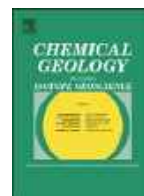




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Significance of apatite REE depletion and monazite inclusions in the brecciated Se–Chahun iron oxide–apatite deposit, Bafq district, Iran: Insights from paragenesis and geochemistry

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ABSTRACT

The Se–Chahun magnetite–apatite deposit (Bafq district, central Iran) comprises several orebodies with large-scale replacement and brecciation textures, and a sodic–calcic alteration envelope. Such members of the iron-oxide copper–gold (IOCG) deposit family commonly exhibit REE enrichment, but the source and evolution of the REE component is arguable. In the Anomaly X orebody, semi-massive ilmenite-rich magnetite and coarse REE-rich fluorapatite formed at 510 ± 8 Ma (U–Pb LA-ICPMS age), at the end of the main regional sodic magmatic event (525 ± 7 Ma). Prior to a major brecciation, a metasomatic event removed Ti and Al from magnetite grain boundaries, and leached primary fluorapatite (BSE-bright) of LREE, Y, Na, Cl, Mg, Mn and Fe, leaving BSE-dark apatite that contained LREE-rich monazite and co-existing vapor- and liquid-dominated fluid inclusions. Subsequent brecciation and hydrothermal infill produced a matrix dominated by actinolite, K-feldspar, biotite, chlorite, calcite, hematite, rutile, and titanite, but apatite was not further metasomatized. It is concluded that P, REE, Ti, Al and Fe were readily transported in the early sodic–calcic fluids, but P and the REE had very restricted mobility (mm's to cm's) in the CO_2 –K–Cl-rich fluids responsible for apatite metasomatism. A role for fluid over-pressuring as a means of increasing the efficacy of apatite REE leaching is circumstantially suggested by the observation that the metasomatic event was terminated by tensile failure. Overall, a case is emerging for fluid-induced nucleation of monazite, and accompanying apatite REE depletion, to be included as a typical but subtle paragenetic feature within the iron oxide–apatite deposit model.

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1. Introduction

The iron oxide–(Cu–Au) deposit style (IOCG) is consistently associated with rare earth element (REE) enrichment, and consequently it is an ideal venue to study hydrothermal REE behavior during and following the emplacement of REE-bearing minerals. One of the most REE-enriched IOCG varieties are the Kiruna-type deposits (Hitzman et al., 1992; Hitzman, 2000), also recently referred to as “IOA” (iron oxide–apatite; Williams, 2010), or P-rich iron oxide deposits (Groves et al., 2010). The classic IOA districts (Kiruna (Sweden), Bafq Mineral Province (BMP; Iran), Chilean Iron Belt, El Laco (Chile)) are attributed to Andean margin processes, and are physically and temporally distinct (with some important exceptions) from economic IOCG mineralization that occurs in some of these regions (Groves et al., 2010). They consist of massive to brecciated, high temperature, magnetite–fluorapatite–calc–silicate bodies that may transgress or be transitional to regional alteration aprons of albite–actinolite $\pm$ K-feldspar $\pm$ phyllic alteration.

They show a common association with evolved felsic intrusions, although the nature of the relationship between intrusions and IOA deposits is an area of substantial argument (Parak, 1975; Hildebrand, 1986; Nyström and Henriquez, 1994; Frietsch and Perdahl, 1995; Barton and Johnson, 1996, 2004; Treloar and Colley, 1996; Broman et al., 1999; Hitzman, 2000; Sillitoe and Burrows, 2002; Williams et al., 2005).

The question of a genetic relationship between IOA and economic IOCG deposits is important to understand for exploration models. A link is supported by the fact that some REE-rich IOCG deposits contain textural evidence of an early IOA stage (e.g., Gawler Province, South Australia: Olympic Dam (Oreskes and Einaudi, 1990) and Oak Dam (Davidson et al., 2007); Carajas district: Sossego deposit (Monteiro et al., 2008)). In most IOCG and IOA deposits, REE enrichment is strongly tied to the formation of P minerals, although allanite, and REE carbonates such as bastnaesite and parisite are also important at some sites (e.g., Olympic Dam; Oreskes and Einaudi, 1990). In an example that illustrates some of the complexity in the P–REE relationship, in the Kiruna district, Edfelt (2007) found that REE compositions of IOCG-associated apatite differ from that of IOA apatite. These aspects reinforce the need to better understand the relationship between REE and P-minerals in the iron oxide-associated clan of Groves et al. (2010).

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IOA deposits, with their high formation temperatures, are a logical place to explore the P-REE relationship. Apatites from these deposits typically contain 2000–6000 ppm REE (Bafq province apatites contain up to 1.75 wt.% REE; Daliran, 2002), and are strongly LREE-enriched, with moderate to strong negative Eu anomalies (Parak, 1975; Frietsch, 1982; Frietsch and Perdahl, 1995). They contrast with the flat REE patterns of anorthosite-related apatites in 'Nelsonites' (apatite-magnetite bodies, e.g., Darling and Florence, 1995). The combined use of back scattered electron imaging (BSE) and LA-ICPMS-based analysis has more recently revealed that apatite can be subject to significant post-depositional REE leaching (Roedder et al., 1987; Harlov et al., 2002), so that it is important to evaluate this possibility before making comparisons to well known apatite end-members (e.g., Belousova et al., 2002). Where REE leaching has occurred in IOA apatite, it is common to observe monazite, and/or xenotime inclusions within the leached zone, or attached to the margins of the leached apatite, and/or within the adjacent calc-silicate-dominated matrix (Harlov et al., 2002; Torab and Lehmann, 2007; Stosch et al., 2010). Experimental studies prove that these monazite and xenotime inclusions typically nucleate after internal redistribution of the apatite REE by a Na–Ca-poor fluid (Harlov and Förster, 2003; Harlov et al., 2005). While this may occur as a part of the typically extensive hydrothermal history of IOA deposits, it may also accompany hydrous metamorphism (Darling and Florence, 1995; Harlov et al., 2002; Edfelt, 2007). Stosch et al. (2010) have used U–Pb dates from apatite-hosted monazite inclusions to contend that the REE redistribution in apatite may even occur during hydrothermal overprinting tens to hundreds of millions of years after IOA formation. Thus it is now uncertain whether apatite REE depletion and consequent formation of monazite inclusions has paragenetic significance within IOA formation models.

Our contribution describes the geology and geochemistry (with emphasis on REE, U and Th) of an IOA deposit, Se–Chahun, from the BMP, Central Iran. The deposit has received little previous attention, but is economically important, and is of interest in the context of the above brief review of REE–P relationships in IOA deposits, because it provides new information on the timing of apatite metasomatism within an IOA paragenesis, and in particular its relationship to brecciation. Our samples were collected from mined outcrops and from drillcore, and were analyzed using transmitted light microscopy, BSE imaging, mineral liberation analysis (MLA), electron microprobe analysis (EMPA), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS) techniques. Numerous samples were used to construct the paragenesis, and our detailed geochemistry was undertaken on 6 of these.

2. Context of the study

2.1. Geological setting of the Bafq Mining District

The BMP is surrounded by fold-and-thrust belts, within the Alpine–Himalayan orogenic system of western Asia. The terrane is divided into three major crustal domains, from east to west: the Lut Block, Tabas Block and the Yazd Block (Alavi, 1991). The Tabas and Yazd blocks are separated by a nearly 600 km long, 80 km wide, arcuate and structurally complex belt (Kashmar–Kerman Tectonic Zone) composed of variably deformed and fault-bound supracrustal rocks (Ramezani and Tucker, 2003). The latter hosts the Bafq mining district. The Kashmar–Kerman Tectonic Zone provides remarkable exposures of the late Neoproterozoic and lower Paleozoic Central Iranian platform successions. An important component of this is the Cambrian Volcanosedimentary Unit (CVSU; Ramezani, 1997), composed of dolomite, limestone, sandstone, shale and bimodal volcanic rocks. Within this sequence, Samani (1993, 1988) recognized the Saghand Formation and the Rizu to Dezu Series (Fig. 1).

The Saghand Formation hosts all IOA deposits in the Bafq district. The formation is crosscut by Zarigan Leucogranite (525 ± 7 Ma, Ramezani and Tucker, 2003) and its equivalent, Narigan Granite in

the north-east and south of the Se–Chahun deposit respectively. These granites are highly silicic, marginally peraluminous trondhjemites (Ramezani, 1997), although Torab and Lehmann (2007) argue that the mildly alkaline character may instead derive from Na–K alteration. All of these features are intruded by unaltered gabbro and late basaltic to dioritic dikes, with uncertain ages (Figs. 1 and 2).

The Early Cambrian tectonic regime has been interpreted as a rift (Berberian and King, 1981; Samani, 1993; Daliran, 2002). Ramezani and Tucker (2003) proposed that this feature was related to a broad-scale Andean margin on the edge of the Proto-Tethyan Gondwanaland supercontinent. This new interpretation is based on the trace element characteristics of the intrusive and volcanic rocks, together with the juxtaposition of the fragmented remains of the margin and cover sequences. This is of some relevance because recent reviews have found a strong association between some iron oxide-associated mineralization and Andean margins (e.g., Hitzman, 2000; Torab and Lehmann, 2007).

Following trondhjemite intrusion, fault block rotation and localized uplift (Jackson and McKenzie, 1984) produced crustal shortening in the Kashmar–Kerman Tectonic Zone (Volcano-Plutonic arc of Torab and Lehmann (2007)). The deformation was generated as accommodation of strike-slip and reverse (thrust) movements on the major fault systems, and for the BMP, the northwest trending Kuhbanan Fault was particularly important (Ramezani and Tucker, 2003) (Fig. 1), although most of the IOA deposits lie on ENE trending smaller faults and fault intersections. The major deposits currently being mined are Chador-Malu (400 Mt), Se–Chahun (140 Mt), and Esfordi (17 Mt); Choghart has a pre-mining reserve of 216 Mt (Torab and Lehmann, 2006). Most examples are massive to semi-massive, show replacement features on their margins, and are variably brecciated to micro-brecciated; ilmenite exsolution is common in magnetite, which is notable, because it is a rare feature in other IOA district examples (Nyström and Henriquez, 1994). Förster and Jafarzadeh (1994) proposed an immiscible liquid magmatic model for these IOA deposits, extrapolating a model previously suggested for Kiruna-type deposits in general (e.g., Nyström and Henriquez, 1994). More recent work (Daliran, 2002; Jami et al., 2007, 2009; Torab and Lehmann, 2007) concluded that hydrothermal fluids played a prominent role in the evolution of at least some deposits, and the source of invoked alkali elements varies from evaporite-derived fluids to evolved felsic magmatic brines. However, Aftabi et al. (2009) considered Esfordi and the other Bafq magnetite–hematite–apatite deposits to be Rapitan-type P-rich banded iron formations.

2.2. Se–Chahun magnetite–apatite mineralization

The Se–Chahun deposit is composed of two major groups of orebodies called the X and XI anomalies (NISCO, 1975). Anomaly XI occurs 3 km northeast of Anomaly X (Figs. 1 and 2). Each anomaly consists of two or three smaller tabular to lens shaped ore bodies (Figs. 2 and 3) in association with many other small bodies. The mineralization is hosted by altered rhyolitic tuff and intercalated shallow-water sandstone, dolomitic limestone and shale (Figs. 1, 2 and 3), representing the middle succession of the Saghand Formation (Samani, 1993). A persistent jaspilite horizon is present in the east of Anomaly X. Most mineralization occurs in sedimentary rocks that are stratigraphically 200 m below this jaspilite, and a relict, variably brecciated, sedimentary banding persists in parts of this Anomaly X. The host rocks and the orebodies are crosscut by E–W-trending normal faults. In addition, late E–W-oriented, unaltered dolerite and dioritic dikes locally crosscut the orebodies and the alteration (Fig. 3).

The Anomaly XI orebodies contain 89% of the ore reserves (average grade of 36–37% Fe), although the massive (with minor banded) magnetite–actinolite ore in Anomaly X has a higher grade (up to 67% Fe; NISCO, 1975; Förster and Jafarzadeh, 1994). The ore in Anomaly XI has a lower phosphorus content (0.08 wt.% P) than that of Anomaly X (0.13 wt.% P). Although we have established a paragenesis jointly

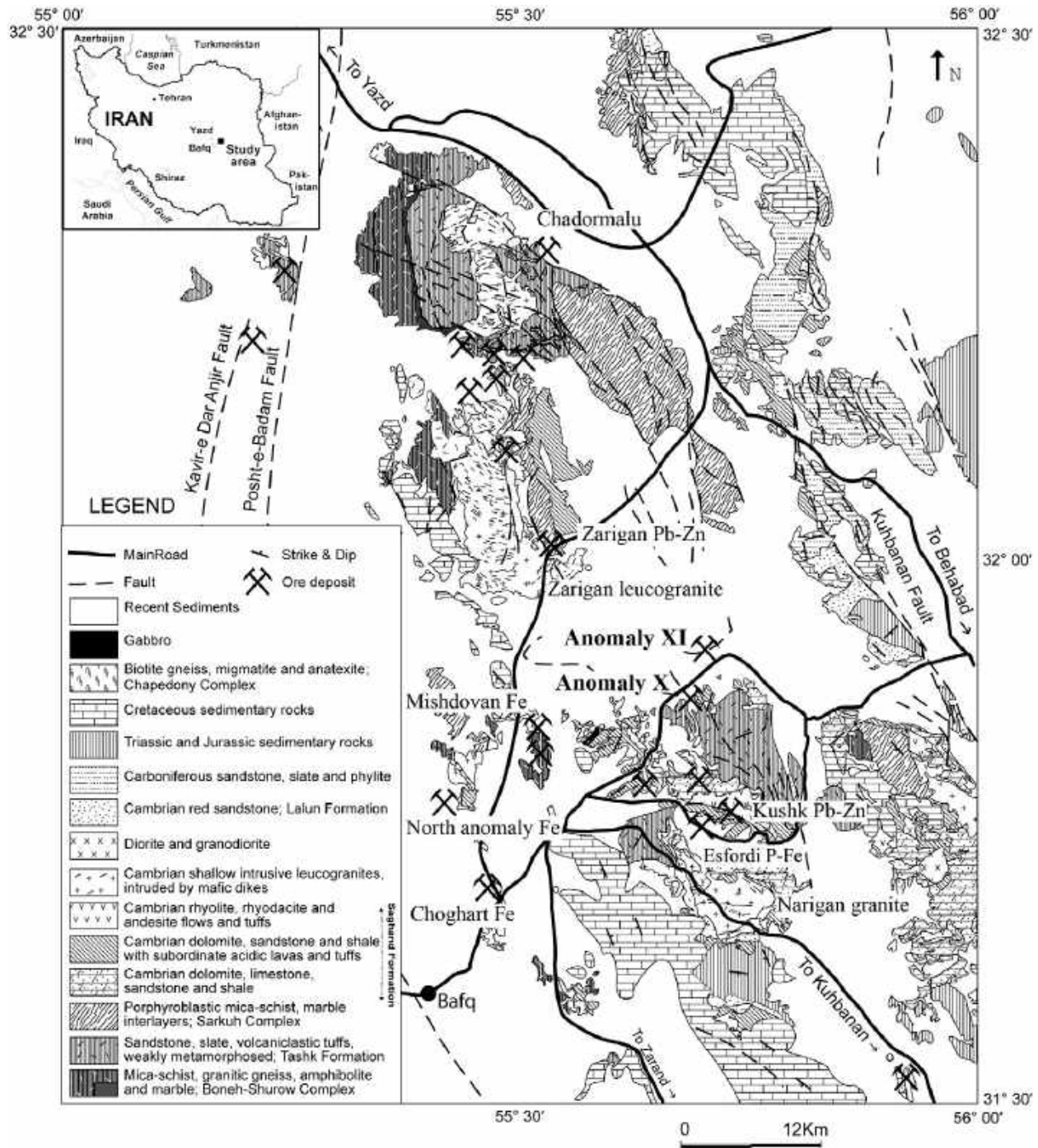


Fig. 1. Simplified regional geological map of Bafq Mineral Province (modified after Haghypour, 1977; Soheili and Mahdavi, 1991; Majidi and Babakhani, 1995; Ramezani and Tucker, 2003; Amini, 2004; Ghaemi and Saidi, 2006; Jami et al., 2007).

across the two orebody groups, all of the detailed geochemistry in this paper derives from Anomaly X; sample locations are provided in table footnotes.

2.3. Orebody and alteration paragenesis

Documentation of the paragenetic sequences (Fig. 4) of hydrothermal alteration and mineralization in the Se–Chahun orebodies was determined using prospect mapping, drill core logging and SEM analysis. The host rocks to both anomalies are strongly altered by both early sodic (chessboard albite) and younger pervasive sodic–calcic alteration (amphibole–albite–magnetite–calcite–epidote–quartz–

titanite–allanite). Magnetite–apatite mineralization is associated with the latter stage. Brecciation is variably developed in this mineralization, with smaller fragment sizes in the apatite zones (up to 2 mm) versus the magnetite zones (up to 7 mm diameter). Although no exotic fragments were observed in the apatite zones, magnetite dominated zones do contain rare fragments of sodic–calcic altered rock. In some places the host rocks are also brecciated, forming albite clasts up to 30 cm across in an actinolite matrix, but field relationships do not permit an understanding of whether this brecciation was contemporaneous with brecciation of the mineralization. A post-brecciation assemblage is present and differs markedly from the pre-brecciation mineralogy. The breccia matrix and post-

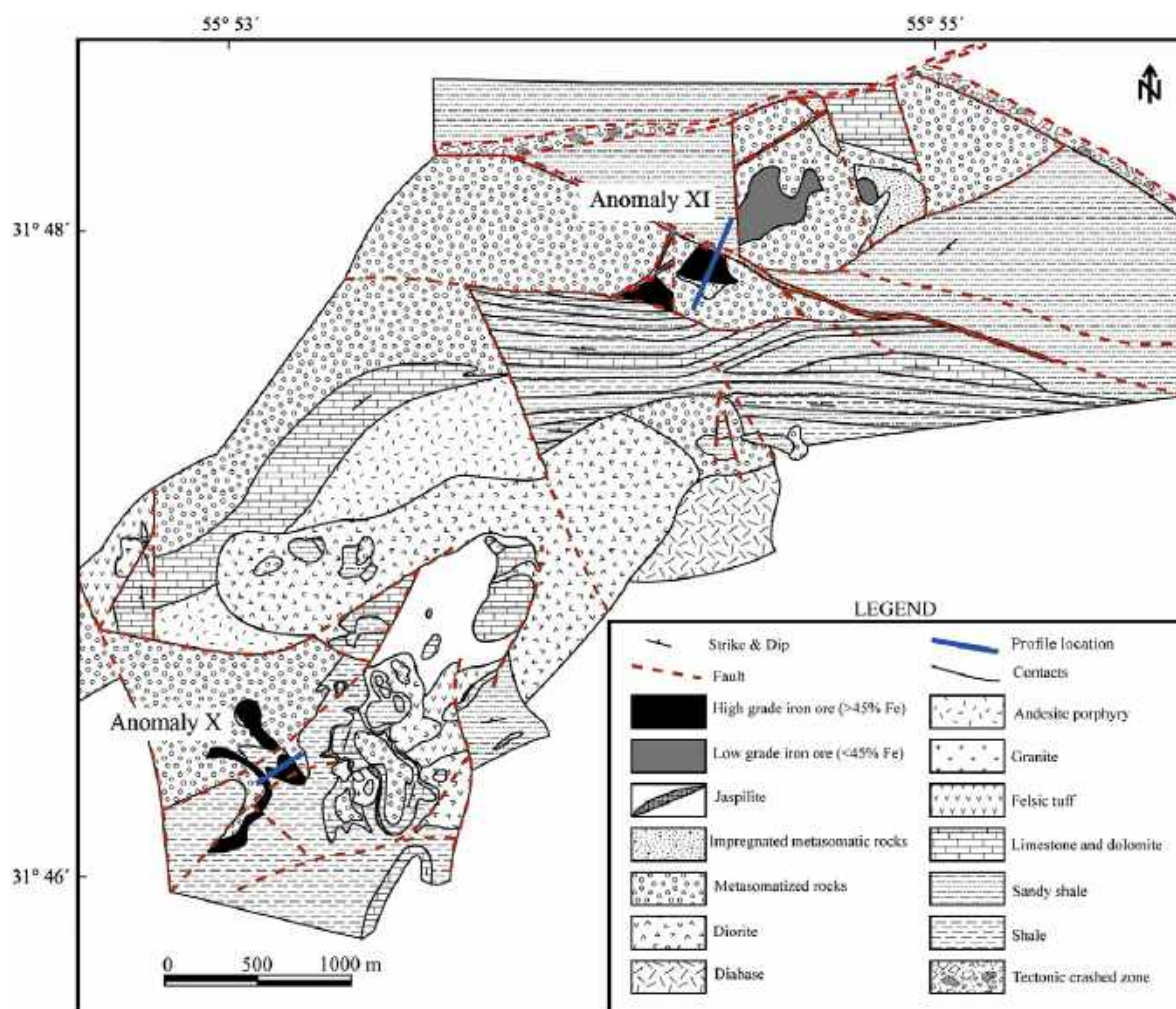


Fig. 2. Simplified geological map of the Se-Chahun deposit, showing Anomalies X and XI (modified after NISCO, 1975). The thick lines are the cross-sections shown in Fig. 3.

breccia veins mainly include K-feldspar, biotite, actinolite (variably altered to chlorite), titanite, ilmenite, sulfide, and rutile. Calcite-quartz-chlorite-(hematite) assemblages commonly comprise the latest infill material (Fig. 5A,C). The rare sulfides are associated with these zones, and are dominated by pyrite with subsidiary chalcocopyrite. In terms of REE-bearing phases, apatite is overgrown by minor monazite, and Th-bearing minerals (mainly huttonite).

3. Detailed petrography of analyzed minerals

3.1. Magnetite

Magnetite (Fig. 5A–D) grain size tends to be bimodal, with one mode averaging 200 μm diameter (up to 1 mm) with a typically more euhedral form (Fig. 5C), whereas the second mode averages 100 μm , and is more typically anhedral. All primary magnetite crystals have cores rich in distinct ilmenite lamellae parallel to the {111} plane (Fig. 5B), but Ti mapping shows that the natural magnetite rims are characterized by a $\sim 50 \mu\text{m}$ wide, smaller scale, speckled ilmenite exsolution texture (Fig. 6A). EMP-based Al mapping shows that the cores are also typically Al-rich, whereas rims are Al-depleted (Fig. 6B). Most magnetite is variably martitized along fractures, {111} planes, and crystal or fragment boundaries (Fig. 5A,B). In brecciated magnetite ore, there is no correlation between Al and Ti enrichment or depletion, and the brecciated margins of coarse magnetite crystals (Fig. 6), but fine fragments display variable Ti contents, and there is a strong tendency for rutile and titanite grains to occur preferentially around these in the

breccia matrix (Fig. 6A). Titanite also occurs as a lining to inter-magnetite carbonate matrix in unbrecciated zones (Fig. 5A,C).

3.2. Apatite

There are two texturally different types of apatite in the Se-Chahun iron ore bodies. The first, present in all orebodies, consists of fine ($< 30 \mu\text{m}$) apatite inclusions within the magnetite grains (Fig. 5C). Due to their small crystal sizes, their chemical analyses were unreliable and they are not evaluated in the chemical section of this paper. The second and dominant group, only observed in Anomaly X, consists of coarse euhedra up to 4 cm long (Fig. 5D), some of which display a relic radiating 'comb' texture suggestive of unidirectional growth from a boundary, similar to observations of some Chilean IOA textures (Treloar and Colley, 1996). The margins of these crystals are distinctly embayed and notched (Fig. 5D). High resolution BSE images of the Se-Chahun apatites show them to have common 'dark' patches and linear stripes overprinting a BSE-bright apatite (Fig. 7A and B). The BSE-dark areas of apatite show a preferred tendency to be oriented parallel to the crystallographic c-axis. Notably, the dark-light patterns show no relationship to breccia block boundaries, which is evidence that the brecciation postdated the development of chemical heterogeneity in the apatite (Fig. 7A, B and C).

In general, numerous fluid and mineral inclusions are scattered within the dark areas (Fig. 7C). However, some dark areas are devoid of inclusions (Fig. 7B). By comparison, bright areas within the apatite contain fewer fluid and solid inclusions.

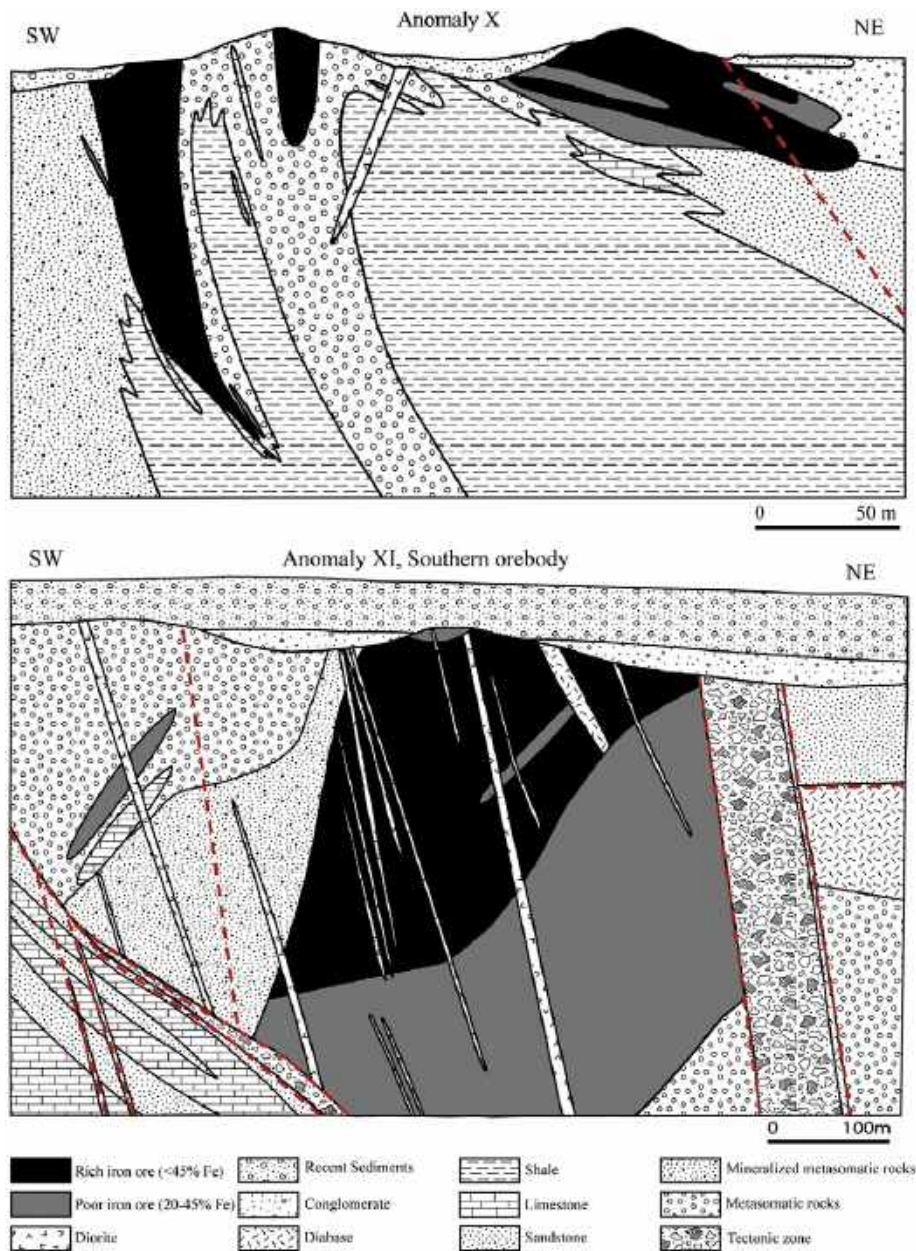


Fig. 3. Simplified cross-sections of Anomaly X and Anomaly XI, southern orebody (modified after NISCO, 1975). Note the anticlinal structure of the rocks in Anomaly X.

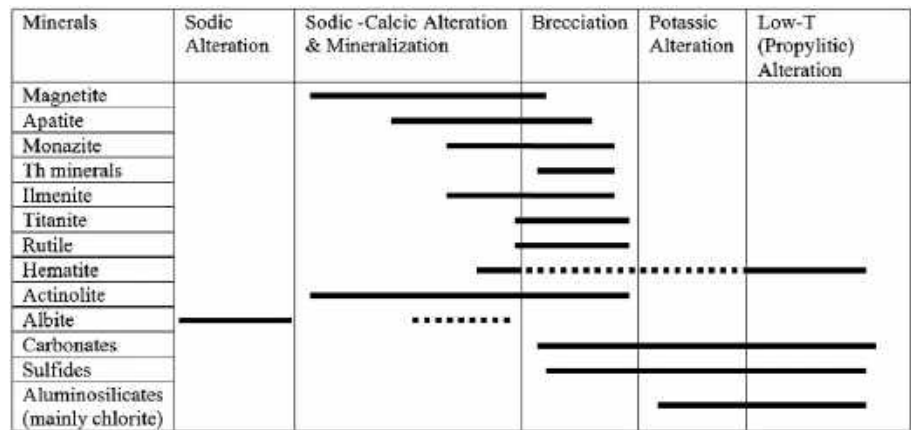


Fig. 4. Paragenetic sequence for the Se-Chahun deposit mineralization.

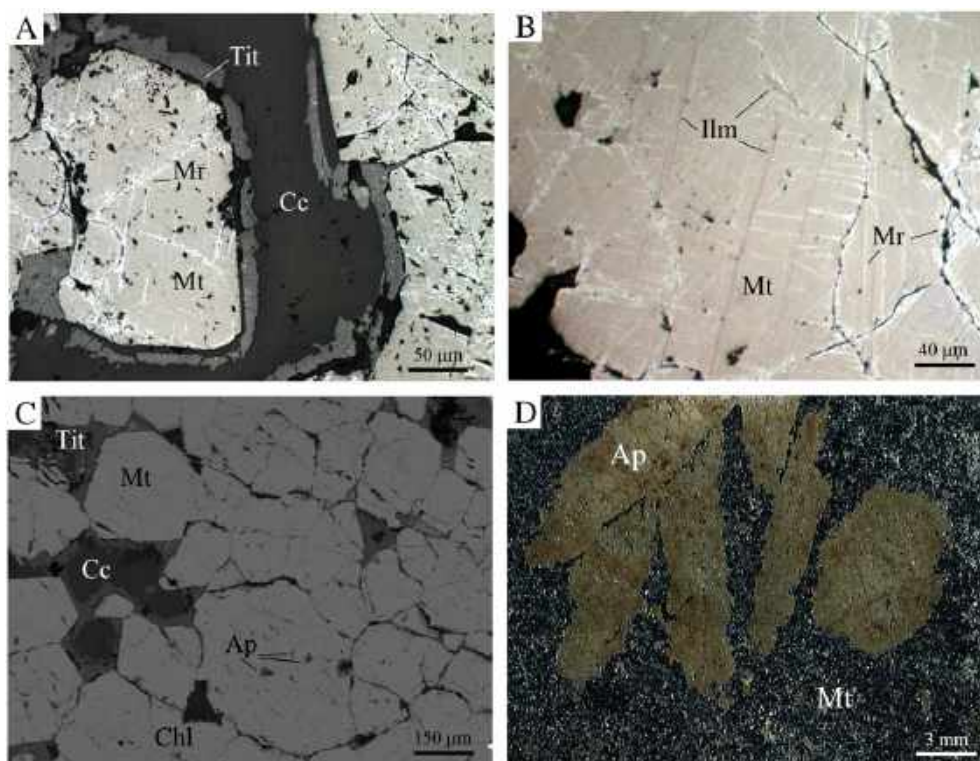


Fig. 5. A) Plane reflected light image (PRLI) showing magnetite with a titanite halo. Calcite has infilled open space (sample 54-38; Anomaly XI). B) Ilmenite lamellae (Ilm) in magnetite (Mt). The light martitised magnetite has formed along cleavage planes (PRLI, To22a; Anomaly X); C) BSE image of primary apatite inclusions in magnetite. Note the occurrence of titanite, chlorite and calcite in the spaces between euhedral magnetite crystals; (54-38; Anomaly XI); and D) A variably brecciated intergrowth of coarse subhedral sheaves of apatite and magnetite crystals (To22; Anomaly X); Abbreviations: Ap = apatite; Cc = calcite; Mt = magnetite; Py = pyrite; Mr = martitised magnetite.

3.3. Monazite

Monazite has at least two different textural forms in the ore zones, corresponding to two different generations. The first generation occurs as solid inclusions (mostly 10–20 μm long, in places up to

120 μm) mainly within elongate domains parallel to the apatite c-axis inside apatite. They are typically euhedral and hexagonal, and are geometrically identical to fluid inclusion shapes within the BSE-dark zones (Fig. 7B and D). They can also be seen to incompletely fill Type 1 and 3 fluid inclusions (see below). The second monazite variety

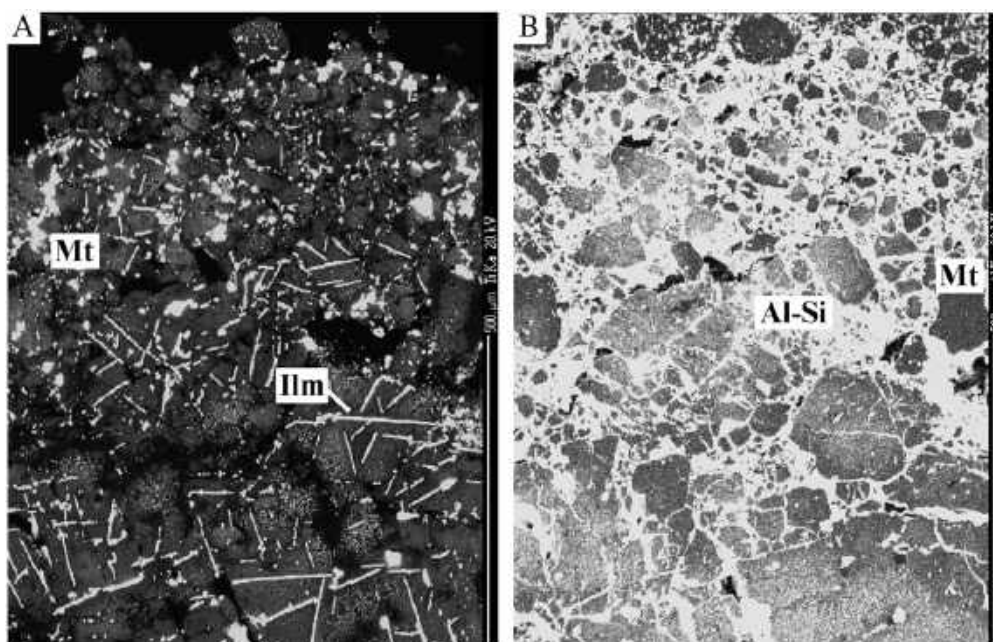


Fig. 6. Element mapping of Se-Chahun magnetite ore, sample To22a, Anomaly X; showing: (A) Ti mapping highlights ilmenite (Ilm) lamellae in magnetite (Mt) as well as small spots of Ti rich materials close to the magnetite rims within the breccia matrix. Ti rich minerals (rutile and titanite) are more common in brecciated zones (top), whereas lamellae are more abundant in the coarse magnetite (bottom). Note the darker areas between lamellae, which shows areas that are depleted in Ti; (B) Al mapping indicates that magnetite (Mt) grain rims are depleted in Al whereas the matrix between magnetite grains is enriched in Al (chlorite and other aluminosilicate minerals).

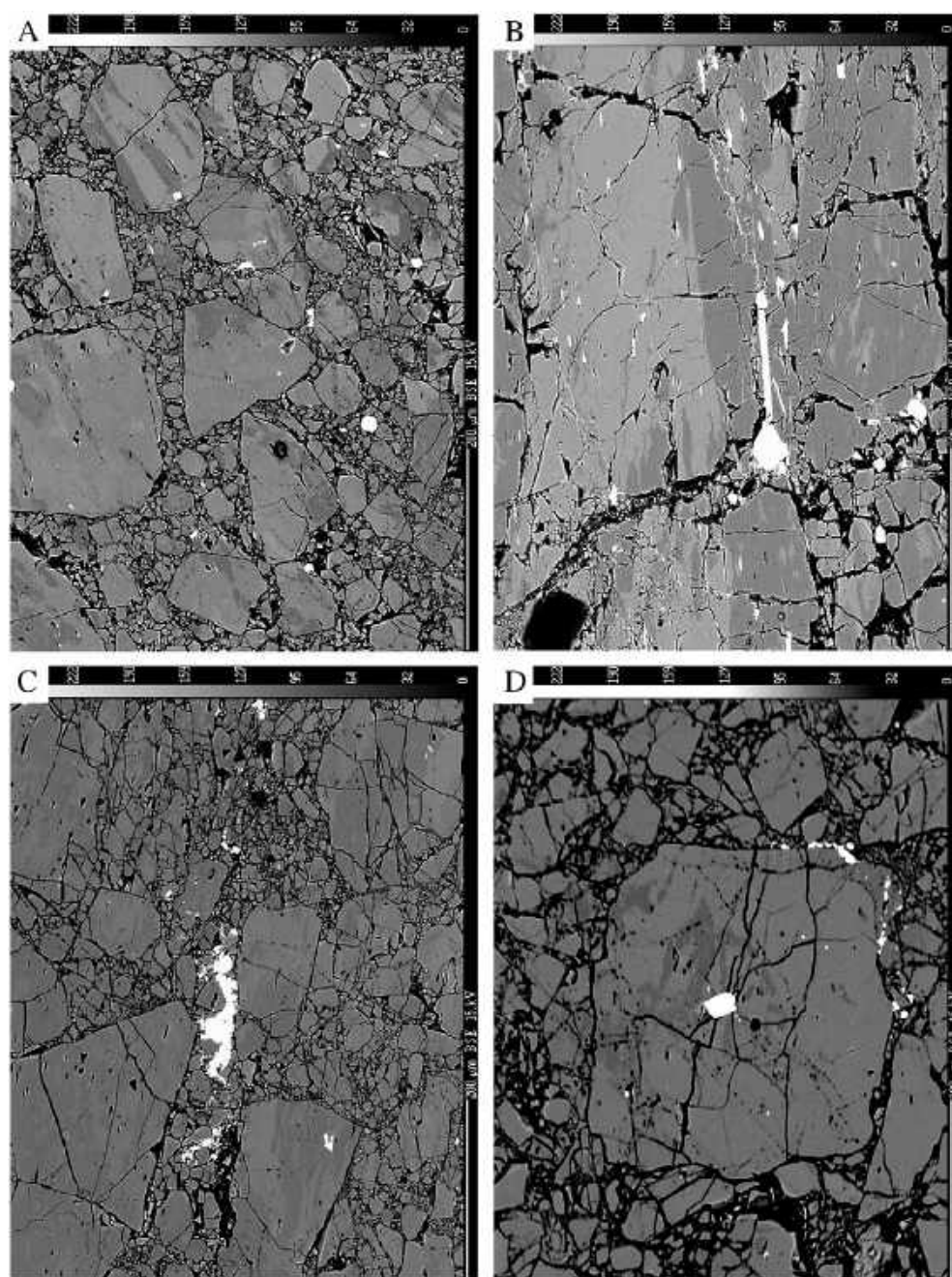


Fig. 7. Back-scattered electron images showing: (A) coarse apatite grains in a brecciated matrix. The apatite grains display a patchy zonation of dark-bright patterns that are crosscut by brecciation. The white spots are monazite crystals (To22a; Anomaly X); (B) Dark-bright patterns in apatite parallel the crystallographic c-axis. The elongate monazite inclusions have formed in the same direction. The monazite crystals in the brecciated areas are mostly anhedral (To22; Anomaly X); (C) monazite morphologies in a brecciated example of mineralization. Note the presence of fluid inclusions (black) in the dark areas (To22a; Anomaly X); (D) A coarse euhedral monazite inclusion in apatite, and small grains of monazite around the apatite grains. The latter formed later in the paragenetic sequence (To22a; Anomaly X).

occurs in the matrix of brecciated apatite domains. Grains occur as aggregates, with irregular shapes and sizes (range 10 μm to 100 μm) (Fig. 7C). Their occurrence only within matrix in the brecciated and fractured areas indicates a post-brecciation timing.

3.4. Fluid inclusions in apatite

Three types of secondary fluid inclusions have been identified in BSE-dark apatite:

Type 1: Liquid-dominated inclusions with minor vapor (typically 90% L + 10% V) (Fig. 8A and B). Some contain accidental crystals of

magnetite and hematite, identified on the basis of their morphology. The majority of inclusions have negative crystal shapes (5–10 μm , Fig. 8A), with elongate varieties being very common (up to 15 μm long, Fig. 8B). They are elongate parallel to the c-axis of the apatite crystals and are commonly associated (attached or adjacent) with various solid inclusions, including monazite (Fig. 9A–C).

Type 2: Three phase inclusions (L + V + S). These are uncommon and small (5–10 μm , Fig. 8C). The single salt shows features consistent with halite.

Type 3: CO_2 -rich vapor inclusions. These are the most abundant and largest fluid inclusions (up to 100 μm long; Fig. 8D). They

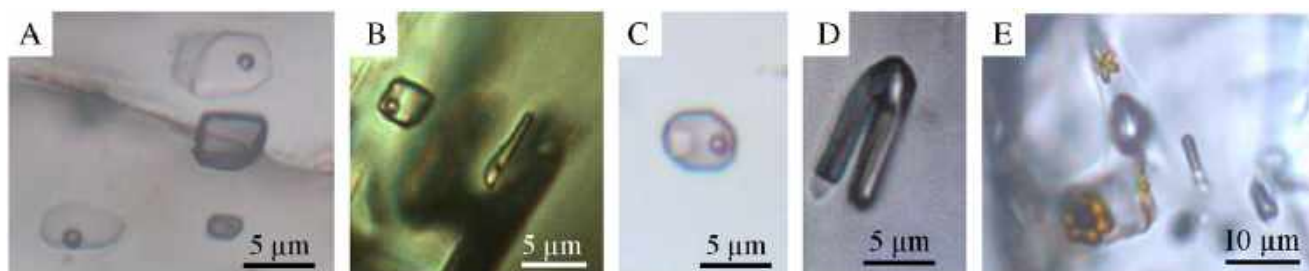


Fig. 8. Representative photomicrographs of the different types of fluid inclusions within the Anomaly X apatite. (A) Two-phase liquid rich fluid inclusions (L + V) and a monophasic gas inclusion; (B) An elongate and a square example of liquid rich fluid inclusions (L + V); (C) Three-phase fluid inclusion; (D) Monophasic gas inclusions; (E) Gas dominated CO₂-rich inclusions which include one or more solid phase(s) mostly iron oxide and hydroxide. A and D are from sample X.205, Anomaly X; B and C derive from sample To22, Anomaly X.

display various shapes, only occur in SEM-dark apatite and can contain accidental crystals of hematite (Fig. 8E), or be attached to monazite (Fig. 9D).

There is also a fluid inclusion generation (two-phase; 90% L + 10% V) that occurs in fine trails cross-cutting all apatite types. It is not clear whether they relate to the brecciating event, or whether they developed during subsequent fluid events.

4. Mineral chemistry of the main REE bearing minerals

4.1. Analytical techniques

4.1.1. EMPA

Mineral analyses were carried out using a SX-100 CAMECA EMPA at the Central Science Laboratory, University of Tasmania. The wavelength dispersive technique was employed. Detection limits for the rare earth elements were 300–1000 ppm. Concentrations of Tb, Ho, Er, and Lu in monazite were routinely measured but their concentrations were below detection limits. The concentrations of U and Pb also were below detection limits (230 and 80 ppm, respectively). Analyses of apatite were performed at 15 kV and 10 nA using a defocused 20 μm diameter beam. The REE in apatite were measured separately using an acceleration voltage of 20 kV, a beam current of 40 nA and a 20 μm beam. The operating conditions for the analysis of monazite were 100 nA, 20 kV, and a 2 μm beam. Operating conditions for the analysis of magnetite (Table 3) included using a 10 μm beam at 10 nA, 15 kV.

4.1.2. LA-ICPMS

Trace element and Pb isotope analyses of minerals of interest, were performed using a Wave UP-213 Laser Ablation System coupled with an Agilent 4500 ICP-MS quadrupole inductively coupled plasma-mass spectrometer (LA-ICPMS) at the University of Tasmania (ARC Center for Excellence in Ore Deposits). Monazite dating was also trialed, but the data yielded ages with errors that were too broad for useful geological application. The laser microprobe incorporates a pulsed Nd:YAG laser

operating at 213 nm and a frequency of 4 Hz. The energy of the beam focused onto the sample surface is attenuated in accordance with the energy appropriate to a suitable crater size (approximately 40 μm) and requires polished samples of approximately 300 μm thickness.

A quadrupole settling time of 5 ms, a dwell time of 25 ms for each element, and a total acquisition time of 100 s were applied for the analysis of the apatite and monazite. After inspection of the spectra, signal intervals for integration were selected in order to avoid those regions which were obviously contaminated or represented signals from small cracks or the glass mount. For the monazite and apatite dating, each analysis was performed by collecting data over an initial 30 s gas background followed by a 30 s period of analysis when the laser was switched on. The glass standard NIST 612 and zircon were used as reference samples for calculating element concentrations.

Each measurement sequence consisted of 2 acquisitions on the standard followed by 10 acquisitions on 10 individual apatite, monazite or magnetite grains and then again 2 acquisitions on the standard. Raw count rates from both the mineral grains and the standards were gas blank-corrected and normalized to the Ca net count rates and the Ca concentration. Element concentrations for each of the apatite grains were calculated by comparison of the Ca-normalized count rates from the apatite with the mean of the four glass standard acquisitions bracketing the 10 apatite analyses. Fe concentrations (72.26%) derived from EMPA analyses were used to normalize the count rates for elements other than Fe during magnetite analysis. Pb isotope analysis used similar methods to those of Woodhead et al. (2009). Lines and spot analyses of various minerals from three separate samples used the standard NIST610 to correct for instrument drift and mass bias.

Apatite dating used a method similar to that described by Meffre et al. (2008), except that the Mud Tank zircons of Black and Gulson (1978) were employed as a primary standard. The apatites were analyzed in 25 mm polished rock mounts using a New Wave solid state 193 nm laser and an Agilent 7500cs quadrupole ICPMS. The samples were ablated in a custom made chamber using a 100 micron beam size at a repetition rate of 10 Hz and fluence around 2 J/cm². We

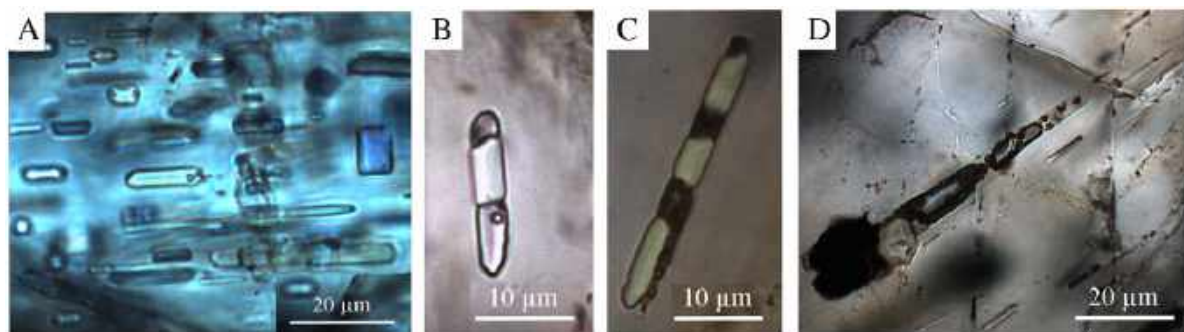


Fig. 9. Photomicrographs showing: (A) Elongate and rectangular monazite and fluid inclusions. Note the orientation of monazite inclusions parallel to the c-axis of the apatite host, and the different orientation of the rectangular inclusion, XPL; (B) A two-phase fluid inclusion that is partly infilled by monazite; (C) A void filled by three monazite segments and gas; (D) Two solid inclusions (dark and light), two vapor inclusions and a small iron oxide inclusion occur in the same channel. All are from sample To22, Anomaly X.

were unable to use the Temora zircons (preferred primary standard; [Meffre et al., 2008](#)) as primary standards because, at the large spot size required for accurate results on the apatite, the count rate on U and Th would have been too high, saturating the detector and causing problems with the age calculations. The Mud Tank zircons were chosen because they have similarly low U contents to the To22 apatite. Ideally a standard apatite would have been used as the primary standard to minimize potential problems associated with ablation of different minerals, but at present no well characterized apatites are available for LA-ICPMS U–Pb work globally. At the large spot size used, very little downhole fractionation of Pb/U was observed (<5%), so we expect only very small effects on the Pb/U ratio as a result of differences in the rate of ablation between zircons and apatite. However, matrix effects are well known in ICPMS. [Black et al. \(2004\)](#) noted that zircons with different compositions but the same age, gave slightly different ages by ICPMS compared to TIMS (up to 3%). Our reported ages may be subject to similar levels of uncertainty due to matrix effects.

4.2. Results

4.2.1. Magnetite

4.2.1.1. EMPA and LA-ICPMS. The representative results of EMPA analysis for magnetite are presented in [Table 1](#), and the results of LA-ICPMS analysis for five magnetite grains are shown in [Table 2](#). The chondrite normalized REE concentration of the magnetite grains shows that Eu has clear negative anomalies ($\text{Eu}/\text{Eu}^* = 0.40\text{--}0.53$) and Ce is weakly depleted ($\text{Ce}/\text{Ce}^* = 0.55\text{--}0.95$). LREE concentrations typically exceed HREE concentrations, reflected in chondrite-normalized La/Yb (La_n/Yb_n) of 3.94–9.48. Time-resolved evaluation of the LA-ICPMS data shows that La cps remain above detection, but are moderately variable when compared to probable magnetite lattice substituents such as V. Additionally, plotting of this time-resolved cps data reveals moderate La–Th–U positive correlations in some but not all analyses. Taken together, this data suggests that REE within the magnetite are probably present as abundant micro-inclusions, although the absence of P from our analytical suite means that we cannot test the hypothesis that these inclusions are REE-phosphates. Given that all apatites measured away from the magnetites possess flat to +Ce anomalies (see 4.2.2), it is unlikely that the –Ce bearing REE patterns documented here derive directly from micro-inclusions of such apatite.

4.2.2. Apatite

4.2.2.1. EMPA. The REE are typically the main influence on BSE response in apatite, but there is also some response from more

Table 1

Trace element concentrations (wt.%) in magnetites (spot analyses, not integrated with ilmenite exsolution features; EMPA data).

Sample*	To22-1	To22-6	To22-9	To22-12	To22-13
SiO ₂	0.04	0.06	<0.04	<0.04	<0.04
TiO ₂	0.42	0.41	0.39	0.22	0.21
Al ₂ O ₃	0.24	0.10	0.26	0.39	0.30
Cr ₂ O ₃	<0.04	<0.04	<0.04	<0.04	<0.04
V ₂ O ₃	0.41	0.44	0.42	0.42	0.40
Fe ₂ O ₃ **	67.9	68.0	67.7	68.0	68.0
FeO	31.3	31.3	31.0	31.0	30.9
MnO	0.07	0.05	0.14	<0.04	0.08
MgO	0.16	0.18	0.22	0.18	0.19
ZnO	0.06	0.01	0.09	0.13	0.10
CaO	<0.02	0.02	<0.02	<0.02	<0.02
CoO	0.01	0.01	0.01	<0.006	<0.006
Total	100.7	100.7	100.3	100.4	100.2

*Sample coordinates: To22 (31°, 52', 35" N; 55°, 41', 18" E).

** Fe₂O₃ and FeO calculated according to [Carmichael \(1967\)](#).

Table 2

Selected trace element concentrations (ppm) in magnetites (laser-ablation ICPMS data).

Sample*	To22a-1	To22a-2	To22a-3	To22a-4	To22a-5
Mg	1885	1589	2433	1859	1744
Al	246	1832	3528	3378	1173
Ca	<450	<450	524	<450	725
Sc	3	1	1	1	1
Ti (%)	2.64	1.33	0.98	1.08	1.21
V	2386	2476	2396	2363	2397
Mn	2070	1443	1247	1146	1539
Co	98.1	82.6	85.3	83.0	86.7
Ni	271.5	263.2	270.7	264.9	275.0
Cu	75.1	14.4	<6	11.1	42.9
Zn	413.7	323.4	817.9	529.6	98.4
Ga	47.7	45.4	44.3	39.4	33.7
Ge	12.9	10.7	12.6	11.3	11.8
As	18.27	<2.4	2.95	2.79	10.5
Sr	14.02	3.28	3.75	2.53	8.94
Y	6.33	1.18	0.70	1.52	4.53
Zr	0.83	0.80	0.48	0.35	1.36
Nb	2.54	0.21	0.69	0.30	0.69
Mo	0.71	0.45	0.46	<0.37	0.39
In	0.20	0.15	0.16	0.16	0.13
Sn	18.2	17.4	17.5	14.0	14.0
Ba	2.93	0.67	6.78	5.60	1.83
La	9.47	1.68	1.32	1.36	6.50
Ce	11.5	2.04	2.34	2.36	6.99
Pr	1.52	0.33	0.27	0.20	0.89
Nd	6.37	1.52	1.12	1.04	3.70
Sm	1.82	0.45	0.33	0.24	0.86
Eu	0.24	0.07	0.03	<0.03	0.16
Gd	1.84	0.28	0.27	0.30	1.08
Tb	0.34	0.07	0.03	0.03	0.18
Dy	1.86	0.29	0.21	0.26	1.28
Ho	0.31	0.05	0.02	0.05	0.25
Er	0.90	0.19	0.11	0.23	0.69
Tm	0.13	0.02	0.02	0.03	0.11
Yb	0.94	0.16	0.10	0.24	0.69
Lu	0.10	0.03	0.01	0.05	0.11
Hf	0.05	0.07	0.04	<0.03	<0.03
Ta	0.37	0.18	0.16	0.11	0.14
W	0.24	<0.03	0.16	0.07	0.19
Pb	1.07	<0.88	<0.88	<0.88	<0.88
Th	1.91	0.73	0.85	0.59	3.58
U	1.14	0.28	0.26	0.18	0.90

*Sample coordinates: To22a (31°, 52', 27" N; 55°, 41', 20" E).

abundant low atomic number elements such as Na, Cl and F ([Pan and Fleet, 2002](#)). The detection limits for the REE by EMPA are between about 800 and 1300 ppm. The OH values were calculated using the equations of [Piccoli and Candela \(2002\)](#). Representative chemical analyses of Anomaly X apatite are presented in [Table 3](#).

Apatite from 3 Anomaly X samples has Cl and F ranges of 0.25–1.25 wt.% and 2.64–3.29 wt.% respectively ([Table 3](#)). Bright apatite is Cl enriched over dark apatite ([Fig. 10](#)). Of the REE, only La, Ce, and Nd were systematically detected in bright apatite (La + Ce + Nd = 6900–19,700 ppm). In dark apatite, none of the routinely sought REE (La, Ce, Nd, Sm, Gd, and Dy) were present at concentrations above their detection limits, but abundances were determined via LA-ICPMS analyses (see below). In all samples, Na₂O, SiO₂, FeO and SO₃ contents in bright areas are significantly higher than those of dark areas ([Table 3](#)). Values for Na₂O and SiO₂ cover a range of 0.10–0.46 and 0.08–0.38 wt.% respectively in the bright areas, and <0.07–0.20 and 0.10–0.27 wt.% respectively in dark areas. SO₃ abundances decrease from 0.06–0.16 wt.% in the bright areas to <0.03 wt.% in the dark areas. There is a clear covariance between Na, Si, and LREEs which is balanced by an increase in CaO and P₂O₅ in the dark areas by up to 0.8 and 0.32 wt.% respectively, supporting previous findings on IOA apatites generally ([Harlov et al., 2002](#); [Pan and Fleet, 2002](#); [Torab and Lehmann, 2007](#)).

4.2.2.2. LA-ICPMS TRAVERSES. Trace element traverses of BSE-dark and -bright areas of two apatite grains were obtained for sample

Table 3

Trace element concentrations (wt.%) in bright and dark parts of the apatites of Anomaly X, measured by EMPA.

Sample*	X.205-2-bright	X.205-5-bright	To22-1-bright	To22-10-bright	X.205-2-dark	X.205-5-dark	X.205-25-dark	To22-11-dark	To22-a-1-dark
P ₂ O ₅	40.15	40.51	40.14	39.88	40.70	41.16	40.78	40.53	40.78
CaO	51.58	52.19	51.56	51.21	53.44	53.24	53.32	53.08	53.09
Na ₂ O	0.24	0.16	0.19	0.33	<0.07	<0.07	<0.07	<0.07	<0.07
SiO ₂	0.20	0.11	0.16	0.30	0.16	0.10	0.15	0.13	0.17
FeO	0.12	0.05	0.36	0.09	<0.04	<0.04	<0.04	0.02	<0.04
SO ₃	0.08	0.05	0.05	0.11	<0.03	<0.03	<0.03	<0.03	<0.03
As ₂ O ₅	<0.04	0.06	0.05	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Y ₂ O ₃	0.18	0.13	0.16	0.23	<0.07	0.13	0.08	0.14	0.09
La ₂ O ₃	0.30	0.22	0.25	0.44	0.10	<0.09	<0.09	<0.09	<0.09
Ce ₂ O ₃	0.76	0.44	0.57	1.00	0.19	<0.1	0.21	0.12	0.25
Nd ₂ O ₃	0.32	0.23	0.25	0.39	<0.14	<0.14	<0.14	<0.14	0.16
EuO	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Cl	1.11	0.74	1.12	1.02	0.25	0.44	0.27	0.52	0.38
F	2.84	2.82	2.76	2.76	3.29	2.97	3.16	3.07	2.94
Total	97.88	97.70	97.60	97.74	98.13	98.04	97.98	97.62	97.87

*Sample coordinates: X.205 (31°, 52', 35" N; 55°, 41', 19" E).

To22a (Fig. 7), to evaluate any spatial control on element abundances. Two traverses (600 and 400 μ m long) from dark to bright areas were analyzed for 34 elements. The results are shown as the average concentration of the elements in equal distances of the traverses (Table 4).

BSE-bright apatite contains the greatest Na, V, Mn, Ge, Zr, Th and U values, but low Fe (<500 ppm). As indicated by EMPA, REE contents are also higher in bright areas (Σ REE = 6296–8931 ppm) compared to dark zones (Σ REE = 3920–4530 ppm). There is evidence of significant relative loss of LREE, because La_n/Yb_n in BSE-light apatite is 16.5–26.0 (av. 21.5) compared to that of dark apatite 9.1–14.8 (av. 12.8). The changes in concentration of analytically dominant elements (Mg, Na, Mn, Fe, La and Sr) through the traverses from dark apatite to bright areas (Fig. 11) are mainly transitional rather than abrupt at the BSE boundary (which is of interest because most experimental work produces abrupt compositional boundaries, e.g., Harlov and Förster, 2003). Na variation most clearly marks the BSE boundary in our apatite, but also shows an erratic behavior consistent with inclusion control, or complex crystallographic control (e.g., Rakovan and Reeder, 1996). In contrast, dark apatite displays inclusion control for La (likely, monazite), Fe and Mg.

The chondrite normalized patterns of REEs in dark and bright areas show that a negative Eu anomaly occurs in both areas, but that the anomaly is more pronounced in the bright areas (Fig. 12). Eu/Eu^* in bright and dark apatite areas is 0.19–0.35 and 0.14–0.29, with average values of 0.27 and 0.20, respectively. A weak +Ce anomaly is present in both dark and bright areas. The Ce/Ce* ratio in dark areas is 1.25–1.61 with an average of 1.43, whereas the ratio in the bright parts is 1.13–1.45 with an average of 1.24. Thus the Ce anomaly is stronger in leached apatite. Our observation of +Ce at Se–Chahun supports a previous observation (Daliran, 2002) that Bafq province apatite has this character, although dark–light BSE character was not assessed in that study.

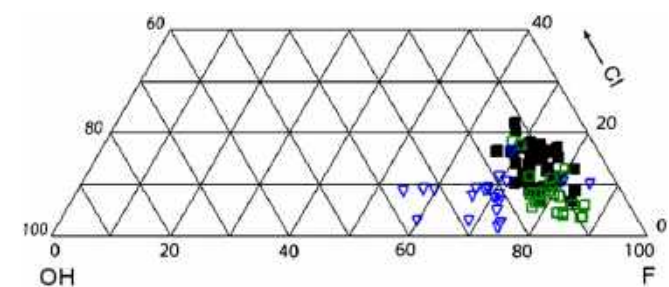


Fig. 10. Ternary plot of the BSE-bright and dark apatite areas (solid and open squares respectively) from the Se–Chahun and Esfordi (triangles) deposits in terms of F–OH–Cl atomic proportions, calculated using the method by Piccoli and Candela (2002) ($n = 81$). The Esfordi apatite data derives from Torab and Lehmann (2007).

The chondrite normalized patterns of BSE-bright apatite are very similar to the REE patterns of apatite within mafic I-type granite (Sha and Chappell, 1999). The apatite values plotted on the Sr vs. Y diagram of Belousova et al. (2002) (Fig. 13), which relates apatite chemistry to genetic association, supports the finding of Torab and Lehmann (2007) that Bafq apatites are chemically very similar to those of other Kiruna-type deposits (Frietsch and Perdahl, 1995). Daliran (2002) and others assert that Bafq deposits show some carbonatite affinities, but this is not supported on the basis of their Sr–Y character, or their lack of positive to flat Eu anomalies (a key carbonatite feature) in their REE patterns. The BSE-dark apatites also plot as Kiruna-type on Fig. 13, which is evidence that, at least at Se–Chahun, grain metasomatism was not severe enough to camouflage the original grain affinity.

4.2.3. Monazite

4.2.3.1. EMPA. Monazite inclusions from all textural associations at Se–Chahun are mainly compositionally very uniform low-Th monazites (<0.60 wt.% ThO₂; Table 5). Globally, hydrothermal monazites have low Th contents (0–1 wt.% ThO₂), whereas igneous monazites have the highest values that are found in nature (3 to >5 wt.% ThO₂; Schandl and Gorton, 2004). A minority of Se–Chahun analyses possessed ThO₂ as high as 1.32 and 1.83 wt.% (Table 5). Torab and Lehmann (2007) and Stosch et al. (2010) used high resolution BSE imaging to discover that Choghart monazite grains possess inner cores rich in ThO₂, and targeted these for dating. In Se–Chahun monazite, SiO₂ and Y₂O₃ contents are also low (0.12–0.78 and 0.14–0.53 wt.%, respectively), both with no systematic variations with respect to the textural position of the monazite. The concentration of As₂O₅ is higher in the monazite aggregates in the breccia (0.11–0.17; Table 5), which is of interest because As is only likely to substitute for P when in its most oxidized +5 state. The characteristic LREE enrichment of monazite (e.g., Chang et al. (1996) and references therein) is expressed most strongly in monazite aggregates from the brecciated matrix (La_n/Yb_n of 581–992.9), compared to apatite-hosted monazite (La_n/Yb_n of 189–460.6). Although Ce in the host dark apatite was preferentially retained, yielding a +Ce anomaly, Ce in the monazite inclusions shows no anomaly. Europium shows a moderate to strong negative anomaly ($Eu/Eu^* = 0.04–0.53$). (Table 5; Fig. 14).

4.3. Apatite dating

Twelve apatite grains from sample To22a were analyzed for U, Th and Pb isotopes (Table 6; Fig. 7). The dating points were within the BSE-bright apatite, which has low U (1–6 ppm) and Th (9–43 ppm) (Table 7), but is the apatite variety that formed with most magnetite. Note that, unlike the Kiruna-type IOCG mineralization in the

Table 4

Trace element concentrations (ppm) in apatites from Anomaly X, Se-Chahun deposit (To22a). All analyses were obtained as a traverse on a single apatite crystal using laser-ablation ICPMS. The concentrations are calculated as the average of concentrations in the equal distances (in μm). The traverse started at the dark part of the apatite and ended at the bright part of it. The interval 245–280 is the boundary between the dark and bright areas.

Sample	105–140	140–175	175–210	210–245	245–280	280–315	315–350	350–385	385–420	420–455	455–490	490–525	525–560	560–595
Na	469	373	531	475	876	1828	2130	1836	2744	2317	2875	2799	2627	3765
Mg	164	172	263	129	74.69	51.29	82.49	114	185	253	299	488	503	468
Si	2156	2167	2262	1212	1095	864	762	654	550	691	592	1785	1662	1630
V	17.74	10.94	6.46	10.52	12.12	6.95	7.78	6.41	5.46	4.92	5.80	40.93	20.69	17.37
Mn	66.83	71.52	84.27	108	86.48	79.77	84.12	88.89	114	144	162	178	187	170
Fe	1544	1396	1031	3094	3194	490	195	223	286	279	441	1420	807	530
Co	0.54	0.54	0.42	0.62	0.36	0.16	0.03	0.08	0.06	0.06	0.11	0.12	0.11	0.05
Ni	0.65	0.87	0.69	0.84	0.40	0.16	0.20	0.10	0.16	0.30	0.32	0.06	0.13	0.37
Ge	13.62	8.55	3.92	3.24	3.50	3.92	3.44	3.59	4.38	4.15	6.16	5.77	8.65	8.73
Sr	264	248	195	184	178	165	182	199	233	255	289	325	357	343
Y	863	788	744	756	835	848	866	826	840	811	869	1315	1403	1367
Cu	1.02	1.72	9.55	3.10	1.40	0.21	0.04	0.04	0.08	0.24	0.32	1.49	0.19	0.06
Zn	1.09	1.09	1.94	1.06	0.29	0.20	0.17	0.17	0.07	0.22	0.18	0.47	0.40	0.10
Al	124	139	675	57.6	19.5	1.85	2.01	8.44	8.45	4.37	6.83	1.65	0.88	24.1
Zr	0.16	0.08	0.09	1.67	1.69	0.62	0.87	0.19	0.03	0.04	0.08	6.27	0.49	0.39
Pb	10.41	4.61	1.60	2.17	6.66	6.34	4.40	2.23	1.35	1.00	1.82	140	11.38	6.44
Th	317	146	31.97	140	857	309	338	58.35	18.88	19.49	46.43	5555	279	130
U	1.67	1.24	1.40	1.60	9.85	7.02	19.66	3.20	1.46	1.54	4.21	389	16.37	8.85
P	31.00	28.54	31.44	32.20	30.61	30.61	27.83	28.95	30.33	27.97	28.63	27.80	28.34	29.34
Ca*	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00	38.00
La	5470	2869	801	564	488	439	592	756	1037	1246	1525	2003	2771	2719
Ce	11493	6487	2505	1878	1793	1516	1824	2250	2848	3223	3910	4975	6495	6718
Pr	1089	622	270	244	224	202	228	259	303	333	387	495	647	658
Nd	3447	2145	1058	966	953	858	933	1010	1117	1190	1359	1723	2216	2200
Sm	383	274	184	180	180	174	173	177	184	188	206	266	333	329
Eu	19.95	16.98	13.34	11.06	10.48	10.63	11.99	11.10	13.41	16.06	19.55	26.32	33.37	32.31
Gd	273	215	168	168	173	165	173	168	172	177	183	251	292	285
Tb	28.32	23.83	20.58	20.98	22.34	21.55	22.48	21.16	21.46	21.98	23.86	33.31	37.87	36.51
Dy	147	129	118	121	130	129	134	129	129	130	139	200	223	218
Ho	26.42	23.50	22.28	23.04	24.91	24.92	26.08	24.37	25.13	25.21	27.22	40.36	43.81	42.25
Er	63.30	57.56	56.78	59.44	65.70	65.06	67.65	64.33	64.28	64.06	69.90	107	117	113
Tm	7.15	6.54	6.73	6.85	8.10	8.26	8.42	7.52	7.76	7.49	8.63	13.50	14.65	13.97
Yb	36.63	34.94	35.89	37.92	43.85	43.76	44.98	41.36	41.90	42.62	47.83	74.97	82.20	79.30
Lu	4.48	4.05	4.19	4.49	5.04	5.25	5.38	4.99	5.04	5.16	5.72	9.08	9.80	9.51

* Average Ca concentration (%) of microprobe analysis in the same sample.

Adirondack Mountains recently dated by U/Pb zircon geochronology (Valley et al., 2009), no hydrothermal zircons were detected in our samples despite systematic search by MLA (an automated SEM instrument). An attempt to date dark apatite was also made. However,

the U–Pb systematics of this apatite proved to be complex due to the inhomogeneous distribution of the U and Th in inclusions, and also due to mobility of the radiogenic Pb produced within these inclusions. Fig. 15 shows that as the laser drilled through each inclusion the

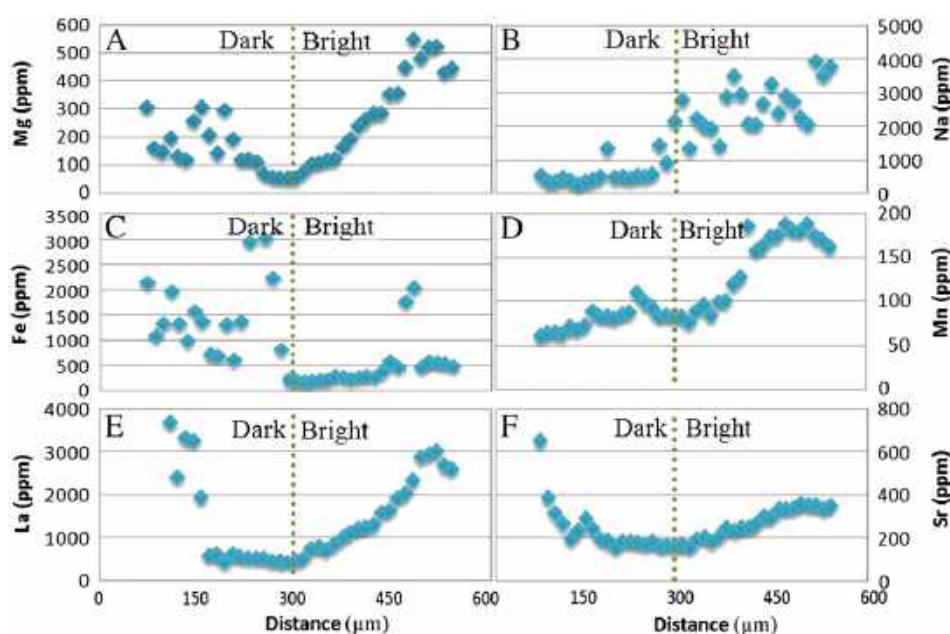


Fig. 11. The changes in concentration of Mg, Na, Mn, Fe, La and along a traverse from a BSE-dark to a BSE-bright area in apatite (To22a, Anomaly X). The dotted line is the border between the dark and bright areas.

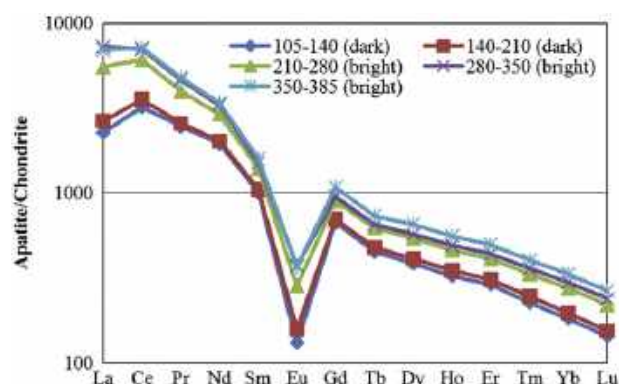


Fig. 12. Chondrite normalized REE distribution patterns of dark and bright areas of apatite from the Se-Chahun ore deposit (To22a, Anomaly X). The patterns show negative anomalies in Eu and slight positive Ce anomalies. Note the lower REE concentration of the dark areas (105–140, 140–210) in the diagrams. Chondrite values are taken from Anders and Grevesse (1989).

apparent $^{206}\text{Pb}/^{238}\text{U}$ age decreased, indicating widespread Pb loss from the inclusions. Correspondingly, the dark apatite analyzed near the inclusions has apparent ages that are much older than adjacent dark apatite, and inclusion-free bright apatite. This is consistent with migration by diffusion of radiogenic Pb from the high U and Th inclusions into the surrounding dark apatite.

By removing dark apatite analyses, and those in bright apatite close to fracture related inclusions, all but one bright apatite data point converged on a weighted average age of 510 ± 8 (at 95% conf. MSWD = 0.94) (see Table 6 and Fig. 16). One bright apatite analysis has a high Pb/U ratio and was drilled in a zone of strongly brecciated crystals to determine if brecciation had affected the U–Pb systematics. The high Pb/U ratio within the brecciated apatite suggests that there is excess radiogenic Pb within the breccia zones (Fig. 16). The brecciated zones are probably contaminated with radiogenic Pb from inclusions that are outside the analyzed area, indicating that Pb mobility within the breccia zones occurred after the rocks were enriched in U and Th, so that radiogenic Pb had time to accumulate and then be remobilized. The accuracy of these results may be subject to matrix effects, as outlined in the Methods section.

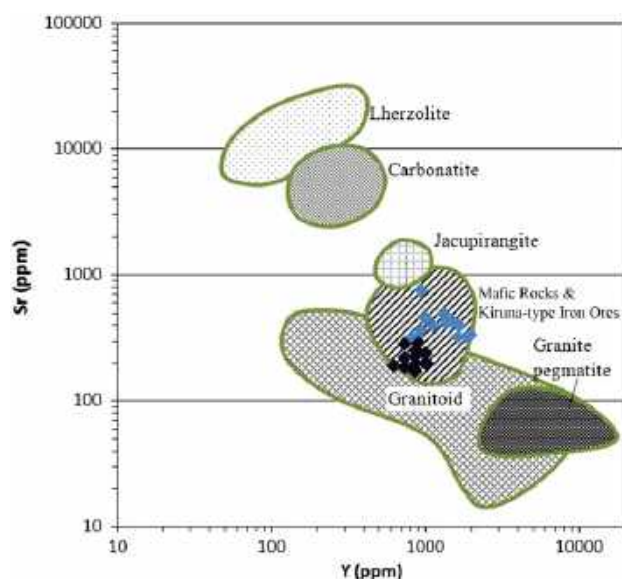


Fig. 13. Y–Sr composition of dark and bright apatite (dark and light solid squares, respectively) from the Se-Chahun deposit, compared to the reference fields of Belousova et al. (2002).

4.4. Pb isotopic composition of minerals

Laser ablation ICPMS Pb isotopic determinations were made on various minerals within Se–Chahun Fe deposit to try to differentiate minerals which formed during or prior to mineralization, from minerals that formed post-brecciation. It was assumed that any minerals that formed during mineralization and contained U should retain a non-radiogenic Pb isotopic composition after correction of the data for *in situ* decay of Th and U. Minerals which formed later should incorporate extra radiogenic Pb into their structure due to the radiogenic decay of the abundant U and Th within the deposit area.

The results were hampered by the low abundance of Pb within the analyzed minerals (Table 7). Pyrite had the highest Pb (9–53.4 ppm; $n=5$) followed by actinolite, magnetite, albite and carbonate. Uranium and thorium Pb values were high compared to Pb in most other minerals, so that a correction had to be made for the *in situ* decay of U and Th. The carbonates did not have enough Pb to enable calculation of ^{204}Pb so that only $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios could be calculated. These ratios indicate a highly radiogenic Pb composition within these minerals.

All of the analyses have relatively low precision for their Pb isotopic composition due to the low Pb, high U and high Th and inhomogeneous distribution of the Pb within these minerals. Minerals with high Pb/U values plot close to the crustal growth curve of Stacey and Kramers (1975), between 300 and 500 Ma (Fig. 16). Minerals with low Pb/U tend to have a very radiogenic isotopic composition. When the *in situ* decay of the U measured in the samples is taken into account, most of the analyses are brought back to a position close to that of the low U minerals, indicating that most of the spread in the uncorrected data results from the decay of the U measured within the minerals. This result suggests that most of the minerals analyzed grew either during or prior to the enrichment in U in the deposit, rather than being added by a much younger event, and that most of the radiogenic Pb produced by U has been little disturbed.

A few of the analyses, such as those from some of the feldspars and magnetites, are over-corrected by the U and Th correction, resulting in analyses moving to a less radiogenic position compared to the main high Pb group of analyses. These minerals have probably lost a little of their radiogenic Pb since they were formed. A single pyrite analysis (19–350) still has a very radiogenic composition even after correction. On close inspection a marked difference between the Pb isotopic compositions of different parts of this pyrite can be observed. On the rim, where the Pb signals are relatively smooth, the ^{206}Pb , ^{207}Pb and ^{208}Pb isotope values are far apart, indicating strongly radiogenic compositions. In the centre, where the Pb is distributed in small inclusions, the Pb isotopes converge, indicating non-radiogenic compositions. The amount of U and Th in the rim is low and not enough to produce the radiogenic Pb measured in that rim. The pyrite is therefore zoned, with a central section having grown during or prior to the U enrichment of the deposit (although post-brecciation) and the outer rim having grown after the production of most radiogenic Pb by U decay.

The production of Th by radiogenic decay can be examined on the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. In general most of the results are compatible with derivation of Pb by *in situ* U decay, but the correction for the *in situ* decay of Th-derived Pb is not as successful, because many analyses fail to return to their original compositions after correction or being overcorrected. This indicates greater mobility of Th-derived Pb in this system compared to U-derived Pb, probably due to the Th-rich minerals being less able to lock Pb within their crystal structure compared to the U-rich minerals within the system.

In summary, the Pb isotope data from actinolite, magnetite, albite and carbonate do not support addition of Pb from an external source after U arrived with magnetite–apatite, but there is Pb-isotope support for the growth of some pyrite after significant radiogenic Pb had evolved from the U.

Table 5

Trace element concentrations (wt.%) in the monazite inclusions in apatite (sample To22a), obtained by EMPA.

Sample	Mnz-1	Mnz-4	Mnz-5	Mnz-13	Mnz-14	Mnz-16*	Mnz-17*	Mnz-19*
P ₂ O ₅	30.42	28.47	29.69	27.01	28.00	28.33	29.28	26.27
SiO ₂	0.12	0.13	0.12	0.78	0.48	0.41	0.51	0.75
ThO ₂	0.60	0.09	0.17	1.32	0.33	<0.08	0.28	1.83
UO ₂	<0.03	0.03	<0.03	0.04	<0.03	<0.03	<0.03	0.05
Y ₂ O ₃	0.46	0.14	0.34	0.25	0.36	0.45	0.25	0.33
La ₂ O ₃	13.10	15.33	14.83	19.32	18.58	18.86	18.11	17.29
Ce ₂ O ₃	30.74	37.01	35.75	33.94	35.58	36.16	36.10	33.11
Pr ₂ O ₃	3.34	3.76	3.70	2.91	2.96	3.12	3.17	3.51
Nd ₂ O ₃	10.65	10.98	11.72	7.51	8.00	9.08	8.54	10.83
Sm ₂ O ₃	0.93	0.75	1.01	0.47	0.49	0.65	0.50	0.89
EuO	<0.03	<0.03	0.07	<0.03	0.04	<0.03	0.05	0.06
Gd ₂ O ₃	0.42	0.22	0.40	0.24	0.27	0.38	0.24	0.27
Dy ₂ O ₃	0.15	<0.09	<0.09	<0.09	0.11	<0.09	<0.09	<0.09
Yb ₂ O ₃	0.05	0.04	0.05	0.05	0.03	0.03	0.02	0.02
CaO	4.71	0.95	1.72	1.37	1.33	0.73	1.97	0.89
FeO	0.06	0.25	0.06	1.24	0.11	0.29	0.05	0.06
PbO	<0.01	0.01	0.01	0.03	<0.01	0.01	0.01	0.04
SO ₃	1.21	<0.04	<0.04	0.86	0.93	0.20	0.67	0.90
Al ₂ O ₃	0.29	<0.02	0.02	0.04	0.16	<0.02	<0.02	0.45
As ₂ O ₅	0.05	<0.03	0.06	<0.03	0.09	0.11	0.15	0.17
Total	97.89	98.09	99.68	97.64	97.82	98.79	99.91	97.78

* Monazite as aggregate in brecciated matrix.

5. Discussion

5.1. Significance of apatite–monazite textures and chemistry

The Se–Chahun IOA ore bodies have the same massive to brecciated textures, high temperature calc–silicate–albite haloes, and LREE-rich geochemical signatures as those of classic Swedish IOA deposits (Hildebrand, 1986; Nyström and Henriquez, 1994; Frietsch and Perdahl, 1995; Belousova et al., 2002; Harlov et al., 2002). The other Bafq district magnetite–apatite deposits also share these features (for instance, Esfordi, Chador-Malu, Choghart; Förster and Jafarzadeh, 1994; Daliran, 2002; Jami et al., 2007; Torab and Lehmann, 2007). Some IOA deposits exhibit complex multi-generational apatite parageneses (e.g., Esfordi and Lakkeh Siah; Jami et al., 2007; Torab and Lehmann, 2007; Stosch et al., 2010), but this is not apparent in our Se–Chahun samples.

REE-leached apatite, and monazite inclusions hosted within this apatite, have been sporadically recognized by earlier literature (for instance, Parak (1973, 1975)), but only in the last decade have they received systematic attention (Harlov et al., 2002; Torab and Lehmann, 2007), and been compared to similar observations in a range of other environments (Pan et al., 1993; Yanagisawa et al., 1999; Pan and Fleet, 2002, amongst others). In the Kiirunavaara IOA deposit (Kiruna district, Sweden) Harlov et al. (2002) contend that the main apatite metasomatism and monazite formation occurred at 700–800 °C (shortly after a magmatic emplacement of the magnetite–apatite), from Cl- and/or

H₂SO₄-enriched brines expelled by the source magma. They show that both massive and brecciated magnetite–apatite ore contains leached apatite with monazite inclusions. However, within the Kiruna district, the Tjarrojakka and Nautanen IOA deposits contain massive apatite that has no evidence of dark–light BSE patterns (Edfelt, 2007). Some IOA deposits in the BMP are also now known to contain abundant dark–light BSE apatite containing monazite inclusions, but there is no systematic documentation of this relationship with respect to widespread brecciation (Torab and Lehmann, 2007; Stosch et al., 2010). Overall, a case is emerging for apatite chemical modification/redistribution to be included as a common but non-ubiquitous feature within the Kiruna-type deposit model, and this case requires testing with further systematic examination of deposit textures.

Experimental studies of the reaction of REE-rich apatite with a range of solutes at a wide range of temperatures and pressures has shown that monazite inclusions form most readily from HCl, KCl or H₂SO₄ dominated fluids that are deficient in Na and Ca (Harlov and Förster, 2003; Harlov et al., 2005). This occurs via preferential dissolution (rather than exsolution or diffusion) of light BSE apatite, and reprecipitation of well-ordered, dark BSE apatite with a micro-porous structure (due to volume differences between chlor- and fluor-apatite). It shows a tendency to align to the apatite c-axis (Yanagisawa et al., 1999; Putnis, 2002), and the edges of affected grains are typically embayed. The monazites grow from REE that are leached and then carried from the reaction front through the dark apatite via nano-channels and then larger micro-channels. Depending on fluid budgets, these monazite precipitates can block the micro-channels, trapping migrating fluids, which terminates the metasomatic process. REE + Y leaching is typically accompanied by sharp reductions in Na, Si and Cl (for instance, Harlov et al., 2005). The important coupled substitutions that achieve charge balancing involve some of these elements, and include (Roedder et al., 1987; Ronsbo, 1989; Fleet and Pan, 1995; Harlov et al., 2002):



and

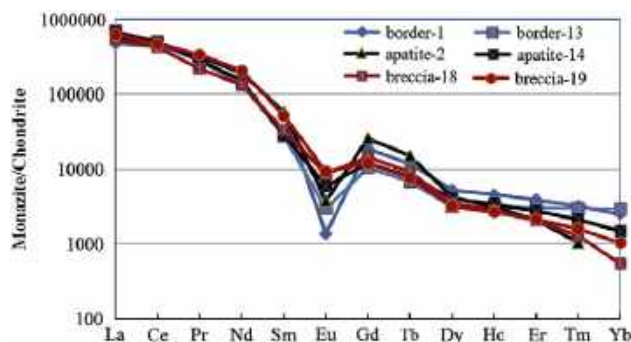


Fig. 14. Chondrite normalized REE distribution patterns of monazite inclusions in the apatite grains (black), monazite aggregate in the brecciated matrix (red) or monazite grains attached to the outside edge of apatites (blue) (To22a, Anomaly X; EMPA values). Chondrite values are taken from Anders and Grevesse (1989).

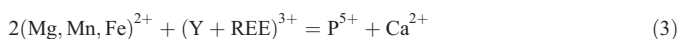
The Se–Chahun apatites are embayed (Fig. 5D), and display the typical Na, Y + REE, and Cl losses that are seen in Harlov's experiments. We also observe Mg, Fe, Mn and Sr loss in dark apatite, and Fe

Table 6

Pb isotopic compositions of apatite in To22a (spot analyses).

Analysis no.	²⁰⁷ Pb/ ²⁰⁶ Pb		²⁰⁶ Pb/ ²³⁸ U		²⁰⁸ Pb/ ²³² Th		²⁰⁷ Pb/ ²⁰⁶ Pb	
	Age	+/- 1 ster	Ratio	+/- 1 RSE	Ratio	+/- 1 RSE	Ratio	+/- 1 RSE
jl02c09	521	10	0.0885	2.0%	0.0251	6.0%	0.0976	2.7%
jl02c10	521	14	0.0909	2.7%	0.0252	6.6%	0.1181	3.8%
jl02c11	513	12	0.0899	2.3%	0.0255	6.2%	0.1215	11.7%
jl02c12	506	12	0.0832	2.4%	0.0240	6.4%	0.0718	3.5%
jl02c13	601	17	0.1033	2.7%	0.0254	6.2%	0.1048	3.2%
jl02c14	479	16	0.0849	3.2%	0.0203	6.5%	0.1315	3.9%
jl02c15	577	45	0.1307	5.8%	0.0352	8.2%	0.2953	3.4%
jl02c16	524	27	0.1019	4.5%	0.0284	7.0%	0.1959	5.5%
jl02c17	516	14	0.1018	2.4%	0.0297	6.4%	0.2057	3.0%
jl02c18	495	41	0.1173	5.8%	0.0280	8.1%	0.3215	6.3%
jl02c19	499	10	0.0868	1.9%	0.0242	6.0%	0.1166	2.8%
jl02c20	510	11	0.0854	2.2%	0.0247	6.3%	0.0870	2.9%
jl18c17			0.609		0.913		0.725	
jl18c18			0.327		0.374		0.495	

enrichment (Fig. 11), with all changes occurring across gradational reaction fronts. We interpret the 150 µm-wide gradational fronts (compared to the sharp fronts seen in experiments) to be the effect of post-depositional diffusion, and this is supported by Pb isotope gradients we observe around monazite inclusions in dark apatite, where the Pb is derived from monazite by U–Th decay (Fig. 15). Although not a key part of our study, the transition element–REE correlations provide evidence that further charge-balanced coupled substitutions may exist in bright apatite, and may contribute to enhanced REE contents:



Although Fe is leached from bright apatite during metasomatism, dark apatite is characterized by a nearly 2–3 fold increase in Fe (Fig. 11) that we attribute to growth of Fe-oxide inclusions in dark apatite (Fig. 8). Given the Fe-budget imbalance, it appears that some of this Fe must have an external (i.e., non-apatite) source. This was not modelled in the Harlov et al. experiments, but could be a natural corollary of the infiltration of a multi-solute fluid.

A major contribution of the Harlov et al. experiments was to show that, although a large range of fluid compositions can produce REE leaching and monazite inclusions in apatite, those fluids cannot have a high activity of Na or Ca, because these elements can enter the apatite structure and maintain charge balance (Harlov et al., 2005). This is a potential paradox for IOA deposits, because these have extensive sodic–calcic alteration haloes formed from sodic–fluid interaction (Hitzman et al., 1992; Broman et al., 1999; Williams et al., 2005).

Recognizing the paradox, Harlov et al. (2002) therefore suggested that the Kiirunavaara fluids evolved to be HCl- and/or H₂SO₄-enriched, whereas Torab and Lehmann (2007) suggested that apatite metasomatism + monazite inclusions occurred due to a switch to a KCl-dominant brine composition in hydrothermal upflow zones, a fact that is consistent with widespread K-feldspar and sericite alteration. Both explanations are consistent with the experimental evidence, and the precise nature of the reacting fluids awaits further fluid inclusion solute analysis. Our own evidence is consistent with the KCl infiltration hypothesis, because our paragenesis (Fig. 4) is similar to that of most other BMP IOA deposits. We are also able to infer that this fluid interaction occurred immediately prior to brecciation, and that it was associated with unmixing of CO₂-rich and aqueous brines, based on our fluid inclusion petrography. By comparison to other IOA deposits above, we can infer that the arrival of these fluids into IOA systems does not always increase over-pressures to the point of rupture, but can still produce significant chemical modification of apatite if the fluids are Na-poor, and apatite is REE-rich. An area of future investigation is whether or not the over-pressures enhance the apatite metasomatic process. Harlov et al. (2002) note that despite being well studied, no monazite-rich apatite is documented in the Chilean IOA systems, and attributes this to a generally Na-rich character of the late fluids. Whether this is the case in brecciated Chilean examples that exhibit unmixed fluid inclusion populations (Rodados Negros; Broman et al., 1999) remains to be seen.

The Se–Chahun site permits some inferences about the nature and behavior of fluids following apatite metasomatism. Decompression associated with brecciation arrested apatite metasomatism, but new monazite and huttonite was precipitated in the breccia matrix. A

Table 7

Pb, Th and U concentrations in different minerals and bright apatite used for dating (values in ppm).

Sample	Mineral	Pb	Th	U	Sample	Mineral	Pb	Th	U
TO22a	apatite	1.4	28	4.7	TO22a	actinolite	2.4	10.1	0.5
TO22a	apatite	1.6	32	5.1	TO22a	actinolite	7.1	9.7	0.5
TO22a	apatite	1.7	37	5.1	TO22a	actinolite	11.5	274.1	3.2
TO22a	apatite	1.3	28	4.9	19–350*	pyrite	9.0	0.1	0.0
TO22a	apatite	1.9	38	4.7	19–350	pyrite	11.7	0.5	0.2
TO22a	apatite	0.3	9	1.0	19–350	pyrite	23.9	0.2	0.0
TO22a	apatite	0.7	9	0.9	19–350	magnetite	4.2	0.8	0.8
TO22a	apatite	1.2	28	2.6	19–350	magnetite	2.2	5.0	1.6
TO22a	apatite	2.1	35	5.6	19–350	carbonate	0.3	0.2	0.1
TO22a	apatite	0.6	15	1.8	19–350	carbonate	0.7	0.9	0.2
TO22a	apatite	2.0	43	5.7	36–50*	pyrite	53.4	0.3	0.1
TO22a	apatite	2.0	41	5.7	36–50	pyrite	44.0	4.3	0.3
TO22a	magnetite	0.6	1.8	0.5	36–50	magnetite	14.5	11.2	4.5
TO22a	magnetite	1.3	1.1	0.4	36–50	magnetite/silicate	2.0	6.8	1.1
TO22a	magnetite	5.1	1.0	0.3	36–50	albite	1.7	4.4	0.7
TO22a	magnetite	2.5	11.1	2.1					

*Sample coordinates: 19–350 (31° 54', 3" N; 55°, 42', 52" E), 36–50 (31° 54', 13" N; 55°, 43', 4" E).

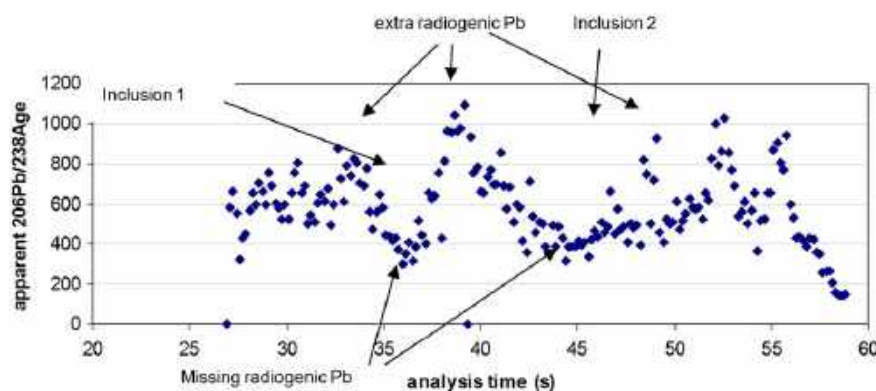


Fig. 15. A time resolved diagram showing how the apparent age (Ma) varied as the laser drilled through the apatite and inclusions in dark apatite (To22a, Anomaly X).

feasible source for the REE in these phases, which would account for the close chemical similarities between the apatite and non-apatite inclusions (Fig. 14), was intra-apatite fluid that drained into the breccia on pressure release. To account for a lack of REE depletion on new apatite fragment boundaries in the breccia, but copious infill by actinolite, K-feldspar, chlorite and hematite, we infer that post-breccia fluids were aqueous and sufficiently Na–Ca-rich to stabilize the apatite structure, preventing further REE depletion. The lack of depletion is less likely to relate to inadequate reaction times, because experiments have demonstrated that the metasomatism proceeds in days to weeks (Harlov and Förster, 2003; Harlov et al., 2005).

5.2. Relationship between magnetite and apatite metasomatism

At Se–Chahun, evidence (Fig. 6) is presented that Ti and Al was leached from magnetite prior to brecciation, and that Ti and Al-rich minerals were deposited in the breccia matrix, and in veins adjacent to breccia. Within the breccia, small magnetite clasts display more variable Ti contents than large fragments, but otherwise there is no evidence that post-breccia fluids leached Ti or Al from magnetite clasts. These observations are consistent with leaching of magnetite by the same fluids that infiltrated the apatite; although the refractory character of the magnetite resulted in only rim leaching. Leaching of Ti and Al from the rims of magnetite grains, and the formation of the Ti-rich minerals such as titanite, rutile and aluminosilicate minerals between magnetite grains, can occur via the activity of acidic K-rich fluids (Gieré, 1989).

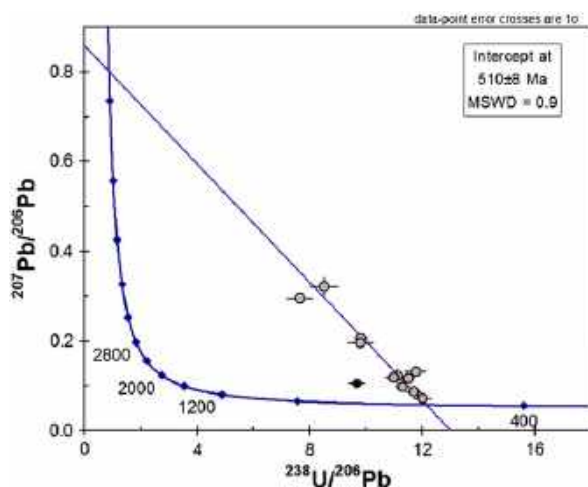


Fig. 16. Reverse concordia diagram for light apatite from sample To22a, Anomaly X. Analyses in grey represent the parts of the apatite that were furthest from a high Th and U inclusion. The analysis in black is from brecciated apatite and was not used for the age calculations.

CO₂-rich fluid is also linked to Ti mobility at high temperatures (Hynes, 1980; Murphy and Hynes, 1986). As both of these fluids are thought to have co-existed prior to brecciation at Se–Chahun, either or both may have produced Ti mobility. Following the brecciation, Ti and Al became unstable in solution, and were reprecipitated across redox and Ca-activity gradients in breccia interstices and adjacent veins, synchronous with significant calc–silicate deposition. This timing could be tested by radiometric dating of the titanite phases (e.g., Romer et al., 1994).

5.3. Age relationships

Although the ages presented here seem to define a reasonable weighted mean age of 510 ± 8 Ma, it is possible that the apatite could have formed slightly earlier depending on whether the apatites retained all Pb, or whether they lost part of it during later thermal events. The fact that bright apatite displays a mixing isochron towards common Pb, suggests that the apatites are likely to have formed early in the history of the deposit, at the same time as the enrichment of the rocks in U. If they had formed later, the decay of U to Pb would have contaminated the apatites with mixtures of common and radiogenic Pb.

The Th–U–Pb monazite dating of the Choghart deposit by EMPA techniques (Torab and Lehmann, 2007) resulted in an average age of $515\text{--}529 \pm 21$ Ma. This work dated monazite cores within larger low U–Th monazite overgrowths, all within brecciated silicate matrix, and the authors note that the low-Th apatite-hosted monazite inclusions were not dateable. Most recently, $^{206}\text{Pb}/^{238}\text{U}$ ages of monazite-free apatite from Bafq district IOA deposits (Lakkeh Siah, Esfordi, Mishdovan and Zarigan) centre between 539 and 527 Ma (Stosch et al., 2010; no errors reported). Our ages for the Se–Chahun apatite (510 ± 8 Ma) are younger but within error of the Choghart high Th monazites. One immediate issue with the high Th–U monazite cores at Choghart is whether they formed hydrothermally, or whether they predate hydrothermal activity, based on their high Th contents, which are atypical of hydrothermal monazite (Schandl and Gorton, 2004). The U–Pb ages of the Zarigan sodic granite (529 ± 16 Ma and 525 ± 7 Ma, Ramezani and Tucker, 2003) have close similarity to these older monazite ages, and overlap with the apatite ages. In addition, host Saghand Formation rhyodacite and dacite porphyry have ages of 528.2 ± 0.8 and 527 ± 1 Ma ages (Ramezani and Tucker, 2003). Thus the formation of magnetite–apatite deposits of the BMP likely occurred after the main intrusion of the Zarigan (and Narigan) granite(s) and the eruption of volcanic rocks of the Saghand Formation, but based on our data could have extended beyond the main magmatic episode, a timing seen in several other IOCG districts (Williams et al., 2005).

We have shown (Section 5.1) that the physical relationships at Se–Chahun require that monazite inclusions in the apatite formed soon after the apatites, and prior to brecciation. This is required because the reaction boundaries in the apatites, to which the

monazite inclusions relate, are themselves truncated by brecciation, and then the breccia was infilled by high temperature calc-silicates and iron oxides (actinolite, titanite, hematite), and then by phyllic alteration minerals. Our Pb isotopic analysis of albite, magnetite and actinolite support this contention, because they require that these minerals grew either during or prior to the enrichment of U at Se–Chahun; that is, the actinolitic matrix to the breccia is not likely to be a young feature. [Stosch et al. \(2010\)](#) find that apatite-hosted monazite inclusions formed at 440 Ma at Choghart, and 130–140 Ma at Gasestan (SE of Se–Chahun), by hydrous fluid overprint. Although we do not have radiogenic ages for our monazite inclusions, our observations of Pb diffusion from them into the surrounding dark apatite ([Fig. 15](#)) mean that would likely yield erroneously young ages; our observations suggest that even high Th monazite cores (e.g., [Torab and Lehmann, 2007](#)) should be reassessed for Pb loss into the surrounding apatite, as one means of assessing the validity of their ages. The physical relationships require that Se–Chahun monazite did not form during the younger events identified by [Stosch et al. \(2010\)](#) in Central Iran, but instead formed as a part of the high temperature evolution of an IOA system.

6. Conclusion

Extensive Na-rich fluid circulation produced large-scale sodic alteration (albitization) in a mixed volcano-sedimentary sequence intruded by sodic granitoids (525 ± 7 Ma). This regional alteration was followed by deposit-related Na–Ca alteration and magnetite–apatite mineralization at 510 ± 8 Ma at Se–Chahun. Main-stage apatite formation was succeeded by a change in fluid chemistry to co-existing CO_2 and K–Cl-rich fluids (the latter requires analytical confirmation), which was followed by brecciation, that is attributed to the accumulation of fluids within and below a magnetite–apatite ‘seal’. The process of leaching of apatite of REE + Y (+ Na, Mg, Mn, Fe) and associated deposition of monazite inclusions in this apatite, operated immediately prior to brecciation, providing circumstantial evidence that over-pressuring may enhance this special mass transfer mechanism (nano-channels; [Harlov et al., 2005](#)). We infer that at the same time, Ti and Al were leached from magnetite crystal rims, providing evidence that the same fluid had different effects on different minerals. No further apatite metasomatism, and only minor leaching of Ti from magnetite, occurred following brecciation, suggesting that complex Na- or Ca-dominated brines began to circulate (which suppress REE leaching in apatite; [Harlov et al., 2005](#)), depositing a Ca–K–Mg–Ti– H_2O -based mineral assemblage. The Se–Chahun evidence supports the case for REE metasomatism of apatite to be recognized as a significant and typical (but not ubiquitous) event in the evolution of IOA deposits, during a transition from NaCl to (proposed) KCl– CO_2 brine dominance that can be associated with brecciation.

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