Some of these samples are from within and some are from equivalent rocks outside the Esfordi mineralised system. As there is evidence of some degree of regional fluid–rock interaction, the samples may be most appropriately considered as ranging from those showing weak alteration to those showing more pronounced alteration. Those showing the more pronounced alteration have somewhat enriched isotopic composition. This is consistent with the character of the fluids inferred from paragenetic assemblages from stages 1 and 2 of the Esfordi mineralised system.

The  $\delta^{18}\text{O}$  values of the actinolite and chlorite separate from various types of ore and intensely altered host rock, ranges between 7.1 to 10.7 ‰. Amphibole separates drawn mainly from stage 2 apatite–hematite–amphibole breccias from the main phosphate ore body and intensely altered rhyolitic tuff which overlie the phosphate body. The amphiboles may be categorised on a textural and compositional basis into (i) a coarser, dark green actinolite which is often overgrown by (ii) a pale coloured, fine and fibrous Ca-rich amphibole.

Oxygen and carbon isotopic values and ratios have been determined for the carbonate fraction of the sample (Table 7.2). The various carbonates forms (pervasive, vein-type and apatite replacement), locations (Fe-rich core, phosphate ore body and the adjacent intensely altered rhyolitic volcanics) and mineralisation stages analysed, the  $\delta^{18}\text{O}$  values are consistently in the range 16.9–24.1 ‰.

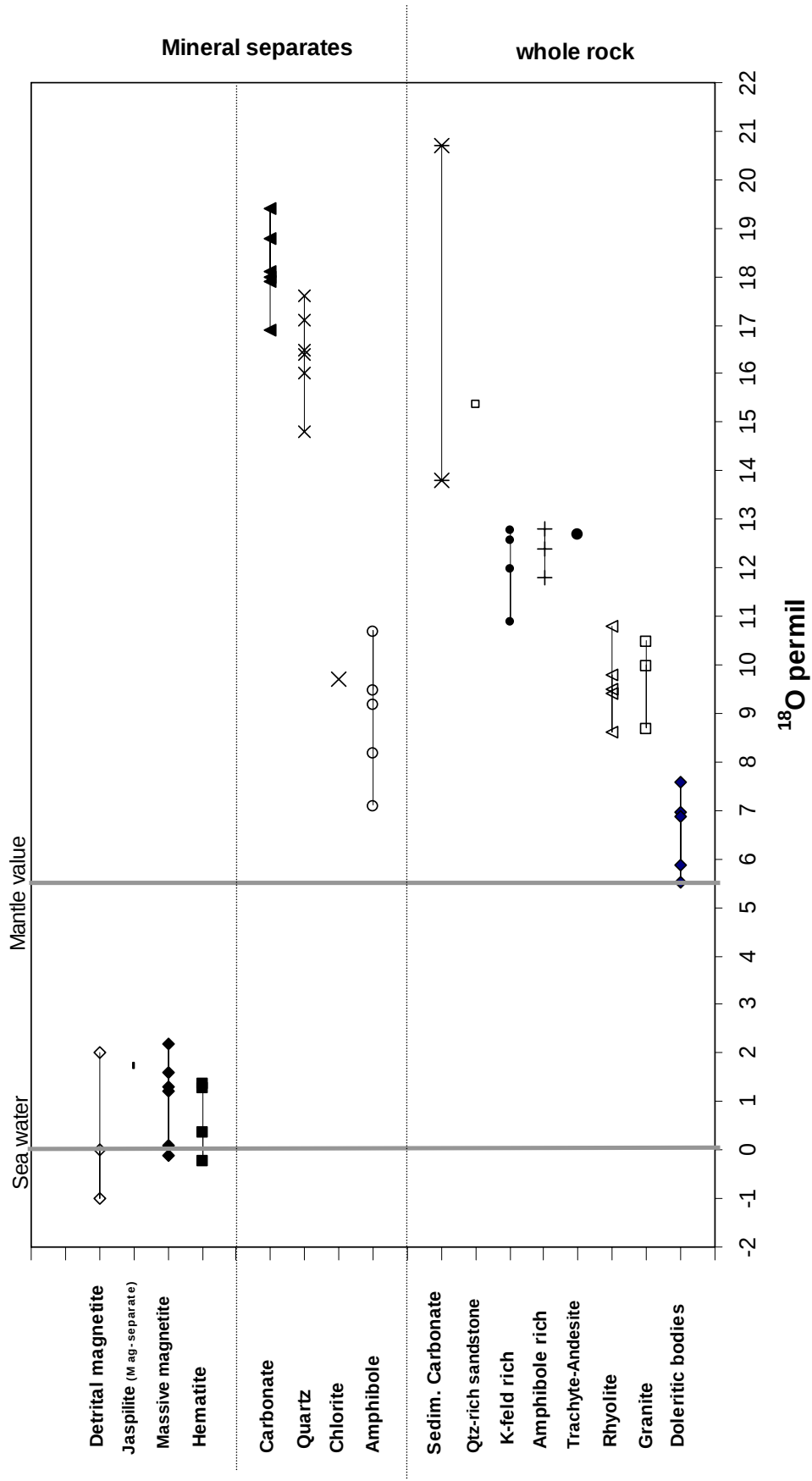
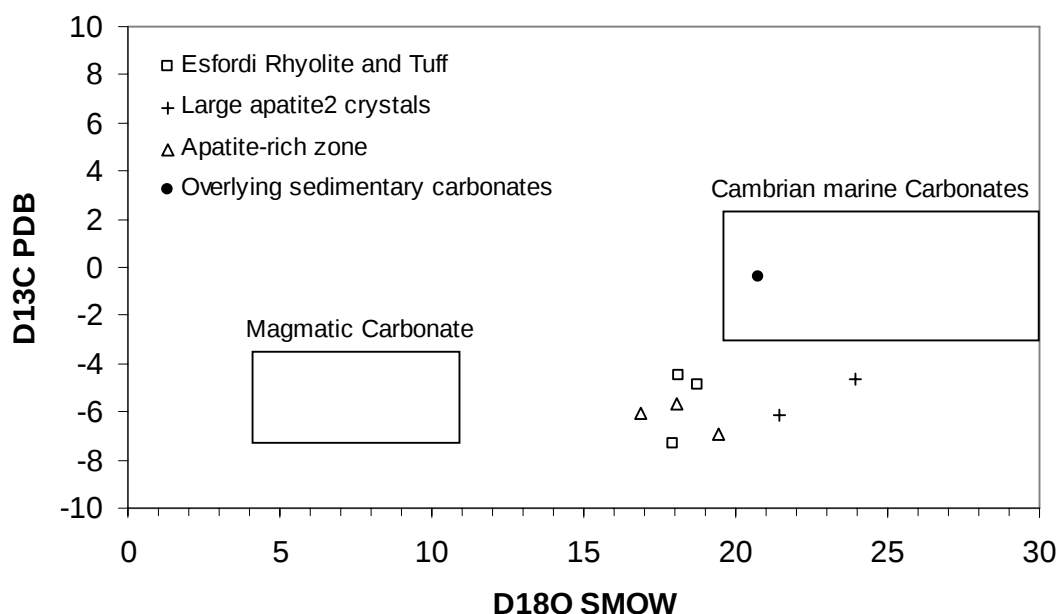


Figure 7.7  $\delta^{18}\text{O}$  values for mineral separates and whole rock analyses for the Esfordi deposit.



**Figure 7.8** Plot of  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  values for carbonate samples from the Esfordi deposit (Cambrian marine carbonate and magmatic boxes after Veizer and Hoefs, 1976 and Ohmoto, 1986).

### 7.3.1 The hydrothermal waters oxygen isotope composition

According to the  $\delta^{18}\text{O}$  values of different mineral phases, the oxygen isotope composition of the waters in equilibrium with these phases calculated (Appendix 4). Based on the Zheng and Simon (1991) constants the magnetite from main Fe-oxide core of the Esfordi system and their equivalent detrital varieties have been deposited from a solution with  $\delta^{18}\text{O}$  range of 6.9–10.1 ‰ at 400 °C. This temperature is the homogenization temperature for the first generation of apatites, which seems to be contemporaneous with the magnetites. Two magnetite samples of the extensively brecciated mineralisation and one of the detrital magnetites in porous tuffaceous sandstone are suggesting a solution with slightly depleted in  $^{18}\text{O}$  composition (7.7, 8.0 and 6.9 ‰ respectively). Due to the shallow depositional environment and the high porosity of the brecciated Fe-oxide ore and tuffaceous sandstone, this shifting of the calculated  $^{18}\text{O}$  composition of solution may caused by mixing with the sea water and/or reequilibrium of the primary magnetite depleted solutions.

The hematite crystals formed at 250 °C as might be expected on the basis of paragenetic association with type 2 apatite, are in equilibrium with solution of 10.8-12.2 ‰, which is in the range of fluids composition calculated for pervasive carbonates and amphibole at 250 °C.

Based on microscopic evidence, the amphiboles (mainly actinolite) deposited in three different generations. The first generations usually show a darker green colour and are mainly associated with brecciated magnetite–apatite ± hematite assemblage. The first generation of apatite with homogenization temperature mode of 400 °C is in equilibrium with this type of actinolite. This type of amphibole shows progressive change to the second generation with rims and patches of lighter colour crystals. In some cases they completely replace the previous generation or occur as well shaped crystals. The second generation is in equilibrium with type 2 apatite with homogenization temperature of 250°C. The last generation of actinolite contains tiny, needle-shape crystals associated with late quartz veins. Due to the mixture of first and second generation of actinolites, the calculated water composition at 250 °C shows a shift from depleted solution (8.3 ‰) to relatively enriched solution (11.8 ‰). This shifting may be caused by progressive mixing of depleted solution in equilibrium with massive magnetite and type 1 apatite (6.9-10.1 ‰) with the enriched solutions in equilibrium with the hematite and type 2 apatite (10.8-12.3 ‰).

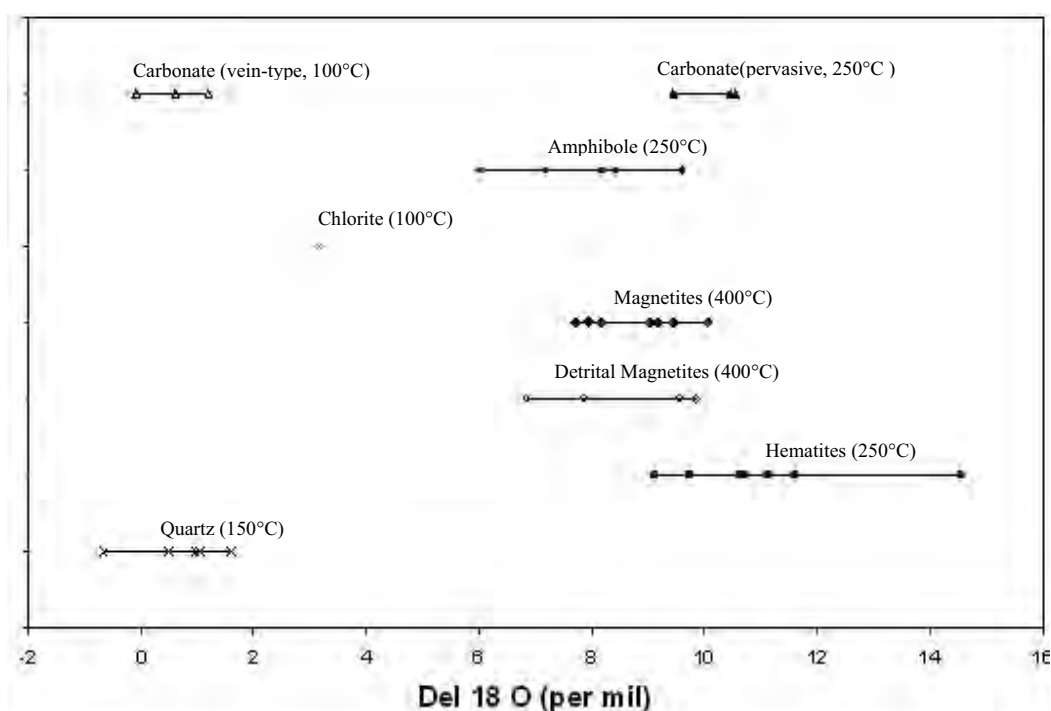
The carbonates (mainly calcite) show two distinct textural forms, pervasive patches in the matrix and vein type. All of the calcites are enriched in  $\delta^{18}\text{O}$  (17.9-19.4 ‰). The samples dominated with pervasive calcite are generally associated with first and second generation of amphiboles and second generation of apatite. Based on 250 °C homogenization temperature of apatite 2, the calculated  $\delta^{18}\text{O}$  value for mineralizing water would be 9.5-10.6 ‰ (Zheng, 1999). This value is consistent with the estimation of water in equilibrium with the hematite associated with type 2 apatite. By using the same

formula, the late vein type calcite dominated samples suggests  $\delta^{18}\text{O}$  for associated fluids of  $-0.1$ – $1.2$  ‰ at  $100$  °C. The calculation of the  $\delta^{18}\text{O}$  value of water in equilibrium with late stage chlorite separate associated with quartz and amphibole also show a  $3.2$  ‰ value at  $100$  °C (Wenner and Taylor, 1973).

The late stage quartz fluid inclusions show a low homogenization temperature range of  $115$ – $195$  °C and mode of  $150$ °C. By using the Zheng (1993) constants the oxygen isotope composition of waters in equilibrium with amphibole 2 at  $100$ °C is  $0.5$ – $2.0$  ‰. The  $^{18}\text{O}$  composition of water based on quartz values at  $150$ °C using Zheng (1993) constants is between  $0.5$  and  $2.1$  ‰. It seems that at the temperature range of  $100$  to  $150$  °C, quartz, chlorite, late vein-type calcite and probably late generation of amphibole are all deposited from same solution with a relatively depleted  $\delta^{18}\text{O}$  value. Such a solution would be consistent with a sea water component. The magnetite associated with jaspillite is consistent with a solution of  $1.8$  ‰ at  $50$  °C using the Mandernack *et al.* (1999) formula.

Such a pattern of composition suggests a continuous history of cooling and mixing of solutions of different affinities. In the first high temperature stage the solution show a relatively enriched values of  $^{18}\text{O}$  ( $6.9$  –  $10.1$  ‰). This value probably caused by either circulating juvenile water through the metamorphic basement rocks or evaporitic part of the CVSU (Saghand Formation or Rizu Series). After the early stage of mineralisation the solutions becomes cooler and enriched in  $^{18}\text{O}$  by mixing with connate and formational waters. These solutions are responsible for hematite-apatite 2 and pervasive type of carbonate deposition.

In the final stages by reducing the supply of the mixture of circulating juvenile and connate water, the sea water starts to penetrate to deeper levels of the system and reduce the  $^{18}\text{O}$  concentration of the solutions. By getting closer to the post brecciation stage, the main water supply changed from juvenile and connate water sources to sea water, which shifts the  $^{18}\text{O}$  composition of the solution towards zero.

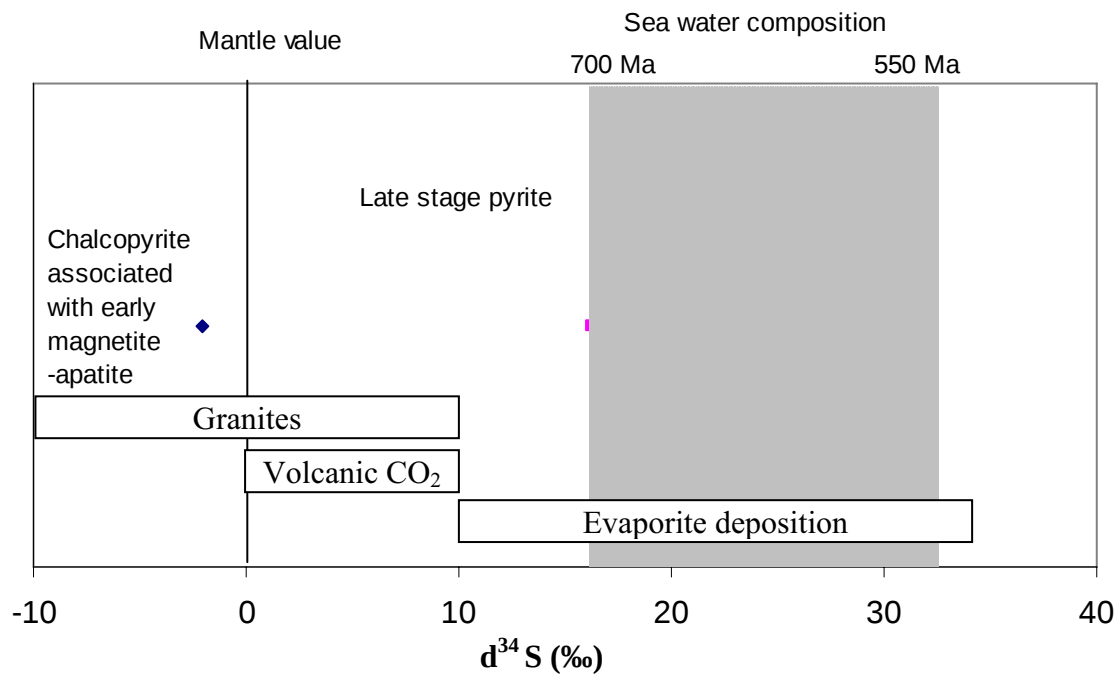


**Figure 7.9 Compositional range of mineralizing solutions based on minerals O isotope ranges.**

## 7.4 SULPHUR ISOTOPE STUDIES

The pyrite crystals in altered porous tuffaceous rocks of the hanging wall and apatite-rich ore of the Esfordi mineralizing system have been separated to give some preliminary sulphur isotopic analyses. These pyrite crystals are mainly associated with late stage minerals such as amphibole 2, carbonates and quartz. A chalcopyrite sample was also separated from massive magnetite ore. A preliminary estimate of the S isotopic composition for disseminated pyrite in late stage assemblages ranges from 16.3 to 30.1 ‰. This overlaps to a significant degree with seawater S from the period 550–700 Ma (Claypool *et al.*, 1980) (Fig 7.10) and is consistent with the O isotopic data from late stage quartz and carbonate.

A chalcopyrite sample, separated from massive magnetite ore, has been also analysed for S isotopes. The chalcopyrite sample shows -2.09 ‰ value, which is lower than the pyrite values.



**Figure 7. 10 Plot of S isotopes of Esfordi pyrite and chalcopyrite.**

## **CHAPTER 8      DISCUSSION AND CONCLUSIONS**

### **8.1      THESIS OBJECTIVES**

The Bafq district constitutes the most significant Fe-oxide and phosphate deposits in the world. It hosts a large number of Fe-oxide deposits with combined reserves of 1,800,000 bt of high grade Fe ore (Taghizadeh, 1976; NISCO 1980).

The Esfordi apatite-magnetite deposit is a P-rich example of the Kiruna-type. Whereas Kiruna and related mineral deposit types have been subjected to extensive study, there remains controversy as to the mechanisms by which such deposits form.

The current study has provided further description of the Esfordi deposit characteristics, relevant to mineral exploration and mining of similar deposits, as well as constraining genetic models for the genesis of the Esfordi deposits, based on detailed mapping of the ore deposit and surrounding alteration envelope, fluid inclusion and stable isotope analysis, REE and trace element geochemistry.

### **8.2      ESFORDI ZONATION AND MINERAL PARAGENESIS**

The Esfordi Fe–P oxide system contains a distinctive pattern of zoning and mineral paragenesis. The main features of this zonation are summarised in Table 8.1. As indicated in Chapter 4, three different zones of apatite mineralisation can be recognised: (i) an inner zone comprises a core of massive Fe-oxides with a peripheral brecciated zone, (ii) an apatite-rich zone overlying and adjacent to the Fe-oxide rich zone and characterised by intense brecciation with localised more massive and less brecciated domains and (iii) a zone of amphibole-rich alteration, extending into the overlying volcanic-volcaniclastic sequence, that hosts low grade P ore. All three zones were affected, to varying degrees, by subsequent brecciation and fluid interaction.

The magnetite in the core of the system typically occurs as a concordant lensoid body with intergrowths of apatite and minor amounts of monazite, allanite, amphibole, chlorite, epidote, calcite and quartz. This contrasts with the funnel-shaped geometry of the Sechahoon the Choghart deposits, proposed by Förster and Jafarzadeh (1994) to be the result of diatremes.

The magnetite is Ti-poor and falls within the typical range of Kiruna-type deposits (Loberg and Hornbahl, 1983) and is well outside the range typical of nelsonites and cumulate magmatic systems in mafic rocks (Dymek and Owens, 2001). The magnetite is variably replaced by hematite. Coarse, bladed hematite with apatite and actinolite, in the more brecciated zones around the margin of the core, have textures interpreted in this study to be the result of open-space filling. The shape of the original euhedral magnetite grains, veins and angular breccia clasts as defined by hematite replacement which may also involve overgrowth.

The most distinctive feature of the Esfordi P–Fe-oxide system is the extensive brecciation and fragmentation, which does not appear to be related to syn- or post-depositional tectonic deformation or post-depositional hydrothermal systems. One mechanism for generating such extensive post-mineralisation brecciation is martitisation, due to low temperature oxidation that produces significant volume increase as the primary magnetite is converted to hematite by O addition (Ohmoto and Skinner, 1983). Some of these textures, however, cannot be readily explained by such oxidation processes and may have been derived from mechanical brecciation or high fluid pressure within a shallow hydrothermal system.

Localised patches of bleaching within zones of otherwise purple apatite 2 at Esfordi are sites where hematite is absent, depleted or replaced by late-stage, low-Ti magnetite. The distribution of these patches appears to be controlled by fractures and brecciated corridors, and an influx of reducing fluids.

The distribution, characteristics and paragenesis of the four types of apatite and associated REE minerals observed at Esfordi are important to understanding the evolution of the system. The sequence of deposition commenced with an early mineralisation stage dominated by magnetite  $\pm$  apatite, which forms the core of the Esfordi system, and was closely followed by hydrothermal episodes dominated by apatite  $\pm$  hematite  $\pm$  actinolite deposition.

The first generation of Esfordi apatite (apatite 1) is associated with the magnetite-rich core of the system, as remnant domains and massive breccia blocks within the overlying phosphate zone. Apatite 1 patches are found as aggregates and disseminations in magnetite-rich groundmass and also as inclusions in magnetite crystals. The early stage amphiboles may be partially or completely altered to chlorite, epidote or even talc in places. The primary magnetite grains are partially replaced by hematite along fractures and crystal borders. Monazite 1 is also present as fine grained solid inclusions in the apatite 1 crystals.

Stage 2 represents the major period of apatite formation (apatite 2) and is characterised by abundant hydrous minerals such as amphibole, extensive brecciation, evidence of fluid activity, remobilization and veining. The mineral assemblage consists of hematite, monazite, xenotime, allanite, actinolite with apatite 2. Apatite 2 is the dominant type in the overlying main phosphate zone where it occurs as large crystals and as the matrix to the widespread breccias and veining as well as the overgrowths on apatite 1.

Both apatite 1 and 2 have been remobilised by the subsequent hydrothermal solutions and replaced by granular apatite. The granular apatite may form corridors along fractures and grain boundaries, mantle other grains and breccia clasts or form pseudomorph of whole apatite 1 or 2 grains.

Granular apatite grains are generally oval with curved rims and display diffuse contacts with other apatite grains at a mesoscopic scale. As a general rule lower

temperatures and higher strain rates favour brittle deformation of minerals, whereas higher temperature and lower strain rates promote ductile deformation (Passchier and Trouw, 1996). The most important processes, modifying grain boundaries are grain boundary migration and grain boundary sliding. Sliding is movement within the plane of the grain boundary and can be considered as a physical dislocation and movement of individual grains or boundaries, whilst migration is normal to it. The stored strain energy, resulting from numerous lattice defects such as dislocations, raises the crystal free energy and produces a less stable crystal than the unstrained counterpart. Strained crystals kept at high temperature have a tendency to recrystallize as a mosaic of unstrained, more stable but smaller grains. This process is fundamentally similar to the process of annealing (Williams *et al.*, 1985). However, if the temperature at which the strained crystals were subjected was relatively high, or if fluid was present along grain boundaries, recovery and recrystallization can continue in the absence of deformation until a minimum internal energy configuration is obtained (Passchier and Trouw, 1996). This process is generally known as static recrystallization. The term annealing is usually used to show processes of recovery and static recrystallization made by passive heating of deformed material (Passchier and Trouw 1996). Similar patterns of strain recovery and recrystallization have been reported in mylonites (Sibson, 1977; Barker, 1990; Best, 2003).

Apatite 1 patches in the magnetite-rich core show fine granular recrystallization similar to mylonites but without any characteristic lineation or foliation. This type of recrystallization is most probably related to recovery of strained crystals formed in the presence of fluids. This recrystallization is most intense developed in apatite 1 patches within the magnetite-rich core of the system, whereas apatite 2 in the overlying massive and brecciated apatite-rich zone display more limited granulation. The clear development of dissolution pores (Figs 4.11 o and p), are marginal to the zones of granular apatite suggest significant role for fluid interaction during the evolution of the Esfordi Fe-P

System. This would indicate that these granular apatites are the residues of interaction with transient fluids.

Stage 3 mineralisation is widespread and represents the major period of a late-stage pervasive carbonate and quartz alteration. This assemblage is characterised by the extensive appearance of carbonates, quartz, apatite 3, amphibole 2, epidote and chlorite. Stage 3 minerals pervasively or diffusively replace earlier apatite, amphibole, and chlorite.

Fig 8.1 illustrates the paragenetic sequence of Esfordi ore zones.

| Stages                     | Stage 1    | Stage 2     | Stage 3    |
|----------------------------|------------|-------------|------------|
|                            | Primary    | Brecciation | Late       |
| Magnetite                  | ██████████ | -----       | -----      |
| Ti-Magnetite               | -----      | -----       |            |
| Ilmenite                   | -----      |             |            |
| <b>Apatite 1</b>           | ██████████ |             |            |
| Monazite 1                 | -----      |             |            |
| Actinolite 1               | ██████████ |             |            |
| Hematite                   | ██████████ | ██████████  | -----      |
| <b>Apatite 2</b>           |            | ██████████  |            |
| <b>Granular apatite</b>    | ██████████ | -----       |            |
| Actinolite 2               |            | ██████████  |            |
| Monazite 2                 |            | ██████████  | -----      |
| Allanite 1                 |            | ██████████  | -----      |
| Allanite 2                 |            | ██████████  | -----      |
| Carbonate (pervasive)      | -----      | -----       | ██████████ |
| Carbonate (vein)           |            |             | ██████████ |
| Bastnaesite and synchysite |            |             | ██████████ |
| Actinolite 3               |            |             | ██████████ |
| <b>Apatite 3</b>           |            |             | ██████████ |
| Quartz                     |            |             | ██████████ |
| Chlorite                   |            |             | ██████████ |
| Epidote                    |            |             | ██████████ |
| Sulphides (py,cp,gn)       |            |             | ██████████ |

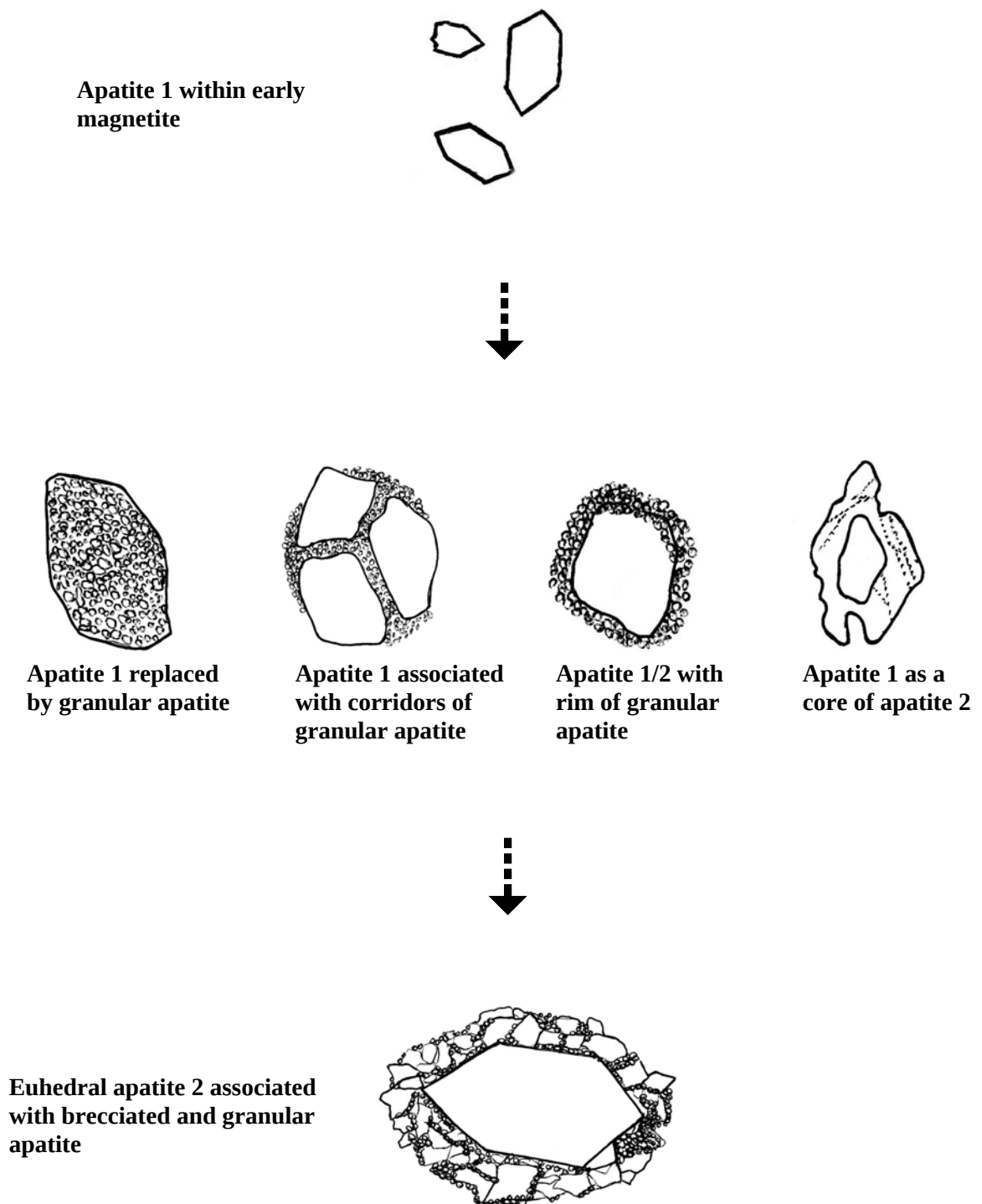
**Figure 8. 1. Paragenetic sequence the mineralizing sequence at Esfordi Fe-P deposit.**

The apatite 3 occurs as a minor phase within late stage carbonate and quartz overprints in both Fe-oxide and phosphate bodies. These overprints are associated with

permeability features such as fractures, reactivated breccias and apatite dissolution corridors as well as with pervasive dissolution of apatite 1 and 2.

Esfordi apatites generally show dominant LREE enrichment similar to that of many Kiruna-type Fe–P systems (Frietsch and Perdahl, 1995). Esfordi apatites are generally F-rich, however apatite 1 and 2 show the highest Cl content among the apatites (average 0.69 and 0.39 wt % respectively). The four types of apatite – 1, 2, granular and 3 – contain average  $\Sigma(\text{La,Ce,Nd})$  values of 1.43, 1.19, 0.22 and 0.11 wt % respectively. Figs 6.18 to 6.20 show the concentration of  $\Sigma(\text{La,Ce,Nd})$ , Cl, F, Y, La, Ce, and Nd within single grains of apatite 2. A zonation with consistent depletion in REE toward the rims of the apatite grains which parallels the paragenetic trend from stage 1 and 2 to later granular and stage 3 apatites.

The existence of trachytic and two sets of doleritic bodies within the host rocks, one partially altered and the other fresh suggests magmatic activity overlapped the mineralisation process.



**Figure 8. 2** Schematic diagram showing the evolution of apatite 1 to apatite 2 and granular apatite. Apatite 3 crystallized as a late stage phase with late quartz and carbonates.

**Table 8. 1** Characteristics of the different types of apatites in the Esfordi system.

|                                    | Stage 2 (Brecciation)                                                                                              |                                                                                                                                                                                                                                             |                                                                                                                                    | Stage 3 (Late)                                                                                                      |
|------------------------------------|--------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
|                                    | Apatite 1                                                                                                          | Apatite 2                                                                                                                                                                                                                                   | Granular apatite                                                                                                                   | Apatite 3                                                                                                           |
| <b>Morphology and colour</b>       | Mosaic of anhedral apatite crystals<br>Granoblastic texture<br>Usually white in color<br>With REM solid inclusions | Large, green, euhedral to subhedral crystals with low solid inclusions<br>Brecciated apatite with deformation tracks and corridors; white, pink or purple anhedral to subhedral crystals<br>Veins and veinlets of hematite and/or magnetite | Granular fine-grained apatite crystals after apatite 1 and 2.<br>White and anhedral crystals in corridors or around apatite grains | Small clear, euhedral to subhedral apatite crystals<br>Always occurred within late stage, quartz or carbonate       |
| <b>Chemistry</b><br>(Average wt %) | La=0.32 Na=0.23<br>Ce=0.77 Si=0.15<br>Nd=0.34<br>F=4.00 Cl=0.69                                                    | La=0.27 Na=0.21<br>Ce=0.67 Si=0.11<br>Nd=0.28<br>F=3.95 Cl=0.39                                                                                                                                                                             | La=0.05 Na=0.08<br>Ce=0.10 Si=0.05<br>Nd=0.07<br>F=5.83 Cl=0.06                                                                    | La=0.03 Na=0.03<br>Ce=0.05 Si=0.03<br>Nd=0.04<br>F=4.99 Cl=0.11                                                     |
| <b>REE minerals</b>                | Monazite 1 as inclusions inside apatite crystals                                                                   | Monazite 2, xenotime and allanite 1 as individual minerals in matrix<br>Allanite is euhedral to subhedral and monazite subhedral to anhedral                                                                                                | Low REE minerals mainly monazite 2 and allanite 2                                                                                  | Allanite 2 and bastnaesite                                                                                          |
| <b>Mineral assemblage</b>          | Magnetite, pyroxene, amphibole I, hematite                                                                         | Hematite, amphibole 2, chlorite, albite, K-feldspar                                                                                                                                                                                         | Hematite, pervasive quartz and carbonate, amphibole II, chlorite                                                                   | Within quartz and carbonate veins; amphibole 3, talc, chlorite, epidote, Fe-hydroxides                              |
| <b>Zone of occurrence</b>          | Main apatite and Fe-oxide zones                                                                                    | Main apatite ore zone<br>Border of main Fe-oxide main ore zone<br>Apatitic veins and stockworks in overlying altered host rocks                                                                                                             | Corridors in apatite 1, brecciated main apatite 2 and apatite veins and veinlets in altered host rock                              | Overprint the older stages specially brecciated main apatite ore<br>Apatite veins and veinlets in altered host rock |

### 8.3 REE MINERALOGY AND GEOCHEMISTRY

Rare earth elements (REE) are characteristically elevated in Kiruna-type magnetite–apatite deposits (Parak, 1975; Frietsch and Perdahl 1995; Kerr, 1998). The REE tend to partition into apatite, but often provide distinctive accessory mineralogies (Harlov *et al.*, 2002). Together with textures and field relationships, these provide insights into both original apatite-Fe-oxide formation and subsequent geological processes.

The high content of REE in apatite 1 and 2 in Esfordi (average 1.43 and 1.19 % respectively) is accompanied by enhanced Si and Na. Granular apatites with low REE levels are interpreted as the result of interaction with fluids permeating through the primary Fe-oxide core of the system. The textural development of granular apatite corridors in with primary apatite particularly in the magnetite-rich core assemblage appears to be related to the most probable routes for these fluids. The depletion of La, Ce and Nd in the granular apatite and low levels presented in apatite 3 is strongly correlated with a corresponding depletion in both Na and Si (Fig 6.16). This is consistent with coupled substitution of trivalent cations such as REE for  $\text{Ca}^{2+}$  in the apatite structure, balanced by substitution of  $\text{Si}^{4+}$  for  $\text{P}^{5+}$  or  $\text{Na}^{+}$  for additional  $\text{Ca}^{2+}$  to balance the electrostatic neutrality as proposed by Pan and Fleet (2002).

The Esfordi monazites demonstrate two distinctive textural forms including monazite 1 inclusions in apatite 1 and 2 and larger monazite 2 crystals in the brecciated matrix and granular domains of the apatite-rich zones where allanite 1 and 2 are also developed.

Pan *et al.* (1993) suggest that the nucleation of monazite in apatite can express by the following reaction between apatite and solution:



This may be applicable to Esfordi where apatite 1 and 2 are enriched in LREE, Na and Si, whereas granular apatites are depleted in LREE and enriched in P and Ca (Fig 6.17).

The different types of monazite regimes occurring in magnetite–apatite ores of the Kiruna area invite comparison with Esfordi. Harlov *et al.* (2002) suggest that monazite at Kiruna originated from REE incorporated into the apatite. The transfer of REE and Y content is considered to have initially take place at high temperature (700-800 °C), during interaction with exsolved magmatic fluids, to form monazite inclusions in the apatite. A further low temperature (~300-400 °C) event during greenschist grade event produced particularly LREE depletion zones in apatite and the formation of monazite grains in the matrix between brecciated apatite grains.

At the Pea Ridge Fe-oxide-REE deposit, Missouri, chondrite normalised whole rock REE patterns show LREE enrichment with a negative Eu anomaly (Kerr, 1998). The abundant hematite occurrence was interpreted to suggest an oxidizing regime results in low  $\text{Eu}^{2+}$  in the hydrothermal fluids. The breccia pipe mineral assemblage of Pea Ridge, suggests that  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{PO}_4^{3-}$  are likely to be the most important REE complexes in the fluids. The strong temperature and pH-dependence of these complexes stability suggest that decrease in the fluid temperature and increase in pH was the main cause of REE minerals deposition.

The reprecipitation of a significant proportion of LREE in the brecciated apatite-rich zone of Esfordi system as monazite 2, overlaps the lower part of this temperature range proposed for the mobilization process proposed at Kiruna. During precipitation and dissolution of apatite, Giere (1996) proposed REE phosphate complexes may play a significant role in this process.

The presence of allanite 1 in the matrix of brecciated apatite in the Esfordi system may be related to local availability of Fe, Si and Al. Similar REE patterns of monazite 2 and allanite 1 may suggest similar source for REE, which, comes from dissolution of

apatite 1 and 2 during the development of granular apatite. Similarly allanite 2 was most likely controlled by the availability of Ca, Si, Al and Fe from partial dissolution of adjacent wall rock amphiboles.

The leached LREE, Na and Si from the apatite 1 and 2 could either crystallize as monazite 1 within apatite crystals or be transported to more brecciated and porous zones and depending on the environmental parameters deposited as monazite 2 and allanite 1.

Previous studies show that allanite can form from the reaction of REE+Th-bearing fluids with pyroxene and plagioclase. Barth *et al.* (1994) concluded that, whereas U may be remobilised, Th effectively remains immobile under a range of hydrothermal condition. The low abundances of Th, U, Si and Ca are typical of monazite associated with apatite and suggest that their chemical components are derived from the apatite (Pan *et al.*, 1993; Harlov *et al.*, 2002). The Esfordi monazites are typically show very low Th and U as well as Ca and Si.

The textural evidence shows that monazite 2 and allanite 1 are in close association with each other in brecciated matrix of apatite-rich zone. The similarity between chondrite normalised pattern of monazite 2 and allanite 1 may indicate a common fluid. The general LREE patterns of the Esfordi allanites are similar to those analyzed in granites and their related hydrothermal systems (Exley, 1980; Ward *et al.*, 1992; Wood and Ricketts, 2000; Hermann, 2002).

Meng *et al.* (2002) pointed out that the F and CO<sub>2</sub>-bearing fluid are capable of redepositing released REE (from precursor minerals such as apatite and monazite) as fluorocarbonates such as bastnaesite, parisite, and synchysite. If the aqueous solution contains sufficient Ca ions, synchysite, theoretically will be stabilised before parisite and bastnaesite. Esfordi bastnaesite and synchysite are associated the late brecciation stage and pervasive replacement of both apatite 1 and 2 by carbonate and quartz. During the late lower temperature stage of Esfordi the REE from apatite1 and 2 are redeposited as

carbonates directly from the replaced apatites rather than by replacement of earlier formed monazite. The association of epidote and amphibole 2 with allanite 2 suggests that these minerals probably developed at a late stage in the Esfordi system evolution.

The Fe-oxide rich core whole rock REE analyses also show greater depletion in La than the other LREE, which may suggest the stronger leaching of La into the solutions. This La is probably in part responsible for deposition of monazite 1 with high La/Ce ratio. After monazite 1 crystallisation and also mixing with less saline waters, the solution was probably relatively depleted in La and the next generation of monazite (monazite 2) and allanite 1 crystallised with lower La/Ce ratio.

Mobilization and fractionation is also reflected in the whole rock REE geochemistry for the mineralised system (Figs. 6.23 and 6.24). The patterns of magnetite-rich core and its brecciated margin demonstrate the subdued LREE enriched pattern ( $La_{cn}/Yb_{cn} = 7.28$  and  $11.41$  respectively) with negative Eu anomalies ( $Eu_{cn}/Eu^*_{cn} = 0.32$ ). This pattern is mainly controlled by granular apatite in the core of the system and minor apatite 2 overprints, the most abundant apatite species. The least LREE enriched sample (R3) has a very strong carbonate overprint on a strong granular apatite development which probably mobilised to the LREE leading to relative HREE enrichment. The apatite-rich ore show stronger LREE enrichment ( $La_{cn}/Yb_{cn} = 23.05$ ) with negative Eu anomalies ( $Eu_{cn}/Eu^*_{cn} = 0.28$ ).

Hass *et al.* (1995) suggest that Cl complexes of LREE are more stable than those of HREE. Based on the fluid inclusion studies (Chapter 6), the salinity of solutions are relatively high. This may explain the LREE depletion of the granular apatites and subsequently, the relative HREE enrichment of the residues in core of the system. The plot of REE differentiation indexes show a trend from low LREE/HREE ratios in magnetite – apatite core compared to higher LREE/HREE ratios in core margin and apatite-rich zone (Fig 6.24).

Frietsch and Perdahl (1995) suggest that the REE patterns of host rocks in relation to those of the Fe-oxide-P mineralisation had been used to indicate the source of the ore. However at Esfordi the least altered volcanics which have average (La/Lu)<sub>cn</sub> of 16.1, (La/Yb)<sub>cn</sub> of 1.2 and (Eu/Eu\*) of 0.9 are markedly different to the ores where the magnetite-rich core (La/Lu)<sub>cn</sub> of 8.2, (La/Yb)<sub>cn</sub> of 7.3 and (Eu/Eu\*) of 0.3 suggesting that this simple genetic linkage may not be readily applied for this system.

The patterns in the jaspilite from Esfordi invite comparison with those from other exhalative iron stones (Fig 8.3). These varying signatures are taken to reflect contributions from sea water, hydrothermal and detrital sources (Herrmann and Hill, 2001). Thus the positive Eu anomaly at Esfordi jaspilite would be attributed to the higher redox condition of the sea water. The oxidizing condition of fluids may be one of the major reasons for the prominent negative Eu anomaly in the ore.

The range of LREE fractionation within many Fe-oxide-P systems reported by Frietsch and Perdahl (1995), and the patterns shown in Fig 8.3 for Esfordi, suggest a range in the extent of apatite dissolution and reprecipitation within different facies of such mineralised systems. Such logic could be extended to the degree of post-mineralisation fluid-apatite interaction in such a system, as suggested by Harlov *et al.* (2002).

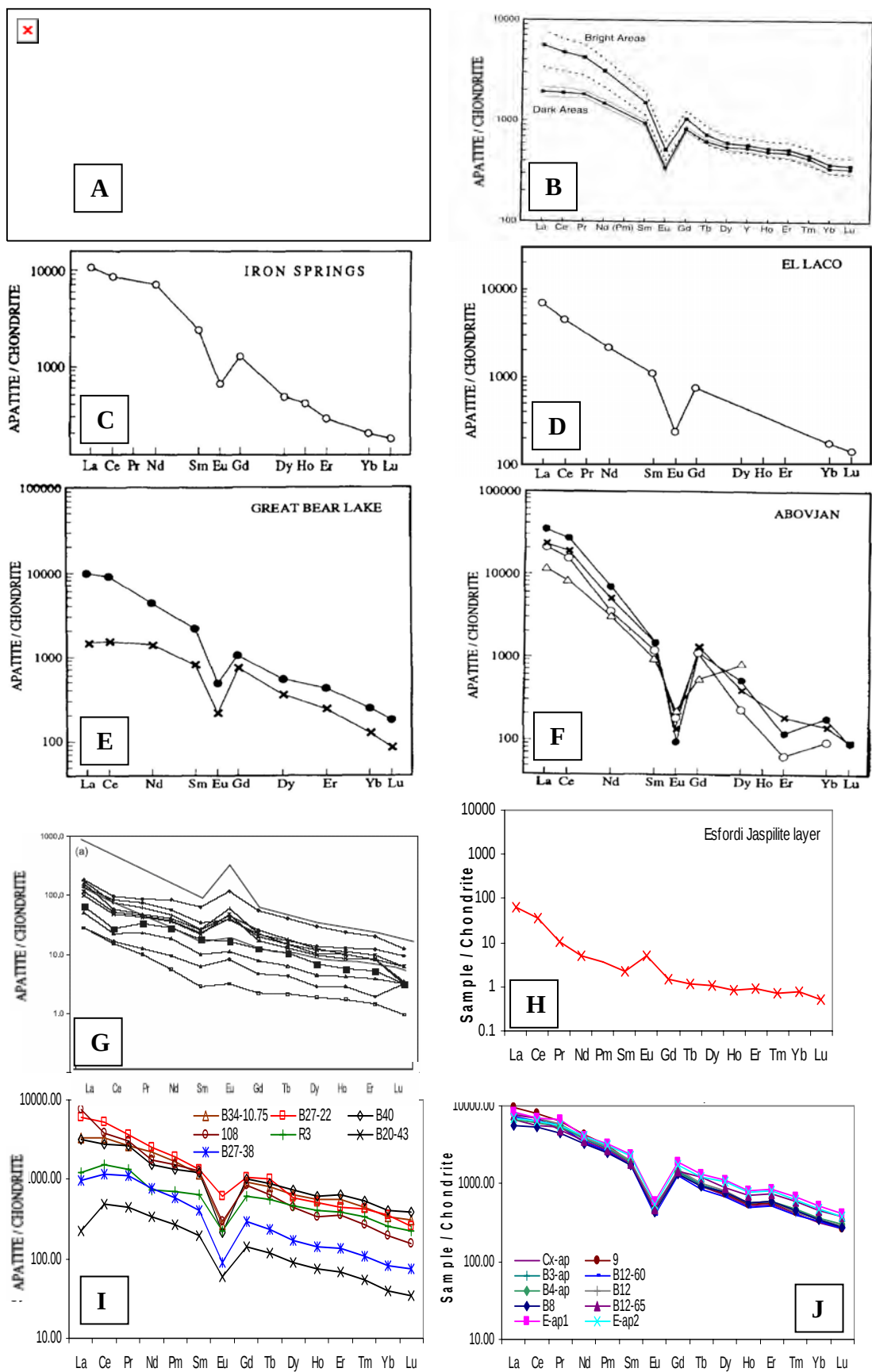


Figure 8.3 (Caption on next page.)

**Figure 8.3** Chondrite normalised REE patterns of a range of Kiruna-type Fe-oxide-P deposits, Mt Isa iron formation and Esfordi jaspilite-magnetite layer.

- A & B: Kiirunavaara, northern Sweden (Frietsch and Perdahl, 1995; Harlov et al, 2002)
- C: Iron Springs, United States (Frietsch and Perdahl, 1995)
- D: El Laco, Fe-oxide ore, Chile (Frutos *et al.*, 1990)
- E: Terra deposit, Great Bear Lake, Canada (Frietsch and Perdahl, 1995)
- F: Abovjan, Russia (Frietsch and Perdahl, 1995 and the references therein)
- G: Soldiers Cap Group iron-formations, Mt Isa Inlier, Australia (Hatton and Davidson, 2004)
- H: Jaspilite-magnetite layer of the Esfordi hanging wall (this study).
- I: Esfordi magnetite-rich core (crosses) and it's marginal breccia (this study)
- J: Esfordi massive and brecciated apatite-rich ore (this study).

## 8.4 FLUID CHARACTERISTICS AND SOURCES

The development of a zoned system of Fe–P oxide mineralisation at Esfordi with distinctive textures consistent with deposition from hydrothermal fluids, the presence of an array of fluid inclusion in apatite and associated quartz together with extensive zones of associated hydrothermal alteration all suggest that hydrothermal fluids have played a significant role in the evolution of this mineralised system.

The use of fluid inclusion data in establishing the origin of apatite in various magnetite–apatite deposits has also proven controversial. A wide temperature range that partially spans potential magmatic processes is indicated by fluid inclusions in apatite and pyroxene at El Laco (Sheets *et al.*, 1997). The apatite fluid inclusion data (in combination with other field relationships and fabrics) indicates deposition of apatite from fluids at sub-magmatic temperatures whereas higher temperatures are inferred from the pyroxene data and is attributed to a heat source from a shallow pluton (Sheets *et al.*, 1997). The sub-magmatic temperatures have been attributed by Broman *et al.* (1999) and Naslund *et al.* (2002), however, to fluid circulation during post-magmatic cooling that followed apatite–magnetite formation by direct crystallisation from oxide melt associated with andesitic volcanism. No fluid inclusions were observed in pyroxenes at Esfordi.

The primary inclusions in stage 1 apatite at Esfordi are observed in remnant domains and the majority of fluid inclusion homogenization temperatures values (375–425 °C) are well below the magmatic temperature range. The salinities and associated solid phases in these stage 1 inclusions are, however, consistent with Ca–K–Na brines that equilibrated with cooling igneous rocks. The ultimate origin of these fluids is less clear. Pollard (2002) has attributed a prominent role in the formation of Fe-oxide–Cu–Au deposits and associated alteration systems to the unmixing of H<sub>2</sub>O–CO<sub>2</sub>–saline fluids derived from CO<sub>2</sub>-bearing magmas. The abundance of CO<sub>2</sub>-rich inclusions in some stage 1 and 2

apatites is too low to suggest such an unmixing role in the generation of the breccia or diatreme systems at Esfordi. No CO<sub>2</sub>-rich inclusions are reported at El Laco (Broman *et al.*, 1999).

The  $\delta^{18}\text{O}$  values for magnetite associated with stage 1 apatite overlap with the range for magnetite reported for typical granitic and rhyolitic rocks by Taylor (1968) and Sheppard (1981) and is thus permissive of a direct magmatic origin. Given the association with apatite 1 containing primary fluid inclusions and the extensive hydrothermal alteration system intimately associated with mineralisation at Esfordi, formation from hydrothermal fluids is also plausible. Such fluids could have been derived from a magmatic source such as the Narigan Granite or rhyolites of the Saghand Formation. Deeply circulating, high temperature fluids exchanging with the underlying Chapedony and Posht-e-Badam Complexes from the metamorphic basement are also possible  $^{18}\text{O}$  sources.

Stage 2 apatite inclusions are derived from grains of more diverse character than stage 1 apatites including coarse, euhedral grains in carbonate–hematite  $\pm$  actinolite veins and interstitial breccia patches, apatite breccia fragments and domains of largely granular grains within breccia fragments. These fluids were significantly cooler (195–295 °C) and more  $\delta^{18}\text{O}$  enriched than fluids trapped in apatite 1. The extent to which these fluids introduced significant amounts of P and Fe into the system or just chemically and physically reworked components already present after apatite 1 deposition is yet to be determined. A similar generation of cooler and more  $\delta^{18}\text{O}$  enriched fluids at El Laco was attributed by Rhodes and Oreskes (1999) to either the boiling of magmatic fluids or contributions of  $\delta^{18}\text{O}$  enriched solutions derived from adjacent basins or salinas. Mineralising fluids from various sources at the Kiruna deposit have been proposed by Harlov *et al.* (2002), based largely on rare earth mineral compositions. These include high temperature fluids associated with crystallisation of associated volcanic rocks and later

influx of lower temperature fluids associated with a greenschist grade metamorphic event. The similar homogenization temperatures for apatites 2, containing coexisting liquid and vapour dominated inclusions, have been interpreted as evidence of boiling, using the criteria of Roedder (1984), and may be linked to the widespread brecciation in both stages of mineralisation and the adjacent wall rocks at Esfordi. The  $\delta^{18}\text{O}$ -depletion in the amphibole, compared with the stage 2 hematites and may be accounted for by late stage amphibole re-equilibrating with stage 3 fluids or inherited from closed system replacement of earlier pyroxene.

A plot of  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  values (Fig 7.8) indicates the composition of carbonate associated with mineralisation falls between the magmatic field and that of marine carbonate (Stakes and O'Neil, 1982) that could be derived from hydrothermal system involving mixing of magmatic and seawater-derived fluids (Ohmoto, 1986; Veizer and Hoefs, 1976). The C isotopes in the carbonate rocks from the overlying Saghand Formation are however typical of marine limestones.

The coolest, most dilute and  $\delta^{18}\text{O}$  depleted fluids trapped in quartz and stage 3 apatite at Esfordi are associated with widespread apatite dissolution. In sub-aerial regimes at El Laco, the isotopic composition of hematite also indicates a late stage interaction between meteoric fluids and the deposit (Rhodes and Oreskes, 1999). The main lithologies and modelling of the fluid inclusion thermometric measurements indicate mineral deposition in a shallow marine environment and, coupled with the O and S isotopic composition of the associated minerals, indicates circulating sea water as the most likely fluid source for the later stage quartz and carbonate.

The extensive magnetite development in stage 1 suggests a relatively reducing nature of the fluids, whereas the stage 2 is dominated by hematite (specularite), granular apatite and apatite 2, which demonstrate a relatively oxidizing nature of this generation of fluids. The stage 2 oxidizing fluids partly convert the primary magnetites to hematite and

the dissolution of apatite 1 and development of granular apatite. In the event of more oxidizing nature of the stage 2 fluids,  $\text{Eu}^{2+}$  concentration were probably very low in the solution leading to the negative Eu anomaly in the primary magnetite-rich core and apatite-rich mineralisation. If plagioclase is stable during any fluid-rock interaction, then exchange of  $\text{Eu}^{2+}$  for  $\text{Ca}^{2+}$  could also give rise to the negative Eu anomaly in any subsequent Fe–P oxide mineralisation.

Fluid inclusion studies (Chapter 7) revealed that mineralizing fluids at Esfordi have been saline (up to 23 wt % NaCl equivalent) and elevated temperatures (up to 505 °C, with peak at 375-425°C for apatite 1, and 195-295 °C for apatite 2) which decreases as the system evolved.

The important REE complexing ligands at temperatures 25-350°C and 25-1000 °C are  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{2-}$  (Wood, 1990, Hass *et al.*, 1995). The stability of these complexes generally decrease with decreasing temperature. Wood (1990); Wood and Williams-Jones (1994) and Hass *et al.* (1995) suggested that the  $\text{Cl}^-$  complexes are the major complexing ligands in saline solutions under acidic condition, whereas  $\text{F}^-$  complexes dominate in neutral pH values, and sulphate, carbonate and phosphate complexes are more important ligands at lower temperatures and moderate pH.

The relatively high F and subordinate Cl content of apatite 1 (Table 6.4) suggest that the potentially important complexing ligand for REE in the first stage of mineralisation was F. The occurrence of considerable carbonates as interbeds in the host rock sequence probably buffered the pH stabilizing more neutral solutions (Salvi and Williams-Jones, 1996) and released significant quantities of Ca and  $\text{CO}_3^{2-}$  into the fluids.

The lower formation temperature of apatite 2 indicated by fluid inclusions studies (195-295°C) along with association with RE phosphates and carbonates such as monazite, xenotime, synchysite and bastnaesite suggests that the  $\text{F}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  concentrations

in fluids may have been high enough to saturate the solution and initiate deposition as temperature declined.

The Cl poor rims of zoned apatite 1 and 2 (Figs 6.19 and 6.20) may indicate that the concentration of the Cl complexes in the fluids decreased with time and temperature. The greater availability of  $\text{PO}_4^{3-}$  with apatite dissolution in this stage resulted in formation of monazite and xenotime whereas in the carbonate replacement of apatite during later stages due to higher concentration of  $\text{CO}_3^{2-}$  led to formation of fluorocarbonate rare earth minerals (synchysite and bastnasite).

REE at Esfordi would be most likely transported dominantly as  $\text{F}^-$  and  $\text{Cl}^-$  complexes in the early stage fluids during the formation of the magnetite–apatite core of the system, whereas  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{2-}$  were dominant complexes with lesser contribution of  $\text{F}^-$  and  $\text{Cl}^-$  in the later stage fluids forming brecciated massive apatite ore and apatite-hematite veins.

Many Fe-Cu-Au and Fe-P deposits are characterised by a distinctive sodic, potassic and calcic alteration of associated host rocks (Barton and Johnson, 1996, 2000; Frietsch *et al.*, 1997; Williams and Pollard, 1998; Pollard, 2000; Haynes, 2000) clearly indicating a key role for fluids in their evolution.

The host rocks to the Esfordi Fe-P oxide deposit show abundant evidence of fluid-rock interaction. This takes the form of 2 major categories of alteration. The Ca-rich alteration, is dominated by actinolite bearing assemblages. Preliminary whole rock chemistry suggest that the introduction of Ca and Mg and the depletion of Ba by way of fluids of  $\sim 250^\circ\text{C}$ . It forms a strata bound zone proximal to the mineralisation, most prominently developed in the hanging wall. This is suggestive of lateral fluid flow rather than from the immediate footwall through the more permeable parts of the volcanoclastic unit. The isotopic composition indicates the fluids involved were likely to be of enriched

character, consistent with interaction with evaporitic rocks documented from Lower Cambrian carbonate sequences in the region (Samani, 1993).

The other type of alteration is characterised by secondary K-feldspar development, which is pervasively developed through the more permeable part of the CVSU. Preliminary whole rock chemistry suggests the introduction of K and Rb and depletion of Na. The more distal distribution suggests a low temperature regime. Barton and Johnson (2000) suggest that this is typical product of diagenetic loss of K from alkaline saline circulating fluids through continental felsic volcanic sequences. This is exemplified by widespread adularia development in ash flows as documented by Hollocher *et al.* (1994) where temperatures of 150-200 °C are inferred on the basis of isotopic data, in response to district scale fluid circulation.

The presence of exotic blocks of sericitic-rich alteration together with various mineralised clasts in the host volcanoclastic unit may indicate the disruption and sedimentation of the upper part of a shallow hydrothermal system during the widespread brecciation episodes.

## **8.5 POTENTIAL Fe–P SOURCES**

There is general acceptance in the literature that the close spatial and temporal association of Fe-oxide-P deposits with igneous rocks is consistent with magma as the direct or indirect source of the Fe and P. There has, however, been a continuing debate (e.g. Naslund *et al.*, 2002) over magmatic separation models versus hydrothermal models to explain the origin of Kiruna-type magnetite–apatite deposits. Uncertainties exist as to the ability of such magmatic models to explain the generation and separation of oxide and silicate melts during the formation of the ore and the role of any associated fluids. At Esfordi a multi-stage mineral paragenesis has produced a range of mineralisation styles including massive breccia, open-space fill, overprinting veins and pervasive replacement.

Mineralogical and textural observations, together with fluid inclusion and stable isotope studies, provide a basis for further assessment of the role of such fluids in the formation of the P–Fe-oxide mineralisation at Esfordi. A comparison with somewhat similar documented deposits and models for their evolution, particularly the source of Fe and P is thus pertinent.

Massive anorthosites host numerous nelsonite bodies (Kolker, 1982; Force, 1991; Owens and Dymek, 1992; McLelland *et al.*, 2001). Some nelsonite bodies occur at or close to anorthosite-granitoid contacts, and an origin through mixing of mafic-felsic magmas is suggested by Clark and Kontak (2004).

In reviewing the experimental and other evidence for immiscibility of silicate melts and Fe-oxide melts into which P is strongly partitioned, Clark and Kontak (2004) identified significant uncertainty as to the degree to which fractional crystallization influences the melt composition prior to immiscibility. Based on the presence of Fe–P rich and silica-poor melt inclusions of variable, but broadly nelsonitic, composition, in the Antauta subvolcanic centre in Peru, Clark and Kontak (2004) concluded that such immiscibility is not the product of Fe enrichment in the residual liquids of a fractionating basaltic magma (as originally suggested by Philpotts, 1967), but the direct result of commingling and mixing of partially crystallised basaltic and/or andesitic and peraluminous rhyodacitic and/or monzogranitic magmas. In similar vein, Matthews *et al.* (1994) interpreted the presence of heterogenous pumice in the Holocene Soncor flow of northern Chile, as the product of the periodic incursion of moderately reduced basaltic-andesitic magma into a chamber of strongly oxidised dacitic magma. Cooling of the hybridizing mafic melt under conditions of increasing O fugacity was envisaged to have driven its composition into a two-liquid field, resulting in the segregation of immiscible melt droplets with up to 80 % FeO<sub>total</sub> and only 2.9 wt % SiO<sub>2</sub>.

In shoshonitic andesite in the Antauta area, Clark and Kontak (2004) observed a series of immiscible mafic globules containing a wide range of compositions – from 25-90 wt %  $\text{Fe}_2\text{O}_3 + \text{MnO} + \text{TiO}_2 + \text{CaO} + \text{P}_2\text{O}_5$ . Such a compositional range was considerably wider than that suggested by Philpotts (1982) might be expected for such immiscible globules. Clark and Kontak (2004) recognised three groups of globules on the basis of their  $\text{P}_2\text{O}_5$  content, ~2 %, 5-13 % and 21 %, and suggested that this difference in composition may be the result of various factors such as (i) depletion of mesostasis melt in the mafic component by nucleation and growth of the metal-rich globules, (ii) varying role of Ti and P to expand the field of immiscibility, (iii) internal heterogeneity of spheres by subsolidus re-equilibration, (iv) decrease in pressure (e.g. subvolcanic magma chamber) causing constriction of the immiscibility field, (v) the effect of oxygen fugacity changes and finally (vi) the influence of equilibration with vapour phase(s) on the original melt composition.

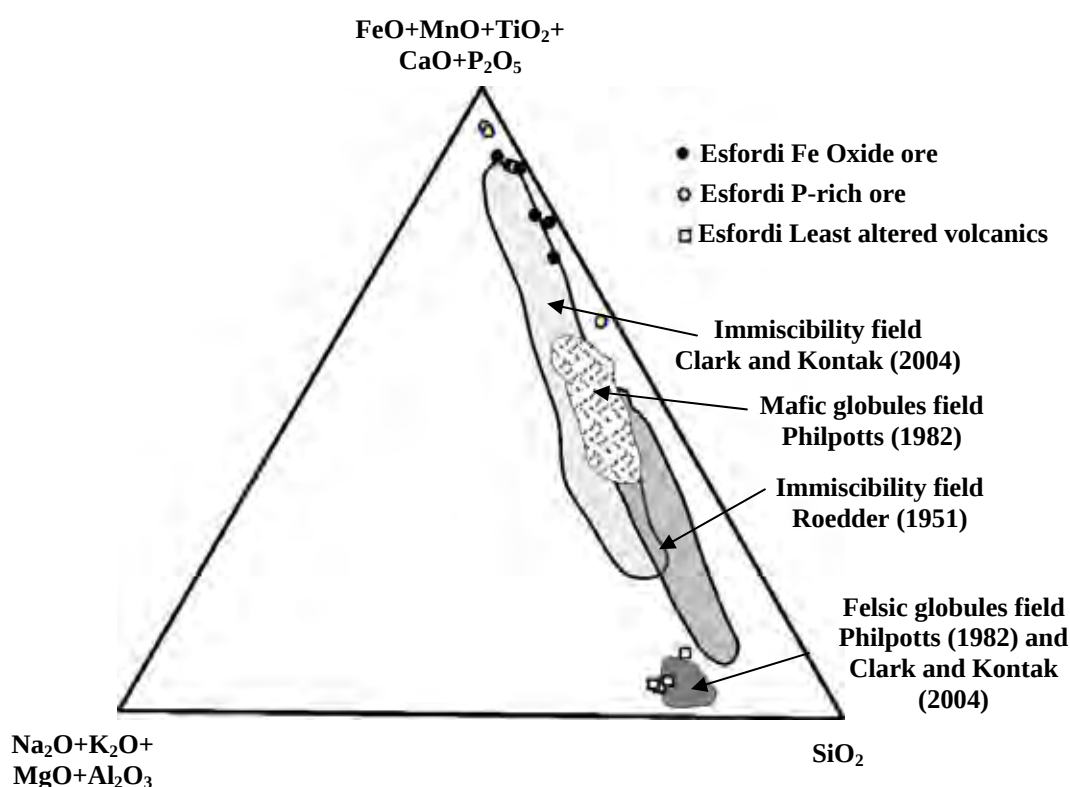
In supporting a magmatic origin, Förster and Jafarzadeh (1994) emphasised the presence of various mesoscopic and microscopic features in a number of Fe-oxide-P deposits in the Bafq district, such as layering, columnar structures and dendritic magnetite, as typical products of melt flow and quenching. Such features are also reported in the Kiruna and El Laco Fe-oxide±apatite deposits by Harlov *et al.* (2002) and Naslund *et al.* (2002), who consider the mineralisation to be the product of direct crystallization from immiscible oxide melts. A common problem with development of magmatic origin models for these deposits, including evidence derived from the mapping of field relationships, has been the subsequent masking effects on key features of hydrothermal alteration. This may be induced by the apparent volatile-rich of magmas associated with these deposits.

Förster and Jafarzadeh (1994) interpreted the pipe-like bodies of massive and brecciated magnetite-dominant mineralisation, within larger heterogenous breccia systems in the Bafq district, to be diatremes and considered the observed effects of hydrothermal

activity to be largely post mineralisation and not significant in the genesis of the deposits. Columnar magnetite or distinctive magmatic flow textures are not, however, recognised at Esfordi. The only feature at Esfordi similar to dendritic magnetite is the remnant patches of intergrowth of stage 1 apatite with magnetite within the Fe-oxide core of the deposit, although field relationships, primary textures and geochemical relationships related to magmatic processes may have been obscured by subsequent hydrothermal fluid activity. Pervasive brecciation in the Fe-oxide core, the P-rich zones and wallrocks at Esfordi is readily apparent, but the close spatial association between liquid and vapour-dominated inclusions in apatites 1 and 2, is more consistent with the shallow boiling of hydrothermal fluids rather than known magmatic processes.

Though there is no direct evidence of an immiscible Fe–P rich liquid at Esfordi, the bimodal character to the volcanism at Esfordi and the syn- intrusive character to mafic bodies in the Narigan Granite provide a scenario where the immiscible Fe-oxide rich melt model of Clark and Kontak (2004), may be plausible in the Bafq region. The metaluminous and peraluminous character of granitic intrusions and associated rhyolitic bodies and the high K content of the mafic bodies are also similar to Antauta. The composition of analysed samples of P and Fe-oxide rich mineralisation and least altered volcanic host rocks at Esfordi plotted on the  $\text{FeO}+\text{MnO}+\text{TiO}_2+\text{CaO}+\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{MgO}+\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  system of Philpotts (1982) overlap with the Antauta data of Clark and Kontak (2004). Daliran (1990) also noted bimodal character of magmatism at the nearby Mishdovan deposit.

In contrast the formation temperature of apatite 1 and 2 are far lower than a magmatic liquid system, based on fluid inclusion studies, although the interaction of dispersed immiscible melt droplets with hydrothermal fluids in a subsurface magma chamber could have produces fluids of the character similar to those detected at Esfordi inclusions.



**Figure 8. 4 Composition of Esfordi Fe-oxide and P-rich mineralisation and least altered volcanics in relation to immiscibility fields of Philpotts (1982) and data from Clark and Kontak (2004).**

A direct role for a primary oxide magmatic melt at Esfordi cannot be precluded on the basis of  $\delta^{18}\text{O}$  data alone, as the values overlap with the general range for magnetites in granites and felsic volcanics (Sheppard, 1981). Despite a similar overlap at the El Laco deposit, Rhodes and Oreskes (1999) proposed a hydrothermal origin for mineralisation based on the similarity between  $\delta^{18}\text{O}$  contents for magnetites displaying fabrics interpreted as magmatic (Frutos and Oyarzun, 1975; Nystrom and Henriquez, 1994) and magnetites displaying field relationships and textures consistent with hydrothermal fluid deposition. The uniformity of magnetite  $\delta^{18}\text{O}$  values within the various styles of mineralisation at Esfordi could be similarly interpreted.

Igneous rocks as sources of Fe and P by way of leaching by hydrothermal fluids from completely solidified rocks of more mafic type is a theme most recently proposed by

Menard (1995) for El Algarrobo Fe deposit, in the Atacama region of Chile. In that district largely using whole rock geochemical analyses and inference from mineralogical data, Menard (1995) recognised five facies within the system, including extensive zones of Fe depletion within dioritic rocks associated with the breakdown of pyroxene, amphibole and magnetite leaving behind assemblages dominated by albite, sphene and rutile. Adjacent zones containing significant magnetite–hematite-actinolite and apatite were considered to sites for deposition from fluids in response to temperature and  $fO_2$  gradients. The widespread development of such Fe depleted rocks has not been observed at Esfordi, nor reported in the Bafq district.

Investigation of calcsilicate alteration systems in NW Queensland and modelling the formation of extensive albitic zones by fluids from two-feldspar granites demonstrate hydrothermal interaction with such igneous rocks can contribute to the formation of Fe-oxide–apatite–actinolite bearing assemblages (Oliver *et al.*, 2004). Extensive zones of secondary albite, however, are not a feature of Esfordi alteration patterns.

## **8.6 ASSOCIATION BETWEEN ESFORDI AND RELATED BAFQ DISTRICT DEPOSITS**

The stratabound lens of Fe-oxides with apatite-rich facies at Esfordi is a P-rich end-member in the range of magnetite–apatite deposits in the Bafq district. The nature and role of fluids in the formation of the Esfordi apatite–magnetite can be considered in terms of previous studies on Kiruna-type apatite deposits in the Bafq district.

Two broad deposit groupings may be made, based on the style of mineralisation, the geometry in relation to host rocks and mineralogy (Daliran, 2002). The first group takes the form of concordant lenses of P-poor Fe-oxides with gradational boundaries, interpreted as the product of precipitation from fluid discharged onto the sea floor, and is exemplified by Mishdovan. Similarly at Esfordi this discharge may have been sub-seafloor and involved mixtures of fluids that had interacted with basement rocks of the Chapedony and

Posht-e-Badam Complexes, fluids derived from underlying igneous rocks during cooling, and fluids derived from interbedded evaporate-bearing portions of the Saghand Formation without a significant seawater component. The second and more common of Daliran's classes, are the massive bodies of apatite-magnetite  $\pm$  hematite with apatite-rich zones as exemplified by Choghart, Sechahoon, Chador Malu and Esfordi. The geometry of these bodies is more variable in relation to the host volcanic and epiclastic rocks.

Discordant, massive magnetite bodies such as Choghart, Chah-Gaz and Chador Malu were classified by Förster and Jafarzadeh (1994) as the product of vent activity in ring grabens surrounding ignimbritic cauldrons. Based on extensive brecciation, they suggested these funnel-shaped bodies were created by a high velocity gas stream and filled with agglomerated intrusive breccia and tuff, subvolcanic intrusive rocks and xenoliths of country rock. Ore textures and other features along the periphery of the apatite-rich zones at Choghart indicate a complex history of deformation and crystallization comparable with those at Esfordi (Daliran, 2002). These discordant ore bodies include magnetic anomaly XIV (comprising 30 steeply-dipping ore bodies) and anomaly XIII from within a 2 km x 6 km area in the middle part of the Bafq - Posht-e-Badam district.

The discordant magnetite bodies were considered by Daliran (2002) to be the product of epigenetic replacement, whereas Förster and Jafarzadeh (1994) considered them the product of crystallization from an immiscible Fe  $\pm$  P melt differentiated from an upper mantle melanephelinitic magma.

Based on evidence at Esfordi, the origin of the breccia bodies is best explained as the result of depositional episodes associated with boiling of isotopically enriched fluids under shallow marine conditions. This is consistent with either of the genetic models (syngenetic submarine hydrothermal and epigenetic replacement) for Fe deposits in the region proposed by Daliran (2002), including those at Mishdovan, Choghart, Chador Malu, the North Anomaly and Esfordi. The broadly conformable geometry of the main

mineralised body with the surrounding volcano-sedimentary sequence, as well as the existence of detrital grains and blocks of magnetite in the tuffaceous sandstones and jaspilitic layers adjacent to and overlying the apatite-rich ore, are also consistent with a syngenetic submarine mineralisation model. These magnetites are associated with relatively small amounts of apatite, implying formation and exposure of the core magnetite mineralisation and associated stage 1 apatite during sedimentation.

The peripheral vein-style mineralisation, containing hematite, stage 2 apatite  $\pm$  magnetite assemblages, together with well-developed hydrothermal alteration zones in the immediately overlying sediments and volcanics, is more consistent with the epigenetic replacement style of mineralisation. The alteration assemblages, dominated by actinolite  $\pm$  clinopyroxene  $\pm$  garnet, are temporally and spatially closely associated with mineralisation dominated by stage 2 apatite, although actinolite-rich lithic clasts are mixed with clasts of the magnetite typically associated with stage 1 apatite. Such calcic assemblages are commonly associated with magnetite–apatite mineralised systems, although the alteration fluids and Ca may be post-mineralisation and derived from sources such as the evaporites that are commonly present in the vicinity of Kiruna-type deposits (Barton and Johnson, 2000). The final overprint by epidote–chlorite alteration displays no obvious spatial link to the late stage carbonate–quartz–stage 3 apatite assemblages.

Jaspilites are associated with almost all Bafq district magnetite–apatite deposits (Förster and Jafarzadeh, 1994) and signal the waning stages of hydrothermal activity in such deposits. In the immediate vicinity of the Esfordi mineralisation, the jaspilite horizon and overlying volcano-sedimentary units are disrupted. The 200m-wide halo of amphibole-rich alteration associated with stage 2 of the Esfordi mineralisation is less intense above this jaspilitic layer.

## 8.7 EVOLUTION OF THE ESFORDI Fe–P OXIDE DEPOSIT

Based on the results of the current study and a comparison of results with previous studies, a relatively simple, four-stage model for the evolution of the Esfordi Fe–P oxide deposit is proposed. The initial stages in the generation of the Fe–P oxide body have not been considered in detail by this study (and hence are largely speculative), however this investigation has provided a basis to evaluate the role of fluids in the subsequent evolution of the Esfordi Fe–P oxide system.

### *Stage 1*

The Esfordi deposit commenced forming in a shallow marine, bimodal volcanic setting within a continental margin tectonic regime. The proto Fe–P oxide body was generated during emplacement of rhyolitic and rhyodacitic ash flows and domes. A prominent role is ascribed to P and Fe-oxide rich liquids formed in response to the mingling of rhyolitic and basaltic silicate liquids. This may have involved segregation of immiscible Fe–P oxide rich droplets, subsequent extrusion and equilibration with fluids near 400°C (a temperature based on the isotope and fluid inclusion data). An alternative process could have involved interaction of immiscible Fe–P oxide rich blebs with fluids at submagmatic temperatures to generate Fe–P rich fluids. Deposition of Fe-oxide and apatite then occurred at, or near, the sea floor in response to cooling and mixing with shallow circulating fluids near 400°C.

### *Stage 2*

Continued circulation of fluids, through a proto Fe–P oxide body shallowly encased in permeable volcanoclastic sediments, produced amphibole-rich alteration and the sealing of the host rocks. A build-up of fluid pressure and subsequent mechanical failure produced widespread brecciation, unroofing of the system, boiling of fluids at or near 250°C and deposition of stage 2 apatite, hematite and actinolite.

### *Stage 3*

Continued volcanoclastic sedimentation, and circulation of magmatic, connate, and sea waters, caused significant dissolution and precipitation of P and Fe-oxide minerals. The granular apatite occurred as the result of dissolution of apatite 1 and 2. Continuing reaction between fluids and wall rock produced the overlying amphibole-rich alteration which mainly developed in the porous, pebbly sandstone.

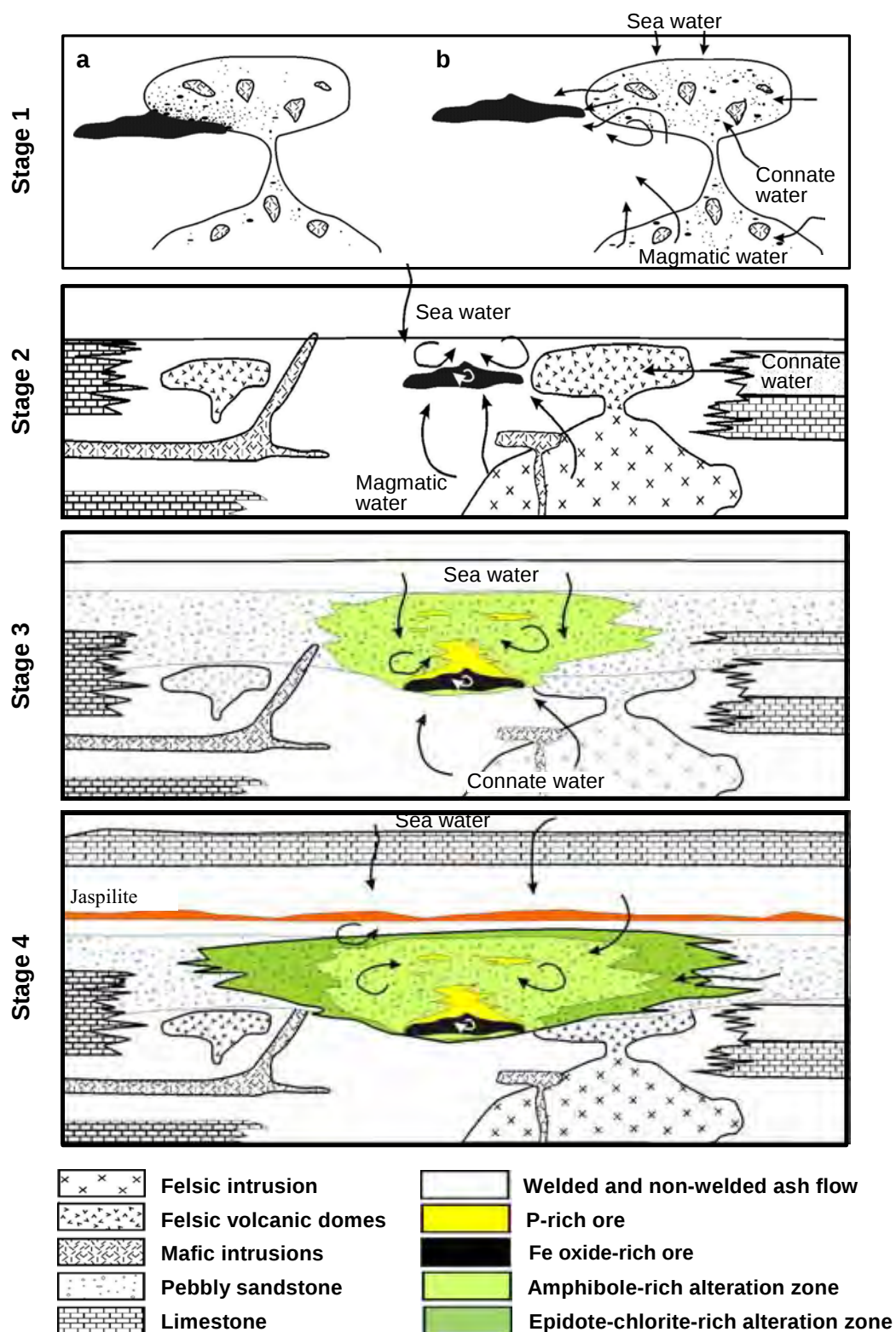
Veins and lenses of Fe–P oxide developed in the porous hanging wall sandstone, which was associated with extensive martitization of the precursor magnetites. Diluted solutions discharged onto the sea floor and produced a thin jaspilite layer.

### *Stage 4*

The circulation of cooler and more dilute solutions of sea water of meteoric character near 100-150 °C produced continued dissolution of apatite 1 and 2 and deposition of carbonate and quartz. The earlier amphibole bearing mineralisation and wall rocks were overprinted by chlorite, epidote, carbonate and sparse sulphides.

Fig 8.6 presents the distribution of the P–Fe ore and the main volcanoclastic and sedimentary package of host rock. As this figure shows the mineralisation is almost restricted to the volcanoclastic suit of lower hanging wall sequence (Chapter 3). Based on field and petrographic evidences these rocks are mainly consists of pebbly sandstone with intercalations of limestone, mafic rocks and jaspilite. These rocks exhibit the highest degree of K and Ca alteration due to their high porosity and permeability, which allow the fluids to penetrate and circulate. Fig 8.6a&b show the extension of the massive Fe-oxide ore body and high grade and low grade apatite ore of the Esfordi mineralizing system. Both ore zones are extended into the hanging wall porous altered volcanoclastic rocks with more development for apatite veins and patches (low grade P ore). Carbonates also occur on both sides of mineralisation in almost the same stratigraphic horizon. This suggests that

carbonates probably played an important role in evolution of the system and ore deposition such as suppressing fluid acidity and supplying Ca to the system.



**Figure 8.5** Schematic four-stage model of the proposed evolution of the Esfordi Fe–P oxide system.

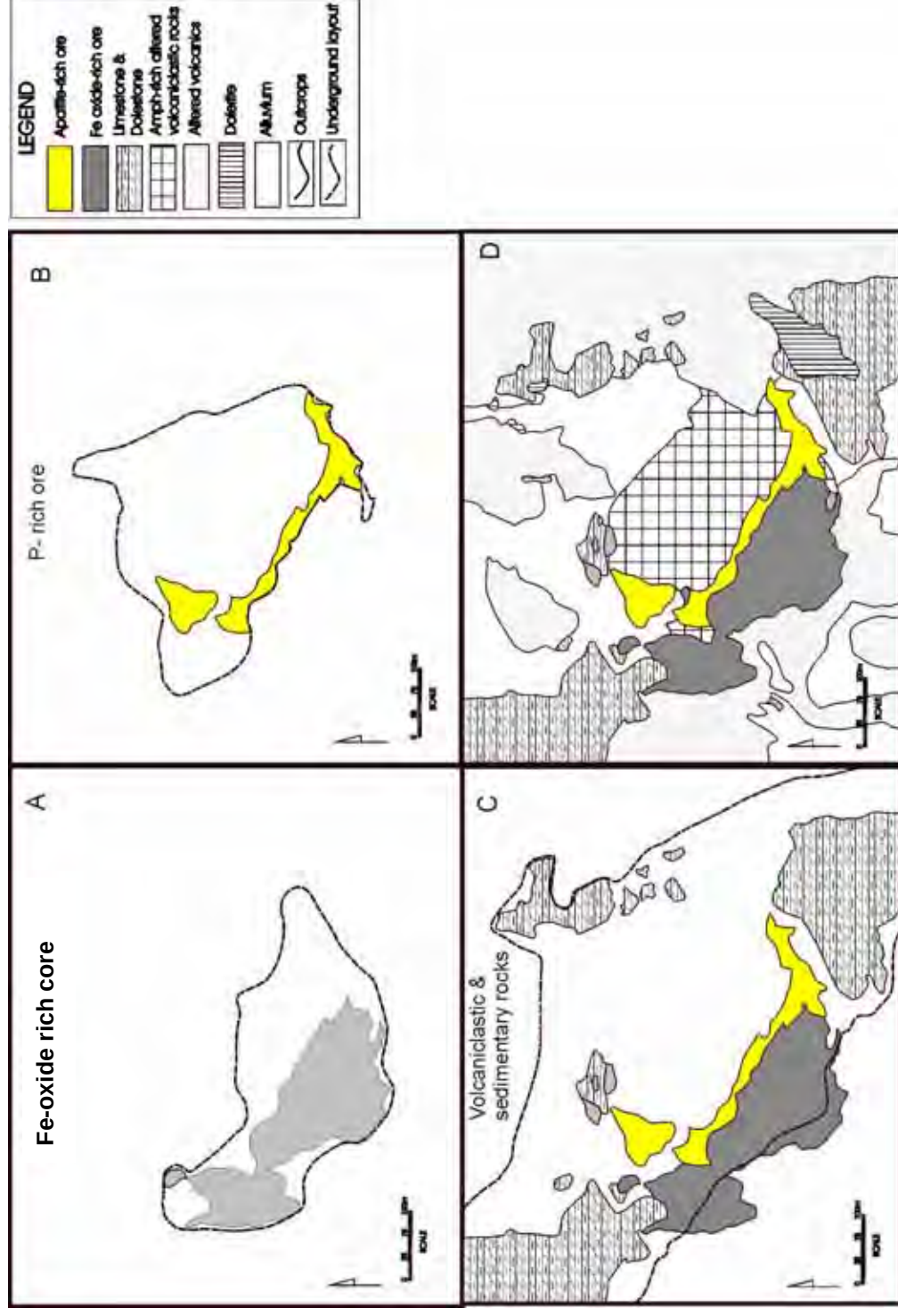


Figure 8. 6 Spatial distribution of ore and host rocks of Esfordi. A: Out crop and projection of Fe-oxide rich core, B: Out crop and projection of P-rich zone, C: Out crops and projection of volcaniclastic and sedimentary rocks, D: Amphibole-rich alteration, felsic and mafic volcanic rocks.

## 8.8 CONCLUSION

The Esfordi Fe–P mineralised system displays substantial similarities with other Kiruna-type Fe-oxide deposits worldwide. It consists of three distinctive ore zones including a stratabound lensoid magnetite-rich core, overlying P-rich ore and low grade P ore associated with an altered sedimentary host rock. Low-permeability welded ash flows form the base to the mineralisation.

Despite the presence of sparse sulphides and the immobile element geochemical patterns, the Esfordi deposit clearly belongs to the Fe-oxide+P-rich end rather than the Fe-oxide–Cu(–Au) end of the Fe-oxide deposit association identified by Hitzman (1992, 2000). The Esfordi system is regionally and locally associated with bimodal magmatism with volcanic arc signature.

Data presented in this study is consistent with the formation of the Esfordi deposit in an evolving hydrothermal system, in a shallow marine volcanic setting, with fluids involved from diverse sources, rather than the deposit being the direct result of quenching of a Fe-oxide+P-rich magmatic melt. The role of fluid interaction with immiscible Fe–P melts in the ultimate derivation of the Fe and P is plausible in the light of the Clark and Kontak (2004) magma mingling model. There is, however, no direct evidence presented by this study to support the Clark and Kontak model. Observations of mineralisation and host rocks at Esfordi reveal a well-developed paragenetic sequence, within a stratabound Fe–P system. A magnetite-rich core to the system, associated with an overlying and peripheral apatite – hematite-rich breccia, has developed within a sequence of carbonate-rich, shallow water sediments and rhyolitic volcanics, which have been subject to intense hydrothermal activity. Rhyolitic pyroclastic and epiclastic units in particular, have been subjected to pervasive K-alteration, whereas assemblages dominated by Ca amphibole are mainly developed proximal to the magnetite–apatite mineralisation. Sericite-rich

alteration observed in breccia clasts and exotic fragments suggesting an overlying sericite-rich alteration zone which brecciated and redeposited with overlying sandstone. The late carbonate-quartz and chlorite-epidote alteration overprints both mineralisation and host rocks and is pervasive through the Bafq region.

Fluid inclusions and stable isotopes at Esfordi, linked to mineral paragenesis observed in textural and field relationships and other geochemical patterns, suggest three different fluid events which range from an early moderately hot and saline stage through progressive cooling and eventual dilution. The earliest paragenetic stage of massive and brecciated magnetite  $\pm$  apatite has associated fluids indicating emplacement at  $\sim 400^{\circ}\text{C}$  as indicated by  $\delta^{18}\text{O}$  values. Such fluids may be of magmatic origin associated with the Narigan Granite or rhyolites of the Saghand Formation, or have exchanged with the underlying metamorphic basement.

The pervasive brecciation associated with large parts of the mineralisation in the hanging wall and the presence of ore material in the overlying sandstone indicates release of pressure from a shallow system. Clasts of magnetite and Ca-rich amphibole in the overlying sandstones are most likely related to mechanical reworking of sea floor accumulations or rapid exhumation of a shallowly buried system.

The paragenetic stage most closely associated with the stratabound breccia zone ore, dominated by apatite–hematite with variable amounts of amphibole and carbonate, is associated with shallow boiling episodes and temperatures ( $\sim 250^{\circ}\text{C}$ ). A source for such a fluid of somewhat enriched isotopic composition could be achieved by mixing the waning original magmatic fluid with more strongly enriched fluids from the underlying and adjacent evaporate-bearing carbonates of the Saghand Formation. Hydrothermal mineralisation and alteration of this shallowly buried magnetite–apatite system continued without significant sea water involvement until the final stages of evolution. The extent to which the main apatite ore body represents a separate introduction of more P-rich fluids or

represents mobilisation of earlier deposited constituents requires further investigation. The dissolution of REE-rich apatite 1 and 2 and the development of REE-poor granular apatite domains with associated REE minerals is clearly related to significant redistribution of P during the brecciation stage. The overlying jaspilite unit, which has less stratigraphic coherence proximal to the Esfordi mineralised system as compared with distal locations, may represent exhalation from the P ore body evolving by sub-seafloor replacement at shallow depth. The jaspilite layer, with its volcanogenic ironstone signature, suggests the ore bearing solutions reached the sea floor. The final, low-temperature (100 to 150°C) paragenetic stage, involving quartz-carbonate±amphibole ±apatite, was associated with fluids that were probably derived from seawater. The isotopic and petrographic evidences suggest that the sparse sulphides are the result of a later hydrothermal event and were largely formed after the formation of the Esfordi P–Fe-oxide bodies.

An important role for composite fluid sources at Esfordi as suggested by Barton and Johnson (2000) for other Fe-oxide deposits is envisaged. These evolving fluids suggest contributions from fluids involved in basement interaction, crystallisation of felsic melts, interaction with interbedded evaporite sequences and sea water. As with other Kiruna-type magnetite–apatite deposits, the Esfordi deposit records the effects of progressive interactions with a range of fluids typical of an arc tectonic regime and which delivers to such deposit types many of their distinctive characteristics.

## 8.9 FUTURE STUDIES

The current investigation represents the first comprehensive investigation of the Esfordi mineralisation. It has been broad in scope and there are various aspects that would benefit from extensions to the study:

- Clarification of the Esfordi district geological setting. This could involve systematic geological mapping to elucidate the volcanic architecture and its relationship to the intercalating sediment packages. In particular, attention could focus on the evidence of magma mixing and generation of Fe–P oxide rich melt inclusions in small intrusive bodies of felsic or more mafic character, where textural evidence was preserved by chilling and where hydrothermal alteration is less pervasive.
- Further investigation of the apatites at Esfordi could include determination of the patterns of O and H isotopes to complement the data for magnetite and hematite. Determination of the full range of REE in the different paragenetic stages, by methods such as laser ablation ICP-MS, is required to quantify REE fractionation trends during the evolution of the apatite-Fe-oxide body with transient fluids.
- Determination of the ages of the mineralisation stages, by Ar-Ar dating of biotites and amphiboles and U-Pb dating of monazites from different paragenetic stages (and compared with U-Pb zircon ages determined by Ramezani and Tucker, 2003).
- More extended examination of the nature of the fluids involved in the evolution of the various paragenetic stages of the mineralisation at Esfordi by the direct chemical determination of fluid inclusions by Raman spectroscopy and other techniques.
- A wider ranging comparative study of the textures, geochemistry and alteration assemblages in P-rich facies of more thoroughly documented Fe-oxide–apatite systems in the region, such as Chador Malu, Choghart and Sechahoon.
- Systematic evaluation of the distribution of the Cl content of apatites in relation to paragenetic stages and their spatial distribution, to improve mine operational procedures designed to meet product specifications by apatite concentrate users.

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Host rocks

| No   | Lithology | Spatial position                                                                      | Mineralogy                                    |
|------|-----------|---------------------------------------------------------------------------------------|-----------------------------------------------|
| 103  | Dolerite  | Doleritic dyke 100 m SE of Esfordi mineralisation                                     | Plg, Pyx, Amp, ser, Bio, epi?, Chl.           |
| 24   | Dolerite  | Large dolerite dike 50 m SE. of Esfordi Fe oxide core near road                       | Amph, Bio, Plg, Ap, Ser, Chl, Fe-oxide, Carb. |
| 28-2 | Dolerite  | Large dolerite dike 100 m E. of Esfordi core, sample from the middle part of the dike | Amph, Bio, Plg, K-feld, Carbonate, Apatite    |
| 90   | Dolerite  | Narigan doleritic dike, 15 km SE of Esfordi                                           |                                               |

| No       | Lithology            | Spatial position                                                    | Mineralogy                                            |
|----------|----------------------|---------------------------------------------------------------------|-------------------------------------------------------|
| 89-1     | Narigan Granite      | 10 km South of Esfordi                                              | Plg, K-feld, Qtz, Serisite                            |
| 93       | Narigan rhyolite     | 15 km South of Esfordi                                              |                                                       |
| NG       | Narigan granite      | Narigan granite close to middle of the stock, 8 km South of Esfordi | K-feld., plg., Qtz, Bio, Ser, Ap., Sph.               |
| 91-2     | Narigan rhyolite     |                                                                     | Embedded Qtz, Plg, K-feld, Chl, Ser, (Sph or rutile?) |
| 85       | Mishdowan granite    | Mishdowan granite, 3 Km NW of Esfordi                               | Plg, K-feld, Qtz, Ser, Zircon/Sph                     |
| RT3      | Rhyolite             | Rhyolite 150 m NE of Esfordi Fe oxide core                          | K-feld., plg., Qtz, Carbonate veins                   |
| 31       | Rhyolite             | Rhyolite 500 m E. of Esfordi core                                   | K-feld., plg., Qtz, Carbonate veins                   |
| 105      | Rhyolite             | Esfordi Rhyolite(Gardaneh), 100 m SE of Esfordi Fe oxide core       | K-feld., plg., Qtz, Carb.                             |
| Bh7-41   | Rhyolite             | Esfordi apatite-rich ore hanging wall (feldspar-rich alt.?)         | Qtz, K-feld, Ser, Chl, Carbonate                      |
| B2-110   | Rhyolite             | Rhyolitic lava, footwall of Esfordi orebody                         | Qtz, K-feld, Ser, Chl, Bio.                           |
| B12-97   | Rhyolite             | K-feld rich altered zone                                            | Qtz, K-feld, bio, ser, carb.                          |
| B64-108  | Rhyolite             | K-feld rich altered zone                                            | K-feld, qtz, Bio, Ser, Carb, (Ap or Sph?)             |
| Bh4-71   | Ash flow             | Hangingwall                                                         | Qtz, Ser, K-feld, Carb.                               |
| B20-75   | Ash flow             | Footwall                                                            | Qtz, Ser, K-feld, Carb.                               |
| 23       | Syenite              | 1.5 Km North of Esfordi                                             | K-feld., plg., amph., Ser.                            |
| 82       | Trachyte             | About 3 Km W. of Esfordi along Bafq road                            | K-feld., plg., Ser, Ep.                               |
| Bh8-65   | Trachyte             | Porphyry rhyolite(lava), 30 m below apatite ore                     | K-feld., plg., Ser, Fe-oxide, Carb.                   |
| Bh10-82  | Trachite             | Footwall, 3-15 m below ore                                          | Plg, Bio, Amph, carb.                                 |
| Bh11-54  | Pebbly Sandstone     | Amph-rich altered sandstone                                         |                                                       |
| B1-13    | Pebbly Sandstone     | Amph-rich altered sandstone                                         |                                                       |
| Bh1-68   | Pebbly Sandstone     | Amph-rich altered sandstone                                         |                                                       |
| B2-134.5 | Calcareous Sandstone | Footwall sandstone with dolomitic intercalations                    |                                                       |
| B2-135   | Limestone            | Silty and sandy limestone                                           |                                                       |
| B2-149   | Limestone            | Limestone with tuffaceous                                           |                                                       |

|              |                            |                                                                 |                                                                      |
|--------------|----------------------------|-----------------------------------------------------------------|----------------------------------------------------------------------|
|              |                            | intercalations, Footwall                                        |                                                                      |
| B3-48        | Pebbly Sandstone           | Amph-rich altered sandstone                                     |                                                                      |
| B4-4         | Pebbly Sandstone           | Amph-rich altered sandstone                                     |                                                                      |
| B9-99        | Pebbly Sandstone           | Amph-rich altered sandstone                                     |                                                                      |
| B12-68       | Pebbly Sandstone           | Amph-rich altered sandstone                                     |                                                                      |
| B64-75       | Pebbly Sandstone           | Amph-rich altered sandstone                                     |                                                                      |
| B20-2        | Altered rhyolite/trachyte? | Amphibole-rich alteration zone, Hanging wall of ap-rich ore     | Amph, K-feld, Bio., Mon?, Zircon?                                    |
| B53-28       | Alt. rhyolite              | Altered volcanic rhyolite; footwall of the Fe-oxide orebody     | Amph, Bio, K-feld, Fe-oxide, Carbonate, Qtz                          |
| B53-41.5     | Amph. Rich rock            | Amph-rich alt., footwall of the Fe-oxide orebody                | Amph, K-feld, Qtz, ser, Carb., Bio.                                  |
| Gr-ac-1      | Amph. Rich rock            | Highly altered rhyolite (Green rock ), Ap-rich ore hanging wall | Amp., chl, K-feld, scapo, serisite, garnet, talc, muscovite, epidote |
| Gr-2         | Amph. Rich rock            | Highly altered rhyolite (Green rock ), Ap-rich ore hanging wall | Amph, K-feld, Chl, Talc, Epi                                         |
| Gr           | Amph. Rich rock            | Highly altered rhyolite (Green rock ), Ap-rich ore hanging wall | Amph, chl, talc, K-feld., Epi                                        |
| B70-15 & 16  | Amph. Rich rock            | Highly altered rhyolite (Green rock ), Ap-rich ore hanging wall | Amph, Epi, Chl, Feld., patches & veins of Fe-oxide+ap+REM            |
| Bh12-14 & 25 | Alt. rhyolitic tuff        | Amph. rich alt. tuff; ap-rich ore hanging wall                  | Amph., Chl., Qtz, ser., bio, Carb.                                   |
| B2-140       | Tufaceous sandstone        | Footwall of the Esfordi orebody                                 | Qtz, tourmaline, Ser, Chl, Amph, Carb.                               |
| B32-111.5    | Tufaceous sandstone        | Footwall of the Esfordi orebody                                 | Otz, Plg, K-feld, Amph, Carbonate, pyrite                            |

#### Ore samples

|          |                        |                                        |                                                         |
|----------|------------------------|----------------------------------------|---------------------------------------------------------|
| B1-12    | Mag-ap core margin     | Main Fe oxide orebody                  | Mag, Hem, Ap1, Ap2, Ann. Ap, Carb, Qtz, Ser, Amp.       |
| B20-43   | Mag.-ap core           | Main Fe oxide orebody                  | Mag, Hem, Ap1, Ap2, Ann. Ap, Carb, Qtz, Mon1, Syn.      |
| B21-43.5 | Mag.-ap core           | Massive magnetite with apatite patches | Mag, Hem, Ap1, Gran. Ap, Carb, Qtz, Mon1.               |
| B27-38   | Mag.-ap core           | Main Fe oxide orebody                  | Mag, Hem, Ap1, Ap2, Ann. Ap, Carb, Qtz.                 |
| R3       | Mag.-ap core           | Main Fe oxide orebody                  | Mag, Hem, Ap1, Ann. Ap, Carb, Qtz.                      |
| B34-10.7 | Mag-ap core margin     | Main Fe oxide orebody                  | Mag, Hem, Ap1, Ap2, Ann. Ap, Carb, Qtz, Ser, Amp.       |
| B38-12   | Mag.-ap core           | Massive and brecciated magnetite       | Mag, Hem, Ap1, Gran. Ap, Carb, Qtz, Mon1.               |
| B40      | Mag-ap core margin     | Main Fe oxide orebody                  | Mag, Hem, Ap2, Ann. Ap, Carb, Qtz.                      |
| B27-22   | Mag-ap core margin     | Main Fe oxide-P orebody                | Mag, Hem, Ap1, Ap2, Ann. Ap, Carb, Qtz, Feld, Amp.      |
| 101      | Brecciated core margin | Main Fe oxide-P orebody                | Mag, Hem, Ap1, Ap2, Ann. Ap, Carb, Qtz, Feld, Amp.      |
| B12-65   | Ap ore                 | Brecciated apatite rich ore            | Fe-oxide, Ap1, Ap2, Ann. ap, Mon1&2, Alla1&2, Amp, Ser, |

|                 |                          |                             |                                                                            |
|-----------------|--------------------------|-----------------------------|----------------------------------------------------------------------------|
|                 |                          |                             | Qtz, Carb.                                                                 |
| B12-60 & B12-38 | Apatite rich ore         | Brecciated apatite rich ore | Fe-oxide, Ap1, Ap2, Ann. ap, Mon1&2, Alla1, Amp, Qtz, Carb.                |
| B4-ap           | Apatite rich ore         | Brecciated apatite rich ore |                                                                            |
| B8-ap           | Apatite rich ore         | Main ap rich zone           | Ap 1&2, Ann. ap, Mon1&2, alla 1&2, Syn, Amph, Fe-oxide, Qtz, Carb.         |
| Cx-ap           | Apatite rich ore         | Massive apatite ore zone    | Ap2, Ann. Ap, Amp, Mon2, Alla1&2, Syn, Carb.                               |
| B9-1 & 5        | Apatite rich ore         | Massive apatite ore zone    | Ap 1&2, mon1&2, monazite, allanite, synchysite, Amph, Fe-oxide, Qtz, Carb. |
| B7-14 & 22      | Apatite rich ore         | Massive apatite ore zone    | Ap 1&2, Rare earth minerals, Amph, Fe-oxide, Qtz, Carb.                    |
| B12-60          | Apatite rich ore         | Brecciated apatite rich ore | Ap 2, Rare earth minerals Amph, Fe-oxide, Qtz, Carb.                       |
| B12-65          | Apatite rich ore         | Brecciated apatite rich ore | Ap 2, Rare earth minerals Amph, Fe-oxide, Qtz, Carb.                       |
| B3-ap           | Apatite rich ore         | Brecciated apatite rich ore | Ap 2, Rare earth minerals Amph, Fe-oxide, Qtz, Carb.                       |
| B2-42           | Massive apatite          | Brecciated apatite rich ore | Ap 1 & 2, RE minerals, Amph, Fe-oxide, Qtz, Carb.                          |
| B21-38          | Massive apatite          | Brecciated apatite rich ore | Ap 1 & 2, RE minerals, Amph, Fe-oxide, Qtz, Carb.                          |
| 106 & 107       | Apatite rich ore         | Brecciated apatite rich ore | Ap 2, RE minerals, Amph, Fe-oxide, Qtz, Carb.                              |
| 108             | Ap patches in core       | Main mag-ap core            | Ap1, ann. Ap, Moz1, Qtz, Carb.                                             |
| E-ap2-1         | Large apatite crystals   | Brecciated apatite ore      | Apatite 2 large crystal                                                    |
| E-ap2-2         | Large ap. crystals       | Brecciated apatite ore      | Apatite 2 large crystal                                                    |
| A11             | Apatite rich ore         | Brecciated apatite ore      | Ap 2, Gran. apatite, RE minerals, Amph, Fe-oxide, Qtz, Carb.               |
| A6              | Apatite rich ore         | Brecciated apatite ore      | Ap 2, Gran. apatite, RE minerals, Amph, Fe-oxide, Qtz, Carb.               |
| EI1, 2 & 3      | Apatite rich ore         | Brecciated apatite ore      | Ap 2, Gran. apatite, RE minerals, Amph, Fe-oxide, Qtz, Carb.               |
| E64-75          | Altered pebbly sandstone | Hangingwall                 | Amph, Pyx, Scapolite, Fe-oxide, Ser, Talc, Chl, Carb.                      |
| B61-5.5         | Altered pebbly sandstone | Hangingwall                 | Amph, Pyx, Scapolite, Fe-oxide, Ser, Talc, Chl, Carb.                      |

## **Appendix 2:**

# **ANALYTICAL TECHNIQUES AND RESULTS**

Following rock crushing and powder preparation, samples were digested by Milestone ETHOS PLUS with MPR-300 medium pressure rotor using HF and HClO<sub>4</sub>/HNO<sub>3</sub> mixed digestion under pressure in sealed teflon vessels in four steps of 10 minute, 220-240 °C temperature and 1000 W microwave power following the procedure outlined by (Dulski, 1994), and LiBO<sub>2</sub> fusion method.

The major elements were determined by X-ray fluorescence (Philips PW1400 XRF sequential Spectrometer) on fused glass disks prepared from a mixture of rock powder and Li-metaborate. Trace elements (Ba, Nb, Rb, Sr, Y, Zr, Ta, Hf, Ti, REE, Pb, U, Th, K and P) were analysed by ICP-MS ( Perkin Elmer SCIEX ICP Mass Spectrometer ELAN 6100).

The overall precision and accuracy for the trace elements were controlled by analysing 3 external standards (For details see Cotten et al. 1995 , Nath et al. 1997 and Bau et al. 1996 ). Due to large variations in the REE contents of the samples, up to several orders of magnitude, dilution factors of 5000, 50 000 and 500 000 were used, resulting in different detection limits relative to the solid sample. Mineralogical compositions were determined on whole rock powder samples by X-ray diffraction Siemens D5000, supplemented by petrographic observation using optical and electron microscopy.

The quantitative analyses of different apatite phases, rare earth phosphates, silicates, carbonates and oxides and some of the associated silicates and carbonates were obtained using a Cameca SX-50 electron microprobe at the electron microscope unit of the University of New South Wales. The microprobe equipped with four wavelength-dispersive spectrometers (WDS) and an energy dispersion attachment (EDS).

The major elements analysed at a voltage of 15 keV and a beam current of 20 nA. Counting times for peak and background determination were 10-30 and 60 s respectively for major elements (P, O, Si, Fe, Ca, Mg, F, Cl), Th and U.

The REE abundances were established at 20 keV, 100 nA beam current, 3  $\mu$ m beam size. Peak overlap corrections were made for Ce-Sm, Gd-Ce and Gd-La, using correction factors determined from the analysis of single REE standards. To minimize peak interference, La, Ce and Y readings were based on  $L\alpha$ -line emissions, Pr, Nd, Sm, Gd, Dy and Er readings are collected on  $L\beta$ , Th on  $M\alpha$  and U on  $M\beta$ -line emissions.

Table 1. Electron microprobe parameters

| Element | Line       | Standard         | Xtal | T-Pk | T-Bgd+ | T-Bgd- | Slope | DL (wt%) |
|---------|------------|------------------|------|------|--------|--------|-------|----------|
| Al      | K $\alpha$ | Sanidine         | TAP  | 10   | 700    | -      | 1.08  | 0.001    |
| Si      | K $\alpha$ | Augite           | TAP  | 30   | 400    | -      | 1.03  | 0.02     |
| P       | K $\alpha$ | Apatite          | PET  | 10   | 1750   | -      | 1.10  | 0.02     |
| Ca      | K $\alpha$ | Diopside         | PET  | 20   | 500    | 500    | -     | 0.01     |
| Mg      | K $\alpha$ | Diopside         | TAP  | 20   | -      | -      | -     | 0.02     |
| Sr      | K $\alpha$ | Celestite        | PET  | 20   | -      | -      | -     | 0.01     |
| Na      | K $\alpha$ | Albite           | TAP  | 20   | -      | -      | -     | 0.01     |
| K       | K $\alpha$ | Sanidine         | PET  | 20   | -      | -      | -     | 0.01     |
| Fe      | K $\alpha$ | Chromite         | LIF  | 20   | -      | 2700   | 0.85  | 0.03     |
| Ti      | K $\alpha$ | Rutile           | PET  | 20   | -      | -      | -     | 0.01     |
| V       | K $\alpha$ | V metal          |      | 20   | -      | -      | -     | 0.01     |
| Cr      | K $\alpha$ | Chromite         |      | 20   | -      | -      | -     | 0.02     |
| Cl      | K $\alpha$ | Tungtupite       | PET  | 30   | -      | -      | -     | 0.01     |
| F       | K $\alpha$ | Flourite         | PCO  | 30   | -      | -      | -     | 0.014    |
| Y       | L $\alpha$ | Xenotime         | PET  | 20   | -      | 1600   | 0.81  | 0.007    |
| La      | L $\alpha$ | LaF <sub>3</sub> | PET  | 20   | 540    | -      | 1.05  | 0.10     |
| Ce      | L $\alpha$ | CeF <sub>3</sub> | PET  | 20   | 1740   | -      | 1.18  | 0.08     |
| Pr      | L $\beta$  | PrF <sub>3</sub> | LIF  | 30   | -      | 500    | 1.00  | 0.01     |
| Nd      | L $\beta$  | NdF <sub>3</sub> | LIF  | 20   | 1930   | 0.83   | 0.83  | 0.07     |
| Sm      | L $\beta$  | Sm               | LIF  | 30   | 300    | 0.97   | 0.97  | 0.12     |
| Gd      | L $\beta$  | REE1             | LIF  | 30   | 500    | -      | -     | 0.02     |
| Dy      | L $\beta$  | REE4             | LIF  | 40   | 305    | 0.98   | 0.98  | 0.02     |
| Er      | L $\beta$  | REE4             | LIF  | 40   | 850    | 0.95   | 0.95  | 0.02     |
| Th      | M $\alpha$ | ThO <sub>2</sub> | PET  | 40   | 1300   | -      | -     | 0.012    |
| U       | M $\beta$  | UO <sub>2</sub>  | PET  | 150  | 1250   | 0.89   | 0.89  | 0.012    |

The XRD detection limit for trace elements (ppm) are as follows:

|     |     |    |     |    |    |   |     |     |    |     |    |     |    |     |    |
|-----|-----|----|-----|----|----|---|-----|-----|----|-----|----|-----|----|-----|----|
| Sb  | Sn  | Cd | Mo  | Nb | Zr | Y | Sr  | U   | Rb | Th  | Pb | As  | Ga | Zn  | Cu |
| 2.9 | 3.9 | 3  | 1.8 | 1  | 1  | 1 | 0.9 | 2.9 | 1  | 2.8 | 2  | 2.5 | 1  | 1.8 | 2  |

|    |     |     |     |    |
|----|-----|-----|-----|----|
| Ni | Co  | Cr  | V   | Ba |
| 2  | 2.9 | 2.9 | 2.9 | 8  |

Table 2: Electron microprobe analyses of amphiboles associated with pyroxene-garnet-scapolite-albite assemblage

|                          | B12-28     | Gr-7       | Gr-8       | Gr-10      | Gr-12      | Gr-17      | Gr-18      |
|--------------------------|------------|------------|------------|------------|------------|------------|------------|
| SiO2                     | 56.331     | 56.370     | 56.399     | 55.788     | 57.281     | 57.891     | 56.692     |
| TiO2                     | 0.070      | 0.030      | 0.050      | 0.000      | 0.100      | 0.000      | 0.200      |
| Al2O3                    | 0.538      | 1.023      | 0.216      | 0.756      | 0.000      | 0.266      | 0.024      |
| FeO                      | 6.393      | 6.268      | 9.306      | 10.093     | 5.752      | 6.472      | 5.624      |
| MnO                      | 1.210      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| MgO                      | 20.087     | 20.043     | 17.469     | 17.741     | 21.292     | 20.710     | 20.802     |
| CaO                      | 13.157     | 9.831      | 12.733     | 11.593     | 13.332     | 11.736     | 13.551     |
| Na2O                     | 0.136      | 2.258      | 0.264      | 0.232      | 0.066      | 0.261      | 0.146      |
| K2O                      | 0.009      | 0.257      | 0.033      | 0.097      | 0.041      | 0.038      | 0.012      |
| Cr2O3                    | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Total                    | 97.932     | 96.080     | 96.471     | 96.300     | 97.864     | 97.374     | 97.051     |
| Si                       | 0.938      | 0.938      | 0.939      | 0.929      | 0.953      | 0.964      | 0.944      |
| Ti                       | 0.001      | 0.000      | 0.001      | 0.000      | 0.001      | 0.000      | 0.003      |
| Al                       | 0.011      | 0.020      | 0.004      | 0.015      | 0.000      | 0.005      | 0.000      |
| Fe                       | 0.089      | 0.087      | 0.130      | 0.140      | 0.080      | 0.090      | 0.078      |
| Mn                       | 0.017      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Mg                       | 0.498      | 0.497      | 0.433      | 0.440      | 0.528      | 0.514      | 0.516      |
| Ca                       | 0.235      | 0.175      | 0.227      | 0.207      | 0.238      | 0.209      | 0.242      |
| Na                       | 0.004      | 0.073      | 0.009      | 0.007      | 0.002      | 0.008      | 0.005      |
| K                        | 0.000      | 0.005      | 0.001      | 0.002      | 0.001      | 0.001      | 0.000      |
| Cr                       | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| sum13                    | 0.119      | 0.119      | 0.116      | 0.117      | 0.120      | 0.121      | 0.119      |
| fe-kor                   | 22.88      | 22.78      | 23.12      | 22.79      | 22.93      | 22.75      | 23.04      |
| Si ges.                  | 7.846      | 7.903      | 8.100      | 7.920      | 7.930      | 7.965      | 7.960      |
| Si(T1)                   | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      |
| Al ges.                  | 0.088      | 0.169      | 0.037      | 0.127      | 0.000      | 0.043      | 0.004      |
| Al IV                    | 0.154      | 0.097      | -0.100     | 0.080      | 0.070      | 0.035      | 0.040      |
| Al VI                    | -0.066     | 0.072      | 0.137      | 0.047      | -0.070     | 0.008      | -0.036     |
| Ti                       | 0.007      | 0.003      | 0.005      | 0.000      | 0.010      | 0.000      | 0.021      |
| Fe tot                   | 0.745      | 0.735      | 1.118      | 1.198      | 0.666      | 0.745      | 0.660      |
| Fe3+                     | 0.240      | 0.404      | 0.000      | 0.425      | 0.140      | 0.491      | 0.000      |
| Fe2+                     | 0.505      | 0.331      | 1.118      | 0.774      | 0.526      | 0.253      | 0.660      |
| Mn                       | 0.143      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Mg                       | 4.171      | 4.189      | 3.740      | 3.755      | 4.394      | 4.248      | 4.354      |
| Cr                       | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Ca                       | 1.964      | 1.477      | 1.959      | 1.763      | 1.977      | 1.730      | 2.039      |
| Na                       | 0.037      | 0.614      | 0.074      | 0.064      | 0.018      | 0.070      | 0.040      |
| Na M4                    | 0.036      | 0.523      | 0.041      | 0.237      | 0.023      | 0.270      | 0.000      |
| Na (A)                   | 0.000      | 0.091      | 0.033      | 0.000      | 0.000      | 0.000      | 0.040      |
| K                        | 0.002      | 0.046      | 0.006      | 0.018      | 0.007      | 0.007      | 0.002      |
| Vac.                     | 0.998      | 0.863      | 0.961      | 0.982      | 0.993      | 0.993      | 0.958      |
| X Mg (Fe <sup>2+</sup> ) | 0.892      | 0.927      | 0.770      | 0.829      | 0.893      | 0.944      | 0.868      |
| Na+K(A)                  | 0.002      | 0.137      | 0.039      | 0.018      | 0.007      | 0.007      | 0.042      |
| Σ (M4)                   | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      |
| Na (M4)                  | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      |
| Vakanz                   | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe |

Table 2: Continued (Electron microprobe analyses of amphibole).

|                          | b12-1      | b12-4      | b12-5      | b12-8      | b12-10     | b12-14     | b12-24     | B12-25     |
|--------------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| SiO2                     | 54.944     | 55.093     | 56.005     | 56.415     | 56.128     | 55.203     | 55.686     | 55.034     |
| TiO2                     | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Al2O3                    | 0.439      | 0.514      | 0.024      | 0.030      | 0.123      | 0.011      | 0.014      | 0.020      |
| FeO                      | 11.315     | 11.532     | 11.534     | 9.881      | 8.590      | 12.696     | 10.402     | 12.590     |
| MnO                      | 0.518      | 0.105      | 0.536      | 0.176      | 0.093      | 0.430      | 0.297      | 0.000      |
| MgO                      | 15.515     | 16.220     | 16.045     | 18.532     | 19.278     | 16.232     | 16.619     | 14.735     |
| CaO                      | 12.029     | 12.496     | 12.908     | 12.712     | 12.385     | 12.552     | 13.014     | 12.588     |
| Na2O                     | 0.107      | 0.082      | 0.026      | 0.125      | 0.225      | 0.115      | 0.019      | 0.071      |
| K2O                      | 0.050      | 0.126      | 0.000      | 0.025      | 0.027      | 0.033      | 0.014      | 0.008      |
| Cr2O3                    | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Total                    | 94.916     | 96.168     | 97.077     | 97.896     | 96.850     | 97.272     | 96.065     | 95.046     |
| Si                       | 0.914      | 0.917      | 0.932      | 0.939      | 0.934      | 0.919      | 0.927      | 0.916      |
| Ti                       | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Al                       | 0.009      | 0.010      | 0.000      | 0.001      | 0.002      | 0.000      | 0.000      | 0.000      |
| Fe                       | 0.157      | 0.161      | 0.161      | 0.138      | 0.120      | 0.177      | 0.145      | 0.175      |
| Mn                       | 0.007      | 0.001      | 0.008      | 0.002      | 0.001      | 0.006      | 0.004      | 0.000      |
| Mg                       | 0.385      | 0.402      | 0.398      | 0.460      | 0.478      | 0.403      | 0.412      | 0.366      |
| Ca                       | 0.215      | 0.223      | 0.230      | 0.227      | 0.221      | 0.224      | 0.232      | 0.224      |
| Na                       | 0.003      | 0.003      | 0.001      | 0.004      | 0.007      | 0.004      | 0.001      | 0.002      |
| K                        | 0.001      | 0.003      | 0.000      | 0.001      | 0.001      | 0.001      | 0.000      | 0.000      |
| Cr                       | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| sum13                    | 0.113      | 0.115      | 0.115      | 0.118      | 0.118      | 0.116      | 0.114      | 0.112      |
| Fe-kor                   | 23.023     | 23.001     | 23.087     | 22.865     | 22.820     | 22.8930    | 23.1270    | 23.1869    |
|                          | 061        | 8479       | 1465       | 6421       | 3792       | 818        | 594        | 795        |
| Si ges.                  | 8.072      | 7.992      | 8.085      | 7.930      | 7.907      | 7.939      | 8.095      | 8.172      |
| Si(T1)                   | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      | 3.820      |
| Al ges.                  | 0.076      | 0.088      | 0.004      | 0.005      | 0.020      | 0.002      | 0.002      | 0.004      |
| Al IV                    | -0.072     | 0.008      | -0.085     | 0.070      | 0.093      | 0.061      | -0.095     | -0.172     |
| Al VI                    | 0.148      | 0.080      | 0.089      | -0.066     | -0.072     | -0.059     | 0.097      | 0.175      |
| Ti                       | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Fe tot                   | 1.390      | 1.399      | 1.392      | 1.161      | 1.012      | 1.527      | 1.265      | 1.563      |
| Fe3+                     | 0.000      | 0.000      | 0.000      | 0.269      | 0.359      | 0.214      | 0.000      | 0.000      |
| Fe2+                     | 1.390      | 1.399      | 1.392      | 0.893      | 0.653      | 1.313      | 1.265      | 1.563      |
| Mn                       | 0.064      | 0.013      | 0.066      | 0.021      | 0.011      | 0.052      | 0.037      | 0.000      |
| Mg                       | 3.398      | 3.508      | 3.453      | 3.883      | 4.049      | 3.480      | 3.602      | 3.262      |
| Cr                       | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      | 0.000      |
| Ca                       | 1.893      | 1.942      | 1.997      | 1.914      | 1.869      | 1.934      | 2.027      | 2.003      |
| Na                       | 0.030      | 0.023      | 0.007      | 0.034      | 0.061      | 0.032      | 0.005      | 0.020      |
| Na M4                    | 0.107      | 0.058      | 0.003      | 0.086      | 0.131      | 0.066      | 0.000      | 0.000      |
| Na (A)                   | 0.000      | 0.000      | 0.004      | 0.000      | 0.000      | 0.000      | 0.005      | 0.020      |
| K                        | 0.009      | 0.023      | 0.000      | 0.004      | 0.005      | 0.006      | 0.003      | 0.002      |
| Vac.                     | 0.991      | 0.977      | 0.996      | 0.995      | 0.995      | 0.994      | 0.992      | 0.978      |
| X Mg (Fe <sup>2+</sup> ) | 0.710      | 0.715      | 0.713      | 0.813      | 0.861      | 0.726      | 0.740      | 0.676      |
| Na+K(A)                  | 0.009      | 0.023      | 0.004      | 0.005      | 0.005      | 0.006      | 0.008      | 0.022      |
| Summe (M4)               | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      |
| Na (M4)                  | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      | Ca-Am      |
| Vakanz                   | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe | Tsch-Reihe |

Table 2 Continue

|                             | mp             | B12-29         | B12-34         | B12-35         | Mj3-3          | Mj3-5          | Mj3-8          | Mj3-10         | Mj3-11         |
|-----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| SiO2                        | 56.190         | 56.887         | 46.704         | 55.217         | 54.767         | 54.586         | 56.456         | 55.838         | 55.065         |
| TiO2                        | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Al2O3                       | 0.118          | 0.087          | 0.259          | 0.009          | 0.277          | 0.300          | 0.123          | 0.278          | 1.114          |
| FeO                         | 8.719          | 8.328          | 12.316         | 12.218         | 9.010          | 9.852          | 8.386          | 9.811          | 7.978          |
| MnO                         | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| MgO                         | 17.896         | 18.494         | 13.819         | 14.877         | 18.884         | 18.281         | 18.185         | 17.141         | 19.521         |
| CaO                         | 13.072         | 12.591         | 16.985         | 12.558         | 12.443         | 12.717         | 12.821         | 12.847         | 11.740         |
| Na2O                        | 0.080          | 0.306          | 0.117          | 0.090          | 0.448          | 0.340          | 0.107          | 0.129          | 1.399          |
| K2O                         | 0.064          | 0.013          | 0.098          | 0.008          | 0.082          | 0.086          | 0.003          | 0.060          | 0.274          |
| Cr2O3                       | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Total                       | 96.139         | 96.706         | 90.298         | 94.978         | 95.911         | 96.162         | 96.082         | 96.104         | 97.090         |
| Si                          | 0.935          | 0.947          | 0.777          | 0.919          | 0.912          | 0.908          | 0.940          | 0.929          | 0.916          |
| Ti                          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Al                          | 0.002          | 0.002          | 0.005          | 0.000          | 0.005          | 0.006          | 0.002          | 0.005          | 0.022          |
| Fe                          | 0.121          | 0.116          | 0.171          | 0.170          | 0.125          | 0.137          | 0.117          | 0.137          | 0.111          |
| Mn                          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Mg                          | 0.444          | 0.459          | 0.343          | 0.369          | 0.469          | 0.454          | 0.451          | 0.425          | 0.484          |
| Ca                          | 0.233          | 0.225          | 0.303          | 0.224          | 0.222          | 0.227          | 0.229          | 0.229          | 0.209          |
| Na                          | 0.003          | 0.010          | 0.004          | 0.003          | 0.014          | 0.011          | 0.003          | 0.004          | 0.045          |
| K                           | 0.001          | 0.000          | 0.002          | 0.000          | 0.002          | 0.002          | 0.000          | 0.001          | 0.006          |
| Cr                          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| sum13                       | 0.116          | 0.117          | 0.100          | 0.112          | 0.116          | 0.116          | 0.116          | 0.115          | 0.118          |
| Fe-kor                      | 23.13          | 23.05          | 23.88          | 23.20          | 22.85          | 22.89          | 23.08          | 23.11          | 22.85          |
| Si ges.                     | 8.089          | 8.080          | 7.793          | 8.192          | 7.843          | 7.847          | 8.090          | 8.072          | 7.768          |
| Si(T1)                      | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          |
| Al ges.                     | 0.020          | 0.015          | 0.051          | 0.002          | 0.047          | 0.051          | 0.021          | 0.047          | 0.185          |
| Al IV                       | -0.089         | -0.080         | 0.207          | -0.192         | 0.157          | 0.153          | -0.090         | -0.072         | 0.232          |
| Al VI                       | 0.109          | 0.095          | -0.156         | 0.194          | -0.110         | -0.102         | 0.110          | 0.120          | -0.047         |
| Ti                          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Fe tot                      | 1.050          | 0.989          | 1.719          | 1.516          | 1.079          | 1.184          | 1.005          | 1.186          | 0.941          |
| Fe3+                        | 0.000          | 0.000          | 0.000          | 0.000          | 0.310          | 0.227          | 0.000          | 0.000          | 0.298          |
| Fe2+                        | 1.050          | 0.989          | 1.719          | 1.516          | 0.769          | 0.958          | 1.005          | 1.186          | 0.644          |
| Mn                          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Mg                          | 3.841          | 3.916          | 3.437          | 3.290          | 4.031          | 3.918          | 3.885          | 3.694          | 4.105          |
| Cr                          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Ca                          | 2.016          | 1.916          | 3.037          | 1.996          | 1.909          | 1.959          | 1.968          | 1.990          | 1.774          |
| Na                          | 0.022          | 0.084          | 0.038          | 0.026          | 0.124          | 0.095          | 0.030          | 0.036          | 0.383          |
| Na M4                       | 0.000          | 0.084          | 0.000          | 0.004          | 0.091          | 0.041          | 0.032          | 0.010          | 0.226          |
| Na (A)                      | 0.022          | 0.000          | 0.038          | 0.022          | 0.033          | 0.054          | 0.000          | 0.026          | 0.157          |
| K                           | 0.012          | 0.002          | 0.021          | 0.002          | 0.015          | 0.016          | 0.001          | 0.011          | 0.049          |
| Vac.                        | 0.966          | 0.997          | 0.941          | 0.976          | 0.951          | 0.931          | 0.999          | 0.963          | 0.794          |
| X Mg<br>(Fe <sup>2+</sup> ) | 0.785          | 0.798          | 0.667          | 0.685          | 0.840          | 0.804          | 0.794          | 0.757          | 0.864          |
| Na+K(A)                     | 0.034          | 0.003          | 0.059          | 0.024          | 0.049          | 0.069          | 0.001          | 0.037          | 0.206          |
| Summe<br>(M4)               | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          |
| Na (M4)                     | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          |
| Vakanz                      | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe |

Table 2: Continue

|                                | Mj3-12         | Mj3-13         | Mj3-17         | B9-10          | B12-65-5       | Gr-13          | Gr-14          | 102-3          | 106-15         |
|--------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| SiO <sub>2</sub>               | 56.134         | 53.974         | 56.487         | 54.210         | 54.079         | 54.377         | 54.454         | 54.750         | 54.406         |
| TiO <sub>2</sub>               | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Al <sub>2</sub> O <sub>3</sub> | 0.327          | 0.499          | 0.460          | 0.652          | 0.023          | 0.190          | 0.333          | 0.961          | 0.829          |
| FeO                            | 8.738          | 13.911         | 4.293          | 14.122         | 12.434         | 10.943         | 9.090          | 4.971          | 12.813         |
| MnO                            | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| MgO                            | 18.556         | 13.634         | 21.811         | 14.746         | 16.220         | 17.646         | 18.036         | 21.670         | 15.870         |
| CaO                            | 12.458         | 12.673         | 13.023         | 12.538         | 12.425         | 13.121         | 12.442         | 10.993         | 11.824         |
| Na <sub>2</sub> O              | 0.085          | 0.122          | 0.130          | 0.182          | 0.099          | 0.076          | 0.271          | 1.979          | 0.432          |
| K <sub>2</sub> O               | 0.083          | 0.010          | 0.159          | 0.018          | 0.013          | 0.013          | 0.033          | 0.502          | 0.060          |
| Cr <sub>2</sub> O <sub>3</sub> | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Total                          | 96.381         | 94.825         | 96.364         | 96.468         | 95.294         | 96.367         | 94.659         | 95.826         | 96.233         |
| Si                             | 0.934          | 0.898          | 0.940          | 0.902          | 0.900          | 0.905          | 0.906          | 0.911          | 0.906          |
| Ti                             | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Al                             | 0.006          | 0.010          | 0.009          | 0.013          | 0.000          | 0.004          | 0.007          | 0.019          | 0.016          |
| Fe                             | 0.122          | 0.194          | 0.060          | 0.197          | 0.173          | 0.152          | 0.127          | 0.069          | 0.178          |
| Mn                             | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Mg                             | 0.460          | 0.338          | 0.541          | 0.366          | 0.402          | 0.438          | 0.447          | 0.538          | 0.394          |
| Ca                             | 0.222          | 0.226          | 0.232          | 0.224          | 0.222          | 0.234          | 0.222          | 0.196          | 0.211          |
| Na                             | 0.003          | 0.004          | 0.004          | 0.006          | 0.003          | 0.002          | 0.009          | 0.064          | 0.014          |
| K                              | 0.002          | 0.000          | 0.003          | 0.000          | 0.000          | 0.000          | 0.001          | 0.011          | 0.001          |
| Cr                             | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| sum13                          | 0.117          | 0.111          | 0.119          | 0.114          | 0.114          | 0.115          | 0.114          | 0.118          | 0.115          |
| Fe-kor                         | 22.92          | 23.212         | 22.902         | 22.99          | 22.90          | 22.91          | 22.93          | 22.76          | 22.85          |
| Si ges.                        | 7.976          | 8.110          | 7.885          | 7.939          | 7.927          | 7.849          | 7.924          | 7.708          | 7.880          |
| Si(T1)                         | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          | 3.820          |
| Al ges.                        | 0.055          | 0.088          | 0.076          | 0.113          | 0.004          | 0.032          | 0.057          | 0.159          | 0.141          |
| Al IV                          | 0.024          | -0.110         | 0.115          | 0.061          | 0.073          | 0.151          | 0.076          | 0.292          | 0.120          |
| Al VI                          | 0.031          | 0.198          | -0.040         | 0.051          | -0.069         | -0.118         | -0.019         | -0.133         | 0.021          |
| Ti                             | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Fe tot                         | 1.038          | 1.748          | 0.501          | 1.730          | 1.524          | 1.321          | 1.106          | 0.585          | 1.552          |
| Fe <sup>3+</sup>               | 0.161          | 0.000          | 0.196          | 0.021          | 0.208          | 0.187          | 0.132          | 0.479          | 0.296          |
| Fe <sup>2+</sup>               | 0.877          | 1.748          | 0.305          | 1.709          | 1.316          | 1.134          | 0.974          | 0.106          | 1.255          |
| Mn                             | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Mg                             | 3.931          | 3.054          | 4.539          | 3.219          | 3.545          | 3.797          | 3.913          | 4.548          | 3.427          |
| Cr                             | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          | 0.000          |
| Ca                             | 1.897          | 2.040          | 1.948          | 1.967          | 1.951          | 2.029          | 1.940          | 1.658          | 1.835          |
| Na                             | 0.023          | 0.036          | 0.035          | 0.052          | 0.028          | 0.021          | 0.076          | 0.540          | 0.121          |
| Na M4                          | 0.103          | 0.000          | 0.052          | 0.033          | 0.049          | 0.000          | 0.060          | 0.342          | 0.165          |
| Na (A)                         | 0.000          | 0.036          | 0.000          | 0.019          | 0.000          | 0.021          | 0.016          | 0.198          | 0.000          |
| K                              | 0.015          | 0.002          | 0.028          | 0.003          | 0.003          | 0.002          | 0.006          | 0.090          | 0.011          |
| Vac.                           | 0.985          | 0.962          | 0.972          | 0.978          | 0.997          | 0.976          | 0.978          | 0.711          | 0.989          |
| X Mg<br>(Fe <sup>2+</sup> )    | 0.818          | 0.636          | 0.937          | 0.653          | 0.729          | 0.770          | 0.801          | 0.977          | 0.732          |
| Na+K(A)                        | 0.015          | 0.038          | 0.028          | 0.022          | 0.003          | 0.024          | 0.022          | 0.289          | 0.011          |
| Summe<br>(M4)                  | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          |
| Na (M4)                        | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          | Ca-Am          |
| Vakanz                         | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe | Tsch-<br>Reihe |

Table 3: Amphibole in Dolerites

|                                | 24-3       | 21-38-7    | 24-2        | 24-5        | 24-6        | 24-7-       | 24-10      | 24-11       |
|--------------------------------|------------|------------|-------------|-------------|-------------|-------------|------------|-------------|
| SiO <sub>2</sub>               | 48.186     | 47.255     | 44.069      | 44.223      | 43.742      | 44.482      | 47.799     | 44.228      |
| TiO <sub>2</sub>               | 1.060      | 0.850      | 0.910       | 1.420       | 0.760       | 0.340       | 1.120      | 0.880       |
| Al <sub>2</sub> O <sub>3</sub> | 11.521     | 10.014     | 12.186      | 11.892      | 11.843      | 11.931      | 6.565      | 12.299      |
| FeO                            | 13.386     | 10.316     | 13.121      | 13.644      | 12.775      | 12.439      | 15.637     | 11.855      |
| MnO                            | 0.000      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| MgO                            | 11.071     | 10.524     | 11.513      | 11.191      | 11.623      | 12.085      | 9.615      | 11.942      |
| CaO                            | 8.047      | 18.587     | 12.158      | 11.815      | 11.852      | 11.769      | 10.275     | 12.027      |
| Na <sub>2</sub> O              | 2.015      | 0.100      | 2.466       | 2.456       | 2.537       | 2.364       | 1.136      | 2.338       |
| K <sub>2</sub> O               | 1.726      | 0.020      | 1.158       | 1.090       | 1.134       | 1.077       | 2.247      | 1.123       |
| Cr <sub>2</sub> O <sub>3</sub> | 0.000      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| Total                          | 97.012     | 97.667     | 97.581      | 97.730      | 96.266      | 96.487      | 94.394     | 96.691      |
| Si                             | 0.802      | 0.786      | 0.733       | 0.736       | 0.728       | 0.740       | 0.796      | 0.736       |
| Ti                             | 0.013      | 0.011      | 0.011       | 0.018       | 0.010       | 0.004       | 0.014      | 0.011       |
| Al                             | 0.226      | 0.196      | 0.239       | 0.233       | 0.232       | 0.234       | 0.129      | 0.241       |
| Fe                             | 0.186      | 0.144      | 0.183       | 0.190       | 0.178       | 0.173       | 0.218      | 0.165       |
| Mn                             | 0.000      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| Mg                             | 0.275      | 0.261      | 0.286       | 0.278       | 0.288       | 0.300       | 0.239      | 0.296       |
| Ca                             | 0.143      | 0.331      | 0.217       | 0.211       | 0.211       | 0.210       | 0.183      | 0.214       |
| Na                             | 0.065      | 0.003      | 0.080       | 0.079       | 0.082       | 0.076       | 0.037      | 0.075       |
| K                              | 0.037      | 0.000      | 0.025       | 0.023       | 0.024       | 0.023       | 0.048      | 0.024       |
| Cr                             | 0.000      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| sum13                          | 0.116      | 0.108      | 0.112       | 0.112       | 0.110       | 0.112       | 0.107      | 0.112       |
| Fe-kor                         | 22.71      | 24.42      | 23.14       | 23.12       | 23.12       | 23.04       | 23.25      | 23.15       |
| Si ges.                        | 6.940      | 7.312      | 6.566       | 6.578       | 6.591       | 6.630       | 7.416      | 6.601       |
| Si(T1)                         | 3.820      | 3.820      | 3.820       | 3.820       | 3.820       | 3.820       | 3.820      | 3.820       |
| Al ges.                        | 1.956      | 1.826      | 2.140       | 2.085       | 2.103       | 2.096       | 1.200      | 2.163       |
| Al IV                          | 1.060      | 0.688      | 1.434       | 1.422       | 1.409       | 1.370       | 0.584      | 1.399       |
| Al VI                          | 0.896      | 1.138      | 0.706       | 0.663       | 0.694       | 0.726       | 0.616      | 0.764       |
| Ti                             | 0.115      | 0.099      | 0.102       | 0.159       | 0.086       | 0.038       | 0.131      | 0.099       |
| Fe tot                         | 1.612      | 1.335      | 1.635       | 1.697       | 1.610       | 1.550       | 2.029      | 1.480       |
| Fe <sup>3+</sup>               | 0.571      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| Fe <sup>2+</sup>               | 1.041      | 1.335      | 1.635       | 1.697       | 1.610       | 1.550       | 2.029      | 1.480       |
| Mn                             | 0.000      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| Mg                             | 2.377      | 2.428      | 2.557       | 2.481       | 2.611       | 2.685       | 2.224      | 2.657       |
| Cr                             | 0.000      | 0.000      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000      | 0.000       |
| Ca                             | 1.242      | 3.082      | 1.941       | 1.883       | 1.913       | 1.880       | 1.708      | 1.923       |
| Na                             | 0.563      | 0.030      | 0.712       | 0.708       | 0.741       | 0.683       | 0.342      | 0.676       |
| Na M4                          | 0.758      | 0.000      | 0.059       | 0.117       | 0.087       | 0.120       | 0.292      | 0.077       |
| Na (A)                         | 0.000      | 0.030      | 0.653       | 0.591       | 0.654       | 0.563       | 0.050      | 0.600       |
| K                              | 0.317      | 0.004      | 0.220       | 0.207       | 0.218       | 0.205       | 0.445      | 0.214       |
| Vac.                           | 0.683      | 0.966      | 0.127       | 0.202       | 0.128       | 0.233       | 0.506      | 0.186       |
| X Mg (Fe <sup>2+</sup> )       | 0.695      | 0.645      | 0.610       | 0.594       | 0.619       | 0.634       | 0.523      | 0.642       |
| Na+K(A)                        | 0.317      | 0.034      | 0.873       | 0.798       | 0.872       | 0.767       | 0.494      | 0.814       |
| Σ (M4)                         | Ca-Am      | Ca-Am      | Ca-Am       | Ca-Am       | Ca-Am       | Ca-Am       | Ca-Am      | Ca-Am       |
| Na (M4)                        | Na-Am      | Ca-Am      | Ca-Am       | Ca-Am       | Ca-Am       | Ca-Am       | Ca-Am      | Ca-Am       |
| Vakanz                         | Tsch-Reihe | Tsch-Reihe | Ed-Pa-Reihe | Ed-Pa-Reihe | Ed-Pa-Reihe | Ed-Pa-Reihe | Tsch-Reihe | Ed-Pa-Reihe |

**Table 4. EMP analyses of Monazite 1 and 2.**

| Type 1 monazite |        |        |        |       |         |        |        |        |        |         |        |        |        |        |        |
|-----------------|--------|--------|--------|-------|---------|--------|--------|--------|--------|---------|--------|--------|--------|--------|--------|
| Label           | 108-16 | 108-26 | 108-28 | 107-4 | 107-4-2 | 107-7  | cx-4   | cx-7   | cx-12  | cx-12-a | 101-1  | 108-9  | 108-14 | 108-17 | 108-12 |
| La              | 10.97  | 10.84  | 11.44  | 11.68 | 13.29   | 12.95  | 15.42  | 16.35  | 14.07  | 14.57   | 14.91  | 12.45  | 9.79   | 12.45  | 10.29  |
| Ce              | 27.87  | 28.73  | 28.03  | 30.11 | 29.64   | 29.91  | 32.37  | 33.50  | 31.62  | 31.84   | 32.53  | 31.10  | 30.02  | 29.83  | 27.11  |
| Pr              | 3.26   | 3.21   | 2.48   | 2.33  | 2.59    | 2.96   | 2.49   | 2.43   | 2.73   | 2.63    | 2.43   | 2.88   | 3.10   | 2.36   | 3.24   |
| Nd              | 11.48  | 10.84  | 10.25  | 9.83  | 8.25    | 9.13   | 7.06   | 6.64   | 7.94   | 7.79    | 7.37   | 8.81   | 11.40  | 9.61   | 12.71  |
| Sm              | 2.17   | 1.76   | 2.28   | 1.28  | 1.32    | 1.87   | 0.59   | 0.44   | 0.65   | 0.61    | 0.65   | 0.88   | 1.68   | 0.77   | 1.32   |
| Gd              | 0.72   | 0.67   | 0.84   | 1.24  | 0.82    | 0.95   | 0.37   | 0.15   | 0.35   | 0.36    | 0.28   | 0.58   | 1.04   | 0.37   | 1.03   |
| Tb              | NA     | NA     | NA     | NA    | NA      | NA     | 0.03   | 0.00   | 0.03   | 0.04    | 0.01   | 0.00   | 0.10   | 0.00   | NA     |
| Dy              | NA     | NA     | NA     | NA    | NA      | NA     | 0.10   | 0.00   | 0.00   | 0.09    | 0.16   | 0.22   | 0.17   | 0.04   | NA     |
| Ho              | NA     | NA     | NA     | NA    | NA      | NA     | 0.00   | 0.00   | 0.00   | 0.00    | 0.10   | 0.03   | 0.07   | 0.08   | NA     |
| Er              | NA     | NA     | NA     | NA    | NA      | NA     | 0.06   | 0.03   | 0.01   | 0.04    | 0.08   | 0.20   | 0.00   | 0.00   | NA     |
| Yb              | NA     | NA     | NA     | NA    | NA      | NA     | 0.00   | 0.00   | 0.00   | 0.00    | 0.02   | 0.06   | 0.00   | 0.00   | NA     |
| Y               | 0.27   | 0.21   | 0.64   | 0.32  | 0.43    | 0.50   | 0.29   | 0.24   | 0.29   | 0.29    | 0.30   | 0.87   | 0.17   | 0.29   | 0.39   |
| Th              | NA     | NA     | NA     | NA    | NA      | NA     | 0.19   | 1.03   | 0.53   | 0.19    | 0.25   | 0.12   | 0.33   | 0.10   | NA     |
| U               | NA     | NA     | NA     | NA    | NA      | NA     | 0.05   | 0.09   | 0.11   | 0.12    | 0.07   | 0.08   | 0.08   | 0.05   | NA     |
| Mg              | 0.00   | 0.00   | 0.00   | 0.00  | 0.00    | 0.00   | 0.00   | 0.00   | 0.00   | 0.00    | 0.01   | 0.00   | 0.00   | 0.00   | 0      |
| Al              | 0.00   | 0.00   | 0.01   | 0.00  | 0.00    | 0.00   | 0.01   | 0.01   | 0.01   | 0.01    | 0.02   | 0.01   | 0.02   | 0.00   | 0.01   |
| Si              | 0.31   | 0.03   | 0.04   | 0.13  | 0.17    | 0.18   | 0.08   | 0.21   | 0.16   | 0.15    | 0.32   | 0.00   | 0.01   | 0.03   | 0.36   |
| P               | 12.50  | 12.76  | 12.82  | 11.73 | 12.96   | 12.65  | 13.21  | 12.73  | 13.00  | 12.92   | 12.84  | 13.18  | 13.11  | 12.92  | 12.27  |
| S               | NA     | NA     | NA     | NA    | NA      | NA     | 0.00   | 0.13   | 0.21   | 0.16    | 0.19   | 0.09   | 0.00   | 0.02   | NA     |
| Ca              | 0.88   | 0.64   | 0.61   | 1.07  | 1.00    | 0.52   | 0.64   | 0.52   | 0.61   | 0.89    | 0.71   | 0.42   | 2.89   | 0.28   | 0.68   |
| Fe              | 0.00   | 0.00   | 0.00   | 0.00  | 0.00    | 0.00   | 0.00   | 0.00   | 0.00   | 0.00    | 0.01   | 0.00   | 0.00   | 0.00   | 0      |
| F               | 1.17   | 1.06   | 1.38   | 1.05  | 0.96    | 0.86   | 0.94   | 0.93   | 0.89   | 0.93    | 0.87   | 0.92   | 0.96   | 1.11   | 1.05   |
| Cl              | 0.05   | 0.13   | 0.01   | 0.05  | 0.06    | 0.02   | NA     | NA     | NA     | NA      | NA     | NA     | NA     | NA     | 0.05   |
| O               | 27.90  | 28.35  | 27.84  | 28.83 | 27.10   | 27.85  | 28.07  | 26.37  | 27.98  | 27.44   | 26.97  | 27.24  | 27.98  | 30.91  | 27.29  |
| Sum             | 99.55  | 99.23  | 98.67  | 99.65 | 98.61   | 100.35 | 101.96 | 101.80 | 101.18 | 101.07  | 101.11 | 100.15 | 102.91 | 101.22 | 97.8   |
| ΣREE            | 56.47  | 56.05  | 55.32  | 56.47 | 55.92   | 57.77  | 58.49  | 59.53  | 57.40  | 57.97   | 58.54  | 57.22  | 57.36  | 55.52  | 55.70  |
| ΣREE+Y          | 56.74  | 56.26  | 55.96  | 56.79 | 56.35   | 58.27  | 58.78  | 59.77  | 57.69  | 58.25   | 58.85  | 58.09  | 57.53  | 55.80  | 56.09  |
| La/Ce           | 0.39   | 0.38   | 0.41   | 0.39  | 0.45    | 0.43   | 0.48   | 0.49   | 0.44   | 0.46    | 0.46   | 0.40   | 0.33   | 0.42   | 0.38   |
| La/Y            | 40.63  | 51.62  | 17.88  | 36.44 | 31.21   | 26.15  | 52.73  | 68.22  | 49.03  | 50.90   | 48.93  | 14.34  | 57.77  | 43.58  | 26.38  |
| La/Nd           | 0.96   | 1.00   | 1.12   | 1.19  | 1.61    | 1.42   | 2.18   | 2.46   | 1.77   | 1.87    | 2.02   | 1.41   | 0.86   | 1.30   | 0.81   |
| ΣHREE           | 0.99   | 0.88   | 1.48   | 1.56  | 1.25    | 1.45   | 0.85   | 0.42   | 0.68   | 0.81    | 0.96   | 1.97   | 1.54   | 0.78   | 1.42   |

**Table 4. Continued.**

|         | Type 2<br>monazite |        |        |        |        |        |       |        |        |       |        |       |       |       |
|---------|--------------------|--------|--------|--------|--------|--------|-------|--------|--------|-------|--------|-------|-------|-------|
| Label   | 106-1              | 107-1  | 107-2  | 107-3  | 107-4  | 107-5  | 107-6 | cx-1   | cx-2   | cx-3  | cx-5   | cx-6  | cx-9  | cx-10 |
| La      | 9.52               | 9.09   | 9.67   | 8.52   | 8.78   | 8.53   | 10.20 | 11.96  | 10.36  | 11.23 | 11.47  | 10.85 | 10.83 | 12.23 |
| Ce      | 26.61              | 30.15  | 30.96  | 29.47  | 29.00  | 28.99  | 29.42 | 30.82  | 31.14  | 30.12 | 31.42  | 30.07 | 29.90 | 30.89 |
| Pr      | 2.40               | 2.96   | 3.15   | 3.43   | 3.14   | 3.14   | 2.84  | 3.02   | 3.22   | 3.18  | 2.91   | 3.05  | 3.23  | 3.02  |
| Nd      | 11.52              | 11.91  | 13.00  | 14.13  | 12.50  | 12.57  | 10.67 | 10.37  | 12.07  | 10.69 | 9.88   | 9.81  | 10.82 | 9.92  |
| Sm      | 2.11               | 2.09   | 2.14   | 2.60   | 2.14   | 2.17   | 1.76  | 1.07   | 1.66   | 1.16  | 0.86   | 1.76  | 1.68  | 0.98  |
| Gd      | 1.03               | 1.13   | 1.25   | 1.44   | 1.19   | 1.43   | 0.97  | 0.66   | 0.91   | 0.70  | 0.38   | 1.02  | 0.94  | 0.58  |
| Tb      | NA                 | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00  | 0.00   | 0.00   | 0.00  | 0.03   | 0.09  | 0.03  | 0.02  |
| Dy      | NA                 | 0.12   | 0.18   | 0.21   | 0.23   | 0.26   | 0.06  | 0.09   | 0.11   | 0.15  | 0.07   | 0.09  | 0.17  | 0.04  |
| Ho      | NA                 | 0.00   | 0.03   | 0.08   | 0.00   | 0.05   | 0.00  | 0.00   | 0.00   | 0.00  | 0.00   | 0.00  | 0.00  | 0.00  |
| Er      | NA                 | 0.10   | 0.13   | 0.14   | 0.04   | 0.17   | 0.00  | 0.07   | 0.09   | 0.13  | 0.00   | 0.04  | 0.01  | 0.05  |
| Yb      | NA                 | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00  | 0.03   | 0.01   | 0.01  | 0.00   | 0.00  | 0.03  | 0.06  |
| Y       | 0.53               | 0.38   | 0.30   | 0.41   | 0.56   | 1.38   | 0.30  | 0.33   | 0.28   | 0.39  | 0.30   | 0.32  | 0.37  | 0.23  |
| Th      | NA                 | 0.00   | 0.00   | 0.45   | 0.79   | 0.37   | 0.24  | 0.00   | 0.02   | 0.39  | 3.31   | 0.12  | 0.20  | 0.00  |
| U       | NA                 | 0.06   | 0.14   | 0.08   | 0.07   | 0.05   | 0.13  | 0.02   | 0.05   | 0.06  | 0.12   | 0.03  | 0.08  | 0.11  |
| Mg      | 0.00               | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00  | 0.00   | 0.00   | 0.05  | 0.00   | 0.00  | 0.00  | 0.02  |
| Al      | 0.00               | 0.01   | 0.02   | 0.00   | 0.01   | 0.02   | 0.03  | 0.02   | 0.01   | 0.01  | 0.02   | 0.00  | 0.02  | 0.01  |
| Si      | 0.09               | 0.00   | 0.02   | 0.00   | 0.00   | 0.00   | 0.10  | 0.12   | 0.08   | 0.10  | 0.14   | 0.07  | 0.06  | 0.11  |
| P       | 11.89              | 13.65  | 13.47  | 13.02  | 12.61  | 12.82  | 12.76 | 12.85  | 12.64  | 12.79 | 12.31  | 12.90 | 12.91 | 12.90 |
| S       | NA                 | 0.17   | 0.00   | 0.04   | 0.14   | 0.10   | 0.02  | 0.04   | 0.00   | 0.08  | 0.00   | 0.00  | 0.00  | 0.01  |
| Ca      | 2.80               | 2.19   | 0.50   | 0.33   | 1.16   | 0.94   | 2.42  | 0.19   | 0.13   | 0.30  | 0.25   | 0.32  | 0.10  | 0.26  |
| Fe      | 0.43               | 0.00   | 0.00   | 0.01   | 0.00   | 0.00   | 0.01  | 0.00   | 0.00   | 0.00  | 0.00   | 0.00  | 0.00  | 0.00  |
| F       | 0.92               | 0.96   | 0.78   | 0.84   | 0.92   | 0.88   | 0.62  | 0.97   | 0.85   | 0.91  | 0.92   | 0.90  | 0.93  | 0.93  |
| Cl      | 0.04               | NA     | NA     | NA     | NA     | NA     | NA    | NA     | NA     | NA    | NA     | NA    | NA    | NA    |
| O       | 27.95              | 26.91  | 26.56  | 26.66  | 29.33  | 28.43  | 26.07 | 27.44  | 27.09  | 26.66 | 26.76  | 26.65 | 26.72 | 27.46 |
| Sum     | 97.84              | 101.87 | 102.29 | 101.86 | 102.61 | 102.27 | 98.63 | 100.07 | 100.71 | 99.12 | 101.14 | 98.12 | 99.02 | 99.82 |
| ΣREE    | 53.20              | 57.55  | 60.51  | 60.02  | 57.03  | 57.30  | 55.91 | 58.10  | 59.57  | 57.36 | 57.02  | 56.78 | 57.64 | 57.78 |
| ΣREE +Y | 53.73              | 57.93  | 60.80  | 60.42  | 57.59  | 58.67  | 56.21 | 58.42  | 59.84  | 57.76 | 57.32  | 57.11 | 58.01 | 58.01 |
| La/Ce   | 0.36               | 0.30   | 0.31   | 0.29   | 0.30   | 0.29   | 0.35  | 0.39   | 0.33   | 0.37  | 0.36   | 0.36  | 0.36  | 0.40  |
| La/Y    | 17.95              | 23.89  | 32.61  | 21.02  | 15.75  | 6.19   | 34.19 | 36.73  | 37.66  | 28.43 | 38.64  | 33.63 | 29.56 | 52.83 |
| La/Nd   | 0.83               | 0.76   | 0.74   | 0.60   | 0.70   | 0.68   | 0.96  | 1.15   | 0.86   | 1.05  | 1.16   | 1.11  | 1.00  | 1.23  |
| ΣHREE   | 1.56               | 1.72   | 1.89   | 2.27   | 2.01   | 3.28   | 1.32  | 1.18   | 1.39   | 1.39  | 0.78   | 1.57  | 1.54  | 0.99  |

**Table 4. Continued.**

| Monazite2 |       |       |              |               |       |        |         |        |       |       |        |         |        |        |  |  |
|-----------|-------|-------|--------------|---------------|-------|--------|---------|--------|-------|-------|--------|---------|--------|--------|--|--|
| Label     | cx-11 | cx-13 | b20-43-<br>4 | B20-43-<br>11 | 101-4 | 101-5  | 108-2   | 108-3  | 101-8 | 101-9 | 108-2  | 108-3-2 | 108-5  | 108-6  |  |  |
| La        | 11.02 | 11.04 | 10.65        | 10.97         | 11.11 | 11.47  | 9.674   | 10.44  | 9.62  | 10.39 | 10.85  | 11.47   | 11.53  | 10.16  |  |  |
| Ce        | 29.47 | 31.40 | 30.81        | 31.21         | 30.72 | 31.56  | 27.48   | 29.52  | 29.23 | 29.40 | 32.21  | 32.89   | 32.17  | 30.65  |  |  |
| Pr        | 3.17  | 2.97  | 2.87         | 2.46          | 3.00  | 2.90   | 3.07    | 3.52   | 3.15  | 3.23  | 3.21   | 2.86    | 2.84   | 3.10   |  |  |
| Nd        | 10.50 | 10.63 | 11.35        | 10.88         | 10.35 | 10.07  | 13.09   | 12.74  | 12.87 | 10.87 | 10.28  | 9.81    | 9.47   | 11.40  |  |  |
| Sm        | 1.49  | 1.42  | 2.39         | 1.35          | 1.20  | 1.48   | 0.88    | 1.12   | 1.90  | 2.02  | 1.33   | 1.20    | 1.02   | 1.79   |  |  |
| Gd        | 0.98  | 0.91  | 1.29         | 1.33          | 0.54  | 0.74   | 0.69    | 0.73   | 1.32  | 1.22  | 0.75   | 0.68    | 0.52   | 1.13   |  |  |
| Tb        | 0.08  | 0.03  | NA           | NA            | 0.15  | 0.15   | NA      | NA     | 0.01  | 0.05  | 0.03   | 0.05    | 0.05   | 0.05   |  |  |
| Dy        | 0.17  | 0.15  | NA           | NA            | 0.02  | 0.08   | NA      | NA     | 0.22  | 0.26  | 0.21   | 0.09    | 0.19   | 0.11   |  |  |
| Ho        | 0.00  | 0.00  | NA           | NA            | 0.00  | 0.02   | NA      | NA     | 0.00  | 0.05  | 0.00   | 0.00    | 0.11   | 0.01   |  |  |
| Er        | 0.01  | 0.16  | NA           | NA            | 0.09  | 0.00   | NA      | NA     | 0.02  | 0.07  | 0.00   | 0.08    | 0.01   | 0.02   |  |  |
| Yb        | 0.02  | 0.00  | NA           | NA            | 0.00  | 0.00   | NA      | NA     | 0.00  | 0.00  | 0.00   | 0.00    | 0.00   | 0.00   |  |  |
| Y         | 0.49  | 0.31  | 0.26         | 0.22          | 0.18  | 0.22   | 0.33    | 0.34   | 0.53  | 0.52  | 0.49   | 0.43    | 0.66   | 0.31   |  |  |
| Th        | 0.03  | 0.53  | NA           | NA            | 0.30  | 0.38   | NA      | NA     | 0.00  | 0.42  | 0.35   | 0.00    | 0.08   | 0.45   |  |  |
| U         | 0.06  | 0.08  | NA           | NA            | 0.00  | 0.08   | NA      | NA     | 0.06  | 0.08  | 0.06   | 0.08    | 0.05   | 0.06   |  |  |
| Mg        | 0.01  | 0.00  | 0.00         | 0.00          | 0.00  | 0.00   | 0       | 0      | 0.01  | 0.00  | 0.00   | 0.00    | 0.00   | 0.00   |  |  |
| Al        | 0.01  | 0.01  | 0.00         | 0.01          | 0.02  | 0.01   | 0       | 0.01   | 0.02  | 0.02  | 0.01   | 0.02    | 0.02   | 0.01   |  |  |
| Si        | 0.10  | 0.07  | 0.08         | 0.11          | 0.14  | 0.12   | 0.82    | 0.1    | 0.10  | 0.45  | 0.00   | 0.01    | 0.05   | 0.00   |  |  |
| P         | 12.96 | 13.06 | 11.98        | 11.91         | 11.93 | 11.64  | 12.44   | 12.21  | 12.26 | 12.53 | 12.99  | 12.96   | 12.73  | 13.03  |  |  |
| S         | 0.01  | 0.06  | NA           | NA            | 0.03  | 0.04   | NA      | NA     | 0.16  | 0.11  | 0.06   | 0.00    | 0.05   | 0.00   |  |  |
| Ca        | 0.23  | 0.09  | 0.05         | 0.06          | 0.69  | 1.03   | 1.16    | 1.23   | 0.65  | 0.61  | 0.56   | 0.12    | 0.35   | 0.40   |  |  |
| Fe        | 0.00  | 0.00  | 0.00         | 0.00          | 0.00  | 1.11   | 0       | 0      | 0.01  | 0.00  | 0.00   | 0.00    | 0.04   | 0.00   |  |  |
| F         | 0.87  | 0.71  | 0.94         | 1.00          | 0.96  | 0.99   | 1.11    | 1.24   | 0.72  | 0.90  | 0.94   | 0.89    | 0.81   | 0.92   |  |  |
| Cl        | NA    | NA    | 0.03         | 0.05          | NA    | NA     | 0.1     | 0.04   | NA    | NA    | NA     | NA      | NA     | NA     |  |  |
| O         | 27.53 | 26.20 | 27.46        | 27.97         | 27.61 | 27.06  | 27.94   | 27.88  | 25.76 | 26.32 | 28.53  | 26.39   | 27.66  | 27.81  |  |  |
| Sum       | 99.22 | 99.84 | 100.15       | 99.53         | 99.06 | 101.15 | 98.7811 | 101.12 | 98.62 | 99.52 | 102.87 | 100.03  | 100.40 | 101.42 |  |  |
| ΣREE      | 56.93 | 58.72 | 59.36        | 58.20         | 57.20 | 58.47  | 54.88   | 58.07  | 58.35 | 57.56 | 58.88  | 59.12   | 57.90  | 58.43  |  |  |
| ΣREE +Y   | 57.41 | 59.03 | 59.62        | 58.42         | 57.38 | 58.68  | 55.21   | 58.41  | 58.88 | 58.08 | 59.37  | 59.56   | 58.56  | 58.74  |  |  |
| La/Ce     | 0.37  | 0.35  | 0.35         | 0.35          | 0.36  | 0.36   | 0.35    | 0.35   | 0.33  | 0.35  | 0.34   | 0.35    | 0.36   | 0.33   |  |  |
| La/Y      | 22.68 | 35.27 | 41.70        | 50.70         | 60.24 | 53.32  | 29.32   | 30.71  | 18.13 | 19.81 | 22.06  | 26.55   | 17.43  | 32.52  |  |  |
| La/Nd     | 1.05  | 1.04  | 0.94         | 1.01          | 1.07  | 1.14   | 0.74    | 0.82   | 0.75  | 0.96  | 1.06   | 1.17    | 1.22   | 0.89   |  |  |
| ΣHREE     | 1.76  | 1.56  | 1.55         | 1.55          | 1.00  | 1.21   | 1.02    | 1.07   | 2.11  | 2.17  | 1.49   | 1.33    | 1.53   | 1.64   |  |  |

**Table 4. Continued.**

| Monazite2 |         |        |          |        |        |        |  |  |  |  |
|-----------|---------|--------|----------|--------|--------|--------|--|--|--|--|
| Label     | 108-8-2 | 108-10 | 108-13-2 | 108-13 | 108-16 | 108-27 |  |  |  |  |
| La        | 9.79    | 10.01  | 8.01     | 9.99   | 10.99  | 9.26   |  |  |  |  |
| Ce        | 29.12   | 30.82  | 30.53    | 30.2   | 31.18  | 29.09  |  |  |  |  |
| Pr        | 2.71    | 3.11   | 3.68     | 2.96   | 2.87   | 2.76   |  |  |  |  |
| Nd        | 8.77    | 11.35  | 14.31    | 12.11  | 9.34   | 12.95  |  |  |  |  |
| Sm        | 0.83    | 1.85   | 1.99     | 1.28   | 1.10   | 1.87   |  |  |  |  |
| Gd        | 0.66    | 1.06   | 0.74     | 0.84   | 0.77   | 0.91   |  |  |  |  |
| Tb        | 0.00    | 0.05   | 0.01     | NA     | 0.03   | NA     |  |  |  |  |
| Dy        | 0.22    | 0.25   | LLD      | NA     | 0.27   | NA     |  |  |  |  |
| Ho        | LLD     | LLD    | 0.12     | NA     | 0.00   | NA     |  |  |  |  |
| Er        | 0.03    | LLD    | LLD      | NA     | 0.05   | NA     |  |  |  |  |
| Yb        | LLD     | LLD    | LLD      | NA     | 0.00   | NA     |  |  |  |  |
| Y         | 0.92    | 0.32   | 0.14     | 0.36   | 1.01   | 0.35   |  |  |  |  |
| Th        | LLD     | 0.68   | LLD      | NA     | 0.01   | NA     |  |  |  |  |
| U         | 0.08    | 0.03   | 0.09     | NA     | 0.10   | NA     |  |  |  |  |
| Mg        | LLD     | LLD    | LLD      | LLD    | LLD    | LLD    |  |  |  |  |
| Al        | LLD     | LLD    | LLD      | LLD    | LLD    | LLD    |  |  |  |  |
| Si        | 0.04    | LLD    | LLD      | 0.12   | LLD    | 0.06   |  |  |  |  |
| P         | 13.34   | 12.75  | 12.88    | 12.12  | 13.04  | 12.18  |  |  |  |  |
| S         | 0.33    | LLD    | LLD      | LLD    | 0.05   | LLD    |  |  |  |  |
| Ca        | 2.76    | 0.32   | 0.15     | 1.01   | 0.47   | 0.7    |  |  |  |  |
| Fe        | 0.07    | LLD    | LLD      | LLD    | LLD    | LLD    |  |  |  |  |
| F         | 0.58    | 0.88   | 0.87     | 1.18   | 0.89   | 1.03   |  |  |  |  |
| Cl        | LLD     | LLD    | LLD      | 0.09   | LLD    | 0.06   |  |  |  |  |
| O         | 27.30   | 26.60  | 26.51    | 26.19  | 26.94  | 27.45  |  |  |  |  |
| Sum       | 97.59   | 100.09 | 100.05   | 98.45  | 99.12  | 98.68  |  |  |  |  |
| ΣREE      | 52.13   | 58.51  | 59.41    | 57.38  | 56.60  | 56.84  |  |  |  |  |
| ΣREE +Y   | 53.05   | 58.83  | 59.55    | 57.74  | 57.62  | 57.19  |  |  |  |  |
| La/Ce     | 0.34    | 0.32   | 0.26     | 0.33   | 0.35   | 0.32   |  |  |  |  |
| La/Y      | 10.59   | 31.35  | 59.14    | 27.75  | 10.84  | 26.46  |  |  |  |  |
| La/Nd     | 1.12    | 0.88   | 0.56     | 0.82   | 1.18   | 0.72   |  |  |  |  |
| ΣHREE     | 1.83    | 1.69   | 1.02     | 1.20   | 2.14   | 1.26   |  |  |  |  |

**Table 5. EMP analyses of Allanite 1 and 2 grains.**

|       | Allanite2 |        |        |        |         |        |        |        |           |         |       |       |  |
|-------|-----------|--------|--------|--------|---------|--------|--------|--------|-----------|---------|-------|-------|--|
| Label | B12-5     | b12-6  | b12-12 | b12-23 | B12-27  | B12-30 | B12-32 | B12-38 | b12-65-13 | B9-21   | B9-23 | B9-24 |  |
| La    | 5.42      | 5.87   | 4.52   | 5.19   | 5.09    | 8.28   | 5.59   | 4.01   | 4.91      | 4.47    | 4.67  | 4.54  |  |
| Ce    | 14.99     | 12.89  | 12.11  | 12.07  | 15.18   | 11.76  | 12.49  | 11.37  | 11.87     | 11.62   | 11.28 | 10.98 |  |
| Pr    | 1.00      | 0.91   | 1.14   | 0.95   | 1.11    | 1.06   | 1.17   | 1.31   | 1.11      | 0.95    | 0.94  | 1.27  |  |
| Nd    | 2.44      | 2.51   | 3.95   | 2.58   | 2.68    | 2.29   | 2.65   | 4.32   | 3.37      | 3.80    | 3.35  | 3.35  |  |
| Sm    | 0.00      | 0.24   | 0.24   | 0.23   | 0.12    | 0.26   | 0.16   | 0.2    | 0.25      | 0.24    | 0.14  | 0.19  |  |
| Gd    | 0.00      | NA     | NA     | NA     | 0.12    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Tb    | 0.00      | NA     | NA     | NA     | 0.00    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Dy    | 0.01      | NA     | NA     | NA     | 0.07    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Ho    | 0.00      | NA     | NA     | NA     | 0.00    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Er    | 0.00      | NA     | NA     | NA     | 0.00    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Yb    | 0.00      | NA     | NA     | NA     | 0.00    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Y     | 0.00      | 0.05   | 0.1    | 0.09   | 0.00    | 0.07   | 0.02   | 0.14   | 0.10      | 0.09    | 0.14  | 0.03  |  |
| Th    | 0.00      | NA     | NA     | NA     | 0.00    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| U     | 0.03      | NA     | NA     | NA     | 0.04    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| F     | 0.12      | 0.27   | 0.44   | 0.28   | 0.08    | 0.54   | 0.6    | 0.38   | 0.42      | 0.49    | 0.38  | 0.48  |  |
| Mg    | 0.12      | 0.08   | 0.36   | 0.06   | 0.19    | 1.06   | 0.53   | 0.17   | 0.21      | 0.17    | 0.1   | 0.09  |  |
| Al    | 4.00      | 4.07   | 4.15   | 3.59   | 3.71    | 5.88   | 6.3    | 4.72   | 4.72      | 5.76    | 4.44  | 5.24  |  |
| Si    | 13.70     | 13.6   | 13.78  | 13.73  | 13.58   | 14.23  | 13.75  | 13.67  | 13.16     | 13.53   | 13.71 | 13.86 |  |
| P     | 0.01      | 0      | 0.03   | 0      | 0.01    | 0.02   | 0.01   | 0.02   | 0.00      | 0.00    | 0.01  | 0.01  |  |
| S     | 0.00      | NA     | NA     | NA     | 0.00    | NA     | NA     | NA     | NA        | NA      | NA    | NA    |  |
| Ca    | 6.79      | 7.4    | 6.64   | 7.84   | 6.76    | 6.96   | 6.98   | 7.07   | 6.91      | 7.35    | 7.65  | 8.1   |  |
| Fe    | 15.69     | 16.77  | 14.4   | 17.09  | 15.89   | 10.07  | 11.65  | 14.46  | 16.98     | 15.12   | 15.7  | 14.51 |  |
| Cl    |           | 0.02   | 0.02   | 0.04   |         | 0.03   | 0      | 0.01   | 0.02      | 0.00    | 0.01  | 0.02  |  |
| O     | 34.96     | 36.15  | 37.7   | 37.09  | 34.48   | 37.8   | 36.96  | 36.46  | 35.87     | 36.39   | 36.85 | 36.72 |  |
| Total | 99.27     | 100.83 | 99.58  | 100.83 | 99.13   | 100.31 | 98.86  | 98.31  | 99.91     | 99.97   | 99.37 | 99.2  |  |
| ΣREE  | 23.8502   | 22.42  | 21.96  | 21.02  | 24.3699 | 23.65  | 22.06  | 21.21  | 21.511    | 21.0777 | 20.38 | 20.14 |  |

**Table 5. Continued**

|       | Allanite1 |         |         |        | Allanite<br>2 |       |        |         |         |         |         |        |        |  |
|-------|-----------|---------|---------|--------|---------------|-------|--------|---------|---------|---------|---------|--------|--------|--|
| Label | b70-6     | b70-8   | b70-9   | B12-37 | B9-22         | B9-17 | B9-18  | cx-8    | cx-8a   | B12-1   | B12-2   | B12-3  | B12-4  |  |
| La    | 5.22      | 4.04    | 3.83    | 3.8    | 3.08          | 3.92  | 2.52   | 4.74    | 4.95    | 3.59    | 4.33    | 4.01   | 4.86   |  |
| Ce    | 13.04     | 11.07   | 10.06   | 12.18  | 8.53          | 11.65 | 7.14   | 13.14   | 13.58   | 11.76   | 13.86   | 14.77  | 14.39  |  |
| Pr    | 1.05      | 0.98    | 0.97    | 1.03   | 0.96          | 0.72  | 0.79   | 0.91    | 0.89    | 1.13    | 1.16    | 1.26   | 1.19   |  |
| Nd    | 2.82      | 3.33    | 3.18    | 4.23   | 3.41          | 3.07  | 2.87   | 2.33    | 2.48    | 3.42    | 3.79    | 3.56   | 3.32   |  |
| Sm    | 0.00      | 0.28    | 0.28    | 0.18   | 0.28          | 0.31  | 0.24   | 0.17    | 0.15    | 0.31    | 0.22    | 0.16   | 0.26   |  |
| Gd    | 0.00      | 0.06    | 0.05    | NA     | NA            | NA    | NA     | 0.05    | 0.03    | 0.18    | 0.08    | 0.01   | 0.13   |  |
| Tb    | 0.00      | 0.00    | 0.00    | NA     | NA            | NA    | NA     | 0.17    | 0.11    | 0.00    | 0.00    | 0.00   | 0.00   |  |
| Dy    | 0.00      | 0.00    | 0.00    | NA     | NA            | NA    | NA     | 0.02    | 0.00    | 0.02    | 0.00    | 0.02   | 0.00   |  |
| Ho    | 0.00      | 0.06    | 0.00    | NA     | NA            | NA    | NA     | 0.00    | 0.00    | 0.00    | 0.02    | 0.06   | 0.16   |  |
| Er    | 0.00      | 0.12    | 0.09    | NA     | NA            | NA    | NA     | 0.12    | 0.00    | 0.08    | 0.01    | 0.07   | 0.07   |  |
| Yb    | 0.01      | 0.01    | 0.02    | NA     | NA            | NA    | NA     | 0.00    | 0.00    | 0.02    | 0.00    | 0.06   | 0.00   |  |
| Y     | 0.01      | 0.00    | 0.02    | 0.06   | 0.06          | 0.08  | 0.11   | 0.03    | 0.08    | 0.13    | 0.10    | 0.05   | 0.06   |  |
| Th    | 0.00      | 0.00    | 0.00    | NA     | NA            | NA    | NA     | 0.07    | 0.06    | 0.00    | 0.13    | 0.00   | 0.10   |  |
| U     | 0.06      | 0.06    | 0.06    | NA     | NA            | NA    | NA     | 0.02    | 0.08    | 0.02    | 0.03    | 0.07   | 0.02   |  |
| F     | 0.06      | 0.01    | 0.01    | 0.51   | 0.32          | 0.27  | 0.33   | 0.12    | 0.11    | 0.09    | 0.09    | 0.09   | 0.09   |  |
| Mg    | 0.00      | 0.00    | 0.00    | 0.16   | 0.07          | 0.06  | 0.05   | 0.18    | 0.14    | 0.02    | 0.04    | 0.06   | 0.16   |  |
| Al    | 4.54      | 5.57    | 6.24    | 4.8    | 6.24          | 6.28  | 7.21   | 3.41    | 3.29    | 6.93    | 5.28    | 4.63   | 4.20   |  |
| Si    | 13.88     | 14.34   | 14.57   | 13.6   | 14.43         | 14.35 | 14.78  | 14.65   | 14.17   | 14.59   | 13.95   | 13.88  | 13.70  |  |
| P     | 0.02      | 0.01    | 0.02    | 0      | 0.02          | 0.03  | 0.09   | 0.15    | 0.08    | 0.00    | 0.01    | 0.01   | 0.00   |  |
| S     | 0.00      | 0.00    | 0.00    | NA     | NA            | NA    | NA     | 0.00    | 0.00    | 0.00    | 0.00    | 0.00   | 0.00   |  |
| Ca    | 7.58      | 8.61    | 9.14    | 6.89   | 9.53          | 9.45  | 10.6   | 6.83    | 6.84    | 8.65    | 7.19    | 7.04   | 6.88   |  |
| Fe    | 15.54     | 14.12   | 13.27   | 14.51  | 13.76         | 13.67 | 13.43  | 14.35   | 15.30   | 11.84   | 13.64   | 15.14  | 15.22  |  |
| O     | 35.80     | 35.54   | 37.86   | 36.97  | 38.35         | 36.23 | 40     | 36.68   | 35.96   | 36.88   | 35.33   | 35.20  | 35.61  |  |
| Total | 99.64     | 98.20   | 99.68   | 98.92  | 99.04         | 100.2 | 100.17 | 98.12   | 98.30   | 99.65   | 99.26   | 100.13 | 100.41 |  |
| Σ REE | 22.1486   | 19.9604 | 18.4878 | 21.42  | 16.26         | 19.67 | 13.56  | 21.6332 | 22.1916 | 20.5009 | 23.4755 | 23.975 | 24.37  |  |

**Table 5. Continued**

|       | Allanite2 |       |       |       |        |        |        |        |        |        |        |        |        |        |        |  |  |  |  |  |
|-------|-----------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|--|--|--|--|
|       | b12-      |       |       |       |        |        |        |        |        |        |        |        |        |        |        |  |  |  |  |  |
| Label | B12-6     | 7bro  | B12-8 | B12-9 | b12-10 | B12-11 | B12-12 | B12-13 | B12-14 | B12-15 | B12-16 | B12-17 | B12-18 | B12-19 | B12-20 |  |  |  |  |  |
| La    | 3.42      | 3.91  | 4.37  | 4.11  | 4.08   | 3.62   | 4.34   | 4.43   | 3.12   | 4.38   | 4.25   | 4.69   | 4.91   | 4.65   | 5.16   |  |  |  |  |  |
| Ce    | 11.70     | 13.71 | 13.50 | 12.84 | 14.18  | 11.14  | 14.07  | 14.29  | 11.07  | 13.86  | 13.80  | 14.53  | 14.59  | 14.39  | 13.60  |  |  |  |  |  |
| Pr    | 1.07      | 1.11  | 1.22  | 1.22  | 1.25   | 1.05   | 1.25   | 1.21   | 1.02   | 1.16   | 1.24   | 1.24   | 1.12   | 1.22   | 1.00   |  |  |  |  |  |
| Nd    | 3.68      | 4.1   | 3.81  | 3.99  | 3.78   | 3.68   | 3.69   | 3.51   | 3.59   | 3.63   | 4.27   | 3.64   | 2.13   | 3.26   | 2.75   |  |  |  |  |  |
| Sm    | 0.27      | 0.12  | 0.35  | 0.37  | 0.22   | 0.44   | 0.32   | 0.22   | 0.48   | 0.25   | 0.48   | 0.09   | 0.04   | 0.20   | 0.05   |  |  |  |  |  |
| Gd    | 0.05      | NA    | 0.12  | 0.22  | 0.09   | 0.19   | 0.12   | 0.06   | 0.23   | 0.15   | 0.05   | 0.00   | 0.00   | 0.07   | 0.02   |  |  |  |  |  |
| Tb    | 0.00      | NA    | 0.00  | 0.00  | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |  |  |  |  |  |
| Dy    | 0.03      | NA    | 0.00  | 0.00  | 0.05   | 0.07   | 0.00   | 0.02   | 0.08   | 0.06   | 0.00   | 0.00   | 0.00   | 0.00   | 0.03   |  |  |  |  |  |
| Ho    | 0.07      | NA    | 0.00  | 0.00  | 0.07   | 0.00   | 0.05   | 0.15   | 0.00   | 0.07   | 0.07   | 0.00   | 0.01   | 0.00   | 0.00   |  |  |  |  |  |
| Er    | 0.06      | NA    | 0.01  | 0.00  | 0.01   | 0.02   | 0.00   | 0.00   | 0.03   | 0.01   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |  |  |  |  |  |
| Yb    | 0.00      | NA    | 0.00  | 0.01  | 0.02   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |  |  |  |  |  |
| Y     | 0.08      | 0.03  | 0.01  | 0.10  | 0.05   | 0.11   | 0.09   | 0.04   | 0.18   | 0.07   | 0.04   | 0.01   | 0.01   | 0.02   | 0.00   |  |  |  |  |  |
| Th    | 0.00      | NA    | 0.05  | 0.02  | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.03   | 0.00   | 0.00   | 0.00   | 0.03   | 0.00   |  |  |  |  |  |
| U     | 0.06      | NA    | 0.01  | 0.04  | 0.00   | 0.05   | 0.05   | 0.08   | 0.02   | 0.00   | 0.04   | 0.09   | 0.07   | 0.07   | 0.02   |  |  |  |  |  |
| F     | 0.03      | 0.36  | 0.10  | 0.11  | 0.10   | 0.05   | 0.06   | 0.13   | 0.11   | 0.11   | 0.08   | 0.06   | 0.12   | 0.12   | 0.04   |  |  |  |  |  |
| Mg    | 0.00      | 0.22  | 0.02  | 0.06  | 0.03   | 0.12   | 0.10   | 0.15   | 0.02   | 0.05   | 0.14   | 0.19   | 0.17   | 0.16   | 0.02   |  |  |  |  |  |
| Al    | 6.67      | 4.57  | 5.39  | 5.97  | 5.23   | 6.58   | 4.60   | 4.35   | 7.92   | 5.24   | 4.46   | 4.14   | 2.59   | 4.34   | 3.27   |  |  |  |  |  |
| Si    | 14.52     | 13.76 | 13.89 | 14.10 | 13.90  | 14.46  | 13.74  | 13.74  | 14.74  | 13.86  | 13.71  | 13.69  | 13.37  | 13.81  | 13.56  |  |  |  |  |  |
| P     | 0.01      | 0.03  | 0.02  | 0.02  | 0.01   | 0.02   | 0.02   | 0.02   | 0.01   | 0.01   | 0.01   | 0.01   | 0.00   | 0.00   | 0.01   |  |  |  |  |  |
| S     | 0.00      |       | 0.00  | 0.00  | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |  |  |  |  |  |
| Ca    | 8.54      | 6.7   | 7.09  | 7.42  | 7.22   | 8.27   | 7.06   | 6.96   | 8.83   | 7.13   | 6.85   | 6.80   | 6.40   | 6.95   | 7.00   |  |  |  |  |  |
| Fe    | 12.29     | 14.84 | 13.95 | 12.92 | 14.01  | 12.12  | 14.88  | 15.20  | 10.49  | 13.74  | 14.55  | 15.21  | 16.39  | 14.70  | 16.87  |  |  |  |  |  |
| O     | 36.73     | 36.44 | 35.66 | 36.21 | 35.75  | 37.33  | 35.22  | 35.44  | 37.56  | 35.69  | 34.78  | 34.96  | 36.51  | 35.91  | 36.31  |  |  |  |  |  |
| Total | 99.29     | 99.9  | 99.57 | 99.74 | 100.05 | 99.33  | 99.69  | 99.99  | 99.50  | 99.52  | 98.80  | 99.36  | 98.45  | 99.90  | 99.71  |  |  |  |  |  |
| ΣREE  | 20.35     | 22.95 | 23.38 | 22.77 | 23.74  | 20.21  | 23.85  | 23.88  | 19.62  | 23.57  | 24.14  | 24.19  | 22.81  | 23.79  | 22.60  |  |  |  |  |  |

**Table 5. Continued**

|       | Allanite2 |        |        |        |        |        |       |       |       |       |       |       |  |
|-------|-----------|--------|--------|--------|--------|--------|-------|-------|-------|-------|-------|-------|--|
| Label | B12-19    | B12-20 | B12-21 | B12-22 | B12-25 | B12-26 | b70-1 | b70-2 | b70-3 | b70-4 | b70-5 | b70-7 |  |
| La    | 4.65      | 5.16   | 4.01   | 4.27   | 4.91   | 4.48   | 2.50  | 1.70  | 1.92  | 1.59  | 2.55  | 2.04  |  |
| Ce    | 14.39     | 13.60  | 14.15  | 13.17  | 14.97  | 15.01  | 7.95  | 5.84  | 8.32  | 6.00  | 7.64  | 6.78  |  |
| Pr    | 1.22      | 1.00   | 1.29   | 1.19   | 1.25   | 1.33   | 0.86  | 0.71  | 1.10  | 0.79  | 0.82  | 0.87  |  |
| Nd    | 3.26      | 2.75   | 3.67   | 3.55   | 3.15   | 3.46   | 2.63  | 2.51  | 3.48  | 3.11  | 2.64  | 2.91  |  |
| Gd    | 0.20      | 0.05   | 0.21   | 0.30   | 0.17   | 0.12   | 0.27  | 0.29  | 0.32  | 0.57  | 0.23  | 0.29  |  |
| Dy    | 0.07      | 0.02   | 0.12   | 0.09   | 0.00   | 0.04   | 0.00  | 0.11  | 0.05  | 0.20  | 0.06  | 0.06  |  |
| Ho    | 0.00      | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |  |
| Er    | 0.00      | 0.03   | 0.02   | 0.00   | 0.00   | 0.00   | 0.00  | 0.00  | 0.04  | 0.03  | 0.00  | 0.03  |  |
| Yb    | 0.00      | 0.00   | 0.00   | 0.01   | 0.12   | 0.00   | 0.03  | 0.05  | 0.00  | 0.04  | 0.00  | 0.02  |  |
| Y     | 0.00      | 0.00   | 0.00   | 0.07   | 0.01   | 0.07   | 0.00  | 0.00  | 0.00  | 0.03  | 0.02  | 0.00  |  |
| U     | 0.00      | 0.00   | 0.00   | 0.00   | 0.00   | 0.01   | 0.00  | 0.00  | 0.06  | 0.00  | 0.00  | 0.00  |  |
| Mg    | 0.02      | 0.00   | 0.00   | 0.03   | 0.02   | 0.01   | 0.05  | 0.06  | 0.03  | 0.08  | 0.01  | 0.00  |  |
| Al    | 0.03      | 0.00   | 0.04   | 0.07   | 0.00   | 0.00   | 1.18  | 0.01  | 0.00  | 0.00  | 0.00  | 0.00  |  |
| Si    | 0.07      | 0.02   | 0.00   | 0.05   | 0.05   | 0.00   | 0.10  | 0.07  | 0.03  | 0.00  | 0.02  | 0.05  |  |
| P     | 0.12      | 0.04   | 0.12   | 0.08   | 0.11   | 0.09   | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |  |
| S     | 0.16      | 0.02   | 0.07   | 0.04   | 0.23   | 0.10   | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |  |
| Ca    | 4.34      | 3.27   | 5.02   | 5.74   | 3.96   | 4.03   | 7.25  | 8.55  | 6.25  | 8.35  | 7.48  | 7.55  |  |
| Fe    | 13.81     | 13.56  | 13.84  | 14.16  | 13.49  | 13.62  | 15.21 | 15.73 | 14.95 | 15.49 | 15.28 | 15.37 |  |
| O     | 0.00      | 0.01   | 0.01   | 0.01   | 0.01   | 0.00   | 0.04  | 0.01  | 0.02  | 0.00  | 0.02  | 0.00  |  |
| Total | 0.00      | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |  |
| Σ REE | 6.95      | 7.00   | 7.12   | 7.59   | 6.68   | 6.68   | 10.56 | 12.27 | 10.50 | 11.86 | 11.06 | 11.41 |  |

**Table 6. EMP analyses of other RE minerals.**

| Label | Britholite |        |        | Xenotime |        |        |       |        |          |       | Synchysite |        |         | Bastnasite |           |  |
|-------|------------|--------|--------|----------|--------|--------|-------|--------|----------|-------|------------|--------|---------|------------|-----------|--|
|       | b70-10     | b70-11 | B12-65 | 107-4-3  | 101-2  | 101-3  | 101-6 | 101-7  | 101-11-1 | B12-7 | B12-23     | B12-24 | Label   | B12-35Bas  | B12-36Bas |  |
| La    | 0.09       | 0.06   | 0.05   | 0.18     | 0.01   | 0.04   | 0.03  | 0.01   | 8.23     | 9.09  | 7.90       | 9.30   | La      | 12.14      | 11.67     |  |
| Ce    | 0.91       | 1.02   | 0.94   | 0.13     | 0.07   | 0.09   | 0.11  | 0.15   | 23.09    | 23.59 | 21.59      | 22.47  | Ce      | 33.84      | 34.41     |  |
| Pr    | 0.22       | 0.35   | 0.29   | 0.00     | 0.00   | 0.05   | 0.00  | 0.00   | 2.01     | 2.19  | 2.07       | 2.29   | Pr      | 2.51       | 2.32      |  |
| Nd    | 1.92       | 2.09   | 1.82   | 0.15     | 0.00   | 0.00   | 0.00  | 0.11   | 8.2      | 8.72  | 7.19       | 8.62   | Nd      | 9.35       | 8.05      |  |
| Sm    | 1.05       | 1.58   | 1.11   | UDL      | UDL    | UDL    | UDL   | UDL    | 1.24     | 1.34  | 1.07       | 1.24   | Sm      | 1.61       | 1.41      |  |
| Gd    | 3.23       | 2.97   | 2.65   | 4.81     | 4.36   | 3.62   | 4.39  | 5.21   | 1.13     | 1.20  | 0.86       | 1.25   | Gd      | 1.27       | 1.76      |  |
| Tb    | 0.41       | 0.53   | 0.58   | 0.52     | 0.63   | 0.47   | 0.63  | 0.72   | UDL      | UDL   | UDL        | UDL    | Tb      | NA         | NA        |  |
| Dy    | 2.80       | 2.46   | 2.66   | 4.73     | 5.35   | 4.12   | 5.30  | 5.13   | 0.47     | 0.29  | 0.34       | 0.54   | Dy      | 0.36       | 0.65      |  |
| Ho    | 0.50       | 0.47   | 0.62   | 0.94     | 1.07   | 0.76   | 1.06  | 0.85   | 0.08     | 0.04  | 0.10       | UDL    | Ho      | 0.06       | 0.12      |  |
| Er    | 2.04       | 1.85   | 2.41   | 3.54     | 3.63   | 3.33   | 3.68  | 3.34   | 0.11     | 0.09  | 0.16       | 0.08   | Er      | 0.11       | 0.21      |  |
| Yb    | 1.37       | 1.86   | 1.75   | 2.39     | 2.58   | 2.43   | 2.59  | 2.38   | 0.05     | 0.07  | 0.05       | 0.03   | Yb      | 0.04       | 0.06      |  |
| Y     | 26.16      | 25.57  | 25.87  | 34.60    | 34.53  | 34.36  | 34.65 | 34.39  | 1.6      | 1.70  | 1.51       | 1.67   | Y       | 1.27       | 1.55      |  |
| Th    | 0.00       | 0.00   | 0.00   | 0.21     | 0.13   | 0.27   | 0.08  | 0.80   | UDL      | UDL   | UDL        | UDL    | Th      | 0.00       | 0.00      |  |
| U     | 0.01       | 0.01   | 0.01   | 0.24     | 0.14   | 0.13   | 0.16  | 0.36   | 0.03     | 0.05  | 0.00       | 0.02   | U       | 0.03       | 0.02      |  |
| F     | 0.37       | 0.52   | 0.46   | 0.08     | 0.00   | 0.00   | 0.01  | 0.00   | 6.91     | 5.32  | 6.04       | 6.08   | F       | 8.46       | 7.78      |  |
| Mg    | 0.00       | 0.00   | 0.00   | 0.00     | 0.00   | 0.00   | 0.00  | 0.00   | UDL      | UDL   | UDL        | UDL    | Mg      | 0.00       | 0.00      |  |
| Al    | 1.85       | 2.16   | 2.06   | 0.00     | 0.00   | 0.00   | 0.00  | 0.00   | 0        | 0.02  | 0.01       | 0.01   | Al      | 0.00       | 0.00      |  |
| Si    | 11.20      | 11.48  | 11.52  | 0.01     | 0.08   | 1.52   | 0.07  | 0.23   | UDL      | UDL   | UDL        | UDL    | Si      | 0.00       | 0.00      |  |
| P     | 0.05       | 0.16   | 0.10   | 14.11    | 15.65  | 13.88  | 15.65 | 15.16  | 0.05     | 0.04  | 0.15       | 0.50   | P       | 0.04       | 0.02      |  |
| S     | 0.01       | 0.01   | 0.01   | 0.00     | 0.01   | 0.01   | 0.00  | 0.00   | 0        | 0.00  | 0.00       | 0.00   | S       | NA         | NA        |  |
| Ca    | 12.79      | 12.57  | 12.71  | 0.32     | 0.09   | 0.17   | 0.09  | 0.22   | 12.36    | 12.69 | 15.18      | 11.61  | Ca      | 0.14       | 0.26      |  |
| Fe    | 1.41       | 1.03   | 1.53   | 0.00     | 0.00   | 2.05   | 0.00  | 0.12   | 0.03     | 0.26  | 0.27       | 0.00   | Fe      | 0.02       |           |  |
| O     | 41.59      | 42.37  | 41.41  | 32.76    | 31.71  | 32.84  | 31.28 | 30.92  | 27.39    | 26.98 | 27.57      | 27.59  | O       | 21.51      | 21.98     |  |
| Total | 109.97     | 111.12 | 110.56 | 99.73    | 100.05 | 100.14 | 99.77 | 100.11 | 92.98    | 93.69 | 92.06      | 93.30  | Total   | 92.76      | 92.27     |  |
| Σ REE | 40.70      | 40.81  | 40.75  | 51.99    | 52.24  | 49.27  | 52.43 | 52.30  | 46.21    | 48.33 | 42.83      | 47.48  | ΣREE +Y | 62.56      | 62.21     |  |

**Table 7 Electron microprobe analyses of magnetites and hematites associated with ore and host rocks of Esfordi mineralization.**

| Wt%                            | Magnetite-rich core |         |        |         |         |         |         |         |         |         | Brecciated core |        |    |    |    |    |
|--------------------------------|---------------------|---------|--------|---------|---------|---------|---------|---------|---------|---------|-----------------|--------|----|----|----|----|
|                                | Mt                  | Mt      | Mt     | Mt      | Mt      | Mt      | Mt      | Mt      | Mt      | Mt      | Mt              | Mt     | Mt | Mt | Mt | Mt |
| Label                          | b40-1               | b40-2   | b40-3  | b40-7   | b40-9   | b40-10  | t40     |         |         |         |                 |        |    |    |    |    |
| SiO <sub>2</sub>               | UDL                 | UDL     | 0.057  | 0.864   | 0.054   | 0.043   | 0.021   | UDL     | 0.034   | 0.059   | 0.049           | 0.043  |    |    |    |    |
| TiO <sub>2</sub>               | 0.303               | 0.046   | 0.091  | 0.086   | 0.038   | 0.074   | 0.767   | 0.084   | 0.024   | 0.160   | 0.035           | 0.204  |    |    |    |    |
| Al <sub>2</sub> O <sub>3</sub> | 0.040               | UDL     | UDL    | 0.081   | UDL     | UDL     | UDL     | 0.018   | UDL     | UDL     | 0.022           | UDL    |    |    |    |    |
| Cr <sub>2</sub> O <sub>3</sub> | 0.018               | 0.021   | UDL    | UDL     | UDL     | UDL     | 0.020   | 0.018   | 0.018   | 0.021   | UDL             | 0.018  |    |    |    |    |
| V <sub>2</sub> O <sub>5</sub>  | 0.333               | 0.287   | 0.215  | 0.253   | 0.258   | 0.227   | 0.356   | 0.331   | 0.343   | 0.355   | 0.294           | 0.294  |    |    |    |    |
| MgO                            | UDL                 | UDL     | UDL    | 0.364   | UDL     | UDL     | UDL     | UDL     | 0.025   | UDL     | UDL             | UDL    |    |    |    |    |
| CaO                            | 0.023               | 0.009   | 0.007  | 0.199   | 0.008   | 0.059   | 0.028   | 0.003   | 0.034   | 0.000   | 0.049           | 0.041  |    |    |    |    |
| MnO                            | UDL                 | UDL     | UDL    | 0.031   | 0.022   | 0.040   | 0.018   | UDL     | 0.012   | UDL     | UDL             | UDL    |    |    |    |    |
| Fe <sub>2</sub> O <sub>3</sub> | 67.610              | 68.618  | 67.891 | 66.674  | 68.145  | 68.851  | 66.639  | 68.036  | 68.036  | 67.881  | 68.563          | 67.163 |    |    |    |    |
| FeO                            | 31.792              | 31.653  | 31.329 | 32.001  | 31.449  | 31.666  | 32.248  | 31.675  | 31.593  | 31.952  | 31.759          | 31.422 |    |    |    |    |
| NiO                            | 0.096               | 0.088   | 0.106  | 0.043   | 0.099   | 0.060   | 0.110   | 0.039   | UDL     | UDL     | 0.035           | 0.032  |    |    |    |    |
| Na <sub>2</sub> O              | UDL                 | 0.066   | UDL    | 0.107   | UDL     | 0.037   | 0.022   | 0.043   | 0.037   | UDL     | UDL             | UDL    |    |    |    |    |
| K <sub>2</sub> O               | UDL                 | UDL     | UDL    | UDL     | UDL     | UDL     | UDL     | UDL     | UDL     | UDL     | 0.027           | UDL    |    |    |    |    |
| TOTAL                          | 100.226             | 100.733 | 99.697 | 100.600 | 100.079 | 101.027 | 100.212 | 100.212 | 100.212 | 100.449 | 100.807         | 99.217 |    |    |    |    |

Table 7 Continued.

| Brecciated core                |        |        |        |         |        |        |         |        |         |         |         |        |         |        |          |        |
|--------------------------------|--------|--------|--------|---------|--------|--------|---------|--------|---------|---------|---------|--------|---------|--------|----------|--------|
| Wt%                            | Mt     | Mt     | Hem    | Mt      | Hem    | Mt     | Hem     | Mt     | Hem     | Mt      | Hem     | Mt     | Hem     | Mt     | Hem      | Hem    |
| Label                          | Rt3-9  | t33    | t33-1  | t39     | t41    | b7-51  | b7-57   | b7-58  | b7-59   | b7-67   | b7-68   | Mt     | Hem     | Mt     | Hem      | E1-60  |
| SiO <sub>2</sub>               | UDL    | UDL    | 0.043  | UDL     | 0.364  | 0.171  | 0.107   | 0.107  | UDL     | 0.043   | 0.043   | 0.107  | UDL     | 0.043  | 0.043    | 0.021  |
| TiO <sub>2</sub>               | 0.649  | 0.033  | 0.083  | 1.601   | 0.100  | 0.033  | 0.083   | 0.033  | 0.050   | 0.050   | 0.033   | 0.033  | 0.050   | 0.033  | 0.033    | 0.100  |
| Al <sub>2</sub> O <sub>3</sub> | 0.092  | UDL    | UDL    | UDL     | UDL    | UDL    | UDL     | UDL    | UDL     | UDL     | UDL     | UDL    | UDL     | UDL    | UDL      | UDL    |
| Cr <sub>2</sub> O <sub>3</sub> | 0.034  | UDL    | UDL    | UDL     | UDL    | UDL    | UDL     | UDL    | UDL     | UDL     | UDL     | UDL    | UDL     | UDL    | UDL      | UDL    |
| V <sub>2</sub> O <sub>5</sub>  | 0.060  | 0.607  | 0.553  | 0.482   | 0.321  | 0.287  | 0.250   | 0.250  | 0.303   | 0.161   | 0.303   | 0.250  | 0.303   | 0.303  | 0.303    | 0.643  |
| MgO                            | 0.000  | 0.017  | UDL    | UDL     | 0.116  | 0.017  | UDL     | 0.033  | UDL     | UDL     | UDL     | 0.033  | UDL     | UDL    | UDL      | 0.050  |
| CaO                            | 0.030  | 0.112  | 0.028  | 0.028   | 0.070  | 0.070  | 0.014   | 0.000  | 0.042   | 0.392   | 0.518   | 0.000  | 0.042   | 0.518  | 0.042    | 0.042  |
| MnO                            | 0.068  | UDL    | UDL    | 0.065   | UDL    | 0.052  | UDL     | 0.013  | UDL     | UDL     | 0.026   | 0.013  | UDL     | 0.026  | UDL      | UDL    |
| Fe <sub>2</sub> O <sub>3</sub> | 67.123 | 67.218 | 98.052 | 95.718  | 66.449 | 98.050 | 99.181  | 67.831 | 99.216  | 98.524  | 67.711  | 67.831 | 99.216  | 67.711 | 97.697   | 97.697 |
| FeO                            | 31.515 | 31.807 | 0.965  | 2.100   | 31.537 | 0.517  | 0.580   | 31.452 | 0.471   | 0.000   | 30.775  | 31.452 | 0.471   | 30.775 | 0.989    | 0.989  |
| NiO                            | UDL    | UDL    | UDL    | UDL     | UDL    | UDL    | UDL     | UDL    | UDL     | UDL     | UDL     | UDL    | UDL     | UDL    | UDL      | UDL    |
| Na <sub>2</sub> O              | 0.029  | UDL    | UDL    | UDL     | UDL    | UDL    | UDL     | UDL    | UDL     | UDL     | UDL     | UDL    | UDL     | UDL    | UDL      | UDL    |
| K <sub>2</sub> O               | 0.035  | UDL    | UDL    | UDL     | UDL    | UDL    | UDL     | UDL    | UDL     | UDL     | UDL     | UDL    | UDL     | UDL    | UDL      | UDL    |
| TOTAL                          | 99.576 | 99.794 | 99.725 | 99.994  | 98.957 | 99.196 | 100.215 | 99.719 | 100.082 | 99.169  | 99.409  | 99.719 | 100.082 | 99.169 | 99.409   | 99.541 |
| Brecciated core                |        |        |        |         |        |        |         |        |         |         |         |        |         |        |          |        |
| Wt%                            | Hem    | Mt     | Mt     | Hem     | Mt     | Hem    | Mt      | Mt     | Mt      | Mt      | Mt      | Mt     | Mt      | Mt     | Mt       | Mt     |
| Label                          | b40-1  | b40-3  | b40-10 | b40-10  | 102-1  | 102-5  | 102-7   | 102-11 | 102-11  | 106-1   | 106-2   | 106-3  | 106-4   | 106-4  | B27-22-3 | Mt     |
| SiO <sub>2</sub>               | 0.028  | 0.024  | 0.063  | 0.045   | 0.043  | 0.043  | 0.024   | 0.015  | 0.015   | UDL     | 0.040   | UDL    | UDL     | UDL    | UDL      | 0.035  |
| TiO <sub>2</sub>               | UDL    | 0.050  | 0.000  | 0.108   | 0.204  | 0.204  | 0.033   | 0.017  | 0.017   | 0.359   | 0.323   | 0.350  | 0.300   | 0.300  | 0.094    | 0.094  |
| Al <sub>2</sub> O <sub>3</sub> | 0.040  | 0.016  | 0.029  | 0.019   | UDL    | UDL    | UDL     | UDL    | UDL     | 0.164   | 0.162   | 0.135  | 0.135   | 0.135  | 0.220    | 0.220  |
| Cr <sub>2</sub> O <sub>3</sub> | UDL    | UDL    | UDL    | UDL     | 0.018  | 0.018  | 0.043   | 0.030  | 0.030   | 0.026   | UDL     | UDL    | UDL     | UDL    | 0.055    | 0.055  |
| V <sub>2</sub> O <sub>5</sub>  | 0.081  | 0.284  | 0.223  | 0.188   | 0.294  | 0.294  | 0.292   | 0.089  | 0.089   | 0.415   | 0.409   | 0.264  | 0.448   | 0.448  | 0.054    | 0.054  |
| MgO                            | UDL    | 0.016  | UDL    | UDL     | UDL    | UDL    | UDL     | 0.018  | 0.018   | UDL     | UDL     | 0.053  | 0.053   | 0.053  | UDL      | UDL    |
| CaO                            | 0.000  | 0.000  | 0.018  | 0.017   | 0.041  | 0.041  | 0.162   | 0.047  | 0.047   | UDL     | 0.015   | UDL    | 0.004   | 0.004  | 0.228    | 0.228  |
| MnO                            | 0.022  | 0.040  | UDL    | UDL     | UDL    | UDL    | 0.019   | UDL    | UDL     | 0.034   | UDL     | UDL    | 0.000   | 0.000  | 0.009    | 0.009  |
| Fe <sub>2</sub> O <sub>3</sub> | 99.563 | 67.602 | 68.182 | 99.987  | 67.163 | 67.163 | 99.044  | 67.956 | 67.956  | 66.537  | 67.031  | 67.313 | 67.003  | 67.003 | 68.169   | 68.169 |
| FeO                            | 0.017  | 31.226 | 31.394 | 0.418   | 31.422 | 31.422 | 0.294   | 30.752 | 30.752  | 31.793  | 32.030  | 31.612 | 31.891  | 31.891 | 30.952   | 30.952 |
| NiO                            | 0.128  | 0.067  | 0.046  | UDL     | 0.032  | 0.032  | UDL     | 0.057  | 0.057   | 0.051   | 0.028   | 0.030  | 0.030   | 0.030  | UDL      | UDL    |
| Na <sub>2</sub> O              | 0.039  | UDL    | 0.025  | 0.020   | UDL    | UDL    | 0.016   | UDL    | UDL     | 0.035   | 0.012   | 0.010  | 0.010   | 0.010  | UDL      | UDL    |
| K <sub>2</sub> O               | UDL    | 0.012  | UDL    | UDL     | 0.006  | 0.006  | UDL     | 0.006  | 0.006   | UDL     | UDL     | UDL    | 0.000   | 0.000  | 0.006    | 0.006  |
| TOTAL                          | 99.880 | 99.327 | 99.956 | 100.793 | 99.217 | 99.217 | 99.911  | 98.982 | 98.982  | 99.387  | 100.039 | 99.761 | 99.864  | 99.864 | 99.816   | 99.816 |
| Clastic Magnetite              |        |        |        |         |        |        |         |        |         |         |         |        |         |        |          |        |
| Wt%                            | Hem    | Mt     | Mt     | Hem     | Mt     | Hem    | Mt      | Mt     | Mt      | Mt      | Mt      | Mt     | Mt      | Mt     | Mt       | Mt     |
| Label                          | b40-1  | b40-3  | b40-10 | 102-1   | 102-5  | 102-7  | 102-11  | 102-11 | 106-1   | 106-2   | 106-3   | 106-4  | 106-4   | 106-4  | B27-22-3 | Mt     |
| SiO <sub>2</sub>               | 0.028  | 0.024  | 0.063  | 0.045   | 0.043  | 0.043  | 0.024   | 0.015  | UDL     | 0.040   | UDL     | UDL    | UDL     | UDL    | UDL      | 0.035  |
| TiO <sub>2</sub>               | UDL    | 0.050  | 0.000  | 0.108   | 0.204  | 0.204  | 0.033   | 0.017  | 0.359   | 0.323   | 0.350   | 0.300  | 0.300   | 0.300  | 0.094    | 0.094  |
| Al <sub>2</sub> O <sub>3</sub> | 0.040  | 0.016  | 0.029  | 0.019   | UDL    | UDL    | UDL     | UDL    | 0.164   | 0.162   | 0.135   | 0.135  | 0.135   | 0.135  | 0.220    | 0.220  |
| Cr <sub>2</sub> O <sub>3</sub> | UDL    | UDL    | UDL    | UDL     | 0.018  | 0.018  | 0.043   | 0.030  | 0.026   | UDL     | UDL     | UDL    | UDL     | UDL    | 0.055    | 0.055  |
| V <sub>2</sub> O <sub>5</sub>  | 0.081  | 0.284  | 0.223  | 0.188   | 0.294  | 0.294  | 0.292   | 0.089  | 0.415   | 0.409   | 0.264   | 0.448  | 0.448   | 0.448  | 0.054    | 0.054  |
| MgO                            | UDL    | 0.016  | UDL    | UDL     | UDL    | UDL    | UDL     | 0.018  | UDL     | UDL     | 0.053   | 0.053  | 0.053   | 0.053  | UDL      | UDL    |
| CaO                            | 0.000  | 0.000  | 0.018  | 0.017   | 0.041  | 0.041  | 0.162   | 0.047  | UDL     | 0.015   | UDL     | 0.004  | 0.004   | 0.004  | 0.228    | 0.228  |
| MnO                            | 0.022  | 0.040  | UDL    | UDL     | UDL    | UDL    | 0.019   | UDL    | 0.034   | UDL     | UDL     | 0.000  | 0.000   | 0.000  | 0.009    | 0.009  |
| Fe <sub>2</sub> O <sub>3</sub> | 99.563 | 67.602 | 68.182 | 99.987  | 67.163 | 67.163 | 99.044  | 67.956 | 66.537  | 67.031  | 67.313  | 67.003 | 67.003  | 67.003 | 68.169   | 68.169 |
| FeO                            | 0.017  | 31.226 | 31.394 | 0.418   | 31.422 | 31.422 | 0.294   | 30.752 | 31.793  | 32.030  | 31.612  | 31.891 | 31.891  | 31.891 | 30.952   | 30.952 |
| NiO                            | 0.128  | 0.067  | 0.046  | UDL     | 0.032  | 0.032  | UDL     | 0.057  | 0.051   | 0.028   | 0.030   | 0.030  | 0.030   | 0.030  | UDL      | UDL    |
| Na <sub>2</sub> O              | 0.039  | UDL    | 0.025  | 0.020   | UDL    | UDL    | 0.016   | UDL    | 0.035   | 0.012   | 0.010   | 0.010  | 0.010   | 0.010  | UDL      | UDL    |
| K <sub>2</sub> O               | UDL    | 0.012  | UDL    | UDL     | 0.006  | 0.006  | UDL     | 0.006  | UDL     | UDL     | UDL     | 0.000  | 0.000   | 0.000  | 0.006    | 0.006  |
| TOTAL                          | 99.880 | 99.327 | 99.956 | 100.793 | 99.217 | 99.217 | 99.911  | 98.982 | 99.387  | 100.039 | 99.761  | 99.864 | 99.864  | 99.864 | 99.816   | 99.816 |

Table 7 Continued.

| Magnetite 2                        |          |           |         |        | Specularite |         |         |           |           |         |         |        |     |     |     |     |     |     |
|------------------------------------|----------|-----------|---------|--------|-------------|---------|---------|-----------|-----------|---------|---------|--------|-----|-----|-----|-----|-----|-----|
| Wt%                                | Mt       | Mt        | Mt      | Mt     | Mt          | Hem     | Hem     | Hem       | Hem       | Hem     | Hem     | Hem    | Hem | Hem | Hem | Hem | Hem | Hem |
| Label                              | B27-22-8 | B27-22-13 | 102-7   | 102-11 | b12-65-8    | E-I-1   | E-I-2   | B27-22-23 | B27-22-24 | 102-1   | 108-8   | E1-71  |     |     |     |     |     |     |
| SiO <sub>2</sub>                   | 0.013    | 0.065     | 0.024   | 0.015  | 0.052       | 0.021   | 0.013   | 0.064     | 0.231     | 0.278   | 0.111   | UDL    |     |     |     |     |     |     |
| TiO <sub>2</sub>                   | UDL      | 0.261     | UDL     | 0.016  | 0.050       | 0.015   | 0.021   | 0.040     | UDL       | 0.108   | 0.090   | 0.083  |     |     |     |     |     |     |
| Al <sub>2</sub> O <sub>3</sub>     | UDL      | UDL       | UDL     | UDL    | 0.010       | UDL     | 0.478   | 0.568     | 0.012     | 0.192   | 0.506   | 0.040  |     |     |     |     |     |     |
| Cr <sub>2</sub> O <sub>3</sub>     | 0.024    | 0.024     | 0.043   | 0.030  | UDL         | 0.026   | 0.015   | 0.035     | UDL       | UDL     | UDL     | UDL    |     |     |     |     |     |     |
| V <sub>2</sub> O <sub>5</sub>      | UDL      | 0.216     | 0.292   | 0.089  | 0.037       | 0.028   | 0.048   | 0.219     | 0.010     | 0.014   | 0.018   | 0.357  |     |     |     |     |     |     |
| MgO                                | UDL      | UDL       | UDL     | 0.018  | 0.583       | 0.002   | 0.017   | 0.870     | 0.069     | UDL     | UDL     | UDL    |     |     |     |     |     |     |
| CaO                                | 0.058    | 0.078     | 0.162   | 0.047  | 0.175       | 0.196   | 0.003   | 0.430     | 0.043     | 0.109   | 0.168   | 0.120  |     |     |     |     |     |     |
| MnO                                | 0.022    | UDL       | 0.019   | UDL    | 0.015       | UDL     | 0.013   | 0.014     | 0.108     | 0.007   | UDL     | UDL    |     |     |     |     |     |     |
| Fe <sub>2</sub> O <sub>3</sub>     | 68.626   | 68.073    | 67.240  | 67.958 | 68.879      | 100.489 | 100.819 | 100.540   | 100.163   | 100.406 | 99.650  | 98.784 |     |     |     |     |     |     |
| FeO                                | 30.828   | 31.741    | 30.911  | 30.750 | 30.034      | UDL     | 0.061   | UDL       | 0.008     | 0.304   | 0.026   | 0.480  |     |     |     |     |     |     |
| NiO                                | UDL      | 0.021     | UDL     | 0.057  | UDL         | UDL     | UDL     | 0.596     | UDL       | UDL     | UDL     | UDL    |     |     |     |     |     |     |
| Na <sub>2</sub> O                  | UDL      | UDL       | 0.016   | UDL    | 0.071       | 0.013   | 0.027   | 0.111     | 0.312     | 0.020   | 0.021   | 0.019  |     |     |     |     |     |     |
| K <sub>2</sub> O                   | 0.019    | 0.017     | UDL     | UDL    | 0.050       | UDL     | 0.013   | 0.032     | 0.012     | 0.015   | 0.017   | UDL    |     |     |     |     |     |     |
| TOTAL                              | 99.575   | 100.482   | 98.691  | 98.981 | 99.836      | 100.784 | 101.490 | 103.376   | 100.649   | 101.423 | 100.570 | 99.868 |     |     |     |     |     |     |
| Volcaniclastic rocks and rhyolites |          |           |         |        |             |         |         |           |           |         |         |        |     |     |     |     |     |     |
| Wt%                                | Mt       | Mt        | Mt      | Mt     | Mt          | Mt      | Hem     | Mt        | Hem       | Mt      | Mt      | Mt     | Mt  |     |     |     |     |     |
| Label                              | T-1      | T-1-2     | T-1-3   | T-1-5  | T-1-6       | T-1-7   | T-1-8   | T-1-9     | Rt3-1     | Rt3-2   | Rt3-4   | Rt3-6  |     |     |     |     |     |     |
| SiO <sub>2</sub>                   | 0.018    | UDL       | 0.007   | 0.033  | 0.014       | 0.022   | UDL     | 0.012     | 0.109     | 0.063   | 0.018   | 0.018  |     |     |     |     |     |     |
| TiO <sub>2</sub>                   | 0.319    | 1.171     | 0.223   | 1.024  | 0.613       | 0.286   | 1.106   | 0.244     | 4.061     | 0.897   | 1.904   | 0.271  |     |     |     |     |     |     |
| Al <sub>2</sub> O <sub>3</sub>     | 0.531    | 0.570     | 0.552   | 0.482  | 0.209       | 0.608   | 0.290   | 0.905     | 0.122     | 0.044   | 0.094   | UDL    |     |     |     |     |     |     |
| Cr <sub>2</sub> O <sub>3</sub>     | UDL      | 0.018     | 0.043   | UDL    | UDL         | 0.031   | 0.065   | UDL       | UDL       | 0.049   | UDL     | UDL    |     |     |     |     |     |     |
| V <sub>2</sub> O <sub>5</sub>      | 0.058    | 0.021     | 0.048   | 0.035  | UDL         | 0.029   | 0.047   | UDL       | 0.128     | 0.088   | 0.054   | 0.027  |     |     |     |     |     |     |
| MgO                                | 0.093    | 0.104     | UDL     | UDL    | UDL         | 0.120   | 0.099   | 0.198     | 0.567     | UDL     | 0.010   | UDL    |     |     |     |     |     |     |
| CaO                                | 0.021    | UDL       | UDL     | UDL    | UDL         | 0.010   | UDL     | UDL       | 0.011     | 0.029   | 0.043   | UDL    |     |     |     |     |     |     |
| MnO                                | UDL      | UDL       | 0.025   | UDL    | UDL         | 0.047   | 0.012   | 0.050     | 0.101     | 0.056   | 0.044   | UDL    |     |     |     |     |     |     |
| Fe <sub>2</sub> O <sub>3</sub>     | 67.910   | 66.463    | 67.980  | 65.934 | 67.016      | 66.986  | 98.469  | 67.113    | 91.790    | 66.615  | 64.343  | 68.036 |     |     |     |     |     |     |
| FeO                                | 31.512   | 32.291    | 31.514  | 31.824 | 31.426      | 30.890  | 0.880   | 30.876    | 2.830     | 31.899  | 32.503  | 31.208 |     |     |     |     |     |     |
| NiO                                | UDL      | UDL       | UDL     | UDL    | UDL         | 0.068   | UDL     | 0.025     | 0.029     | 0.036   | 0.014   | UDL    |     |     |     |     |     |     |
| Na <sub>2</sub> O                  | UDL      | UDL       | UDL     | UDL    | UDL         | UDL     | 0.019   | UDL       | UDL       | 0.023   | UDL     | UDL    |     |     |     |     |     |     |
| K <sub>2</sub> O                   | UDL      | 0.017     | 0.014   | UDL    | UDL         | UDL     | UDL     | UDL       | 0.010     | 0.080   | 0.037   | 0.036  |     |     |     |     |     |     |
| TOTAL                              | 100.463  | 100.642   | 100.396 | 99.443 | 99.287      | 99.096  | 100.967 | 99.425    | 99.748    | 99.777  | 99.027  | 99.567 |     |     |     |     |     |     |

Table 7 Continued.

| Volcaniclastic rocks           |        |        | Jaspilite |        |        |        | Dolerite |        |        |        |        |        |
|--------------------------------|--------|--------|-----------|--------|--------|--------|----------|--------|--------|--------|--------|--------|
| Wt%                            | Mt     | Mt     | Mt        | Mt     | Mt     | Mt     | Mt       | Mt     | Mt     | Mt     | Mt     | Mt     |
| Label                          | Rt3-8  | Rt3-7  | E-Ra-1    | E-Ra-2 | E-Ra-3 | E-Ra-4 | E-Ra-1   | 24-2   | 24-6   | 24-7   | 24-7-2 | 24-10  |
| SiO <sub>2</sub>               | 0.010  | 0.007  | 0.030     | UDL    | 0.010  | UDL    | 0.030    | 0.108  | 0.042  | 0.082  | 0.032  | UDL    |
| TiO <sub>2</sub>               | 2.709  | 1.497  | 0.300     | 0.417  | 0.100  | 0.037  | 0.020    | 5.354  | 7.279  | 9.064  | 10.314 | 11.340 |
| Al <sub>2</sub> O <sub>3</sub> | 0.110  | UDL    | 0.265     | 0.491  | 0.208  | 0.151  | 0.265    | 1.560  | UDL    | UDL    | 0.013  | UDL    |
| Cr <sub>2</sub> O <sub>3</sub> | 0.044  | UDL    | UDL       | UDL    | UDL    | UDL    | UDL      | 0.326  | 0.337  | 0.286  | 0.233  | 0.281  |
| V <sub>2</sub> O <sub>5</sub>  | 0.100  | 0.039  | UDL       | UDL    | UDL    | 0.047  | 0.018    | 0.431  | 0.298  | 0.409  | 0.478  | 0.343  |
| MgO                            | 0.289  | UDL    | UDL       | UDL    | UDL    | UDL    | UDL      | 0.052  | UDL    | 0.021  | 0.000  | 0.029  |
| CaO                            | 0.028  | 0.037  | UDL       | UDL    | UDL    | UDL    | UDL      | 0.043  | UDL    | 0.048  | 0.024  | 0.099  |
| MnO                            | 0.081  | 0.075  | UDL       | UDL    | UDL    | UDL    | UDL      | 0.296  | 0.830  | 1.157  | 1.216  | 1.468  |
| Fe <sub>2</sub> O <sub>3</sub> | 62.631 | 65.115 | 68.395    | 67.411 | 67.685 | 68.568 | 68.735   | 55.101 | 53.082 | 49.812 | 47.228 | 45.125 |
| FeO                            | 32.772 | 31.962 | 31.574    | 31.443 | 30.811 | 31.167 | 31.268   | 36.651 | 37.129 | 38.900 | 40.051 | 40.046 |
| NiO                            | 0.046  | 0.028  | UDL       | UDL    | UDL    | UDL    | UDL      | 0.028  | 0.092  | 0.004  | 0.000  | 0.071  |
| Na <sub>2</sub> O              | 0.000  | 0.013  | UDL       | UDL    | UDL    | UDL    | UDL      | 0.017  | UDL    | UDL    | 0.028  | 0.006  |
| K <sub>2</sub> O               | 0.032  | 0.035  | UDL       | UDL    | UDL    | UDL    | UDL      | 0.040  | UDL    | UDL    | UDL    | 0.010  |
| TOTAL                          | 98.820 | 98.761 | 100.567   | 99.773 | 98.818 | 99.977 | 100.336  | 99.951 | 99.090 | 99.783 | 99.590 | 98.801 |

**Table 7 Continued.**

|                                    | <b>Dolerite</b> |        | <b>N.Dolerite</b> |         |         | <b>Trachyte</b> |         |          |
|------------------------------------|-----------------|--------|-------------------|---------|---------|-----------------|---------|----------|
| Wt%                                | Mt              | Mt     | Mt                | Mt      | Mt      | Hem             | Mt      | Mt       |
| <b>Label</b>                       | 24-15           | 24-15  | 90-2              | 90-4    | 90-4-2  | 90-7            | 10-82-4 | 10-82-13 |
| <b>SiO<sub>2</sub></b>             | 0.064           | 0.054  | 0.100             | 0.104   | 0.169   | 0.103           | 0.384   | 0.328    |
| <b>TiO<sub>2</sub></b>             | 8.005           | 9.635  | 12.412            | 3.520   | 1.918   | 10.384          | 0.093   | 0.386    |
| <b>Al<sub>2</sub>O<sub>3</sub></b> | 0.023           | 0.566  | UDL               | UDL     | UDL     | UDL             | 0.190   | 0.200    |
| <b>Cr<sub>2</sub>O<sub>3</sub></b> | 0.524           | 0.285  | 0.543             | 0.054   | 0.126   | 0.593           | 0.027   | 0.165    |
| <b>V<sub>2</sub>O<sub>5</sub></b>  | 0.338           | 0.485  | 0.538             | 0.375   | 0.303   | 0.405           | 0.222   | 0.157    |
| <b>MgO</b>                         | UDL             | UDL    | 0.017             | 0.019   | UDL     | 0.032           | UDL     | UDL      |
| <b>CaO</b>                         | 0.058           | 0.015  | 0.151             | 0.102   | UDL     | 0.047           | 0.142   | 0.023    |
| <b>MnO</b>                         | 0.110           | 0.843  | 0.419             | 0.021   | 0.000   | 0.975           | 0.015   | 0.028    |
| <b>Fe<sub>2</sub>O<sub>3</sub></b> | 50.739          | 47.435 | 42.069            | 61.842  | 64.322  | 77.412          | 66.782  | 65.707   |
| <b>FeO</b>                         | 38.384          | 39.691 | 42.516            | 35.221  | 33.519  | 8.965           | 31.694  | 31.634   |
| <b>NiO</b>                         | 0.004           | 0.114  | 0.072             | 0.065   | 0.175   | 0.033           | 0.000   | 0.000    |
| <b>Na<sub>2</sub>O</b>             | UDL             | 0.023  | 0.050             | 0.012   | 0.021   | UDL             | 0.046   | 0.013    |
| <b>K<sub>2</sub>O</b>              | UDL             | UDL    | 0.028             | 0.002   | 0.006   | 0.011           | 0.025   | 0.023    |
| <b>TOTAL</b>                       | 98.250          | 99.123 | 98.840            | 101.332 | 100.535 | 98.950          | 99.551  | 98.627   |

**Table 8. XRF analytical results**

| Wt %                           | Massive magnetite-rich core |        | Brecciated rim of the Fe-oxide core |        | Massive apatite ore |       | Brecciated apatite ore with carbonate overprint |        |        | Jaspilite |
|--------------------------------|-----------------------------|--------|-------------------------------------|--------|---------------------|-------|-------------------------------------------------|--------|--------|-----------|
| sample                         | B20-43                      | B27-38 | B34-11                              | B40    | Bh12-65             | Cx-ap | 108                                             | B27-22 | R3     | 10        |
| SiO <sub>2</sub>               | 18.33                       | 9.74   | 9.94                                | 9      | 3.47                | 4.07  | 32.96                                           | 2.71   | 16.49  | 29.52     |
| TiO <sub>2</sub>               | 1.58                        | 0.96   | 0.46                                | 0.49   | 0.05                | 0.04  | 0.07                                            | 0.02   | 1.76   | UDL       |
| Al <sub>2</sub> O <sub>3</sub> | 0.16                        | 0.15   | UDL                                 | UDL    | UDL                 | UDL   | UDL                                             | 0.1    | UDL    | 0.26      |
| Fe <sub>2</sub> O <sub>3</sub> | 69.70                       | 66.91  | 22.67                               | 52.97  | 3.23                | 2.14  | 19.52                                           | 7.46   | 16.59  | 62.38     |
| MnO                            | 0.02                        | 0.03   | 0.01                                | 0.05   | 0.07                | 0.08  | 0.06                                            | 0.04   | 0.03   | 0.12      |
| MgO                            | 0.53                        | 0.23   | 0.62                                | 1.21   | 0.99                | 0.95  | 0.96                                            | 0.56   | 1.39   | 0.15      |
| CaO                            | 4.56                        | 11.33  | 37.46                               | 19.85  | 51.27               | 51.59 | 25.02                                           | 50.11  | 35.52  | 3.83      |
| Na <sub>2</sub> O              | 0.12                        | 0.34   | 0.42                                | 0.32   | 0.68                | 0.82  | 0.42                                            | 0.32   | 0.48   | 0.09      |
| K <sub>2</sub> O               | UDL                         | 0.05   | 0.08                                | 0.02   | 0.15                | 0.16  | 0.09                                            | 0.03   | 0.11   | UDL       |
| P <sub>2</sub> O <sub>5</sub>  | 2.47                        | 5.53   | 22.25                               | 11.39  | 32.64               | 33.65 | 16.33                                           | 32.73  | 22.12  | 0.08      |
| SO <sub>3</sub>                | UDL                         | UDL    | 0.19                                | UDL    | 0.44                | 0.46  | 0.24                                            | 0.14   | 0.31   | UDL       |
| L.O.I                          |                             | 3.29   | 4.54                                | 2.82   | 0.39                | 3.55  | 2.63                                            | 4.75   | 4.58   | 2.6       |
| Total                          | 97.47                       | 98.56  | 98.64                               | 98.12  | 93.38               | 97.51 | 98.3                                            | 98.91  | 99.38  | 99.03     |
| Trace elements (ppm)           |                             |        |                                     |        |                     |       |                                                 |        |        |           |
| Sn                             | 45                          | 52.7   | 1.9                                 | 44.8   | LLD                 | LLD   | 23.1                                            | LLD    | 43.6   | 55.4      |
| Cd                             | 17.5                        | 17.9   | 3.3                                 | 10.5   | 6.6                 | 18    | 7.6                                             | 11     | LLD    | 13.2      |
| Mo                             | LLD                         | 4.8    | LLD                                 | LLD    | LLD                 | LLD   | 2                                               | LLD    | 2.2    | 126.1     |
| Nb                             | 3.6                         | 1.7    | LLD                                 | LLD    | LLD                 | 5.9   | 1                                               | LLD    | 21.6   | 2.9       |
| Zr                             | LLD                         | LLD    | 22.4                                | LLD    | 28.9                | 30.6  | 26.7                                            | 30.2   | 28.9   | LLD       |
| Sr                             | 34.3                        | 117.2  | 408.6                               | 151.6  | 367.9               | 408.4 | 381.3                                           | 410.7  | 268.7  | 44.3      |
| U                              | LLD                         | 12.5   | 11                                  | 7.7    | 10.6                | 8     | 6.4                                             | 13.6   | 6.2    | 5.7       |
| Rb                             | LLD                         | LLD    | 12.9                                | 1.8    | 24.4                | 22    | 11.6                                            | 21.2   | 15.6   | LLD       |
| Th                             | 14.7                        | 37     | 64.5                                | 71.2   | 97.3                | 71    | 51.8                                            | 78.7   | 66.5   | 3.6       |
| Pb                             | 5.7                         | 6.1    | 5.3                                 | 6.4    | 6.3                 | 8.1   | 4.2                                             | 8.4    | 7.6    | 6.5       |
| As                             | 17.3                        | 19.9   | 114.9                               | 83.9   | 109.2               | 88.3  | 24.3                                            | 106.6  | 146.4  | 29.5      |
| Ga                             | 32                          | 22     | 3.5                                 | 16.3   | 2.2                 | 0.01  | 2.2                                             | LLD    | LLD    | 2         |
| Zn                             | 17.8                        | 13.6   | 10.1                                | 15.2   | 9.3                 | 4.2   | 3.6                                             | LLD    | 7.1    | 19.2      |
| Cu                             | 11.3                        | 17.8   | 33.4                                | 20.2   | 36.3                | 31.9  | 27.1                                            | 320.5  | 20.9   | 74.5      |
| Ni                             | 121.5                       | 14.9   | LLD                                 | LLD    | LLD                 | LLD   | LLD                                             | LLD    | LLD    | 5.8       |
| Co                             | LLD                         | LLD    | 23.9                                | LLD    | LLD                 | LLD   | 22.9                                            | LLD    | 15.2   | LLD       |
| Cr                             | LLD                         | LLD    | LLD                                 | 10.3   | LLD                 | LLD   | LLD                                             | LLD    | 39.7   | 208.2     |
| V                              | 2189.6                      | 1265.7 | 252.7                               | 749.8  | 128.2               | 34.8  | 315.4                                           | 40.7   | 114.4  | 11.4      |
| La                             | 77.26                       | 323.00 | 1145.7                              | 1068.3 | 2551.6              | NA    | 2582.4                                          | 2056.7 | 406.6  | 22.6      |
| Ce                             | 443.5                       | 1060.0 | 3058.7                              | 2553.7 | 6477.6              | 5073  | 3469.5                                          | 4721.3 | 1363.3 | 33.4      |
| Pr                             | 54.38                       | 132.58 | 324.77                              | 319.98 | 599.46              | NA    | 363.65                                          | 444.91 | 158.24 | 1.41      |
| Nd                             | 213.6                       | 495.1  | 1383.4                              | 964.4  | 2282.2              | NA    | 1148.1                                          | 1644.2 | 477.09 | 3.55      |
| Sm                             | 38.00                       | 80.14  | 222.02                              | 234.63 | 361.99              | NA    | 243.72                                          | 263.31 | 125.81 | 0.51      |
| Eu                             | 4.34                        | 6.68   | 19.24                               | 15.43  | 35.06               | NA    | 21.69                                           | 45.66  | 16.02  | 0.44      |
| Gd                             | 36.42                       | 78.42  | 239.00                              | 258.66 | 369.96              | NA    | 223.60                                          | 282.16 | 161.73 | 0.44      |
| Tb                             | 5.45                        | 10.97  | 37.14                               | 41.10  | 55.88               | NA    | 30.19                                           | 48.17  | 26.53  | 0.07      |
| Dy                             | 26.36                       | 52.13  | 190.66                              | 216.39 | 264.20              | NA    | 134.66                                          | 176.89 | 142.38 | 0.40      |
| Ho                             | 5.72                        | 11.31  | 43.14                               | 48.18  | 55.16               | NA    | 26.34                                           | 40.60  | 31.70  | 0.07      |
| Er                             | 13.67                       | 27.60  | 110.86                              | 127.05 | 148.89              | NA    | 69.38                                           | 89.50  | 79.17  | 0.22      |
| Tm                             | 1.72                        | 3.44   | 14.34                               | 16.99  | 19.16               | NA    | 8.43                                            | 13.32  | 10.77  | 0.03      |
| Yb                             | 8.73                        | 18.22  | 76.02                               | 91.27  | 97.82               | NA    | 42.76                                           | 78.71  | 56.49  | 0.19      |
| Lu                             | 1.17                        | 2.57   | 10.34                               | 12.99  | 12.61               | NA    | 5.38                                            | 8.78   | 7.62   | 0.02      |

**Table 8. Continued.**

|      | Ap. Ore | Ap. Ore | Ap. Ore | Ap. Ore | Fe ore | Fe ore | Fe ore       | carbonate-<br>rich ap ore | Jaspilite |
|------|---------|---------|---------|---------|--------|--------|--------------|---------------------------|-----------|
| Name | B12-7   | B27-22  | B40     | 108     | B20-43 | B27-38 | B34-<br>10.7 | R3                        | 10        |
| Ba   | 11.9    | 6.2     | 6.6     | 1825.6  | 17.4   | 15.7   | 12.3         | 11.2                      | 96.2      |
| Ce   | 6477.6  | 4721.3  | 2553.8  | 3469.6  | 443.5  | 1060.0 | 3058.8       | 1363.4                    | 33.5      |
| Dy   | 264.2   | 176.9   | 216.4   | 134.7   | 26.4   | 52.1   | 190.7        | 142.4                     | 0.4       |
| Er   | 148.9   | 89.5    | 127.1   | 69.4    | 13.7   | 27.6   | 110.9        | 79.2                      | 0.2       |
| Eu   | 35.1    | 45.7    | 15.4    | 21.7    | 4.3    | 6.7    | 19.2         | 16.0                      | 0.4       |
| Ga   | 4.2     | 0.0     | 20.3    | 80.6    | 33.3   | 24.6   | 6.5          | 3.0                       | 0.0       |
| Gd   | 369.9   | 282.2   | 258.7   | 223.6   | 36.4   | 78.4   | 239.0        | 161.7                     | 0.4       |
| Ho   | 55.1    | 40.6    | 48.2    | 26.3    | 5.7    | 11.3   | 43.1         | 31.7                      | 0.1       |
| La   | 2551.6  | 2056.7  | 1068.3  | 2582.4  | 77.3   | 323.0  | 1145.7       | 406.6                     | 22.6      |
| Lu   | 12.6    | 8.8     | 13.0    | 5.4     | 1.2    | 2.6    | 10.3         | 7.6                       | 0.0       |
| Mn   | 370.8   | 301.6   | 432.2   | 380.5   | 241.0  | 262.8  | 305.4        | 116.3                     | 1017.1    |
| Nd   | 2282.2  | 1644.2  | 964.4   | 1148.1  | 213.6  | 495.1  | 1383.4       | 477.1                     | 3.6       |
| Ni   | 169.6   | 0.0     | 542.1   | 222.9   | 511.3  | 346.3  | 350.6        | 255.3                     | 0.0       |
| Pb   | 26.4    | 1.7     | 11.9    | 19.3    | 16.1   | 11.7   | 17.1         | 33.5                      | 5.2       |
| Pr   | 599.5   | 444.9   | 319.9   | 363.7   | 54.4   | 132.6  | 324.8        | 158.2                     | 1.4       |
| Sm   | 361.9   | 263.3   | 234.6   | 243.7   | 38.0   | 80.1   | 222.0        | 125.8                     | 0.5       |
| Sr   | 402.9   | 577.6   | 152.9   | 433.1   | 30.2   | 113.6  | 403.9        | 301.5                     | 43.5      |
| Tb   | 55.9    | 48.2    | 41.1    | 30.2    | 5.5    | 10.9   | 37.1         | 26.5                      | 0.1       |
| Th   | 129.1   | 14.3    | 54.8    | 54.3    | 8.5    | 20.7   | 62.4         | 76.6                      | 0.9       |
| Tm   | 19.2    | 13.3    | 17.0    | 8.4     | 1.7    | 3.4    | 14.3         | 10.8                      | 0.0       |
| U    | 14.9    | 9.3     | 6.9     | 8.8     | 1.7    | 15.9   | 8.5          | 6.4                       | 4.4       |
| V    | 0.0     | 74.8    | 0.0     | 0.0     | 0.0    | 0.0    | 0.0          |                           | 36.0      |
| Y    | 1606.5  | 995.8   | 1057.8  | 611.0   | 131.9  | 260.3  | 1234.7       | 709.5                     | 1.4       |
| Yb   | 97.8    | 78.7    | 91.3    | 42.8    | 8.7    | 18.2   | 76.0         | 56.5                      | 0.2       |

**Table 8. Continued.**

|                                | Gabbro    |        | Doleritic<br>dykes |        |         |        | Granites |         |           |         |
|--------------------------------|-----------|--------|--------------------|--------|---------|--------|----------|---------|-----------|---------|
|                                | Mishdovan | W. Esf | Esfordi            | Esford | Narigan | Esford | Narigan  | Narigan | Mishdovan | Narigan |
| sample                         | 86        | 76     | 24                 | 28     | 90      | 103    | 89-1     | 93      | 85        | 91-2    |
| SiO <sub>2</sub>               | 51.83     | 69.49  | 47.77              | 46.12  | 44      | 46.41  | 74.06    | 79.39   | 77.68     | 72.43   |
| TiO <sub>2</sub>               | 1.16      | 0.1    | 2.59               | 2.72   | 3.21    | 1.243  | 0.25     | 0.32    | 0.17      | 0.34    |
| Al <sub>2</sub> O <sub>3</sub> | 18.1      | 10.47  | 14.89              | 13.65  | 13.35   | 15.98  | 13.71    | 11.05   | 12.52     | 14.26   |
| Fe <sub>2</sub> O <sub>3</sub> | 7.58      | 2.55   | 11.72              | 12.83  | 14.27   | 9.64   | 1.07     | 0.94    | 0.85      | 1.72    |
| MnO                            | 0.11      | 0.07   | 0.16               | 0.18   | 0.14    | 0.18   | 0.02     | 0.02    | 0.01      | 0.02    |
| MgO                            | 5.95      | 1.22   | 5.9                | 6.84   | 8.62    | 8.42   | 0.55     | 0.36    | 0.24      | 0.79    |
| CaO                            | 8.49      | 4.2    | 5.38               | 6.2    | 6.16    | 11.16  | 1.15     | 0.68    | 0.35      | 0.9     |
| Na <sub>2</sub> O              | 3.71      | 0.56   | 4.63               | 3.87   | 3.53    | 2.05   | 4.02     | 5.77    | 5.66      | 7.02    |
| K <sub>2</sub> O               | 0.88      | 7.69   | 2.96               | 2.84   | 1.51    | 0.836  | 4.28     | 0.33    | 1.92      | 0.46    |
| P <sub>2</sub> O <sub>5</sub>  | 0.12      | 0.05   | 0.89               | 0.93   | 0.95    | 0.12   | 0.06     | 0.04    | 0.02      | 0.07    |
| SO <sub>3</sub>                |           | 0.05   | 0.04               | 0.09   |         | 0.023  | 0.02     | 0.03    | 0.03      |         |
| L.O.I                          | 1.75      | 4.33   | 2.75               | 3.51   | 3.87    | 3.97   | 1.15     | 0.96    | 0.8       | 1.68    |
| FeO                            |           |        |                    |        |         |        |          |         |           |         |
| Total                          | 6.82      | 2.29   | 10.55              | 11.55  | 12.84   | 8.67   | 0.96     | 0.84    | 0.76      | 1.55    |
| Total                          | 99.68     | 100.78 | 99.65              | 99.78  | 99.61   | 96.3   | 100.34   | 99.89   | 100.25    | 99.69   |
| Sb                             | LLD       | LLD    | LLD                | LLD    | LLD     | 3.3    | 4.9      | 6.6     | 7.3       | 7.9     |
| Sn                             | 8.3       | 4      | 11.9               | 5.1    | 9.8     | UDL    | LLD      | LLD     | LLD       | LLD     |
| Cd                             | LLD       | LLD    | 3.3                | LLD    | LLD     | 6.8    | LLD      | LLD     | LLD       | LLD     |
| Mo                             | 2.2       | LLD    | 6.3                | 3.3    | 3       | 1      | LLD      | 2       | 2.6       | LLD     |
| Nb                             | 5.7       | 4.6    | 81.6               | 78.2   | 66      | 3.8    | 5.7      | 6.1     | 3.2       | 5.6     |
| Zr                             | 59.2      | 85.9   | 580.6              | 501.7  | 371.8   | 80     | 125.4    | 121.2   | 119.4     | 119.2   |
| Y                              | 20.4      | 5.4    | 33.8               | 35.3   | 38.5    | 22.3   | 23       | 3.7     | 1.3       | 12.7    |
| Sr                             | 273.1     | 70.5   | 747.9              | 739    | 378.2   | 399.8  | 99.8     | 58.5    | 71.5      | 56.6    |
| U                              | LLD       | LLD    | 2.9                | LLD    | 4.3     | LLD    | LLD      | LLD     | LLD       | 5       |
| Rb                             | 23.1      | 127    | 78.5               | 83.4   | 44.7    | 22.6   | 95.6     | 22.4    | 35.2      | 28      |
| Th                             | LLD       | 6.1    | 14                 | 16.7   | 8.5     | LLD    | 8.9      | 4.5     | 19        | 9.3     |
| Pb                             | 8.6       | 22.8   | 15.3               | 16.3   | 6.1     | 10.4   | 8.9      | 7       | 5.5       | 5.5     |
| As                             | LLD       | 11.3   | 4.1                | 2.6    | 4.7     | LLD    | 2.5      | 2.9     | LLD       | 8.9     |
| Ga                             | 16.7      | 10.5   | 26.2               | 23.9   | 23.7    | 16.8   | 15.9     | 10      | 14        | 14.8    |
| Zn                             | 60        | 71.6   | 149.4              | 190.7  | 115     | 91.5   | 18.3     | 14.7    | 11.8      | 17      |
| Cu                             | 57.1      | 10.2   | 47.4               | 35.3   | 20.1    | 50     | 8.9      | 11      | 10.5      | 12.4    |
| Ni                             | 55.5      | 9.3    | 103.8              | 133.9  | 214.2   | 131.9  | 5.8      | 9       | 9.4       | 5.4     |
| Co                             | 27.7      | 34.8   | 33.5               | 37.7   | 38.2    | 60.6   | LLD      | LLD     | LLD       | 49      |
| Cr                             | 124.6     | LLD    | 233.1              | 260.3  | 356.9   | 423.9  | 121.2    | 202.8   | 257.8     | LLD     |
| Ce                             | 21.78     | 46.94  | 155.46             | 171.68 | 160.94  | 13.98  | 36.55    | 44.41   | 27.48     | 45.57   |
| V                              | 195.9     | 22.2   | 204                | 221.4  | 263.5   | 197.8  | 40.1     | 48.1    | 25.7      | 48.1    |
| Ba                             | 223.2     | 1306.5 | 772.5              | 627.3  | 631.7   | 660.3  | 778.3    | 56.9    | 506.6     | 57.5    |

**Table 8. Continued.**

|                                | Least altered volcanics |          |        |        | K-feld rich rocks |         |         |       |
|--------------------------------|-------------------------|----------|--------|--------|-------------------|---------|---------|-------|
|                                | E. Esf                  | gardaneh |        |        |                   |         |         |       |
| sample                         | 31                      | 105      | Bh8-65 | Bh7-41 | B2-110            | Bh12-97 | B64-108 | RT3   |
| SiO <sub>2</sub>               | 70.19                   | 70.69    | 74.17  | 70.76  | 73.38             | 75.93   | 64.81   | 70.14 |
| TiO <sub>2</sub>               | 0.18                    | 0.19     | 0.23   | 0.14   | 0.21              | 0.16    | 0.56    | 0.19  |
| Al <sub>2</sub> O <sub>3</sub> | 11.18                   | 11.98    | 12.62  | 10.48  | 11.56             | 10.67   | 14.64   | 12.14 |
| Fe <sub>2</sub> O <sub>3</sub> | 1.5                     | 2.05     | 2.56   | 1      | 2.31              | 1.09    | 2.17    | 1.72  |
| MnO                            | 0.05                    | 0.03     | 0.01   | 0.04   | 0.11              | 0.02    | 0.03    | 0.005 |
| MgO                            | 0.87                    | 0.63     | 0.68   | 2.35   | 2.37              | 1.01    | 2.1     | 0.21  |
| CaO                            | 2.78                    | 1.83     | 0.79   | 2.41   | 0.06              | 1.3     | 1.92    | 1.7   |
| Na <sub>2</sub> O              | 0.34                    | 0.45     | 5.27   | 0.36   | 0.36              | 0.46    | 0.46    | 0.31  |
| K <sub>2</sub> O               | 8.53                    | 9.54     | 2.64   | 7.45   | 8.26              | 6.9     | 9.67    | 10.37 |
| P <sub>2</sub> O <sub>5</sub>  | 0.05                    | 0.04     | 0.06   | 0.03   | 0.05              | 0.05    | 0.14    | 0.03  |
| SO <sub>3</sub>                | 0.19                    | 0.01     | 0.32   | 0.03   | 0.03              | 0.1     | 0.11    | 0.06  |
| L.O.I                          | 3.32                    | 2.07     | 1.81   | 4.57   | 1.29              | 2.36    | 4.11    | 2.17  |
| FeOTotal                       | 1.35                    | 1.84     | 2.30   | 0.99   | 2.08              | 0.98    | 1.95    | 1.55  |
| Total                          | 99.18                   | 99.51    | 101.2  | 99.62  | 99.99             | 100.05  | 100.72  | 97    |
| Sb                             | 4.3                     | LLD      | LLD    | 5.2    | 3.4               | 5.1     | LLD     | 2     |
| Sn                             | LLD                     | LLD      | 2      | 7.8    | 42                | LLD     | LLD     | LLD   |
| Cd                             | LLD                     | LLD      | LLD    | LLD    | LLD               | LLD     | LLD     | 4.1   |
| Mo                             | 2.6                     | 3        | 5.4    | LLD    | LLD               | 6       | 5.4     | 1.9   |
| Nb                             | 5.6                     | 4.1      | 7      | 2.9    | 6.4               | 6.2     | 7.2     | 5.2   |
| Zr                             | 159                     | 159.1    | 189.3  | 144.9  | 153.6             | 139.1   | 312.2   | 173.7 |
| Y                              | 28.7                    | 14.7     | 16.4   | 4.6    | 9.7               | 6.3     | 12.9    | 70.8  |
| Sr                             | 64.8                    | 39.6     | 47.5   | 32.4   | 24.3              | 35.4    | 56.3    | 62.5  |
| U                              | 2.9                     | 6.9      | 4.9    | 3.3    | 3.9               | LLD     | 4.2     | 4.4   |
| Rb                             | 179.9                   | 152.6    | 48.9   | 162.9  | 96.6              | 133.9   | 236.2   | 161   |
| Th                             | 16                      | 17.7     | 21.1   | 7.9    | 10.2              | 11.8    | 12.6    | 9.4   |
| Pb                             | 4.9                     | 4.5      | 4.6    | 5      | 4.2               | 4.6     | 5       | 4.4   |
| As                             | 8.7                     | 5.4      | 3.6    | 5.2    | 4.7               | 3.4     | 5.7     | 6.9   |
| Ga                             | 11.9                    | 20.9     | 13.8   | 13.3   | 11.6              | 7.5     | 16.1    | 9.1   |
| Zn                             | 10.3                    | 11.7     | 10.7   | 9.9    | 16.8              | 10.3    | 20.8    | 8.3   |
| Cu                             | 31.8                    | 16.9     | 9.6    | 9.5    | 13.6              | 11.4    | 10.5    | 13    |
| Ni                             | 8.3                     | 15.9     | 8.7    | 10.6   | 23.9              | 10.2    | 10.3    | LLD   |
| Co                             | LLD                     | LLD      | 3.3    | LLD    | 3.4               | LLD     | LLD     | 44.8  |
| Cr                             | 85.3                    | 121.4    | 146.9  | 100.3  | 146.5             | 124.2   | 52.3    | LLD   |
| Ce                             | 24.11                   | 56.83    | 51.46  | 55.01  | 56.35             | 18.47   | 99.34   | 37.14 |
| V                              | 34.3                    | 27.1     | 33     | 25.2   | 28                | 29.5    | 69.5    | 19.2  |
| Ba                             | 2888.5                  | 550.5    | 612.9  | 550.5  | 466.2             | 1072.8  | 1120.5  | 668.9 |

**Table 8. Continued.**

|          | Amph-Chl. Rich |        |        |         |        | Tuffaceous rocks |        |         |
|----------|----------------|--------|--------|---------|--------|------------------|--------|---------|
|          |                |        |        |         |        |                  |        |         |
| sample   | B53-41.5       | B20-2  | B21-13 | Gr-ac-1 | GR     | Bh11-45          | Bh1-13 | Bh12-25 |
| SiO2     | 51.29          | 55.22  | 55.86  | 46.65   | 46.65  | 57.2             | 56.41  | 75      |
| TiO2     | 0.18           | 0.19   | 0.49   | 0.71    | 0.71   | 0.87             | 0.44   | 0.2     |
| Al2O3    | 9.53           | 7.62   | 0.15   | LLD     | LLD    | 9.42             | 10.48  | 11.49   |
| Fe2O3    | 4.54           | 6.44   | 17.08  | 11.21   | 11.21  | 8.56             | 7.83   | 2.21    |
| MnO      | 0.04           | 0.09   | 0.09   | 0.19    | 0.19   | 0.1              | 0.08   | 0.02    |
| MgO      | 4.53           | 10.37  | 12.1   | 12.33   | 12.33  | 6                | 6.62   | 2.01    |
| CaO      | 10.4           | 9.83   | 12.74  | 20.1    | 20.1   | 6.82             | 5.5    | 0.73    |
| Na2O     | 0.66           | 3.42   | 0.76   | 0.46    | 0.46   | 1.54             | 0.4    | 0.58    |
| K2O      | 6.15           | 1.37   | 0.01   | 0.04    | 0.04   | 2.08             | 2.97   | 5.61    |
| P2O5     | 0.04           | 0.03   | 0.08   | 0.05    | 0.05   | 0.71             | 0.46   | 0.05    |
| SO3      | 0.1            | 0.04   |        | 0.07    | 0.07   | 1.3              | 1.09   | 0.19    |
| L.O.I    | 13.81          | 3.06   | 0.96   | 9.03    | 9.03   | 7.34             | 7.46   | 2.54    |
| FeOTotal | 4.09           | 5.799  | 15.37  | 10.09   | 10.09  | 7.709            | 7.05   | 1.99    |
| Total    | 101.27         | 97.68  | 100.32 | 100.84  | 100.84 | 101.94           | 99.74  | 100.63  |
| Sb       | 3              | LLD    | LLD    |         | LLD    | LLD              | LLD    | 6.7     |
| Sn       | 10.9           | 55.4   | 16.9   | 12.7    | 9.1    | 11.5             | 20.4   | 5.3     |
| Cd       | LLD            | LLD    | LLD    |         | 5.3    | LLD              | LLD    | LLD     |
| Mo       | LLD            | LLD    | LLD    |         | 0.9    | 13.1             | 7.7    | 2.1     |
| Nb       | 3.2            | 3      | 2.8    | 3.7     | 1.9    | 15.2             | 9.9    | 5.4     |
| Zr       | 170.8          | 111.6  | 43.6   | 290.5   | 125.7  | 149.7            | 146.5  | 155.5   |
| Y        | 58.6           | 160    | 145.4  | 64.1    | 100.3  | 32               | 49     | 13.6    |
| Sr       | 68.4           | 178.2  | 19.9   | 341.9   | 242.7  | 101.3            | 92     | 76.7    |
| U        | 9.7            | LLD    | LLD    |         | 3.4    | 4.4              | 4.6    | 4.7     |
| Rb       | 123.1          | 47.3   | 3      | 51.3    | 15.7   | 61.4             | 81.5   | 144.4   |
| Th       | 12.7           | 40     | LLD    | 10.5    | 16.5   | 12.4             | 10.4   | 16      |
| Pb       | 4.7            | 4.9    | 4      | 6.3     | 7.2    | 5.7              | 5.5    | 3.6     |
| As       | 2.9            | LLD    | 4      |         | LLD    | 11.3             | 14.7   | 22.4    |
| Ga       | 16.4           | 10.6   | 6.7    | 19.8    | 11     | 13.2             | 13.2   | 10.5    |
| Zn       | 73.3           | 22.6   | 43.2   | 105.6   | 65.5   | 71.5             | 60.7   | 12.2    |
| Cu       | 9              | 11.6   | 12     | 30.4    | 31.5   | 16.1             | 21.2   | 9.2     |
| Ni       | 16.9           | 10.7   | 46.6   | 96.3    | 15.6   | 31.6             | 27.4   | 8.8     |
| Co       | 12             | 14     | 30.6   | 35.3    | 21.6   | 19.7             | 16.8   | LLD     |
| Cr       | 23.9           | 51.8   | 113.7  | 42.1    | 7      | 160.7            | 120.2  | 80.3    |
| Ce       | 106.86         | 165.71 | 144.9  | 241.4   | 102.51 | 142.63           | 180.55 | LLD     |
| V        | 126            | 133.8  | 335.9  | 163.8   | 114.3  | 141.4            | 110.9  | 35.2    |
| Ba       | 498.4          | 328.1  | LLD    | 240.4   | 165.9  | 700.3            | 1059.9 | 3105.8  |

**Table 9. Normative calculation of igneous rocks chemical data of Esfordi and Bafq area.**

|                                  | Narigan Granite |        |        |        |        |       | Mishdovan granite | N.Esf. Syenite | W.Esf. Trachyte | Esfordi Rhyolite |        |        |
|----------------------------------|-----------------|--------|--------|--------|--------|-------|-------------------|----------------|-----------------|------------------|--------|--------|
|                                  | 89-1            | 93     | 91-2   | NG1    | NG2    | NG3   | 85                | 23             | 82              | RT3              | 31     | 105    |
| SiO <sub>2</sub>                 | 74.06           | 79.39  | 72.43  | 76.8   | 75.4   | 76.25 | 77.68             | 56.89          | 53.84           | 70.14            | 70.19  | 70.69  |
| TiO <sub>2</sub>                 | 0.25            | 0.32   | 0.34   | 0.22   | 0.13   | 0.02  | 0.17              | 0.19           | 0.17            | 0.191            | 0.18   | 0.19   |
| Al <sub>2</sub> O <sub>3</sub>   | 13.71           | 11.05  | 14.26  | 14.52  | 12.71  | 13.26 | 12.52             | 19.33          | 16.52           | 12.14            | 11.18  | 11.98  |
| Fe <sub>2</sub> O <sub>3</sub> T | 1.07            | 0.94   | 1.72   | 0.71   | 1.02   | 0.29  | 0.85              | 4.77           | 6.64            | 1.72             | 1.5    | 2.05   |
| MnO                              | 0.02            | 0.02   | 0.02   | 0.04   | 0.02   | 0.03  | 0.01              | 0.13           | 0.08            | 0.005            | 0.05   | 0.03   |
| MgO                              | 0.55            | 0.36   | 0.79   | 0.35   | 0.14   | 0.05  | 0.24              | 1.01           | 0.59            | 0.21             | 0.87   | 0.63   |
| CaO                              | 1.15            | 0.68   | 0.9    | 1.27   | 0.73   | 0.92  | 0.35              | 1.11           | 5.93            | 1.7              | 2.78   | 1.83   |
| Na <sub>2</sub> O                | 4.02            | 5.77   | 7.02   | 4.76   | 5.31   | 4.95  | 5.66              | 7.05           | 3.54            | 0.31             | 0.34   | 0.45   |
| K <sub>2</sub> O                 | 4.28            | 0.33   | 0.46   | 0.42   | 3.43   | 3.28  | 1.92              | 6.05           | 6.7             | 10.369           | 8.53   | 9.54   |
| P <sub>2</sub> O <sub>5</sub>    | 0.06            | 0.04   | 0.07   | 0.01   | 0.03   | 0.02  | 0.02              | 0.11           | 0.11            | 0.028            | 0.05   | 0.04   |
| LOI                              | 1.15            | 0.96   | 1.68   | 1.21   | 0.86   | 0.91  | 0.8               | 3.04           | 6.19            | 2.17             | 3.32   | 2.07   |
| Sr                               | 99.8            | 58.5   | 56.6   | 287    | 65     | 61    | 71.5              | 243.9          | 148.5           | 62.5             | 64.8   | 39.6   |
| Ba                               | 778.3           | 56.9   | 57.5   | 265    | 250    | 257   | 506.6             | 259.2          | 283.9           | 668.9            | 2888.5 | 550.5  |
| Ni                               | 5.8             | 9      | 5.4    | 4      | 5      | 4     | 9.4               | 6.3            | 7.1             | 0                | 8.3    | 15.9   |
| Cr                               | 121.2           | 202.8  | 2.2    |        |        |       | 257.8             | 55.8           | 65.2            |                  | 85.3   | 121.4  |
| Zr                               | 125.4           | 121.2  | 119.2  | 28     | 29     | 54    | 119.4             | 1014.3         | 946.5           | 173.7            | 159    | 159.1  |
| total                            | 100.34          | 99.89  | 99.69  | 100.31 | 99.78  | 99.98 | 100.22            | 99.68          | 100.31          | 98.983           | 98.99  | 99.5   |
| Minerals                         | Norm Wt%        |        |        |        |        |       |                   |                |                 |                  |        |        |
| Quartz                           | 35.6            | 47.83  | 37.35  | 48.46  | 33.75  | 36.44 | 41.22             | 9.68           | 19.91           | 30.42            | 36.59  | 33.39  |
| Plagioclase                      | 30.6            | 43.42  | 47.07  | 37.78  | 41.38  | 39.55 | 41.56             | 32.76          | 10.46           | 0                | 0      | 0      |
| Orthoclase                       | 25.23           | 1.95   | 2.72   | 2.48   | 20.33  | 19.38 | 11.35             | 35.87          | 39.48           | 61.93            | 50.94  | 56.67  |
| Corundum                         | 3.1             | 2.27   | 4.65   | 6.68   | 0.97   | 2.02  | 2.33              | 6.45           | 7.21            | 0.92             | 1.96   | 1.66   |
| Hypersthene                      | 1.37            | 0.9    | 1.97   | 0.87   | 0.35   | 0.12  | 0.59              | 2.52           | 1.47            | 0.52             | 2.19   | 1.57   |
| Rutile                           | 0.24            | 0.31   | 0.32   | 0.17   | 0.11   | 0     | 0.17              | 0.05           | 0.09            | 0.18             | 0.13   | 0.17   |
| Ilmenite                         | 0.02            | 0.01   | 0.04   | 0.09   | 0.04   | 0.04  | 0                 | 0.27           | 0.16            | 0.02             | 0.1    | 0.04   |
| Magnetite                        | 0               | 0      | 0      | 0      | 0      | 0.04  | 0                 | 0              | 0               | 0                | 0      | 0      |
| Hematite                         | 1.07            | 0.94   | 1.73   | 0.71   | 1.02   | 0.26  | 0.85              | 4.79           | 6.62            | 1.74             | 1.52   | 2.06   |
| Apatite                          | 0.14            | 0.09   | 0.16   | 0.02   | 0.07   | 0.05  | 0.05              | 0.25           | 0.25            | 0.07             | 0.12   | 0.09   |
| Zircon                           | 0.03            | 0.03   | 0.03   | 0      | 0      | 0.01  | 0.03              | 0.21           | 0.19            | 0.03             | 0.03   | 0.03   |
| Calcite                          | 1.98            | 1.14   | 1.46   | 2.29   | 1.26   | 1.62  | 0.63              | 1.77           | 10.33           | 3.05             | 5.12   | 3.23   |
| Na2CO3                           | 0.67            | 1.11   | 2.53   | 0.49   | 0.74   | 0.47  | 1.26              | 5.47           | 3.92            | 2.04             | 2.65   | 1.59   |
| Total                            | 100.08          | 100.04 | 100.03 | 100.04 | 100.02 | 100   | 100.1             | 100.1          | 100.1           | 100.92           | 101.36 | 100.53 |

Table 9. Continue

|                                  | Trachyte | Rhyolite |        |        |        |        |        |        |          |          |  |
|----------------------------------|----------|----------|--------|--------|--------|--------|--------|--------|----------|----------|--|
|                                  | Bh8-65   | Bh7-41   | ER1    | ER2    | ER3    | ER4    | ER5    | ER6    | ER7      | ER8      |  |
| SiO <sub>2</sub>                 | 74.17    | 70.76    | 72.06  | 74.85  | 74.21  | 73.16  | 71.62  | 72.21  | 73.3     | 72.35    |  |
| TiO <sub>2</sub>                 | 0.23     | 0.14     | 0.25   | 0.15   | 0.16   | 0.18   | 0.15   | 0.14   | 0.09     | 0.2      |  |
| Al <sub>2</sub> O <sub>3</sub>   | 12.62    | 10.48    | 12.36  | 9.72   | 11.57  | 12.28  | 11.84  | 11.02  | 10.37    | 11.58    |  |
| Fe <sub>2</sub> O <sub>3</sub> T | 2.56     | 1        | 3.14   | 2.88   | 2.16   | 2.71   | 2.84   | 3.12   | 0.53     | 0.82     |  |
| MnO                              | 0.01     | 0.04     | 0.04   | 0.02   | 0.02   | 0.02   | 0.04   | 0.06   | 0.09     | 0.04     |  |
| MgO                              | 0.68     | 2.35     | 0.59   | 0.41   | 0.61   | 1.24   | 0.92   | 0.94   | 0.44     | 1.43     |  |
| CaO                              | 0.79     | 2.41     | 0.86   | 0.92   | 1.29   | 2.29   | 3.26   | 2.61   | 2.21     | 3.15     |  |
| Na <sub>2</sub> O                | 5.27     | 0.36     | 6.03   | 2.82   | 1.23   | 0.51   | 0.69   | 0.21   | 0.15     | 0.14     |  |
| K <sub>2</sub> O                 | 2.64     | 7.45     | 2.02   | 3.64   | 6.46   | 5.18   | 5.27   | 7.02   | 8.4      | 5.59     |  |
| P <sub>2</sub> O <sub>5</sub>    | 0.06     | 0.03     | 0.08   | 0.09   | 0.06   | 0.18   | 0.05   | 0.04   | 0.12     | 0.06     |  |
| LOI                              | 1.81     | 4.57     | 3.11   | 3.83   | 2.47   | 2.13   | 3.61   | 3.25   | 3.69     | 4.81     |  |
| Sr                               | 47.5     | 32.4     |        |        |        |        |        |        |          |          |  |
| Ba                               | 612.9    | 550.5    |        |        |        |        |        |        |          |          |  |
| Ni                               | 8.7      | 10.6     | 2.89   | 2.75   | 1.66   | 2.2    | 12.1   |        | 0.43     | 0.66     |  |
| Cr                               | 146.9    | 100.3    |        |        |        |        |        |        |          |          |  |
| Zr                               | 189.3    | 144.9    | 92.3   | 246.7  | 153.8  | 274.5  | 59.1   | 149.2  | 121.6    | 182.5    |  |
| total                            | 101.2    | 99.62    | 100.54 | 99.33  | 100.24 | 99.88  | 100.29 | 100.62 | 99.39104 | 100.1651 |  |
| Minerals                         | Norm     | wt%      |        |        |        |        |        |        |          |          |  |
| Quartz                           | 42.03    | 38.88    | 48.65  | 60.7   | 48.45  | 51.5   | 49.94  | 43.65  | 40.73    | 48.72    |  |
| Plagioclase                      | 29.77    | 0        | 21.01  | 0      | 0      | 0      | 0      | 0      | 0        | 0        |  |
| Orthoclase                       | 15.48    | 44.2     | 11.88  | 21.63  | 38.06  | 30.67  | 31.03  | 41.25  | 49.94    | 32.98    |  |
| Corundum                         | 3.89     | 2.42     | 6.03   | 5.83   | 4.57   | 6.67   | 6.13   | 3.39   | 1.28     | 5.52     |  |
| Hypersthene                      | 1.67     | 5.88     | 1.47   | 1.02   | 1.52   | 3.09   | 2.29   | 2.32   | 1.1      | 3.56     |  |
| Rutile                           | 0.23     | 0.1      | 0.2    | 0.13   | 0.14   | 0.16   | 0.1    | 0.07   | 0        | 0.15     |  |
| Ilmenite                         | 0        | 0.08     | 0.09   | 0.04   | 0.04   | 0.04   | 0.09   | 0.13   | 0.17     | 0.09     |  |
| Magnetite                        | 0        | 0        | 0      | 0      | 0      | 0      | 0      | 0      | 0.03     | 0.00     |  |
| Hematite                         | 2.54     | 1        | 3.12   | 2.9    | 2.15   | 2.71   | 2.83   | 3.1    | 0.51     | 0.81     |  |
| Apatite                          | 0.14     | 0.07     | 0.19   | 0.21   | 0.14   | 0.42   | 0.12   | 0.09   | 0.28     | 0.14     |  |
| Zircon                           | 0.04     | 0.03     | 0.01   | 0.04   | 0.03   | 0.06   | 0.01   | 0.03   | 0.03     | 0.03     |  |
| Sphene                           | 0        | 0        | 0      | 0      | 0      | 0      | 0      | 0      | 0        | 0        |  |
| Calcite                          | 1.31     | 4.29     | 1.35   | 1.45   | 2.16   | 3.66   | 5.68   | 4.53   | 3.68     | 5.46     |  |
| Na <sub>2</sub> CO <sub>3</sub>  | 2.93     | 6.51     | 6.02   | 7.76   | 3.64   | 1.25   | 2.65   | 2.98   | 5.04     | 5.77     |  |
| Total                            | 100.06   | 103.47   | 100.02 | 101.71 | 100.9  | 100.23 | 100.87 | 101.54 | 102.79   | 103.23   |  |

Table 9. Continue

|                                  | Doleritic dykes |        |        |        |
|----------------------------------|-----------------|--------|--------|--------|
|                                  | 24              | 28-Feb | 90     | 103    |
| SiO <sub>2</sub>                 | 47.77           | 46.12  | 44     | 46.41  |
| TiO <sub>2</sub>                 | 2.59            | 2.72   | 3.21   | 1.243  |
| Al <sub>2</sub> O <sub>3</sub>   | 14.89           | 13.65  | 13.35  | 15.98  |
| Fe <sub>2</sub> O <sub>3</sub> T | 11.72           | 12.83  | 14.27  | 9.64   |
| MnO                              | 0.16            | 0.18   | 0.14   | 0.18   |
| MgO                              | 5.9             | 6.84   | 8.62   | 8.42   |
| CaO                              | 5.38            | 6.2    | 6.16   | 11.16  |
| Na <sub>2</sub> O                | 4.63            | 3.87   | 3.53   | 2.05   |
| K <sub>2</sub> O                 | 2.96            | 2.84   | 1.51   | 0.836  |
| P <sub>2</sub> O <sub>5</sub>    | 0.89            | 0.93   | 0.95   | 0.12   |
| LOI                              | 2.75            | 3.51   | 3.87   | 3.97   |
| Sr                               | 747.9           | 739    | 378.2  | 399.8  |
| Ba                               | 772.5           | 627.3  | 631.7  | 660.3  |
| Ni                               | 103.8           | 133.9  | 214.2  | 131.9  |
| Cr                               | 233.1           | 260.3  | 356.9  | 423.9  |
| Zr                               | 580.6           | 501.7  | 371.8  | 80     |
| total                            | 99.64           | 99.69  | 99.61  | 100.01 |
| Minerals                         | Norm            | Wt %   |        |        |
| Quartz                           | 0               | 0      | 1.12   | 2.74   |
| Plagioclase                      | 43.62           | 36.11  | 30.48  | 47.33  |
| Orthoclase                       | 17.73           | 16.96  | 9.04   | 4.96   |
| Corundum                         | 2.66            | 3.19   | 5.93   | 0.83   |
| Hyperssthene                     | 6.55            | 16.83  | 29.82  | 28.19  |
| Rutile                           | 0               | 0      | 0      | 0      |
| Ilmenite                         | 4.98            | 5.22   | 6.19   | 2.37   |
| Magnetite                        | 5.16            | 5.65   | 6.29   | 4.22   |
| Hematite                         | 0               | 0      | 0      | 0      |
| Apatite                          | 2.09            | 2.18   | 2.22   | 0.28   |
| Zircon                           | 0.12            | 0.1    | 0.07   | 0.01   |
| Sphene                           | 0               | 0      | 0      | 0      |
| Calcite                          | 6.32            | 8.07   | 8.92   | 9.1    |
| Na <sub>2</sub> CO <sub>3</sub>  | 0               | 0      | 0      | 0      |
| Total                            | 100.16          | 100.15 | 100.15 | 100.12 |

**Table 10 Calculated  $\delta^{18}\text{O}$  values for waters in equilibrium with mineral phases**

| Sample No | Mineral | Rock type                                       | $\delta^{18}\text{O}$ | $\delta^{18}\text{O}$ of Water |        |        |        |        |        |        |        |        |                      | Reference |
|-----------|---------|-------------------------------------------------|-----------------------|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|----------------------|-----------|
|           |         |                                                 | SMOW                  | 100 oC                         | 150 oC | 200 oC | 250 oC | 300 oC | 350 oC | 400 oC | 450 oC | 500 oC |                      |           |
| B12-65    | Qtz     | Purple Ap. between main Fe and ap ores bodies   | 16.5                  | -4.6                           | 1.0    | 4.9    | 7.5    | 9.5    | 10.9   | 12.0   | 12.8   | 13.5   | zheng (1993a)        |           |
| B8        | Qtz     | Disseminated Fe-oxide in a qtz-carbonate matrix | 17.1                  | -4.0                           | 1.6    | 5.4    | 8.1    | 10.0   | 11.5   | 12.6   | 13.4   | 14.0   | zheng (1993a)        |           |
| 104       | Qtz     |                                                 | 16.0                  | -5.2                           | 0.5    | 4.3    | 7.0    | 8.9    | 10.4   | 11.4   | 12.3   | 12.9   | zheng (1993a)        |           |
| 107       | Qtz     | Main Fe ore with patches of ap -qtz-carbonate   | 16.4                  | -4.7                           | 1.0    | 4.8    | 7.5    | 9.4    | 10.8   | 11.9   | 12.7   | 13.4   | zheng (1993a)        |           |
| B12-9     | Qtz     | Vein type quartz                                | 17.6                  | -3.5                           | 2.14   | 5.96   | 8.64   | 10.58  | 12.01  | 13.09  | 13.9   | 14.57  |                      |           |
| Bh1-13    | Mag     | Altered Lapilli tuff                            | 10.6                  | -10.5                          | -4.9   | -1.1   | 1.6    | 3.6    | 5.0    | 6.1    | 6.9    | 7.6    |                      |           |
| Bh1-13    | Hem     | Altered Lapilli tuff                            | 1.3                   | 12.6                           | 12.8   | 12.6   | 12.2   | 11.7   | 11.2   | 10.6   | 10.1   | 9.6    | Zheng & Simon (1991) |           |
| B52-42    | Hem     |                                                 | 1.4                   | 12.6                           | 12.9   | 12.7   | 12.3   | 11.8   | 11.2   | 10.7   | 10.2   | 9.7    | Zheng & Simon (1991) |           |
| 104       | Hem     | Main mag ore (martitized)                       | -0.2                  | 11.1                           | 11.3   | 11.1   | 10.7   | 10.2   | 9.7    | 9.1    | 8.6    | 8.1    | Zheng & Simon (1991) |           |
| 107       | Hem     | Main Fe ore with patches of ap -qtz-carbonate   | 0.4                   | 11.7                           | 11.9   | 11.7   | 11.3   | 10.8   | 10.3   | 9.7    | 9.2    | 8.7    | Zheng & Simon (1991) |           |
| V2        | Hem     |                                                 | 2.3                   | 13.6                           | 13.8   | 13.6   | 13.2   | 12.7   | 12.2   | 11.63  | 11.1   | 10.6   | Zheng & Simon (1991) |           |
| 101       | Hem     | ap. Rich zone                                   | 5.2                   | 16.5                           | 16.7   | 16.5   | 16.1   | 15.6   | 15.1   | 14.53  | 14.0   | 13.5   | Zheng & Simon (1991) |           |
| B4        | Hem     | brecciated tuff                                 | 1.8                   | 13.1                           | 13.3   | 13.1   | 12.7   | 12.2   | 11.7   | 11.13  | 10.6   | 10.1   | Zheng & Simon (1991) |           |
| 52        | Hem     | Specularite in main P zone                      | 11.1                  | 22.4                           | 22.6   | 22.4   | 22.0   | 21.5   | 21.0   | 20.5   | 19.9   | 19.4   | Zheng & Simon (1991) |           |
| 10        | Mag     | Fe-oxide-jaspilite layer                        | 1.7                   | 8.9                            | 9.9    | 10.3   | 10.3   | 10.1   | 9.9    | 9.6    | 9.2    | 8.9    | Zheng & Simon (1991) |           |

**Table 10 Continued**

| Sample No | Mineral | Rock type                                             | $\delta^{18}\text{O}$ | $\delta^{18}\text{O}$ of Water |        |        |        |        |        |        |        |        | Reference               |
|-----------|---------|-------------------------------------------------------|-----------------------|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|-------------------------|
|           |         |                                                       | SMOW                  | 100 °C                         | 150 °C | 200 °C | 250 °C | 300 °C | 350 °C | 400 °C | 450 °C | 500 °C |                         |
| 32-2      | Mag     | Detrital mag.                                         | -1.0                  | 6.2                            | 7.2    | 7.6    | 7.6    | 7.4    | 7.2    | 6.9    | 6.5    | 6.2    | Zheng & Simon (1991)    |
| 106       | Mag     | Mag layers in tuffaceous sandstone (Gardaneh)         | 2.0                   | 9.2                            | 10.2   | 10.6   | 10.6   | 10.4   | 10.2   | 9.9    | 9.5    | 9.2    | Zheng & Simon (1991)    |
| 32-1      | Mag     | Fe-oxide as small layers in rhyolite or sandstone     | 0.0                   | 7.2                            | 8.2    | 8.6    | 8.6    | 8.4    | 8.2    | 7.9    | 7.5    | 7.2    | Zheng & Simon (1991)    |
| 32-1      | Mag     |                                                       | -0.02                 | 7.1                            | 8.2    | 8.5    | 8.6    | 8.4    | 8.2    | 7.8    | 7.5    | 7.1    | Zheng & Simon (1991)    |
| B12-65    | Mag     | Purple Ap. Zone between main Fe and ap ores bodies    | 1.6                   | 8.8                            | 9.8    | 10.2   | 10.2   | 10.0   | 9.8    | 9.5    | 9.1    | 8.8    | Zheng & Simon (1991)    |
| B12-9     | Mag     | Main Apatite ore                                      | 1.2                   | 8.4                            | 9.4    | 9.8    | 9.8    | 9.6    | 9.4    | 9.1    | 8.7    | 8.4    | Zheng & Simon (1991)    |
| 102       | Mag     | Main Fe ore, mag. Veins in an ap-qtz-carbonate matrix | 2.2                   | 9.4                            | 10.4   | 10.8   | 10.8   | 10.6   | 10.4   | 10.1   | 9.7    | 9.4    | Zheng & Simon (1991)    |
| B40       | Mag     | Main Fe ore with ap., qtz and carbonate               | -0.1                  | 7.0                            | 8.0    | 8.4    | 8.5    | 8.3    | 8.0    | 7.7    | 7.4    | 7.0    | Zheng & Simon (1991)    |
| B1-2      | Mag     | Main Fe ore                                           | 1.3                   | 8.5                            | 9.5    | 9.9    | 9.9    | 9.7    | 9.5    | 9.2    | 8.8    | 8.5    | Zheng & Simon (1991)    |
| B54-42    | Mag     | core mt                                               | 0.3                   | 7.5                            | 8.5    | 8.9    | 8.9    | 8.7    | 8.5    | 8.2    | 7.8    | 7.5    | Zheng & Simon (1991)    |
| B20-43    | Mag     | Hem (martite), Main Fe ore                            | 0.1                   | 7.3                            | 8.3    | 8.7    | 8.7    | 8.5    | 8.3    | 8.0    | 7.6    | 7.3    | Zheng & Simon (1991)    |
| B2-42     | Mag     | secondary mt                                          | 4.7                   | 11.9                           | 12.9   | 13.3   | 13.3   | 13.1   | 12.9   | 12.6   | 12.2   | 11.9   | Zheng & Simon (1991)    |
| B20-17    | Mag     | secondary mt                                          | 6.8                   | 14.0                           | 15.0   | 15.4   | 15.4   | 15.2   | 15.0   | 14.7   | 14.3   | 14.0   | Zheng & Simon (1991)    |
| B12-38    | Chl     |                                                       | 9.7                   | 3.2                            | 5.7    | 7.4    | 8.7    | 9.6    | 10.3   | 10.9   | 11.4   | 11.8   | Wenner & Taylor (1971). |
| B12-65    | Amph    | Purple Ap. between main Fe and ap ore bodies          | 7.1                   | -1.6                           | 2.1    | 4.5    | 6.0    | 7.1    | 7.8    | 8.3    | 8.6    | 8.8    | Zeng (1993)             |
| B54-42    | Amph    | Brecciated ap.                                        | 8.2                   | -0.5                           | 3.3    | 5.6    | 7.2    | 8.2    | 8.9    | 9.4    | 9.7    | 9.9    | Zeng (1993)             |
| B9        | Amph    | Main Apatite ore                                      | 9.2                   | 0.5                            | 4.3    | 6.6    | 8.2    | 9.2    | 9.9    | 10.4   | 10.7   | 10.9   | Zeng (1993)             |
| Gr-ac-1   | Amph    | Highly alt.rhyolite with garnet-amph                  | 9.5                   | 0.8                            | 4.5    | 6.8    | 8.4    | 9.5    | 10.2   | 10.6   | 11.0   | 11.2   | Zeng (1993)             |

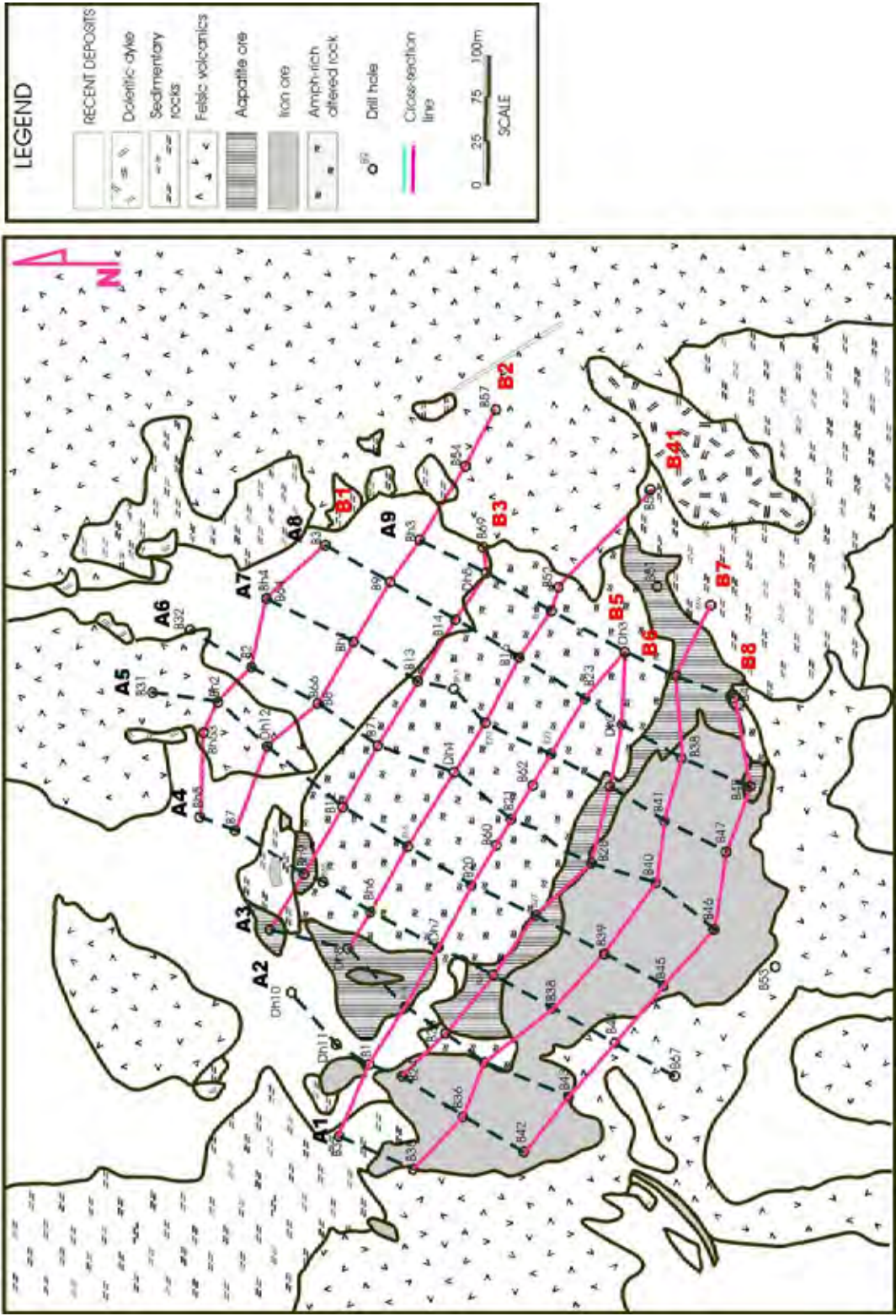
**Table 10 Continued.**

| Sample No | Mineral             | Rock type                                | δ <sup>18</sup> O | δ <sup>18</sup> O of Water |        |        |        |        |        |        |        |        |                       | Reference |
|-----------|---------------------|------------------------------------------|-------------------|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|-----------------------|-----------|
|           |                     |                                          |                   | 100 °C                     | 150 °C | 200 °C | 250 °C | 300 °C | 350 °C | 400 °C | 450 °C | 500 °C |                       |           |
| B20-17    | amph                | Alt. tuff, top of ap-rich zone           | SMOW<br>10.7      | 2.0                        | 5.7    | 8.0    | 9.6    | 10.7   | 11.4   | 11.8   | 12.2   | 12.4   | Zeng (1993)           |           |
| B8        | Carbonate           | pervasive                                | 16.9              | 1.0                        | 6.7    | 11.2   | 14.9   | 17.9   | 20.4   |        |        |        | Kim and O'Neil (1997) |           |
| 101       | Carbonate calcite   | pervasive                                | 18                | 2.1                        | 7.8    | 12.3   | 16.0   | 19.0   | 21.5   |        |        |        | Kim and O'Neil (1997) |           |
| B4        | Calcite             | pervasive (altered tuffaceous sandstone) | 17.9              | 2.0                        | 7.7    | 12.2   | 15.9   | 18.9   | 21.4   |        |        |        | Kim and O'Neil (1997) |           |
| B12-94    | Calcite             | vein dominated                           | 18.1              | 2.2                        | 7.9    | 12.4   | 16.1   | 19.1   | 21.6   |        |        |        | Kim and O'Neil (1997) |           |
| Bh12-86   | Calcite             | vein dominated                           | 18.8              | 2.9                        | 8.6    | 13.1   | 16.8   | 19.8   | 22.3   |        |        |        | Kim and O'Neil (1997) |           |
| 102       | Carbonate (calcite) | vein dominated                           | 19.4              | 3.5                        | 9.2    | 13.7   | 17.4   | 20.4   | 22.9   |        |        |        | Kim and O'Neil (1997) |           |
| B8        | Carbonate (calcite) | pervasive                                | 16.9              | -1.3                       | 3.81   | 7.13   | 9.45   |        |        |        |        |        | Zeng (1999)           |           |
| 101       | Carbonate (calcite) | pervasive                                | 18                | -0.2                       | 4.91   | 8.23   | 10.6   |        |        |        |        |        | Zeng (1999)           |           |
| B4        | Calcite             | pervasive (altered tuffaceous sandstone) | 17.9              | -0.3                       | 4.81   | 8.13   | 10.5   |        |        |        |        |        | Zeng (1999)           |           |
| B12-94    | Calcite             | vein dominated                           | 18.1              | -0.1                       | 5.01   | 8.33   | 10.7   |        |        |        |        |        | Zeng (1999)           |           |
| Bh12-86   | Calcite             | vein dominated                           | 18.8              | 0.6                        | 5.71   | 9.03   | 11.4   |        |        |        |        |        | Zeng (1999)           |           |
| 102       | Carbonate (calcite) | vein dominated                           | 19.4              | 1.2                        | 6.31   | 9.63   | 12     |        |        |        |        |        | Zeng (1999)           |           |

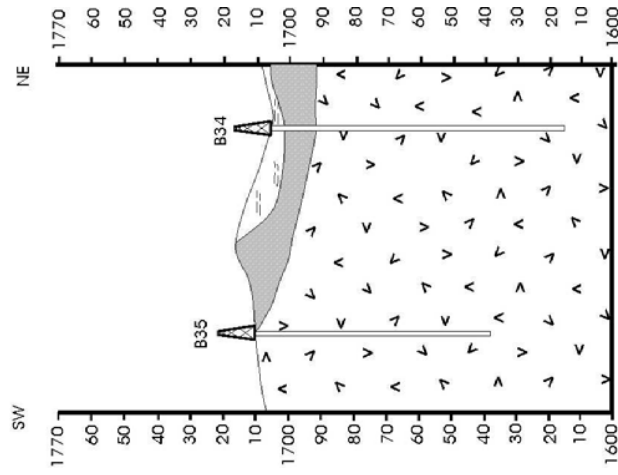
**Appendix 3:**

**GEOLOGICAL MAP  
AND CROSS-SECTIONS OF  
ESFORDI P-FE OXIDE DEPOSIT**

Geological Map and cross-sections Of Esford P-Fe oxide deposit

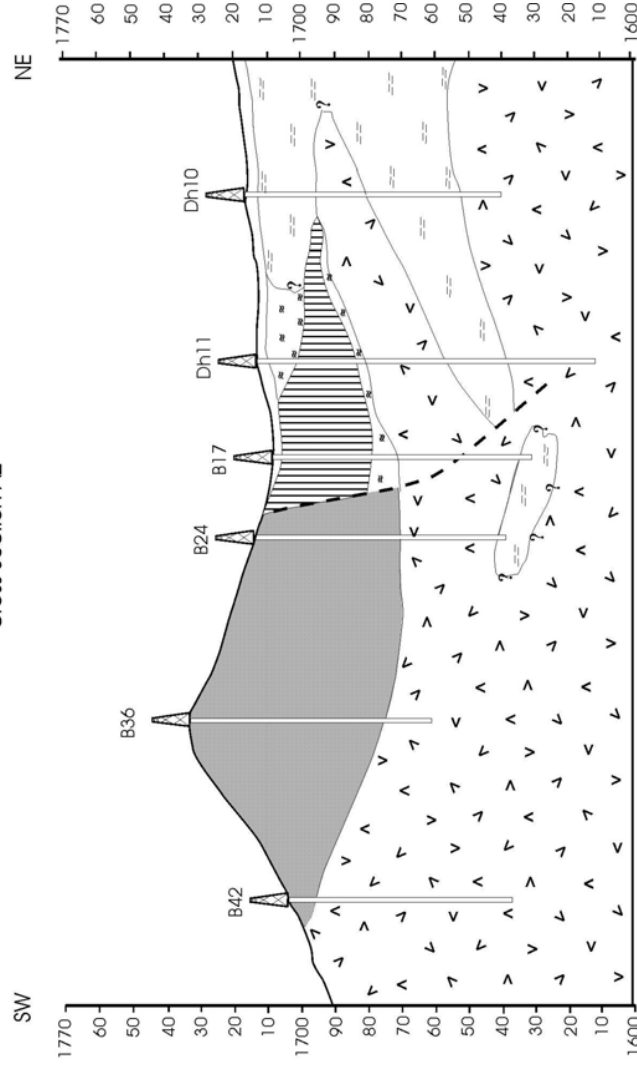


Cross Section A1

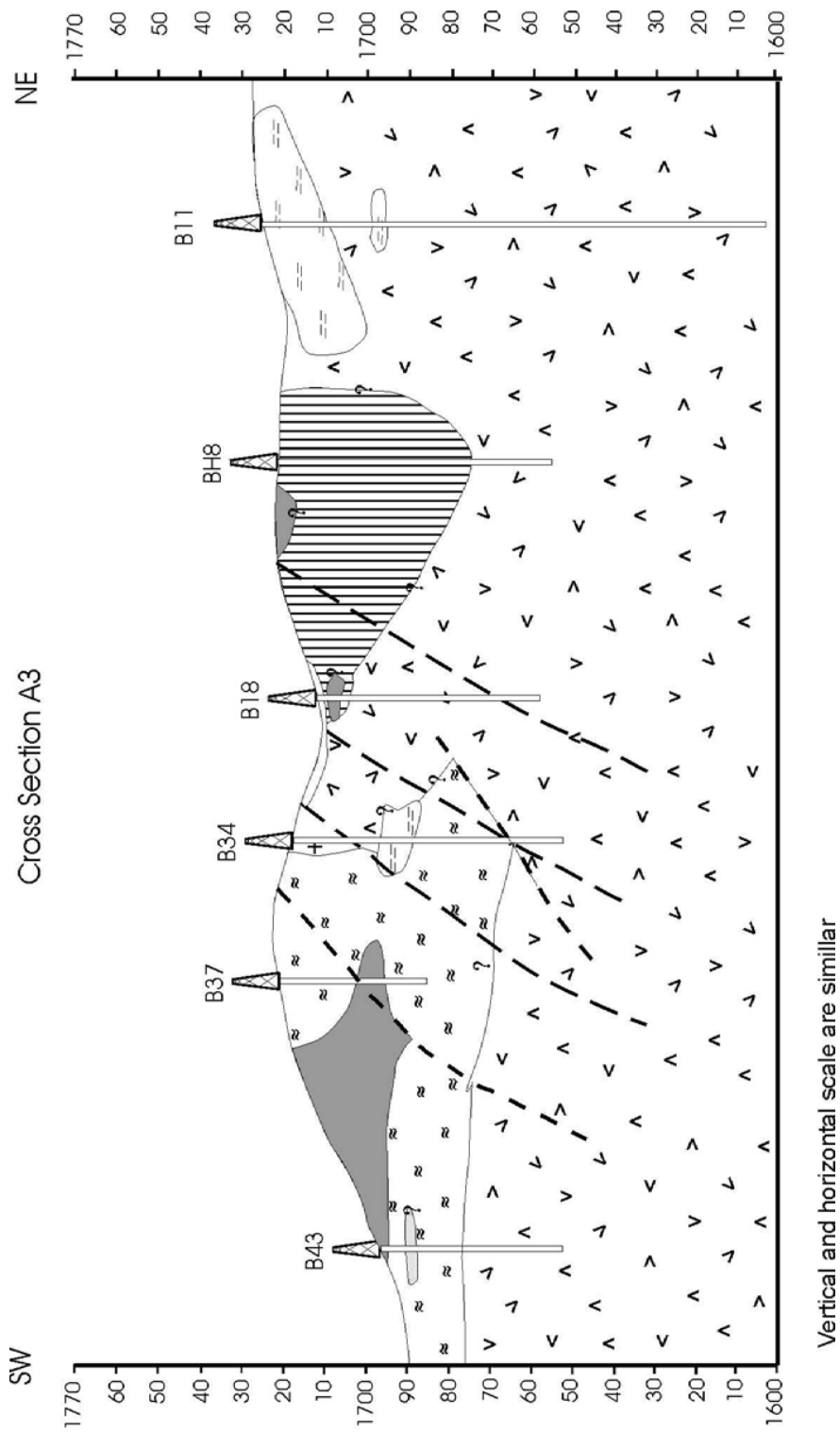


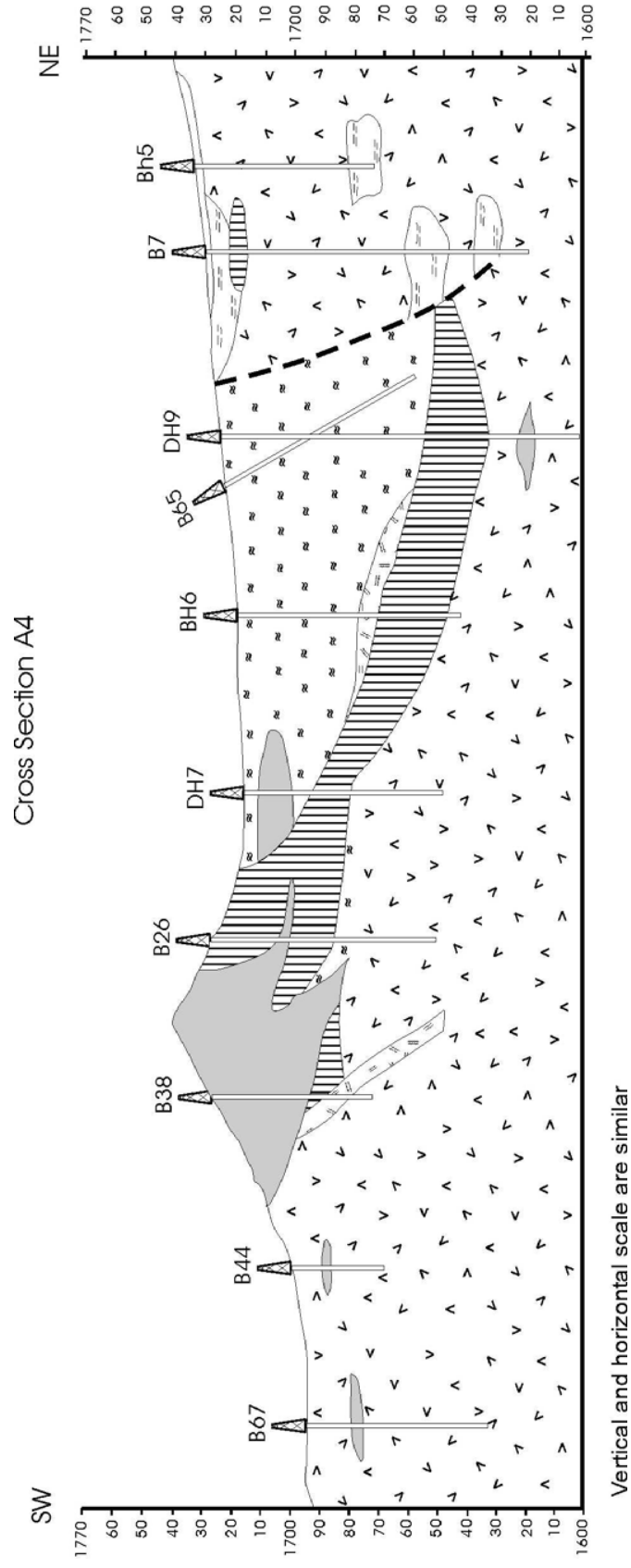
Same vertical and horizontal scale

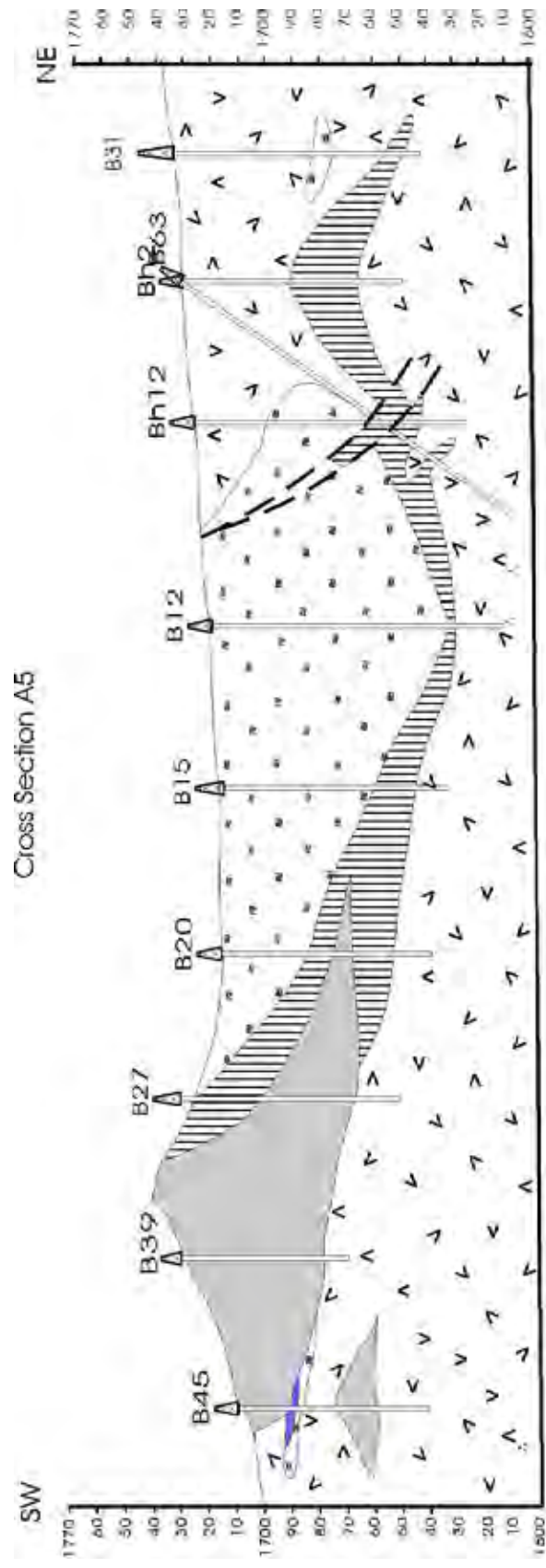
Cross Section A2



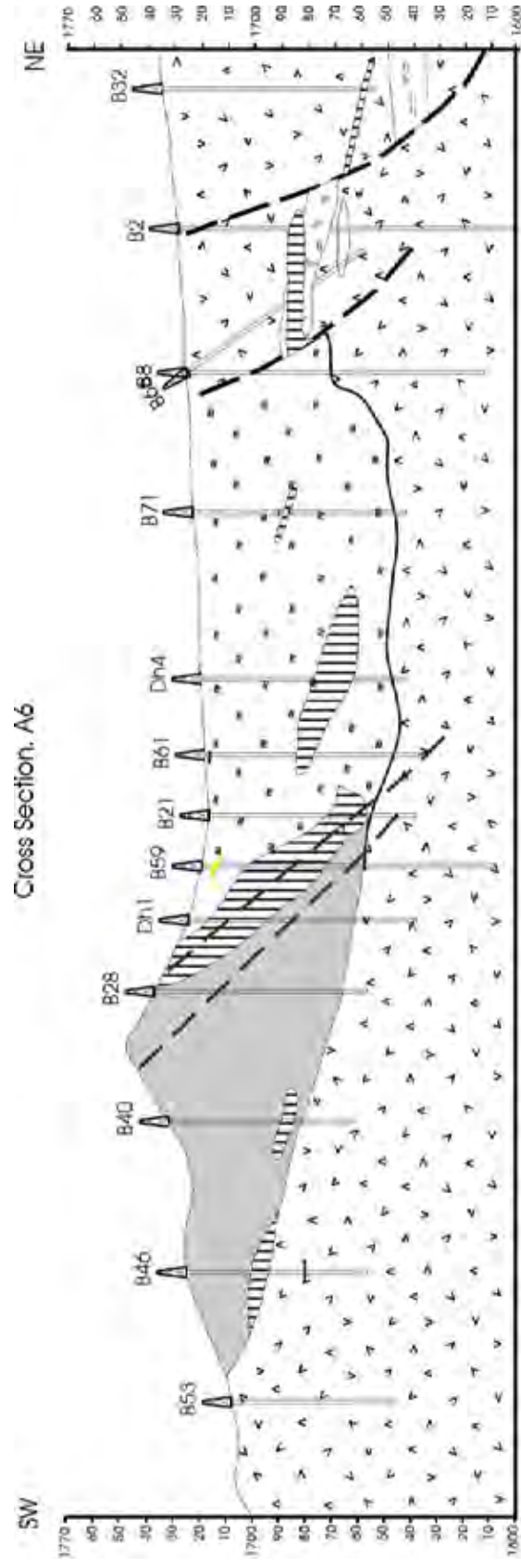
Vertical and horizontal scale are similar





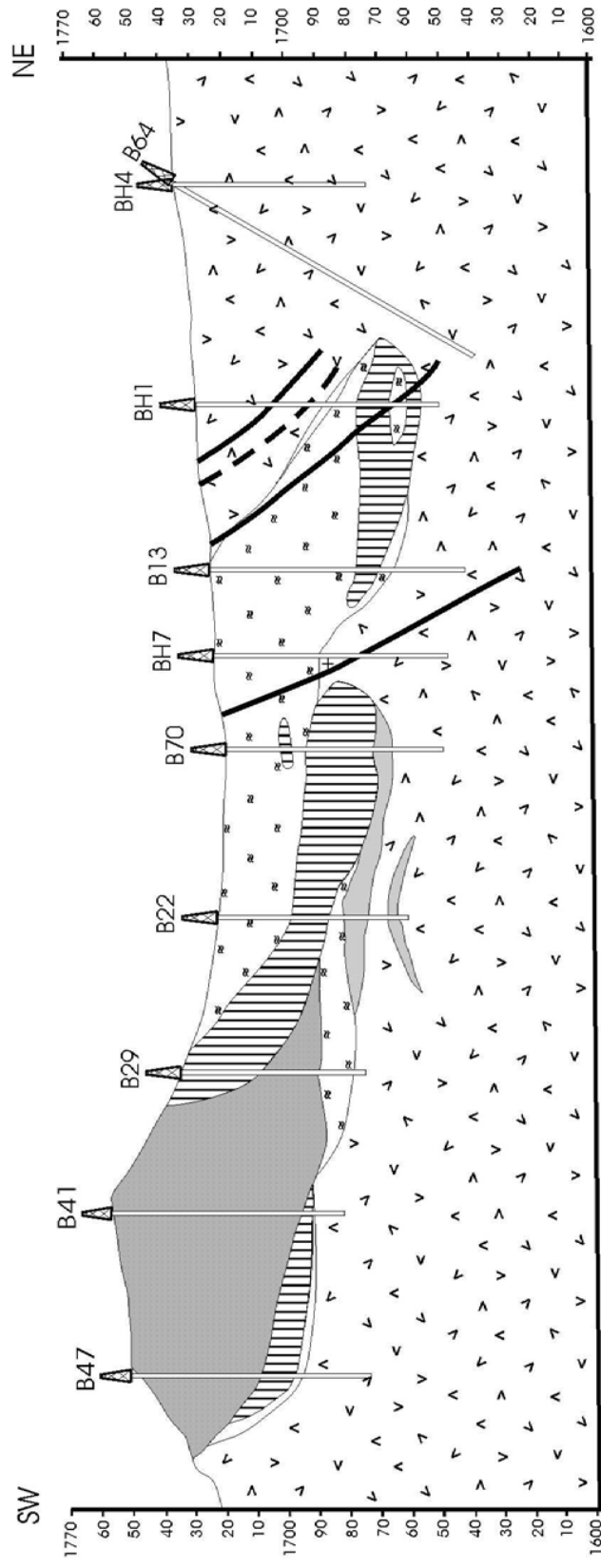


Vertical and horizontal scale are similar



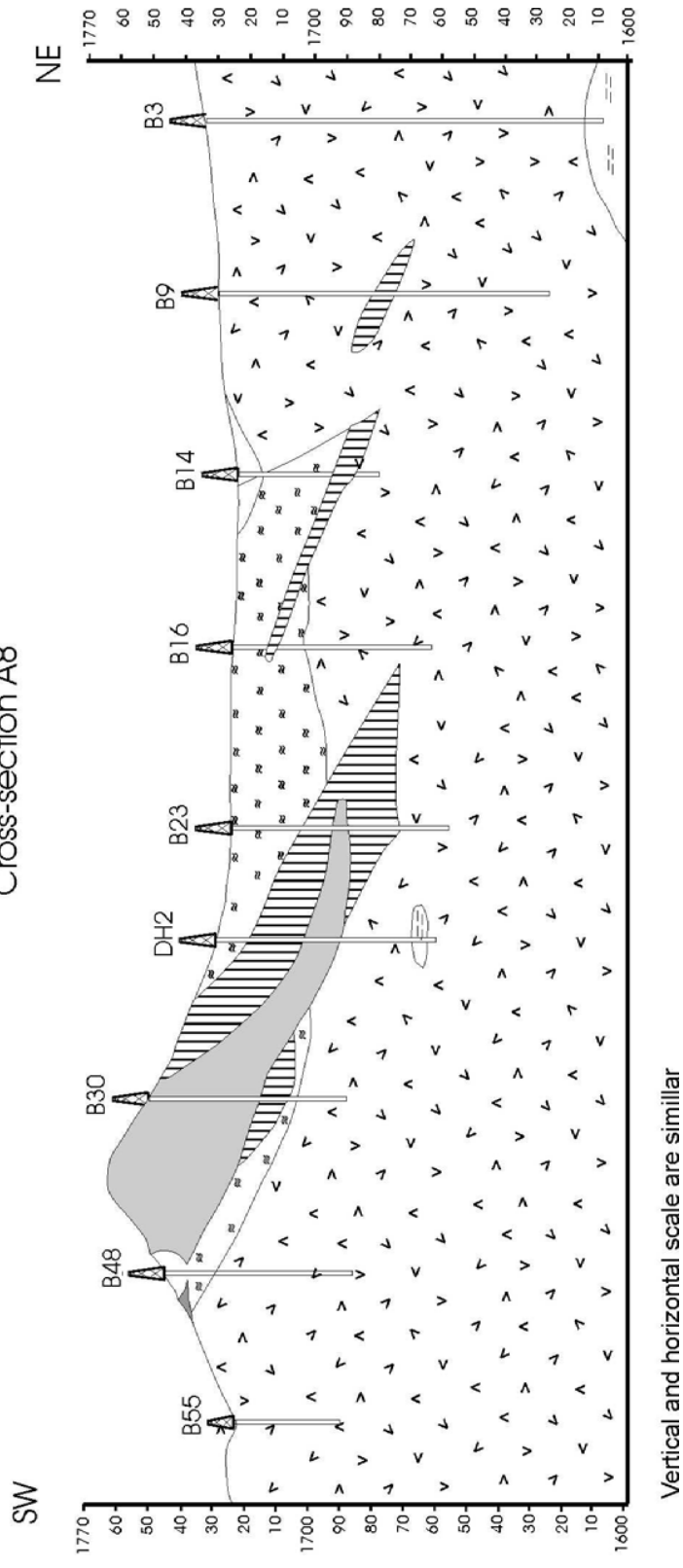
Vertical and horizontal scale are similar

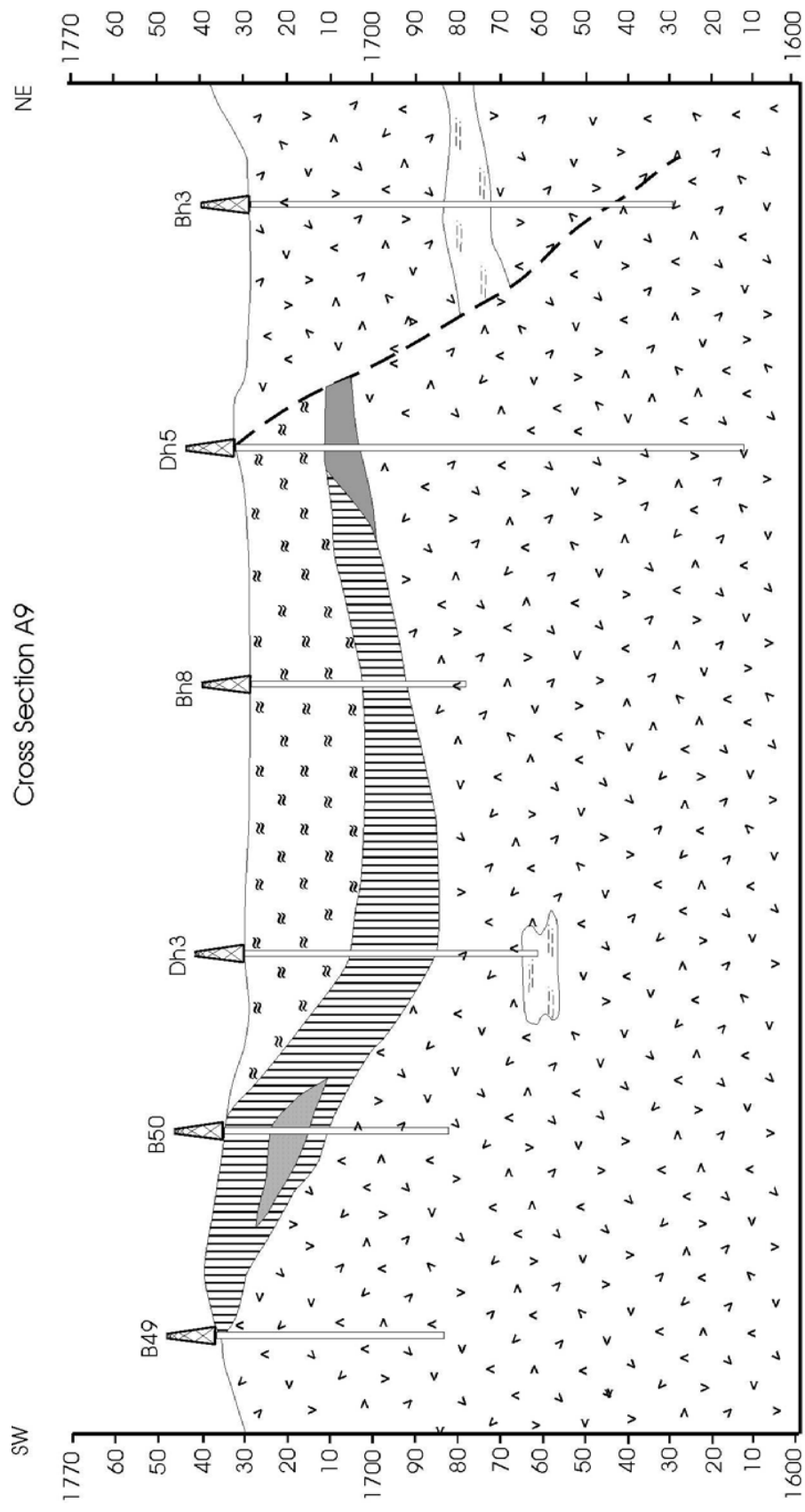
Cross Section A7



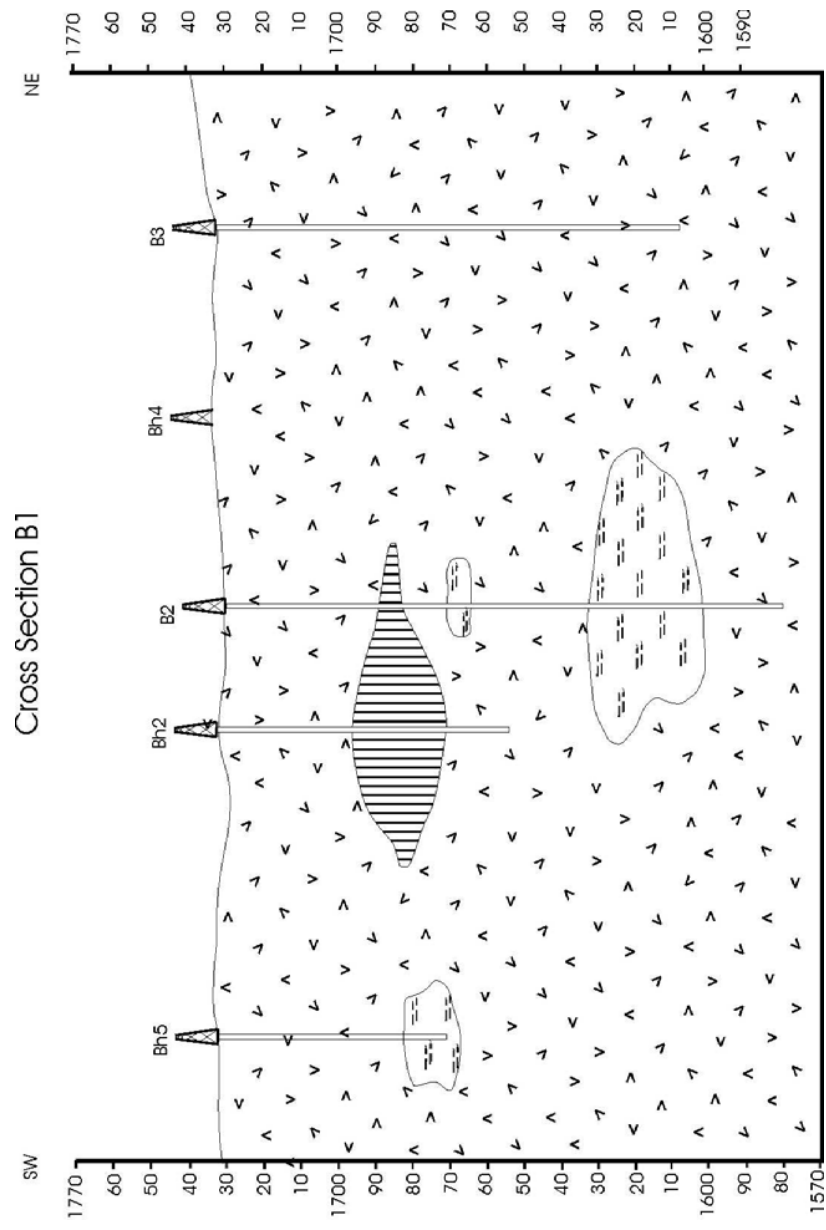
Vertical and horizontal scale are similar

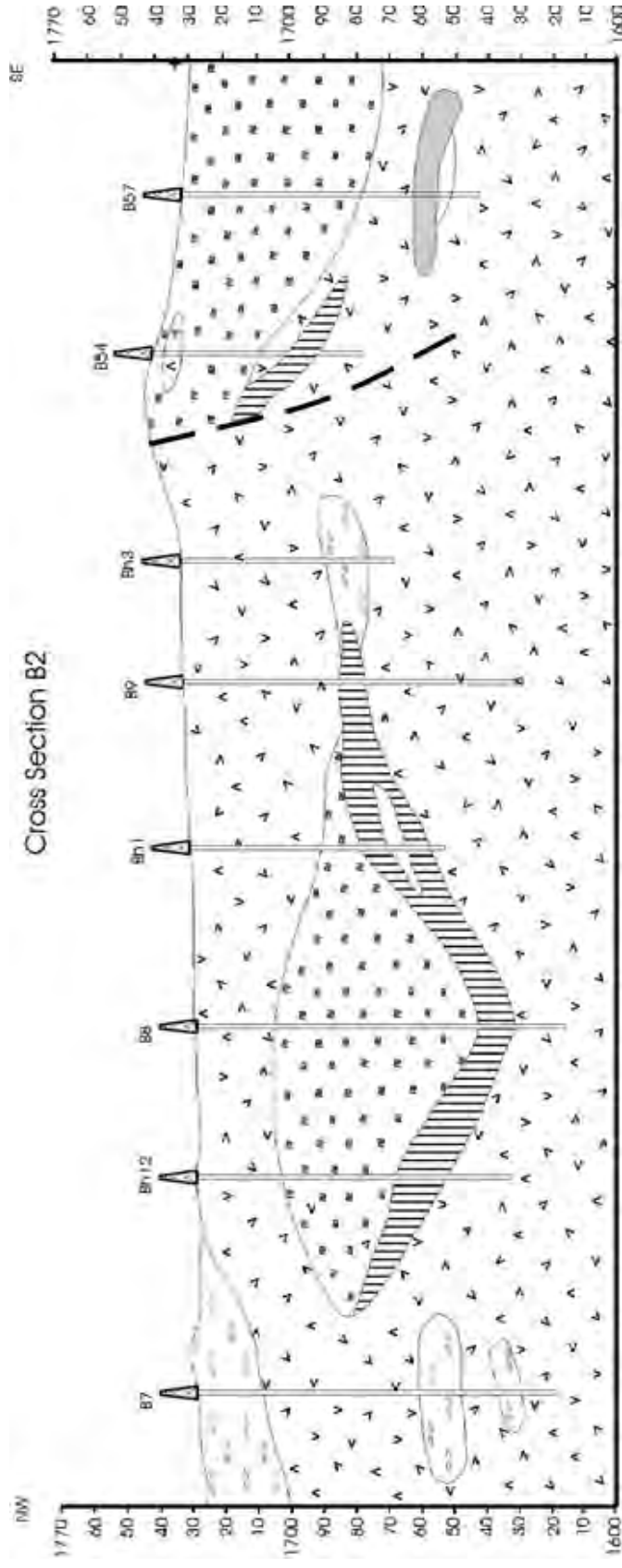
Cross-section A8

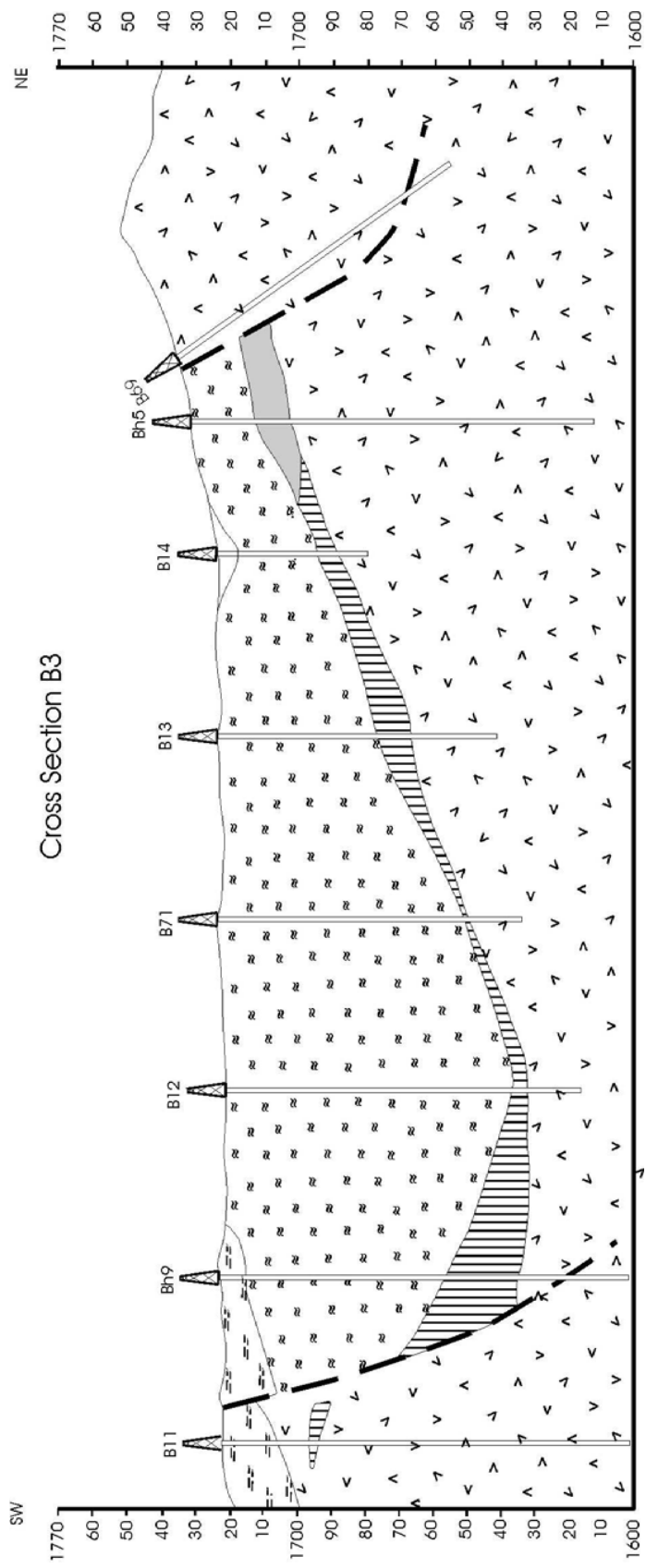


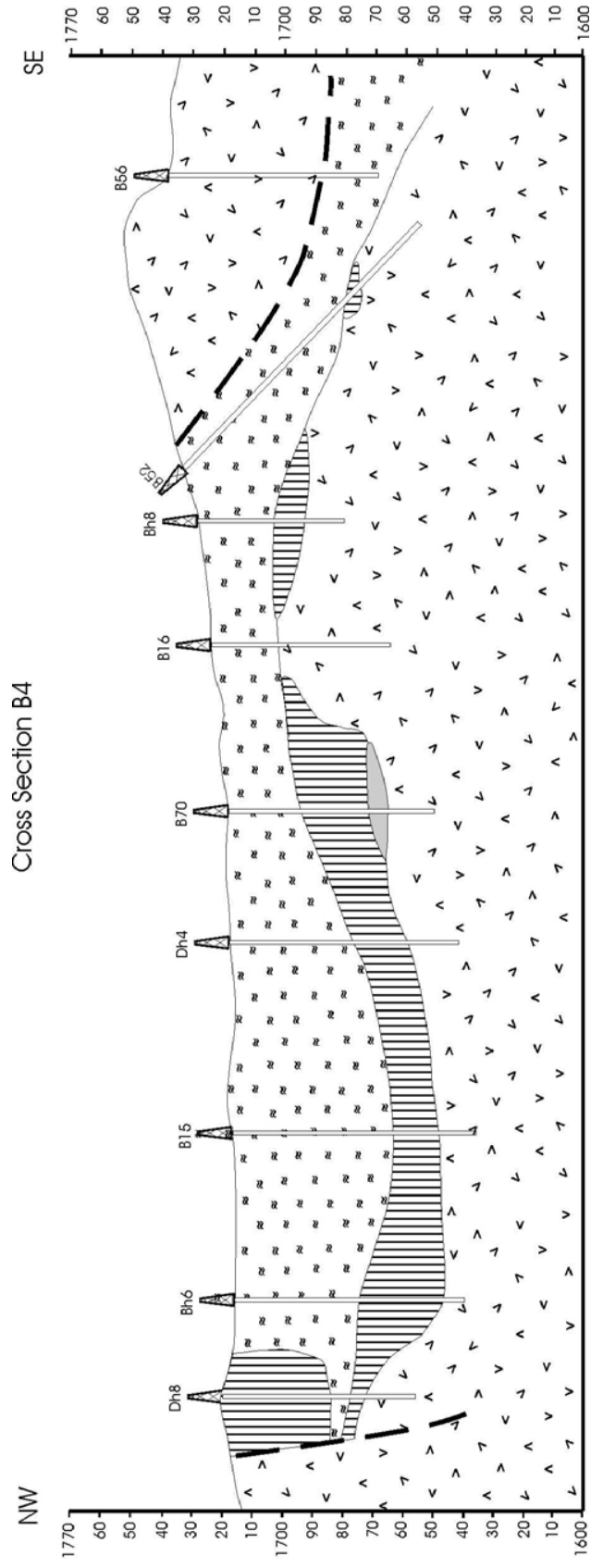


Vertical and horizontal scale are similar

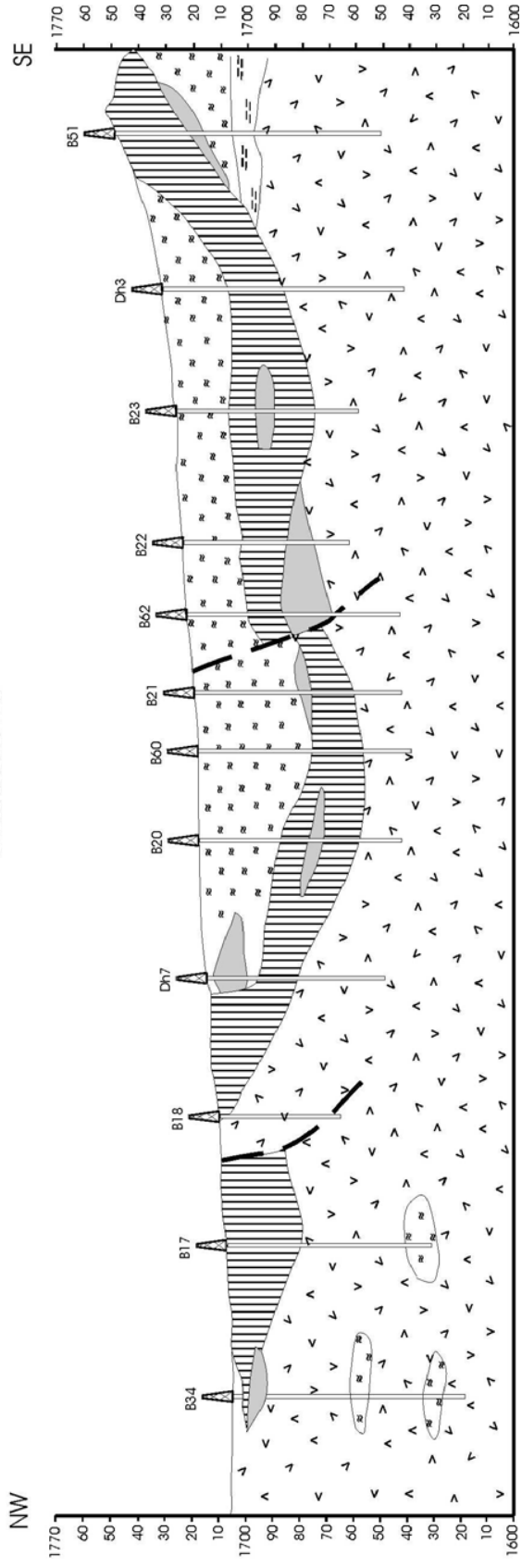




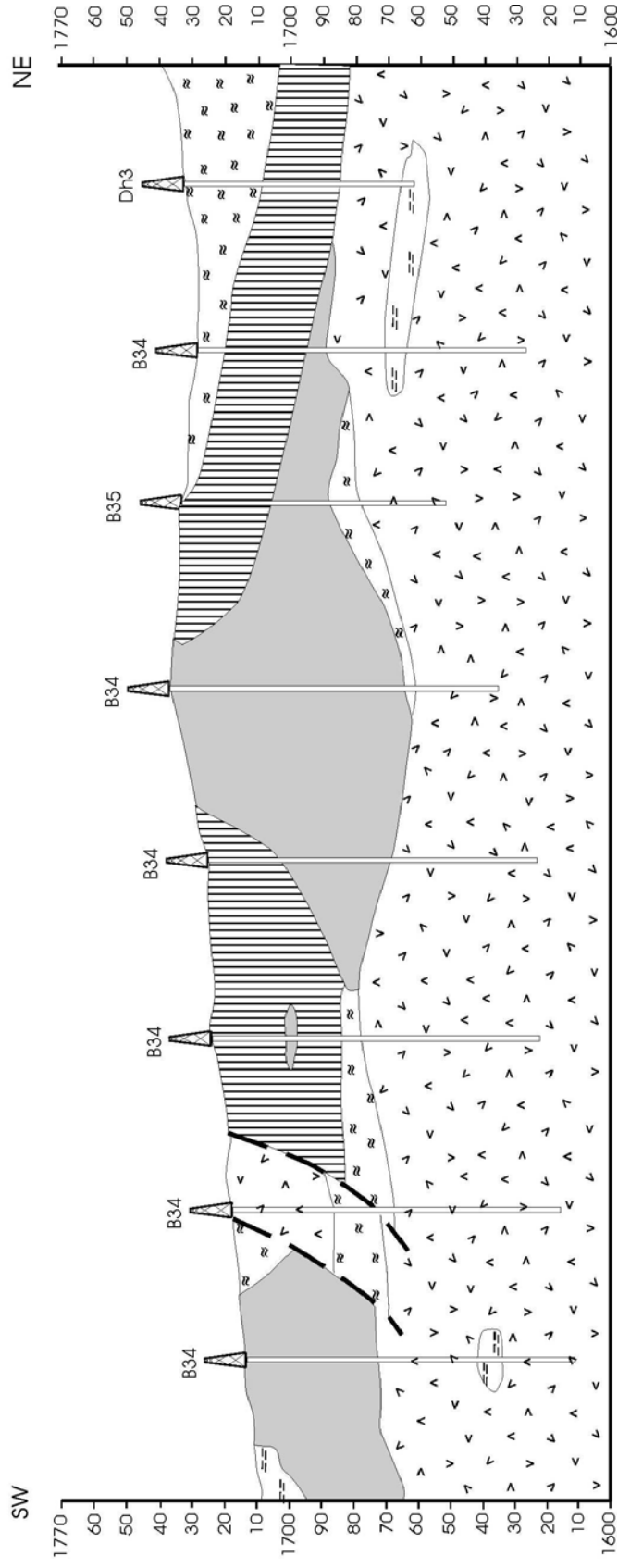




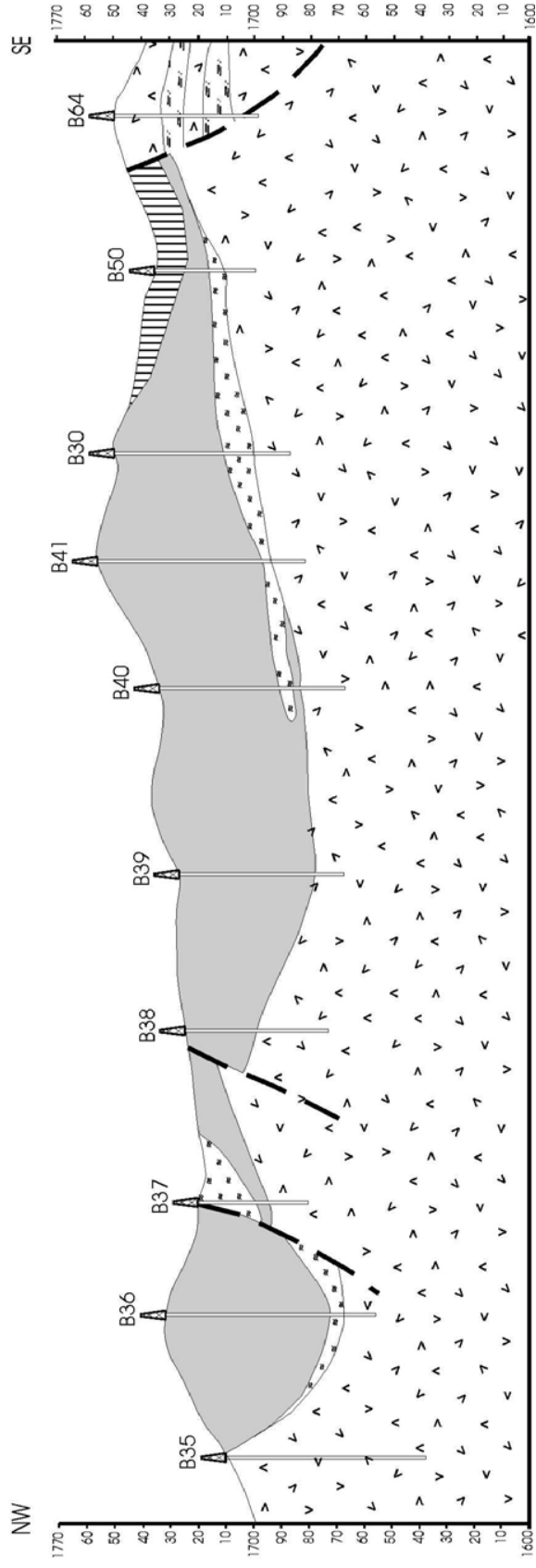
Cross Section B5



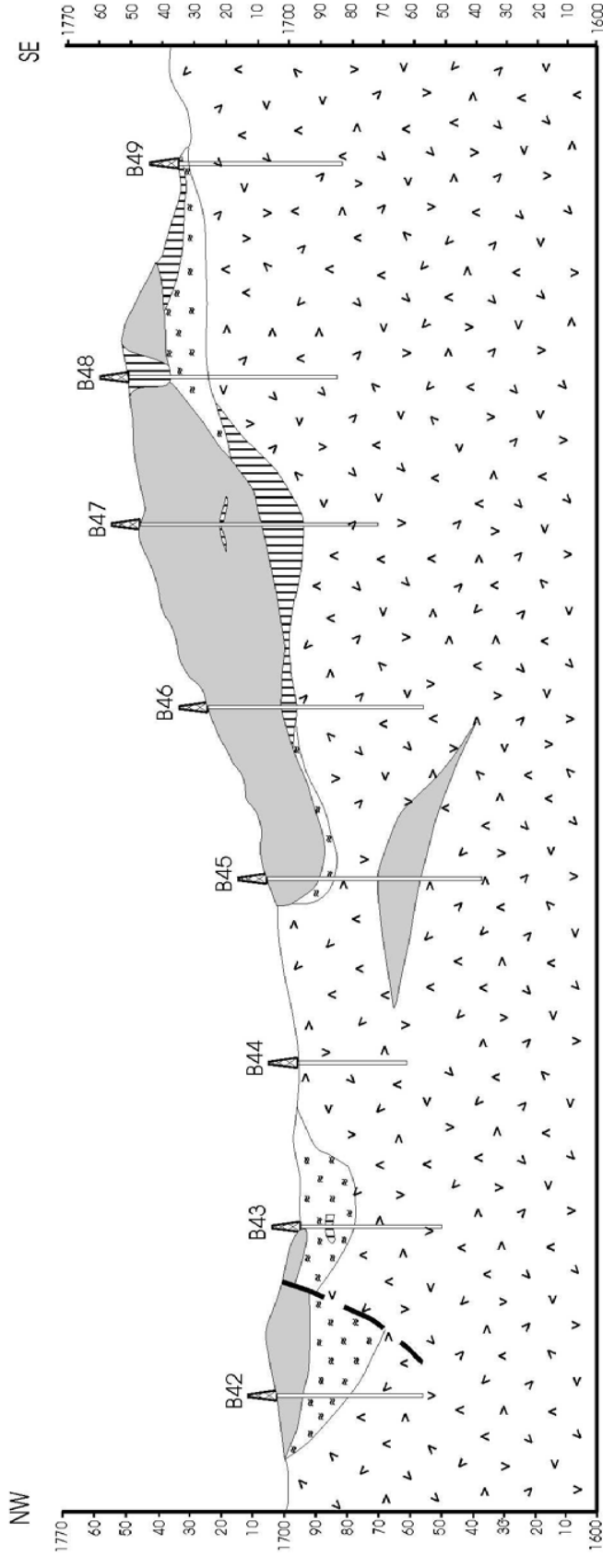
Cross Section B6



Cross Section B7



Cross Section B8



## Appendix 4 :

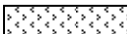
### DRILL-HOLES AND RELATED CHEMICAL ANALYSES

More than 90 shallow (31-150 m with average 80 m) drill-holes were drilled in the Esfordi during 3 episodes of exploration. Location of these drill-holes are illustrated in appendix 3.

More than 65 bore holes are presented in this appendix. All the core samples have been analyzed for major elements including Si, Al, Mg, Fe, Ca and P by the Phosphate Exploration Project, Iranian Ministry of Mines and Metals.

The general lithology of the bore holes are also presented. The lithological data are partly adopted from Esfordi mine core logs and the core logging done in this project.

#### Lithological Legend

|                                                                                     |                                   |
|-------------------------------------------------------------------------------------|-----------------------------------|
|  | Apatite-rich ore                  |
|  | Fe-oxide rich ore                 |
|  | Rhyolite & rhyolitic tuff         |
|  | Welded & non-welded ash flow tuff |
|  | Agglomerate                       |
|  | Altered volcaniclastic rocks      |
|  | Limestone & dolomite              |
|  | Shale and mudstone                |
|  | Sandstone & siltstone             |
|  | Mafic volcanic rocks              |

