Hydrothermal Overprint of the Chador-MaluKiruna-type Deposit (Bafq District, Central Iran) and Associated REE Mobilization: Evidence from Mineralogy and Geochemistry

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Abstract. This paper presents a discussion of possible mobilization of the apatite-hosted REE during hydrothermal overprint of the Chador-Malu Kiruna-type iron oxide-apatite deposit and their subsequent uptake by the adjacent actinolite-rich host rocks based on mineralogical and geochemical evidence. The formation of apatite-hosted monazite inclusions during apatite REE leaching is proposed to be a mineralogical control on REE mobility which would provide the HREE with a preferential opportunity for mobilization. Using a scanning electron microscope, it is shown that the apatite-hosted monazites are most abundant in the samples from the eastern periphery of the northern ore body having contact with a suite of actinolite-rich metasomatic rocks (metasomatites). The bulk REE patterns of the metasomatites closely associated with the monazite inclusion-rich ores shows elevated HREE patterns which would suggest the uptake of the mobilized HREE by these actinolite-rich host rocks. No significant LREE mobility could be interpreted from the REE patterns. The chloride-rich overprinting fluid compositions proposed by experimental studies and suggested for similar deposits at both the Kiruna and Bafq districts are consistent with the restricted REE mobility that could be interpreted from the bulk REE geochemistry of the host rock samples, and thus might be the case in the Chador-Malu iron oxide-apatite system.

Keywords: Bafq, iron oxide-apatite, REE geochemistry, REE mineralogy.

Introduction

The REE comprise a coherent group of elements in which the different elements show similar chemical behavior. However, there are differences in their geochemical behavior which arise predominantly from the absence of electrons in the outer shells (5d) of the REE, the regular filling of their inner levels (4f), and the consequent gradual and systematic variation in their ionic radii with atomic number, for any given oxidation state, geochemically for the 3+ state, with Eu existing also in the 2+ and Ce in the 4+ states (see e.g., Henderson, 1996 for the ionic radii).

Rare earth elements form high field strength (HFS) cations (ionic potential > 2.0) with their field strength (which is thought of as the electrostatic charge per unit surface area of the cation) increasing from La to Lu. As a generalization, the HFS elements are immobile (Rollinson, 1993). However, many exceptions are documented (see e.g., Humphris, 1984). The REE are mobile in certain geochemical systems involving aqueous media, as evidenced by analytical data for many natural waters including fluid inclusions, and also by enhanced concentrations of REE in metasomatized rocks; however, the mobility is limited and has led to-some usage of the REE as immobile for modeling particular processes such as rock alteration (see Henderson, 1996). Strict immobility, even over small distances, has been documented for dry metamorphic systems (e.g., Muecke et al., 1979; Merriman et al., 1986). However, Humphris (1984) concluded that there is no simple relationship between the degree of mobility of the REE and rock type or metamorphic grade, and emphasized the mineralogical (1) and fluid (2) controls, which may be illustrated with reference to the example of the REE being more susceptible to be released from a glassy basalt during alteration than from a crystalline rock of the same composition mineralogical control), and the REE being subject to mobilization by halogen-rich fluids in a rock in which they would otherwise be immobile through the movement of an aqueous fluid (fluid control) (see Rollinson, 1993).

The complexing behavior of REE at high temperatures and pressures have widely been studied and reviewed e.g., Brookins, 1989; Humphris, 1984; Wood, 1990, Millero, 1992; Henderson, 1996). The halides comprise some of the more important complexing groups in hydrothermal systems, as evidenced not only by direct observations (see e.g., Brookins, 1989), but also by the presence of REE-rich
fluoride-bearing minerals in some hydrothermal deposits (e.g., Ebya, 2012). The REE form strong complexes with the fluoride ion and comparatively weak complexes with the chloride ion (Henderson, 1996); however, Ragnarssottir (in Henderson 1996) has shown that for saline granitic fluids at 500°C, the dominant species are LnCl\(^{2+}\) and LnF\(^{2+}\), the latter being more important for the HREE.

The Kiruna-type deposits, also recently referred to as “IOA” (iron oxide-apatite; Williams, 2010), or P-rich iron oxide deposits (Groves et al., 2010), are one of the most important non-sedimentary types of economic iron oxide-rich deposits in the world. They are characterized by magnetite-hematite-apatite mineralogy and their associated halos of high temperature sodic-calcic alteration minerals (see e.g., Frietsch and Perdahl, 1995; Williams et al., 2005, among others). The formation of this group of deposits, however, has been subject to substantial controversy e.g., Frietsch and Perdahl, (1995) and various genetic models have been proposed. Researchers put forward two different genetic models involving magmatic (e.g., Frietsch, 1978, 1984; Nyström and Henriquez, 1994; Naslund et al., 2002; Jonsson et al., 2013) and hydrothermal processes (e.g., Hitzman, 2000; Barton and Johnson, 2000; Daliran, 2002, Daliran et al., 2007; Smith et al., 2013). However, whether considering a magmatic or a hydrothermal genetic model for iron oxide-apatite deposits, it is now revealed that apatite can be subject to significant post-depositional REE leaching (Roedder et al., 1987; Harlov et al., 2002). A case has emerged for post-mineralization (even as late as tens to hundreds of million years; Stosch et al., 2011) monazite nucleation in apatite, and simultaneous apatite REE depletion during hydrothermal overprint, which is proposed to be included as a typical but non-ubiquitous feature within the kiruna-type iron oxide–apatite deposit model (Bonyadi et al., 2011). This phenomenon (presence of monazite-richapatites) has been observed in certain Baqf district iron oxide-apatite deposits (Jamí, 2005; Torab and Lehmann, 2007; Stosch et al., 2011; Bonyadi et al., 2011; Sabet-Mobarhan-Talab et al., 2015) as well as in the Swedish deposits (Parak, 1975,Harlov et al., 2002), but not in the Chilenian iron oxide-apatite systems (Harlov et al., 2002).

Apatite REE leaching and monazite formation in the classic Kiirunavaara deposit (Sweden) was ongoing through the infiltration of Cl- and/or H\(_2\)SO\(_4\)-enriched brines at 700–800°C, which were originated from the source magma subsequent to the magmatic emplacement of the Fe-P melt (Harlov et al., 2002). Likewise, the infiltration of a KCl- or KCl-CO\(_2\)-dominant brine has been proposed for the apatite REE leaching and monazite nucleation in the Baqf district deposits (Torab and Lehmann, 2007; Bonyadi et al., 2011). Experiment has also shown that monazite nucleation occurs most readily through the interaction of HCl-, KCl-, or H\(_2\)SO\(_4\)-dominated fluids with REE-rich apatite (300-900°C and 0.5-1 Gpa; Harlov and Förster, 2003; Harlov et al., 2005). However, it was demonstrated that Na- or Ca-dominated brines stand aside from the large range of - fluid compositions that can produce REE leaching and monazite inclusions in apatite, as Na and Ca can enter the apatite structure, maintain charge balance, and suppress the REE leaching process (Harlov et al., 2005).

Sabet-Mobarhan-Talab et al. (2015) studied the geology and geochemistry of the Chador-Malu deposit, and pointed out the effects of hydrothermal overprint, including the formation of apatite-hosted monazite inclusions, in the iron oxide-apatite body (see also Sabet-Mobarhan-Talab and Aliinia, 2014). This monazite formation could be assumed as a mineralogical control on possible mobilization of the apatite-hosted REE during overprinting events. Additionally, the main host rock to the iron oxide-apatite deposit is an amphibole-rich metasomatite (see below), which, considering the compatibility of REE in the amphibole structure (e.g., Rollinson, 1993), would uptake the mobile REE in the case of any mobilization. Accordingly, an attempt in the present study has been made to investigate apatite-hosted monazite formation in the Chador-Malu iron oxide-apatite body, and to examine the REE patterns of the adjacent amphibole-rich rocks in order to establish any possible relationship between them and to pinpoint potential REE mobilization. The methodology is designed based on the assumption that the REE patterns of the low-REE content host rocks (e.g., Sabet-Mobarhan-Talab, 2014; Sabet-Mobarhan-Talab et al., 2015) would be highly susceptible to increase in bulk-rock REE concentrations in the case of REE uptake.

**Geological Setting**

The Chador-Malu iron oxide-apatite deposit is located in the Baqf district, which is part of the Central Iranian micro plate in the Alpine-Himalayan orogenic system. A series of intersecting regional-scale faults divide the Central Iranian Terrane into three major crustal domains, namely the Lut, Tabas, and Yazd Blocks, among which lies a more that 1000-km-long, and up to 80-km-wide, arcuate and structurally complex belt, called the Kashmir-Kerman volcano-plutonic arc (Ramezani and Tucker, 2003), which hosts the Baqf district and the Early Cambrian volcanic and plutonic rocks of Central Iran (Fig. 1).

A model proposed for the Early Cambrian tectonics and magmatism in the Baqf district is crustal extension associated with intracontinental rifting. It has been proposed that this rifting event formed an aborted rift associated with alkaline magmatism, including alkaline volcanic rocks, alkaline granites, and carbonatites (e.g., Samani, 1988, 1998; Daliran, 1990, 1999, 2002; Förster and Jafarzadeh, 1994). However, attributing the regional-scale arcuate faults of the Baqf district (Fig. 1) to a back-arc extensional setting, Ramezani and Tucker (2003) suggested that the Kashmir-Kerman volcano-plutonic arc represents an active continental-margin environment in relation to subduction under the Central Iranian microplate and closure of a Proto-Tethys ocean in the Early Cambrian.
Fig. 1 Structural map of eastern Central Iran (modified after Ramezani and Tucker, 2003; Torab, 2008). The arcuate Kashmar-Kerman volcano-plutonic arc encompasses the Bafq district which covers the area between Bafq and Saghand and hosts the most important iron oxide-apatite deposits.

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The Early Cambrian sequence in Central Iran consists of a complex set of volcano-sedimentary rocks which extends from Poshte-Badam to Zarand and hosts the most important iron oxide-apatite, Pb-Zn, and U ore deposits in Iran (Samani, 1988) (Fig. 1). The volcanic rocks vary from felsic to mafic in composition and include rhyolite, agglomeratic tuff, splitic lava, and diabase, but dominantly rhyolitic rocks, most of which having been subject to widespread alkaline metasomatism (K-feldsparization and albitization; e.g., Daliran et al., 2007). The sedimentary rocks consist of dolomites, dolomitic limestones, and evaporites (Torab, 2008). Ramezani and Tucker (2003) assigned an Early Cambrian age (529-554 Ma) for the volcanic suites of this volcano-sedimentary unit and named this sequential unit as the Cambrian Volcano Sedimentary Unit (CVSU).

Intruded into the CVSU, as well as into the Upper Precambrian metamorphic rocks, are plutonic bodies of mostly granitic composition (locally associated with diorite and gabbro-diorite dikes or sills), which are quite common in Central Iran, of which the Zarigan, Narigan, and the Chador-Malu granites are located in the Bafq district (Fig. 2). Based mainly on their high sodium contents, Berberian and Berberian (1981) described these granitic intrusions as alkali granite. The same was considered by later researchers (e.g., Samani, 1988; Förster and Jafarzadeh, 1994; Daliran, 2002; Ghorbani, 2013); however, Torab (2008) contends that these rocks are calc-alkaline intrusions affected by widespread sodic alteration (albitization), and suggests an evaporitic source for Na. Ramezani and Tucker (2003) defined an age of 525±7 Ma and 529±16 Ma (U-Pb on zircon) for the Zarigan and the Chador-Malu granites respectively. Stosch et al. (2011) determined the U-Pb apatite age for major iron oxide-apatite deposits in the Bafq district (527-539 Ma). These ages fell entirely within the age range of the felsic plutonic rocks of the Bafq district (including those mentioned above) dated by Ramezani and Tucker (2003) (525-547 Ma; U-Pb on zircon).
The northern ore body of the Chador-Malu deposit (this study; Fig. 3) has the shape of an upright cylinder with several horizontal extensions and is more than 600 m deep. The southern ore body is a flat-lying lens, interpreted as magnetite lava flow or sill. These two ore bodies accompanied by two other magnetic anomalies in the Chador-Malu area are arranged in north-northeast-south-southwest direction along the eastern segment of the ring fracture zone shown in (Fig. 2) (Fürster and Jafarzadeh, 1994).

According to field observations, the main host rock of the northern ore body is a highly altered actinolite-rich CVSU rhyolite, documented under the name “metasomatite” (Moghtaderi et al., 2007), and locally known as “Green Rock” (Jami, 2005; Torab, 2008). Comprising the main host rock of major iron oxide-apatite deposits in the Bafq district (see e.g., Jami, 2005; Torab, 2008; Bonyadi et al., 2011; Sabet-Mobarhan-Talab et al., 2015), this metasomatic rock is widespread in the region and is thought to be the consequence of a multistage regional metasomatism (Daliran et al., 2007) in relation to the intrusion of the Cambrian plutonic rocks.

**Host rock alterations**

The actinolite-rich metasomatites comprise the main host rock to the northern ore body of the Chador-Malu deposit (Fig. 3). The main host rock alteration is actinolitization (Fig. 4a&b). Which gives the host rocks a distinctive green appearance; however, sodic (albitization) and potassic (K-feldspar and sericitization) alterations can also be observed and are related to the earlier stages of regional metasomatism in the Bafq district (see also Daliran et al., 2007; Fig. 4c&d). Quartz represents the late stage of hydrothermal alteration in the host rock (see also Daliran et al., 2007; Fig. 4e). The host rocks have locally undergone Fe-
Metasomatism (Sabet – Mobarhan - Talab et al., 2015) which occurred subsequent to their multistage alteration, resulting in the growth of magnetite grains on the alteration quartz (late stage) and other alteration minerals (Fig. 4).

Fig. 4 Photomicrographs of the metasomatic host rocks in thin section (Sabet-Mobarhan-Talab et al., 2015). (a & b) Actinolitization in the host metasomatite. Note the magnetite grains in b. c) K-feldspar and albite in the host metasomatite representing the potassic and sodic alterations respectively. Quartz represents the late stage of alteration. Note the magnetite growth on actinolite and quartz, and the actinolite crystal on albite, which demonstrate the order of crystallization. d) Sericitization in the host metasomatite. Note the magnetite grains on sericitized K-feldspar. e) Quartz growth on actinolite crystal occurred during the late stage of alteration (Act: actinolite; Qtz: quartz; Mt: magnetite; K-feld: potassium feldspar; Alb: albite).

Samples, analytical methods, and chemical compositions

Six host rock samples were analyzed for major and trace element concentrations by ICP-MS (Perkin Elmer Nexion 300Q) and ICP-OES (Perkin Elmer Optima 7300DV) at Lab West Minerals Analysis, Malaga, Western Australia. A portion of the pulverized sample was accurately weighed into a PTFE tube, and a mixture of acids, including hydrofluoric acid, was added. The tube was then placed into a pressure vessel and sealed. The samples underwent digestion at high temperature and pressure (up to 200°C and 20 Bar). After digestion, the samples were diluted to a predetermined volume, ready for analysis. The resulting data were collated and assessed for performance of internal quality control results (blanks, duplicates and certified reference materials) following Lab West’s MMA-04 multielement analysis technique. The results are presented in (Table 1).

Over forty silver-coated polished sections were prepared from apatite-bearing ores, and were studied under BSE imaging using a Philips XL-30 scanning electron microscope at Amirkabir University of Technology.
Apatite-hosted monazite inclusions were frequently observed in the samples collected from the peripheral zone of the northern ore body at different locations, but were most ubiquitous at the eastern periphery having contact with the metasomatites (Fig. 3). Two different locations were selected at these contacts, and two host rock samples of 1 meter spacing were collected adjacent to the contacts at either location (hereinafter called the Contact Host Rock samples, abbreviated CHR). The CHR sample with the lowest REE content has the highest Na and K concentrations (Table 1). Demonstrating the relatively high abundance of feldspar minerals as a consequence of sodic and potassic alterations, which rarely dominate the mineral composition of the metasomatic host rocks, giving them a felsic appearance. However, actinolite-rich metasomatites (Green Rocks), which are the dominant host rock type of the Chador-Malu deposit (see above), demonstrate the prevailing nature of calcic alteration at the Chador-Malu area (see also Moghtaderi et al., 2007) in comparison with the sodic and potassic types, and comprise the three CHR samples with higher REE contents than the feldspar-rich sample described (Table 1). Additionally, two host rock sample of the dominant actinolite-rich mineralogy were collected from two different locations with a distance from the contact and the CHR samples (hereinafter called the Off-Contact Host Rock samples, abbreviated OCHR). The sample locations are presented in (Table 1) based on the local coordinate system used in the Chador-Malu mine (see Fig. 3). The variation in the intensity of the dominant alteration types is illustrated in (Fig. 5).

Table 1. REE, P, Na, K and Ca, composition of the host rocks (all concentrations in ppm unless indicated otherwise).

<table>
<thead>
<tr>
<th>Sample</th>
<th>DL (ppm)</th>
<th>CHR1a</th>
<th>CHR1b</th>
<th>CHR2a</th>
<th>CHR2b</th>
<th>OCHR1</th>
<th>OCHR2</th>
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<td>Act-rich</td>
<td>Act-rich</td>
<td>Felds-rich</td>
<td>Act-rich</td>
<td>Act-rich</td>
<td></td>
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<td>10509.3</td>
<td>10503.5</td>
<td>10503.5</td>
<td>10511.2</td>
<td>10516.1</td>
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<td>10040.7</td>
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<td>10031.9</td>
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<td>0.28</td>
<td>1.82</td>
<td>1.20</td>
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<td>K (%)</td>
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<td>0.32</td>
<td>1.70</td>
<td>0.72</td>
<td>2.90</td>
<td>2.50</td>
<td>1.10</td>
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<tr>
<td>Ca (%)</td>
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<td>4.15</td>
<td>4.30</td>
<td>1.70</td>
<td>4.90</td>
<td>4.60</td>
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<tr>
<td>P</td>
<td>5</td>
<td>470</td>
<td>320</td>
<td>240</td>
<td>350</td>
<td>430</td>
<td>640</td>
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<tr>
<td>La</td>
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<td>155</td>
<td>105</td>
<td>67.3</td>
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<tr>
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<td>191</td>
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<td>123</td>
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<tr>
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<td>121</td>
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<td>430.4</td>
<td>120.08</td>
<td>263.9</td>
<td>438.4</td>
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CHR1a and CHR1b are collected with approx. 1 meter spacing at the same sampling location.

CHR2a and CHR2b are collected with approx. 1 meter spacing at the same sampling location.

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<tr>
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<th>CHR1b</th>
<th>CHR2a</th>
<th>CHR2b</th>
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<td>7.35</td>
<td>3.43</td>
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<td>0.284</td>
<td>0.295</td>
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**Fig. 5** Variation diagram showing the intensity of the dominant types of alteration in the host rock samples (Table 1) REE, P, Na, K, and Ca composition of the host rocks (all concentrations in ppm unless indicated).

**Results**

**REE mineralogy and apatite-monazite relations**

Apatite-hosted monazites were most frequently observed in samples from the eastern periphery having contact with the metasomatites (Fig. 3). But were rare toward the interior of the cylindrical ore body of the Chador-Malu iron oxide-apatite deposit. Select BSE images of monazite inclusions in the Chador-Maluapatites are shown in (Fig. 6, 7).

The circled magnetite-hosted bright mineral in (Fig. 6a) is native gold which was only observed once (Fig. 8). Apatite-hosted non-phosphorous LREE-rich mineral inclusions (e.g., fluorocarbonates), which have been observed in the Bafq district deposits (e.g., Jami 2005), were also very rare (Fig. 9). The relative density of La and Ce elemental maps in (Figure 9c, d). Which indicates the higher concentration of Ce than La, may match certain members of the bastnäsite-group minerals (Fleischer, 1978).

The heterogeneous pattern observed in the apatites under high-contrast backscattered electron (BSE) imaging (Fig. 6b, c) is called BSE-dark and BSE-bright phases (see e.g., Torab and Lehmann, 2007; Bonyadi et al., 2011). These apatite phases are contrasting due mainly to the different concentrations of REE and some trace elements. Since the REE has high atomic weights, they produce more backscattered electrons (e.g., Torab, 2008), so that adjacent REE-rich and REE-depleted zones in apatite display bright and dark domains respectively, as it is observed in the present case. Monazite inclusions are commonly associated with the BSE-dark phase (e.g., Bonyadi et al., 2011) (Fig. 6b& c).
Fig. 6 Backscattered Electron (BSE) images of the Chador-Maluapatites. a) Monazite-rich apatite. The abundant bright spots are monazite inclusions. The one circled bright mineral associated with magnetite is native gold (see Fig. 8). b & c) Apatite-hosted monazite inclusions associated with the BSE-dark phase. d) An example of inclusion-free apatite mostly associated with the interior of the cylindrical ore body.

Fig. 7 Backscattered Electron (BSE) image and elemental maps of an apatite-hosted monazite inclusion. a) A euhedral monazite inclusion. b-d) Elemental maps of P, La, and Ce for “a”.

Fig. 8 Backscattered Electron (BSE) image (a) and elemental map of Au (b) for the native gold circled in (Fig. 6a).

Fig. 9 Backscattered Electron (BSE) image and elemental maps of an apatite-hosted non-phosphorous LREE-rich mineral inclusion. a) The mineral inclusion hosted in apatite and its magnified image at top right. b-d) Elemental maps of P, La, and Ce for the magnified image in “a”.

Such monazite inclusions as they are observed in the case of Chador-Malu (Fig. 6a-c, Fig. 7) may nucleate through REE redistribution in apatite during fluid-mineral interaction (e.g., Harlov and Förster, 2003; Harlov et al., 2005). This involves the preferential dissolution of BSE-light-apatite, and the reprecipitation of micro porous BSE-dark apatite, during which monazites grow from the REE that were leached and carried from the reaction front through the BSE-dark apatite via nano- and micro-channels (Bonyadi et al., 2011). Monazite nucleation in apatite involves the following general reaction (Harlov et al., 2002):
BSE-bright apatite + Ca^{2+} and P^{5+} (fluid) = (1)
SE-dark apatite + monazite + Si^{4+} and Na^{+} (fluid)
And may also be expressed by the following charge-compensated coupled substitutions (e.g., Fleet and Pan, 1995; Harlov et al., 2002):

Na^{+} + (Y + REE)^{3+} = 2Ca^{2+} (2)
And
Si^{4+} + (Y + REE)^{3+} = P^{5+} + Ca^{2+} (3)

**Bulk-Rock REE Pattern**

Fig. 10 shows the chondrite-normalized REE patterns of the host rock samples. All CHR samples show flat HREE patterns (Gd/Lu)_N = 1.02-1.91), particularly between Ho and Lu, and have similar REE contents except for the feldspar-rich sample (CHR2b) with relatively low REE concentrations. Additionally, the three CHR samples with similar higher REE contents also have similar negative Eu anomalies (Eu/Eu' = 0.32-0.46), whereas the one with lower REE content displays a relatively small negative Eu anomaly (Eu/Eu' = 0.61) (Fig. 10). However, the two OCHR samples how chondrite-normalized REE patterns with negative slope and relatively high LREE/HREE fractionation ((La/Lu)_N = 12.33 & 17.17), but negative Eu anomaly similar to the amphibole-rich CHRs, yet slightly greater in extent (Eu/Eu' = 0.28 & 0.29) (Fig. 10). Finally, the LREE patterns of all host rocks except the feldspar-rich sample are remarkably similar, but with varying LREE contents (Table 1).

![Fig. 10 Bulk-rock REE patterns of the host rock samples. Chondrite values from Anders and Grevesse (1989).](image-url)

**Discussion**

The chondrite-normalized REE patterns of the CHR samples have flat HREE portions and thus suggest HREE mobility (the translocation of the HREE into the host rocks) at least in the eastern peripheral zone of the northern ore body of the Chador-Malu iron oxide-apatite system, whereapatite-hosted monazite inclusions were most ubiquitous (see above). This supports the assumption that the monazite formation in the Chador-Maluapatites would be a mineralogical control on possible REE mobility. Used as control group, the two OCHR samples were collected a short distance away from the contact locations (see Table 1 for the coordinates), since a restricted if any mobility of the REE was expected (based on the restricted mobility of the REE reported from similar cases; e.g., Bonyadi et al., 2011). The OCHR samples show similar REE patterns with higher LREE/HREE fractionation ((La/Lu)_N = 12.33 & 17.17) than the CHR samples, supporting the assumption of restricted REE mobility in the Chador-Malu iron oxide-apatite system, which might be due to the relatively weak complexes that the REE would form with the chloride ion (compared to the fluoride ion; Henderson, 1996) and/or a limited amount of the REE that would be...
released from the mineral phase (see below). This interpretation of the REE patterns is also consistent with a mobility of mm’s to cm’s for the REE in CO₂-K-Cl-rich over printing fluids in the Se-Chahuniron oxide-apatite deposit proposed by (Bonyadi et al. 2011).

Mineralogical changes during fluid-rock interaction are considered to have a significant control over the degree of REE mobility (e.g., Humphris 1984; Rollinson, 1993). During apatite REE leaching and redistribution, the LREE would be mostly partitioned into the nucleating monazite considering their compatibility in its structure (Clark 1984), and therefore would not be released from the mineral phase significantly. However, the heavier REE would be more sufficiently released from the apatite structure and supplied into the fluids phase, and thus might be provided with a preferential opportunity to be mobilized either through complexing (since they are more susceptible to complexing than the LREE; Humphris, 1984), or as free ions. The latter holds true in acid pH conditions, a case proposed for the Kiruna-type deposits (H₂SO₄-dominant over printing fluids; Harlov et al., 2002), and the former is more likely otherwise (Henderson, 1996). Thus it could be proposed that monazite formation during apatite REE leaching as it is demonstrated in the present case might be a mineralogical control (Humphris, 1984) on REE mobilization.

The range of proposed fluid chemistry for such apatite-hosted monazite formation (see Harlov et al., 2002; Harlov and Förster, 2003; Harlov et al., 2005), particularly those proposed for the Bafq district iron oxide-apatite deposits (KCl-dominant brines; Torab and Lehman, 2007; Bonyadi et al., 2011), is consistent with the chondrite-normalized REE patterns of the host rock samples from Chador-Malu (Fig. 10). Which could be interpreted as an indication of restricted REE mobility. Although no micro analytical data is presented for the chemistry of overprinting fluids at Chador-Malu, the assumption that the fluid chemistry proposed for the geologically- and geochemically-similar Bafq district deposits (Torab and Lehman, 2007; Bonyadi et al., 2011) might also be the case in the Chador-Malu systems supported by the restricted REE mobility suggested above, which might possibly be due to the weak complexing of the REE with the chloride ion. This would be a fluid control (Humphris, 1984) on REE mobility which would provide the appropriate halogen ligand for REE complexing in the Chador-Malu iron oxide-apatite system to produce such REE patterns (Fig. 10).

The feldspar-rich sample with the lowest REE content (CHR2b) also has the smallest negative Eu anomaly (Eu/Eu²⁺ = 0.61); however, the three other CHR samples (actinolite-rich) have relatively high REE contents and greater negative Eu anomalies (Eu/Eu²⁺ = 0.32-0.46) than the feldspar-rich sample (Fig. 10). The partitioning of Eu between fluid and solid phases in a hydrothermal system depends on its valency state which, in turn, is strongly temperature-dependent at any given oxygen fugacity (Henderson 1996). Sverjensky (1984) argues that above 250°C the dominant europium form is likely to be Eu²⁺ (single ion or complex), whereas at 25°C the trivalent state will be almost exclusively present. Thus considering the high temperatures proposed for the apatite leaching and monazite formation in the Kiruna-type deposits (e.g., 700–800°C; Harlov et al., 2002), and shown in the experiment (e.g., 300-900°C; Harlov and Förster, 2003; Harlov et al., 2005), a thermochemical reduction of Eu³⁺ to Eu²⁺ in the fluid phase following its release from apatite structure might be proposed, which would be consistent with the relatively small negative Eu anomaly of the feldspar-rich sample (CHR2b; Fig. 10). Since the divalent Eu is compatible in most feldspar structures (e.g., Rollinson, 1993).

Similarly, actinolite would have a prominent role in the uptake of mobilized REE (particularly the HREE) and producing the bulk-rock REE patterns with flat HREE portions (Fig. 10), which is consistent with the compatibility of REE (particularly the HREE) in the amphibole structure (e.g., Rollinson, 1993).

All host rocks except the feldspar-rich sample (CHR2b) show similar LREE patterns (Fig. 10). While the relatively high LREE contents of the amphibole-rich CHR samples (Table 1) might suggest LREE mobilization and enrichment into these rocks, their remarkably similar LREE patterns to the off-contact samples (OCHR1&2) do not support important LREE mobilization, since relatively disturbed LREE patterns would be expected if there were significant LREE mobility.

Conclusions

The bulk REE geochemistry of the amphibole- and feldspar-rich host rock samples from the eastern contact of the northern ore body of the Chador-Malu iron oxide-apatite system suggests the mobilization of apatite-hosted HREE and their uptake by the actinolite-rich metasomatic host rocks adjacent to the contacts. It is proposed that the overprinting-related monazite formation within apatite might be a mineralogical factor controlling the mobility of REE in the Chador-Malu Kiruna-type iron oxide-apatite deposit and similar systems. Although it is largely speculative, this case suggests that the HREE might be released and have
a preferential opportunity to be mobilized (even though over very short distances) during fluid-mineral interaction, REE redistribution, and monazite nucleation, a mineral structure that partitions the lighter rare earth elements. The chemical compositions proposed for the fluids responsible for monazite formation in apatite in similar cases and relevant experiments (see above) are likely to hold true for the Chador-Malu system, since they suggest the appropriate complexing ligand (chloride ion) which would be consistent with the restricted HREE mobility interpreted from the contrasting CHR and OCHRREE patterns. The range of temperatures proposed for such overprinting processes in the relevant cases and experiments (>300°C) might also be the case in the Chador-Malu, since it is consistent with the relatively small extent of Eu anomaly in the feldspar-rich host rock (Fig. 10). Which would suggest the thermochemical reduction of Eu⁴⁺ to Eu²⁺ in high temperatures subsequent to its release from apatite structure and entering the fluid phase, a form that is compatible in the feldspar structure.

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