

# The use of trace elements in Fe-oxides as provenance and petrogenetic indicators in magmatic and hydrothermal environments

Sarah A.S. Dare, Sarah-Jane Barnes, Julien Méric, Alexandre Néron  
*Université du Québec à Chicoutimi (UQAC), Chicoutimi, Québec, Canada, G7H 2B1*

Georges Beaudoin, Emilie Boutroy  
*Université Laval, Québec, Québec, Canada, G1V 0A6*

**Abstract.** In order to use trace element composition of magnetite as an indication of its origin it is necessary to understand the processes that control the trace element concentrations in magnetite. We have characterised trace element distribution in magnetite, using laser ablation ICP-MS, from magmatic ore deposits (Fe-Ti-V-P and Ni-Cu-PGE) where the paragenetic sequences are well constrained. Changes in composition of the liquid, driven by crystal fractionation, are recorded by magnetite in both silicate and sulfide melts. The composition of magnetite is sensitive to co-crystallizing phases, with marked depletion in Ti when ilmenite crystallizes before magnetite and in Cu when a sulfide liquid segregates. Multi-element variation diagrams show that magmatic magnetites have chemical signatures distinct from hydrothermal magnetite due to differences in fluid composition and different conditions of formation (e.g., competing phases, redox and temperature). Chemical fingerprinting of magnetite from the magnetite 'lava flows' of El Laco, northern Chile, provides new evidence to support the hydrothermal alteration model rather than a magmatic origin.

**Keywords.** Magnetite, trace elements, laser ablation-ICP-MS, provenance, El Laco

## 1 Introduction

Magnetite forms under a wide variety of conditions, crystallizing at high temperature from silicate, sulfide and carbonatite magmas or it can precipitate at lower temperatures from hydrothermal fluids. These different conditions may lead to distinctive trace element signatures for the magnetite. Recent analytical developments make it possible to determine a much wider range of trace elements than previously. Thus it may become possible to use the trace element signature of magnetite as petrogenetic and provenance indicators.

One problem is how to establish which trace element variations are significant. Modern laser ablation-ICP-MS systems provide results for ~ 20-25 elements. Some studies have been carried out using a statistical approach (e.g., Dupuis and Beaudoin 2011; Nadoll et al. 2012). Other studies have concentrated on petrogenesis (e.g., Reguir et al. 2008; Dare et al. 2012). Our current studies consider well characterized samples from different settings to establish which elements are the most diagnostic and which processes have the most effect. These studies could then be applied to less well understood examples or provenance studies. For example, we show that the difference observed in the behaviour of trace elements between magnetite of

magmatic and hydrothermal origin permits a re-evaluation of the nature of the fluid (Fe-rich melt or hydrothermal) involved in forming the enigmatic magnetite 'lava flows' of El Laco, northern Chile (Nyström and Henriquez 1994; Sillitoe and Burrows 2000).

## 2 Methodology

To characterise magnetite formed from high temperature silicate melts we have analysed magnetite in Fe-Ti-V-P deposits from both layered intrusions, such as the Bushveld (South Africa) and Sept-Iles (Quebec, Canada) Complexes, and massif-type anorthosites, such as Lac St. Jean (Quebec, Canada). Magnetite from Sudbury and Voisey's Bay Ni-Cu-Platinum-Group-Element (PGE) sulfide deposits (Canada) represent magnetite formed from sulfide liquids. Samples from hydrothermal and low temperature environments include examples of Fe-oxide-Copper-Gold (IOCG) from Ernest Henry (Australia), porphyry-Cu from Morococha (Peru) and banded iron formation from Thompson Ni Belt (Manitoba, Canada). Samples from the El Laco area represent our test case.

The LA-ICP-MS system used at LabMaTer, UQAC, is a Resonetics M-50 193nm laser coupled with an Agilent ICP-MS. An international reference material (GSE-1g) was used for calibration and Fe used as the internal standard. A beam size of 55 – 80 µm was used so that any fine-grained exsolution lamellae (e.g., ilmenite, spinel) were incorporated into the analysis to better represent the initial composition of the Fe-Ti oxide (Dare et al. 2012). The data are presented in order of increasing compatibility with magnetite and normalized to average crust (Fig. 1). We find that these types of diagrams help to investigate the behaviour of trace elements during crystallization of magnetite from different melt compositions (silicate and sulfide) and anomalies due to the competition for an element among co-crystallizing phases (e.g., magnetite, ilmenite and sulfide) are more readily observed.

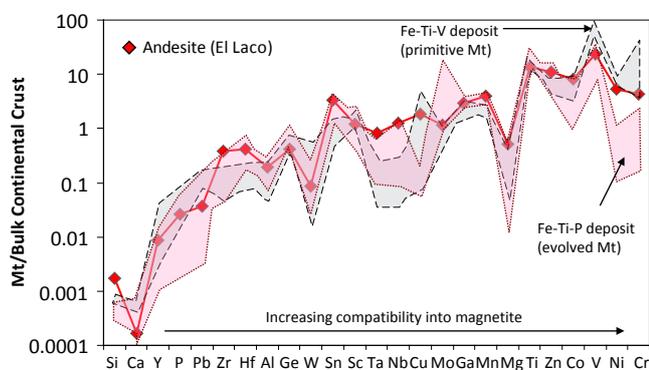
## 3 Magnetite records changing melt composition

The concentration of an element in magnetite depends

on: a) the concentration of the element in the liquid from which it crystallizes, b) whether other minerals are crystallizing at the same time and competing for the element and c) the partition coefficient of the element into magnetite. As a high temperature melt cools, crystal fractionation changes the composition of the residual liquid according to the partitioning behaviour of elements into the crystallizing phases. In two relatively simple and well-constrained systems (silicate and sulfide melts) we can demonstrate the effect fractionation of the melt has on the composition of magnetite (Figs. 1-2).

### 3.1 Magnetite from silicate melts

Magmatic Fe-oxide deposits commonly crystallize from an evolved silicate melt (~ intermediate in composition) at the top of layered intrusions. The lowest Fe-oxide layers of the Bushveld (free of apatite) are richest in V (~ 1.5 wt.%) whereas the uppermost Fe-oxide layers (Fe-Ti-P deposit) are poor in V and contain apatite (Barnes et al. 2004). Oxygen fugacity ( $fO_2$ ) controls whether Ti-rich magnetite crystallizes from the magma before (oxidizing conditions) or after (reducing conditions) ilmenite (Toplis and Carroll 1995). In the layered intrusions studied ( $fO_2 \sim FMQ$ ), Ti-rich magnetite (6–12 wt.% Ti) crystallized either before or at the same time as ilmenite. Both magnetite and ilmenite from the first and last Fe-oxide layers (~ 2 km apart for the Bushveld Complex) were analysed to document the change in composition of trace elements during crystal fractionation of silicate magma (Fig. 1).



**Figure 1.** Multi-element variation diagram for magnetite (Mt) from magmatic Fe-oxide deposits. Magnetite from Fe-Ti-V deposits (grey field) can be distinguished from those from Fe-Ti-P deposits (pink field) using a few critical elements such as Cr, Ni, V, Mo, Nb and Ta. Order of increasing compatibility of elements into magnetite is taken from Dare et al. (2012). Si and Ca determined by electron microprobe using the trace mode of Dupuis and Beaudoin (2011).

Both magnetite (Fig. 1) and ilmenite record fractionation of the magma. Elements sequestered during crystallization of mafic minerals (e.g., olivine, pyroxene) are highest in concentration in magnetite from the lowest layers (V < 1.5 wt. %, Mg < 1 wt. %, Cr < 6000 ppm, Ni < 500 ppm and Co < 200 ppm) and decrease up section. Correspondingly, elements that are incompatible during fractionation (Cu, Ga, Ge, Hf, Mn, Mo, Nb, Sc, Sn, Ta, Ti, W, Zn and Zr) increase up section and are concentrated in magnetite from the uppermost layers

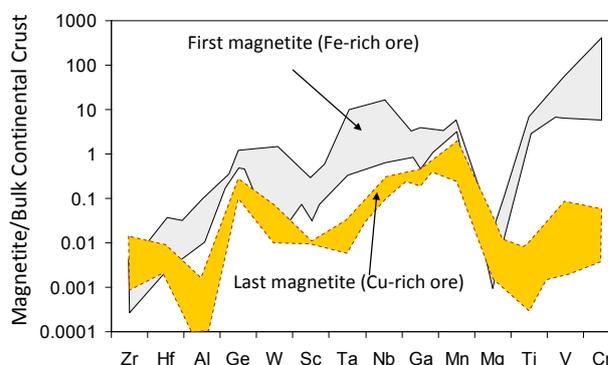
(i.e. Fe-Ti-P deposit).

Magnetite composition is also sensitive to specific co-crystallizing phases. The crystallization of ilmenite before magnetite in some anorthosite-hosted Fe-oxide deposits results in magnetite being relatively depleted in elements that preferentially partitioned into early-forming ilmenite, i.e. Ti (3–6 wt.%), Hf, Mg, Mn, Nb, Sc, Ta, W and Zr. Co-crystallization of trace amounts of sulfides, which can segregate towards the end of fractionation (i.e. in Fe-Ti-P deposits), results in depletion of Cu (highly chalcophile) in magnetite relative to other incompatible elements such as Nb and Mo (Fig. 1). However, co-crystallization of apatite will not have any discernable effect on magnetite chemistry because elements that are concentrated into apatite (Ca, P, Y and REE) are highly incompatible in magnetite and generally absent in all magmatic magnetite.

### 3.2 Magnetite from sulfide melts

Ni-Cu-PGE deposits form when immiscible sulfide melt separates from a mafic-ultramafic melt, collecting highly chalcophile elements (i.e. Ni, Cu, PGE) and some mildly chalcophile elements (e.g., Co, Sn, Zn, Mo, Pb) but very little lithophile elements. The main phases to crystallize from a sulfide melt (1180 – 850°C) are first Fe-rich sulfides poor in Pt and Pd, which form pyrrhotite and pentlandite at lower temperatures (< 600°C), followed by Cu-rich sulphides (which form chalcopyrite and cubanite) and typically associated with Pt-Pd-minerals. Primary magnetite (< 15 wt. %) is commonly present in massive sulfide ore where it crystallized from sulfide melt at high temperature (~1000°C). Magnetite from Ni-Cu-PGE deposits can be distinguished from magnetite in hydrothermal ore deposits by their high Ni + Cr content (Dupuis and Beaudoin 2011).

In these deposits, magnetite also records the fractionation history of the sulfide melt (Dare et al. 2012). Yet the composition and behaviour of trace elements in magnetite is different to that in a silicate melt: (a) the composition of sulfide melt (enriched in chalcophile elements) is different to that of silicate melt (enriched in lithophile elements) and (b) crystallizing phases that compete with magnetite are different.



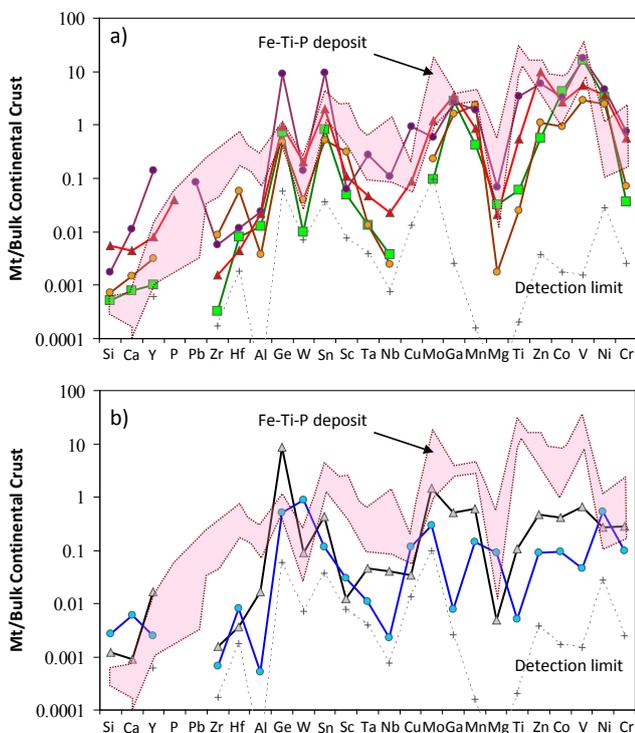
**Figure 2.** Multi-element variation diagram (lithophile elements only) for magnetite (Mt) from Ni-Cu-PGE deposits. Modified from Dare et al. (2012).

As there is no competition with co-crystallizing

silicate minerals, all of the lithophile elements in the sulfide melt are controlled by crystallization of magnetite (Fig. 2). Thus early-forming magnetite in Fe-rich ore is enriched in all of the lithophile elements (< 2 wt.% Ti, V and Cr), which are gradually depleted in the residual melt so that later-forming magnetite in the Cu-Pt-Pd-rich ore contains the lowest concentrations of all these elements (< 50 ppm). Thus the Cr-Ti-V content of magnetite can identify whether the ore is Cu-Pt-Pd rich or Fe-rich and Pt-Pd poor (Dare et al. 2012). Of the chalcophile elements, only Ni, Co, Zn, Sn and Mo are present in magnetite, the concentration of which depends on competition from co-crystallizing sulfides (Fe-rich or Cu-rich).

#### 4 Comparison between magmatic and hydrothermal magnetite

Hydrothermal magnetites have distinctly different chemical signatures to magmatic magnetite (Fig. 3). In particular, they have lower concentrations for many of the trace elements that are common in magmatic magnetite (e.g., Ti, Al, Zn and Mo). Magnetite from low temperature hydrothermal environments appears to have the lowest overall abundance of trace elements (Fig. 3b). Elements that are typically absent in magmatic magnetite, i.e. highly incompatible into magnetite (Si, Ca, Y, P and REE), can be enriched in magnetite from some hydrothermal settings (Fig. 3a). The different signature of hydrothermal magnetite must reflect their different liquid composition and conditions of formation (e.g., temperature, redox and competing phases).



**Figure 3.** Multi-element variation diagrams to compare magnetite (Mt) from magmatic (pink field) and hydrothermal settings: a) High temperature magmatic-hydrothermal deposits such as IOCG (circle), IOA (square) and porphyry (triangle); b) Low temperature hydrothermal settings such as BIF (triangle)

and carbonate veins in serpentinite (circle). In a) samples of IOCG from Ernest Henry (orange: this study) and Bafq, Iran (purple: Bonyadi et al. 2010), IOA from Othrys ophiolite, Greece (Green: Mitsis & Economou-Eliopoulos, 2001) and porphyry from Morococha (this study). All samples in b) are from Thompson Ni Belt (this study).

Another important difference between magmatic and hydrothermal magnetite is the behaviour of Ni and Cr. In magmatic settings their behaviour is coupled, with Ni/Cr ratios  $\leq 1$ , as they are both compatible during fractionation of silicate magmas. In contrast, in many high temperature hydrothermal settings, for example skarn, IOCG, Fe-oxide-apatite (IOA) and porphyry, their behaviour is decoupled and Ni/Cr ratio of magnetite is much higher ( $\geq 1$ ). This is probably related to a difference in solubility and/or mobility for Ni compared to Cr in many types of hydrothermal fluids.

#### 5 Are the magnetite ‘lava flows’ of El Laco (Chile) magmatic or hydrothermal?

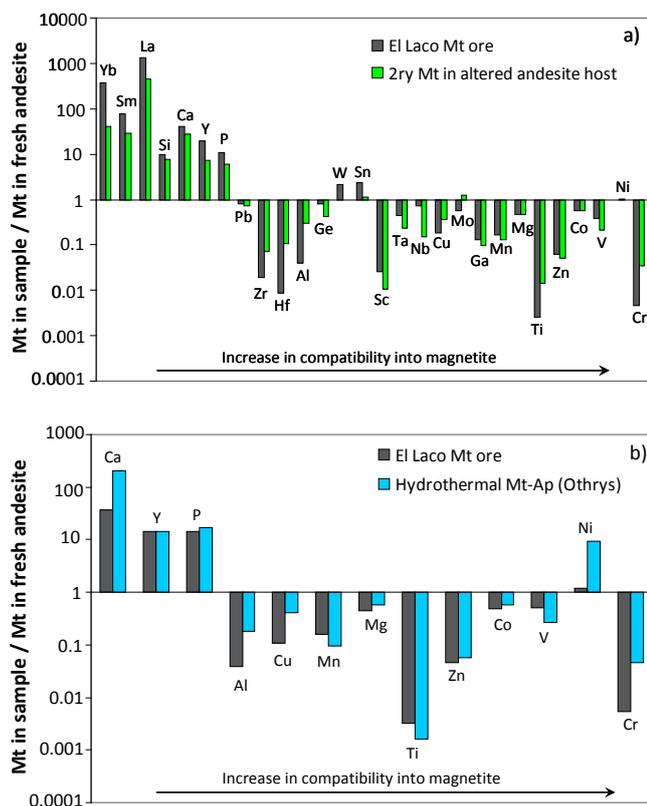
The 2 Ma stratovolcano of El Laco hosts Fe-oxide deposits (500 Mt at 60% Fe) on surface and immediately below (< 300 m depth). The deposits are classified as a ‘Kiruna-type’ or IOA (Fe-oxide-apatite) subgroup of IOCG deposits and comprises Ti-poor (< 0.1 wt.%) magnetite with minor hematite, apatite and clinopyroxene. The origin of El Laco deposits, and many other Kiruna-type deposits, has been debated for a long time. At El Laco, magnetite ore takes the form of lava flows which led many workers to argue their formation from an Fe-oxide liquid that erupted from the volcano (e.g., Nyström and Henriquez 1994). However, studies on alteration assemblages surrounding the deposits were used to argue that magnetite ore formed by hydrothermal replacement of the andesite lava flows (Rhodes et al. 1999; Sillitoe and Burrows 2000). What can be learned from chemical fingerprinting of the magnetite from both the ore and host rocks?

Our samples of magnetite ore are representative of the magnetite “lava flows” as they have the same compositional range as magnetite concentrates analysed by Nyström and Henriquez (1994) for all of the El Laco deposits. Fresh andesite host rocks at El Laco contain phenocrysts of Ti-rich magnetite, of typical magmatic composition (Fig. 1). However, magnetite from El Laco massive ore has a distinctly different composition to magmatic magnetite in the host andesite (Fig. 4) indicating that the ore magnetite was not in equilibrium with a silicate melt:

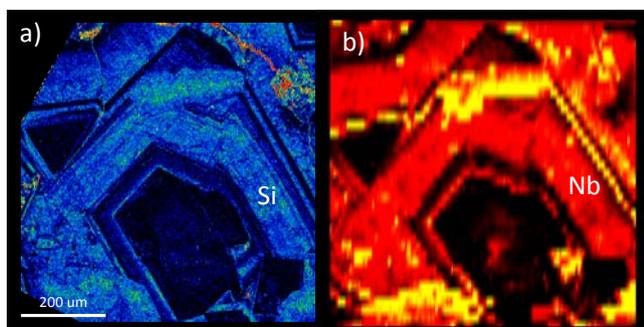
- 1) Magnetite from El laco ore is depleted in many elements but in particular those considered relatively immobile in hydrothermal fluids, e.g., Ti, Al, Cr, Zr, Hf and Sc (Fig. 4a);
- 2) Magnetite is enriched in elements that are highly incompatible into magnetite (REE, Si, Ca, Y and P) and normally in very low abundance in magmatic magnetite (Fig. 4a) but can be enriched in magmatic-hydrothermal magnetite (Figs. 3a and 4b) from IOCG and IOA (Mitsis and Economou-Eliopoulos 2001; Bonyadi et al. 2010);
- 3) The behaviour of Ni and Cr is decoupled with ratios

> 1, typical of magnetite from IOCG, IOA and skarns;  
 4) Oscillatory zoning of Si, Ca, Mg and REE in El Laco magnetite is similar to that found in skarn magnetite (Fig. 5).

Furthermore, magnetite of clear secondary origin in the altered host rock has the same composition (Fig. 4a) and compositional zoning as magnetite from the El Laco massive ore. Thus the chemical fingerprint of magnetite from the El Laco “lava flows” supports the hydrothermal model of alteration of andesite lava flows rather than a magmatic origin.



**Figure 4.** Composition of magnetite (Mt) from El Laco ore (black) compared to a) secondary (2ry) magnetite in altered andesite host of El Laco and b) hydrothermal magnetite deposited together with apatite (Ap) in a mantle shear zone of the Othrys ophiolite, Greece (LA-ICP-MS data from Mitsis and Economou-Eliopoulos (2001)). All samples normalized to primary magnetite in the fresh andesite of El Laco.



**Figure 5.** Chemical maps of zoned magnetite from El Laco massive ore: a) Si by electron microprobe (beam size 3 μm) and b) Nb by laser ablation ICP-MS (beam size 19 μm). In a) Si-rich zones (blue) contain ~ 1.5 wt.% Si.

## Conclusions

The main processes that control the composition of magnetite in magmatic systems are 1) the partitioning behaviour of an element into magnetite, 2) composition of the liquid, which changes during crystal fractionation, and 3) competition for an element among co-crystallizing phases. Trace element signatures of magnetite from different environments (i.e., magmatic and hydrothermal) are distinct and can be used in provenance studies. As such the chemical signature of magnetite from the El Laco ‘lava flows’ indicate a hydrothermal rather than a magmatic origin.

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