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**Trace elements in magnetite from porphyry Cu-Mo-Au deposits in
British Columbia, Canada**

Dante Canil^{*1}, Carter Grondahl^{1,3}, Terri Lacourse², Laura K. Pisiak¹

¹ School of Earth and Ocean Sciences, University of Victoria, Victoria, BC, Canada

² Department of Biology, University of Victoria, Victoria, BC, Canada

³ current address: Department of Earth Sciences, University of Toronto, Toronto, ON,
Canada

* Corresponding Author: Dante Canil

E-mail: dcanil@uvic.ca

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Abstract

This study examines trace elements in hydrothermal magnetite from five porphyry Cu-Mo-Au deposits and two skarns in British Columbia, Canada. Trace element concentrations vary several orders of magnitude both within and between magnetite from skarn and porphyry deposit settings. The heterogeneous composition of hydrothermal magnetite may in part be due to the short duration, low temperature and multiple-fluid events that attend the formation of porphyry ore deposits. Principal component analysis shows two dominant patterns of trace element abundances in hydrothermal magnetite. Firstly, positive correlations of Ti, Al and V, which account for nearly 40% of the total variation in magnetite, are inferred to depend on temperature and oxygen fugacity. Secondly, antithetic abundances of lower valence cations (Co, Mn) with higher valence cations (Sn and Mo) may reflect variations in the redox potential, acidity and metal speciation of hydrothermal fluids. The Cu/Fe and Mn/Fe ratios calculated for fluids in equilibrium with the hydrothermal magnetite using experimental partitioning data are similar to those measured directly in brines trapped in quartz-hosted fluid inclusions from porphyry Cu-Mo-Au deposits.

1. Introduction

Magnetite is a widespread accessory mineral that forms in many different geologic settings and host rocks. Hydrothermal magnetite occurs in porphyry Cu-Mo-Au deposits as disseminated grains, massive aggregates, veins, intergrowths and replacements of other minerals such as hematite (Nadoll et al., 2014). The amount of magnetite associated with mineralization in typical porphyry deposits can locally exceed 10% by volume (Leitch et al., 1995; Sillitoe, 1973, 1997; Sinclair, 2007). In shallow porphyry systems, Fe^{2+} -chloride complexes can react with H_2O or aqueous SO_2 to precipitate magnetite. This mechanism may be the means by which oxidized S species in fluids exsolved from magma are reduced, leading to sulfide mineralization (Simon et al., 2004; Richards, 2014). Hydrothermal magnetite crystallization with chalcopyrite, bornite, and chalcocite in porphyry systems is favoured at high temperature and $f\text{O}_2$, and low $f\text{S}_2$ (Beane and Titley, 1981).

Magnetite is a cubic inverse spinel (space group $Fd3m$) with general formula AB_2O_4 where A and B are tetrahedral (Fe^{3+}) and octahedral (Fe^{3+} and Fe^{2+}) coordination sites, respectively. A variety of cations can substitute on the A and B sites in magnetite, an inverse spinel (O'Neill and Navrotsky, 1984). Previous work has demonstrated the potential of the composition of detrital magnetite for sediment provenance (Grigsby, 1990; Razjigaeva and Naumova, 1992). More recent studies have focussed on the trace element chemistry of magnetite as a prospecting tool for many types of ore deposits (Dupuis and Beaudoin, 2011; Nadoll et al., 2012; 2014; Dare et al., 2012; 2014). Building upon the work of Dupuis and Beaudoin (2011), a comprehensive survey of the trace element chemistry of over 1400 magnetite analyses by Nadoll et al. (2012, 2014) distinguished grains in hydrothermal, igneous and metamorphic settings. Nadoll et al. (2014, 2015)

presented more than 900 analyses for magnetite from the porphyry setting - one data set from the Ertzberg deposit (Indonesia) with trace elements determined by electron microprobe (EMP) and the remainder from eight deposits in New Mexico and Arizona, USA employing LA ICPMS. The latter work showed considerable overlap in trace element abundances for magnetite from many settings, but with important discriminating power for Mg, Al, Ti, V, Mn, Co, Zn and Ga. Nadoll et al. (2015) presented a diagram to discriminate porphyry from skarn magnetite based on covariation of Al, Mn, Ti and V, but noted considerable overlap in the transition between these two types of hydrothermal magnetite. Dare et al. (2014) also show how hydrothermal magnetite is distinct from that in igneous rocks based on the covariation of Ti, Ni and Cr.

In this paper, we expand the study of trace elements in hydrothermal magnetite from porphyry and skarn deposits by examining settings in the Canadian Cordillera, one of which (Island Copper) is well-characterized for its temperature of formation (Arancibia and Clark, 1996). Our primary purpose is to apply magnetite trace element chemistry to inform about the physical conditions of formation, or the chemical attributes of fluids in hydrothermal settings that may control the substitution of trace elements in the magnetite structure. This information will lead to a better understanding of the general trace element fingerprint in hydrothermal magnetite that may be indicative of porphyry mineralization.

2. Deposit Geology and Setting

We studied magnetite in 12 samples from five porphyry deposits and two endo-skarn bodies in the Canadian Cordillera (Figure 1, Table 1). In most cases, we studied two to four polished sections of each sample. Magnetite in these samples occurs as massive

aggregates, disseminated grains, stringers or in quartz veins (Table 1). Further petrographic details of each sample are given in Appendix 1.

2.1 Island Copper

Island Copper is a Cu-Mo-Au deposit hosted in a Jurassic (165 Ma) calc-alkaline monzonite stock and rhyodacite dykes that intrude Bonanza Group volcanic rocks of the Wrangellia Terrane (Perello et al., 1995; Friedman and Nixon, 1995). Skarn and vein-style mineralization is locally prominent. Most ore at Island Copper is associated with early-stage magnetite alteration surrounding a barren intrusive core (Arancibia and Clark, 1996).

2.2 Pine

Pine is a Cu-Au deposit hosted in calc-alkaline quartz monzonite that intrudes coeval quartz- and feldspar-phyric crystal tuffs of the Toodoggone Formation in the Quesnel Terrane. Associated hydrothermal events leading to mineralization have an age of 199 Ma (Dickinson, 2006).

2.3 Endako

Endako is a low-F Mo deposit (Pond, 2013). Mineralization is in a series of en echelon molybdenite-quartz-pyrite veins and mineralized fractures, and occurs in four-distinct fault-bounded zones hosted within calc-alkaline biotite monzogranite and granodiorite of the Jurassic-Cretaceous Francois Lake suite in the Triassic-Eocene Endako batholith (Whalen et al., 2001; Pond, 2013). Three stages of molybdenite mineralization are dated using the Re-Os method to be between 145 to 154 Ma (Selby and Creaser, 2006)

2.4 Copper Mountain

Copper Mountain is a porphyry Cu-Au deposit hosted in alkaline syenite and diorite of the early Jurassic (203 Ma) Copper Mountain Stock (Preto et al., 2004; Logan and Mihalynuk,

2014) that intrudes Triassic Nicola Group volcanic rocks of the Quesnel Terrane (Holbek and Noyes, 2013). Mineralization consists of veins, stockworks, breccias, and disseminations, with hypogene chalcopryrite, bornite, and chalcocite. Skarns can also occur where porphyry systems are in contact with carbonate rocks (Beane and Titley, 1981b). Our single sample is from skarn associated with porphyry type mineralization at Copper Mountain (Holbek and Noyes, 2013; Preto, 1972).

2.5 Mt. Polley

Mt. Polley is a Cu-Au deposit hosted in alkaline diorite and monzonite of the Late Triassic Mt. Polley Intrusive Complex (205 Ma) which intrudes Triassic Nicola Group volcanic rocks of the Quesnel Terrane (Rees, 2013). Hydrothermal breccias are commonly associated with main zones of mineralization. Samples were taken from the Junction zone ('Flank'), the Boundary zone ('Breccia'), and the summit of Mt. Polley ('summit').

2.6 Argonaut/Iron Hill

The Argonaut or Iron Hill deposit is a massive magnetite-garnetite skarn (Black, 1952) produced at the contact of mid-Jurassic calc-alkaline Island Plutonic Suite quartz monzonite with Triassic Quatsino limestone country rock of the Wrangellia Terrane. A body of massive magnetite contains abundant Fe silicates (andradite, hedenbergite and gedrite) and accessory chalcopryrite, and pyrite.

2.7 Port Renfrew

This is not an ore deposit but a massive sheet-like magnetite skarn body four meters in thickness produced at the contact of diorite of the early Jurassic West Coast Complex (195 Ma) with Triassic Quatsino limestone of the Wrangellia Terrane (Canil et al., 2013). The rock is entirely pure massive magnetite.

3. Methods

Rock samples were cut to cm-thick slices on a rock saw and then trimmed to 1 – 2 cm cubes, mounted in epoxy and polished. Samples were viewed with a reflected light microscope to assess the abundance, size, and [shape](#) of magnetite grains. Samples were then examined for micro-inclusions using a Hitachi S-4800 scanning electron microscope (SEM) at the University of Victoria. Major and minor element composition of magnetite was determined using a Cameca SX-50 electron microprobe (EMP) at the University of British Columbia. Between 10 to 20 grains in each sample were analyzed using a 5 micron beam at 15 kV, 20 nA with counting times of 20 seconds for Fe, Ti and Mn, and 60 sec count times for Mg, Al, Si, Ca, Cr, V and Ni. Back-scattered electron imaging was used to avoid grain boundaries, fractures or grains with inclusions. The EMP analyses were recalculated according to spinel stoichiometry (Table 2). The elements Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Sn, Ta, W and Re were determined in magnetite by laser ablation inductively coupled plasma mass spectrometry (LA ICPMS; Jackson et al., 1992) using a 213 nm Nd YAG laser focused to spot of 30 microns for grains smaller than 100 microns, and up to 80 microns for larger grains. Each analysis involved collection of a 20 - 30 second background followed by ablation for up to 30 seconds depending on grain size. Ablated material was carried in He-Ar gas to an Element ICP MS. Time resolved spectra were exported offline and processed to derive element concentrations following Longerich et al. (1996) using Fe determined by EMP as an internal standard. NIST SRM 611, 613, and 615 glasses were used for standardization for every 10 unknowns. Analysis of a standard basalt glass (BCR2-g) was used to check accuracy and precision every 10

unknown analyses (Table 2). The EMP and LA ICPMS analyses were performed on the same grains, but not identical spots on those grains. The LA ICPMS time resolved spectra were in some cases edited for obvious inclusions that were intersected by the laser at depth in the grain (e.g. high Cu - sulfides, high Si - quartz). In less than 10% of all cases the signal from inclusions in the spectra was too significant to edit, and the analysis discarded.

Accuracy of trace elements based on analysis in BCR2g glass over a one year period is within 10% of accepted values for all elements except Al (14%), Cu (14%), Zn (22%), Ga (29%), and Sn (16%). We report all data that are above the limit of detection as characterized by three times the standard deviation of the background (Table 2 - Appendix). For LAICPMS analysis, Al, Sc, Ti, V, Mn, Cr, Mo, Cu, Co, Ni, Zn, Ga and Sn are detectable in most magnetite grains (Table 2) but we did not determine Cr, Zn and Ga in every sample. In some samples Nb was below detection limit. In almost all samples Ta, W, and Re were near or below detection limit (Table 2). Because Cr, Zn, Ga, Ta, W and Re were not comprehensively determined in all samples in our dataset they will not be discussed further.

To better reveal the relationships between trace elements as well as similarities in the composition of magnetite from various settings (skarn, porphyry and igneous) we conducted principal component analysis (PCA). We combined our data on hydrothermal magnetite (Table 2, e-Appendix) with a dataset of magnetite grains from glacial till near Mt. Polley. [Based on their Ti, Ni and Cr contents and the classification of Dare et al. \(2014\), more than 90% of these till grains are from igneous bedrock sources \(Pisiak et al., 2014\).](#) To further randomize the dataset we also included magnetite octahedra of metamorphic origin from river gravels near Serro, Minas Gerais, Brazil (Dorieguetto et al. 2003). The

Mt. Polley till and Serro data were obtained in the same LA ICPMS lab and thus are internally consistent with the hydrothermal magnetite data from the porphyry and skarn deposits. Principal component analysis (PCA) was conducted on the correlation matrix of the LA ICPMS magnetite data ($n=295$ samples) after log transformation (Aitchison et al. 2002). Log-ratio transformation was not used because that approach emphasizes elements with high relative variance, irrespective of absolute concentration (e.g., Baxter et al., 2005). Regardless, as explained by Aitchison et al. (2002), log and log-ratio transformations are more or less equivalent in the case of trace element data, particularly in a case such as ours where magnetite is nearly pure Fe_3O_4 , and the total of all trace elements accounts for less than 5% of the total bulk composition.

Elements that were not analyzed on many of the samples (Cr, Ga) or had concentrations below or near the detection limit in most samples (Ta, W, Re) were excluded from the PCA. For the remaining elements, only 7.5% of the observations were below the detection limit, about half of which were for Nb. Following on previous convention, these observations were assigned values of one-half the detection limit (Sanford et al., 1993; Farnham et al., 2002; Grunsky and Kjarsgaard, 2008). Nevertheless, the PCA results do not change significantly if Nb is excluded, nor do they change if all censored values are removed from the dataset: PCA returns more or less the same patterns of separation and clustering in both elements and deposit types when the censored values are excluded.

4. Results

Viewed under reflected light, alteration of magnetite to hematite was noted along fractures and grain boundaries in many samples. Chalcopyrite and pyrite in all the samples is less abundant than magnetite, and occurs as veins, disseminated grains, and as inclusions and fracture fill within magnetite (Fig. 2). Many of the massive magnetite grains were free of inclusions, but in some samples the SEM imaging revealed sparse <10 micron-sized inclusions of quartz, apatite, titanite and more rarely rutile, barite, argentite, chalcopyrite and native gold.

The EMP analyses show the hydrothermal magnetite in all samples (Table 1) is essentially pure and stoichiometric Fe_3O_4 with minor Ti, Al, Mn and V. All samples have less than 0.5% ulvospinel ($\text{USp} - \text{Fe}_2\text{TiO}_4$) component (Table 2). Magnesium is consistently low (< 0.1 wt%). Concentrations for the low mass elements (Mg, Si, Ca) determined by LA ICPMS were spurious, possibly due to the use of Fe as the internal standard, which is in low concentration in NIST glasses. Because there is considerable heterogeneity in many of the more complex porphyry samples, two large and petrographically homogeneous massive magnetite samples (Argo and LHG – Table 1) were used to compare results of the LA ICPMS and EMP methods. For the trace elements that are above the detection limit of EMP (~ 250 ppm) we found good agreement between these two methods (Fig. 3).

Of all the trace elements, Al, Ti, V and Mn are consistently in highest concentrations in hydrothermal magnetite. The high standard deviations of the mean of analyses show there is considerable variation within samples for many trace elements (Table 2). Nevertheless, the trend of the variation in a sample generally reflects the trend between samples. For example, Al shows a regular positive correlation with Ti and Mn

within individual samples that reflects the overall trend of all samples together (Fig. 4). On the other hand, V is nearly constant in each sample and shows no such covariation with Al between samples (Fig. 4).

Elements that show significant variation in hydrothermal magnetite within and between localities are summarized in plots of medians and quartiles (Fig. 5, 6, 7). The Ti levels are homogeneous within samples and similar between samples at a given deposit, but vary between deposits from high values (up to 10,000 ppm) at Island Copper to less than 100 ppm at Copper Mountain (Fig. 5a). For V, hydrothermal magnetite from each porphyry deposit shows almost no intra-sample variation, but significant variation between deposits (Fig. 5b). Skarn deposits in our dataset are consistently low in both V and Ti (Fig. 5a,b). Manganese shows an opposite trend to Ti, with low values at Island Copper (< 1000 ppm) to higher values (up to 10,000 ppm) at Mt. Polley (Fig. 5c). Most of the porphyry and skarn deposits studied have overall Ti and V that match well with magnetite from porphyries and skarns in the southwest USA and Ertzberg, Indonesia studied by Nadoll et al. (2014, 2015). Magnetite from Mt. Polley stands out as being relatively Mn-rich compared to all other porphyry deposits in British Columbia and elsewhere (Fig. 5c).

Cobalt concentrations follow Mn and both of these elements are opposite in trend to that of Ni (Fig 6 a,b). Island Copper, Pine and Mt. Polley show significant inter-sample variations for Co, Ni or both (Fig. 6). Copper abundances are the most heterogeneous both within and between samples, and show no clear covariation with any other element (Fig. 6c). Most of the magnetite from the British Columbia deposits contains < 30 ppm Cu but extremely high values (up to 5000 ppm) are observed in the Mt. Polley flank samples

(Figure 5c). High Cu in magnetite was also reported for a small number of analyses (n = 16) in **porphyry** deposits in the southwestern USA (Nadoll et al., 2014).

Tin contents in magnetite tend to be homogeneous within porphyry deposits but show notable variation between localities from ~ 10 - 20 ppm at Island Copper to < 2 ppm at Mt. Polley (Fig. 7a). Molybdenum in magnetite from all deposits is < 10 ppm (Figure 7b). The triad of Sn, Mo and Sc are consistently high in some deposits (Island Copper) and notably low in others (Mt. Polley), but are all positively correlated with one another (Fig. 7) and anti-correlated to Mn (Fig. 5c).

Magnetite at Copper Mountain is similar in element abundances to the Argo and Renfrew skarn samples (Table 2, Fig. 6a). Compared to porphyry magnetite all skarn samples are relatively impoverished in trace elements, as was also observed by Nadoll et al. (2014, 2015).

The PCA examines the relationship of all trace elements in magnetite we studied from porphyry, skarn and igneous settings and produces element loadings that can be described in a general way as the magnitude of correlations or covariances observed between all the variables. The PCA reveals two dominant trends. Axes 1 and 2 account for 60% of the variation in trace element composition (Fig. 8). Axis 1 shows strong negative loadings of Ti, Al and V, accounting for 38.6% to the total variation present in the data (Fig. 8a). Axis 2 accounts for 21.4% of the variation and clearly separates strong positive loadings for Sn and Mo from negative loadings for lower valence cations Co and Mn. Element loadings also show clear affinity between Sc and Nb (Fig. 6a). On the PCA plot of samples (Fig. 6b), magnetite grains that are similar in composition plot as clusters, and when further from the origin their chemistry is dominated by fewer elements. The distinct

element fingerprint of each deposit or setting is clear by their relative position along Axis 1 (Ti, Al, V) (Fig. 6b). For example, magnetite from the skarn deposits is impoverished in these latter three elements, relative to those from porphyries and from the igneous grains that make up the majority of the till (Pisiak et al, 2014).

5. Discussion

5.1 Causes of trace element variation in magnetite within and between deposits

Limited experimental work on hydrothermal magnetite shows its composition is dependent on temperature, fO_2 , and fluid composition (Buddington and Lindsley, 1964; Ilton and Eugster, 1989; Simon et al. 2004). Although the details of these parameters are not well constrained for all the ore deposits we sampled, we can use existing petrology from key samples, and limited experimental data on fluid compositions and spinel solid solutions to understand some of the trace element trends in hydrothermal magnetite.

Titanium is a common element in magnetite, entering as a coupled substitution $2Fe^{3+} \rightleftharpoons Ti^{4+} + Fe^{2+}$ favoured at high temperature in ulvospinel-magnetite solid solutions (Buddington and Lindsley, 1964). Titanium is very insoluble in fluids (Mysen, 2012) and its concentrations in magnetite from hydrothermal settings are also likely controlled solely by temperature. Quartz-hosted fluid inclusions in the magnetite-amphibole-quartz alteration zone of the Island Copper record temperatures of 650 - 720°C (Arancibia et al. 1995). Higher Ti contents than the maximum at Island Copper (10,000 ppm – Fig. 4a) are only observed in magnetite from igneous rocks (Nadoll et al. 2014; Dare et al. 2014).

Aluminium shows a positive correlation with Ti in magnetite (Fig. 4a). The solubility of both Ti and Al in the magnetite structure show a positive temperature

dependence (Turnock and Eugster, 1962; O'Neill and Navrotsky, 1984). Experimentally-produced magnetite in felsic igneous rock bulk compositions crystallized at temperatures above 700°C contains greater than 10,000 and 4000 ppm Ti and Al, respectively (Fig. 4a). Porphyry deposit mineralization is inferred to occur at temperatures below 580°C (Richards, 2014; Seo et al. 2012). If 700°C is assumed to be a generous upper temperature limit for porphyry deposit formation, this would correspond to maximum Ti and Al content of ~ 10,000 and 4000 ppm, respectively, in hydrothermal magnetite from this setting (Fig. 4a).

In magnetite, V is present as V^{3+} , V^{4+} or V^{5+} , but with an ionic radius nearly identical to Fe^{3+} , V^{3+} is the dominant cation (Toplis and Corgne, 2002; Balan et al. 2006). The V^{4+}/V^{3+} in magnetite varies with fO_2 but there is only a ~ 3 % change in the proportion of V^{4+} in magnetite over five orders of magnitude in fO_2 (FMQ-2 to FMQ+3) at 1195°C (Bordage et al., 2011). There are no valence data for V in magnetite at the much lower temperatures of porphyry deposit formation. Vanadium abundances in magnetite from this study are the most homogeneous of all trace elements within samples, but vary by two orders of magnitude between deposits (Fig. 4b; 5). Variations in V between samples might reflect fO_2 differences of the magmas that produced fluid to form hydrothermal magnetite, or may simply be due to the mineral assemblage coexisting with magnetite (e.g. biotite, ilmenite) which can differentially partition V^{3+} and V^{4+} (Bordage et al. 2011). The dominance of V^{3+} in magnetite, however, and its general trend following Ti in all but one sample (Fig. 4a; Fig. 5) suggest that V may also be principally controlled by temperature in hydrothermal settings.

We observe high and widely variable concentrations of Cu in hydrothermal magnetite with levels in the Mt. Polley flank samples being quite exceptional (> 1000 ppm

Cu, Figure 6c). Weight percent levels of Cu^{2+} can substitute for Fe^{2+} in the magnetite structure, as evidenced by a complete solid solution along the join $\text{CuFe}_2\text{O}_4 - \text{Fe}_3\text{O}_4$ (Zaki, 2007). On the other hand, experiments shows less than ~50 ppm Cu in magnetite in equilibrium with Cl- or S-bearing fluids at 700 °C, or with rhyolite melt at 700 °C (Ilton and Eugster, 1989; Simon et al. 2006; 2008). High Cu in magnetite could be explained by the presence of Cu in minute sulfide inclusions. For example, only 0.01% of chalcopyrite containing 30 wt.% Cu included in magnetite would produce a bulk Cu content of 30 ppm. Few sulfide inclusions were recognized in our magnetite samples using SEM. Even in the most Cu-rich magnetite from Mt. Polley flank, with up to 5000 ppm Cu, we observed only rare, tiny sulfide inclusions (< 3 μm). We cannot rule out that more inclusions were intersected beneath the mineral surface imaged by SEM, or that nanoinclusions (e.g. Hough et al. 2008) are a source of Cu intersected by the laser at depth. For these reasons, the high and widely variable concentrations of Cu in hydrothermal magnetite remain suspect and enigmatic.

At the $f\text{O}_2$ of formation of porphyry deposits (> FMQ+3 - Richards, 2014), Sn occurs in silicate melt as Sn^{4+} (Linnen et al., 1996). High Sn has been measured in spinel from slags and is interpreted as Sn^{4+} in substitution for Ti^{4+} in $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{TiO}_4$ solid solutions (Wang et al., 2012). Relatively high Sn values are observed in magnetite from the Island Copper, Pine and Endako deposits (Fig. 7). Granitoids in the Endako deposit are high in Sn (Whalen et al., 2001) suggesting that the entire Endako igneous system shows Sn enrichment. All of Sn, Mo, and Sc show positive correlations with one another in magnetite in our dataset (Fig. 7). The Endako and Island Copper deposits have high Mo grades and their magnetite is also notably enriched in Mo and Sc. Granitoid-hosted Mo and

Sn deposits have an association with F-rich magmas or fluids (Mutschler et al., 1981) and these elements along with Nb and Sc have a strong affinity to F in fluids (Webster and Holloway 1990; Shchekina and Gramenitskii, 2008). Thus, the concentrations of Sn, Mo, and Sc in hydrothermal magnetite appear to be dominated by fluid chemistry (Cl/F) as highlighted below.

Several trace elements in hydrothermal magnetite correlate with one another (Dare et al. 2014; Nadoll et al., 2012, 2014, 2015) as expected by crystal chemical constraints in the spinel structure (O'Neill and Navrotsky, 1984). [Using discriminant measures to identify elements that are important in the bulk compositions of magnetite, Nadoll et al. \(2015\) showed that: \(1\) Mg and Mn are predominant compositional influences in skarn magnetite, \(2\) Mg, Ti, V, Mn and Co govern hydrothermal porphyry magnetite and \(3\) Ti, Mn, Al, Zn and V are key in igneous magnetite.](#) In contradistinction, the PCA of our dataset (Fig. 8) is a cogent reflection of the variations in all trace elements that substitute in the magnetite crystal structure, whether the magnetite is of any origin (hydrothermal or igneous).

The disposition of elements on the PCA axes is predictive and can be shown to be consistent with some of the intensive variables under which a magnetite may have formed in either a hydrothermal or igneous setting. For example, Axis 1 of the PCA involving Ti, Al and V is explicable by temperature being the major control on the composition of hydrothermal or igneous magnetite (Fig. 8a) as described above using experimental data. The varying temperature within and between each deposit or setting is expressed by the groupings of magnetite along Axis 1, with highest-temperature igneous samples from till on the left, intermediate-temperature porphyry samples in the middle, and low-temperature skarn samples to the far right (Fig. 8b).

Irrespective of Ti and V contents that are affected by temperature, Axis 2 separates magnetite grains rich in Co and Mn from those depleted in these elements, but enriched in the high valence cations Sn and Mo and to some degree Sc and Nb (Fig. 8). The disposition of these two element groups on Axis 2 may mirror their relative behaviour and affinity for certain ligands in hydrothermal fluids as measured in several natural and experimental fluid-melt partitions. For example, Mn partitions preferentially into fluid over magnetite and its concentration in fluid increases with chlorinity (Ilton and Eugtser, 1989; Zajacz et al. 2008). We are unaware of any work on fluid/melt partitioning of Co but being divalent it is expected to behave similar to Mn. In contrast to Mn, Mo prefers hydroxyl species and its partitioning in fluids does not change appreciably with chlorinity (Keppler and Wyllie, 1991). For example, the separation of Mo from Cu in porphyry systems shows strong evidence of being due to small differences in redox potential and the acid-base balance of magmatic fluids, with Mo-rich fluids favoured at more reduced and acidic conditions (Seo et al. 2012). Tin solubility in fluids increases with fO_2 and peraluminosity of the coexisting melt (Keppler and Wyllie, 1991) and like Mo shows an association with F well known empirically in certain classes of granitoid-hosted ore deposits (Webster and Holloway, 1990). Although F shows no clear influence on the behaviour of Mo or Sn in fluids in experiments (Keppler and Wyllie, 1991), it might simply be a diluent of Cl, favouring higher Mo and Sn in settings having Cl-poor hydrothermal fluids that precipitate magnetite.

We can use experimental data to derive the metal contents or ratios of such fluids from which the hydrothermal magnetite in our study formed. Ilton and Eugster (1989) measured partitioning of Mn and Cu between magnetite and fluid ($K_d = (Me/Fe)_f / (Me/Fe)_{mt}$, where 'Me' is Mn or Cu) at 200 MPa to as low as 650°C, near the

inferred upper temperature limit of 700°C for the formation of samples in our study. Using their K_d values at 650°C, we derive the Cu/Fe and Mn/Fe in fluids in equilibrium with the mean and median Cu/Fe and Mn/Fe in magnetite from each deposit (Fig. 9). The results at 650°C can be considered minima for Cu or Mn, as lower temperatures would favour greater partition of these metals into fluid relative to magnetite. The Cu/Fe and Mn/Fe we calculate for fluids in equilibrium with hydrothermal magnetite from the British Columbia porphyry deposits are comparable to those measured directly in vapour and brine inclusions from three large well-studied porphyry Cu deposits (Fig. 7). The data from the Bingham, Alumbrera and Grasberg deposits suggests Cu partitions significantly into vapours over brines (Ulrich et al. 1999; Landtwing et al. 2005). With the exception of the extremely high Cu values in magnetite from the Mt. Polley Flank, the Cu/Fe in fluids estimated for the porphyry deposits we studied would suggest hydrothermal magnetite in all cases was in equilibrium with brines, not vapour. Because there is less fractionation of Mn between brine and vapour (Ilton and Eugster, 1989), we cannot use this metal to differentiate unequivocally a brine from vapour source.

5.2 Magnetite as an indicator mineral for porphyry Cu deposits

In British Columbia, several porphyry Cu-Mo-Au deposits occur in arc terranes that accreted to form the Canadian Cordillera (Figure 1). Although there are many arc-related intrusions in the Cordillera, only a small fraction of these are mineralized. Furthermore, large tracts of the province are covered by glacial overburden. Given an understanding of the glacial history of the region, basal till geochemistry and mineralogy indicative of primary source bedrock can be used to follow trends up-ice, possibly to mineralized source rocks (Levson, 2001; Averill, 2001). With the rare exception of chalcopyrite (Plouffe et al.

2012; Hashmi et al. 2014) many of the obvious diagnostic minerals that form in porphyry Cu deposits (bornite, molybdenite, clay minerals) weather quickly under surface conditions and may not serve reliably as indicator minerals in glacial deposits. Magnetite is an ideal indicator mineral because it is robust during erosion and transport, exhibits compositional variation depending on its source rock, and has physical properties that make for convenient separation from sediment samples (Grigsby, 1990).

Dupuis and Beaudoin (2011) investigated the trace element content of magnetite determined by electron microprobe from a variety of mineral deposits, and developed discrimination diagrams for the different sources of magnetite. Their work defines fields for porphyry and skarn deposits on the basis of the abundances of Ti, V, Ni, Cr, Mn in magnetite. Much of the data from this study do not plot in their narrow porphyry field from the Dupuis and Beaudoin (2011) study (Fig. 10a). Their efforts were built upon by Nadoll et al.(2014, 2015) using a much larger database of LA ICPMS analyses, who noted more transitional trace element chemistry between magnetite in skarn and porphyry settings. The means of samples from our study plot within Nadoll et al.(2015) skarn and porphyry fields on a plot of Al+Mn versus Ti+V (Fig. 10b).

Dare et al.(2014) show igneous magnetite has high Ti and low Ni/Cr relative to that of hydrothermal origin (Fig. 10c). This distribution is wholly commensurate with our inferences from PCA (Fig. 8) and a compilation of experimental data on Ti and Al in magnetite (Fig. 4a). The means of all samples from the porphyry deposits in British Columbia plot within the 'hydrothermal' field in Figure 10c, and it may serve as a robust first-order classification of ore-related magnetite during in a till exploration program.

In the application of trace element concentrations in magnetite as an indicator mineral, it is important to address the order-of magnitude variation in trace elements observed even in a single sample (Fig. 4). The mineral assemblages and chemistry of trapped fluids from porphyry systems show that many variables (T, fO_2 , fluid composition) are at play during different times in the formation of a porphyry deposit (Arancibia and Clark, 1996; Landtwing et al. 2005; Seo et al. 2012). The range of these variables might be preserved in the composition of magnetite. For example, Mn varies widely for porphyry magnetite in British Columbia, the southwest USA and Ertzberg deposits (Fig. 5c). If Mn in magnetite is controlled by fluid acidity or chlorinity, as observed experimentally (Ilton and Eugster, 1989) and inferred from the PCA in our study (Fig. 8), the variation in this element within and between deposits would suggest a wide variety of fluid chlorinities during the stage precipitating hydrothermal magnetite. Indeed, the Mn/Fe measured in fluids in quartz-hosted inclusions from porphyry deposits varies nearly an order of magnitude (Ulrich et al. 1999; Landtwing et al. 2005), a range bracketed by all the ore deposits in this study (Fig. 9).

Furthermore, porphyry deposits can form over remarkably short lifetimes (tens of years) and at temperatures below 700°C (Cathles and Shannon, 2007; Richards, 2014). Using the formula $x = (Dt)^{1/2}$ with diffusion rates (D) measured in magnetite (Van Orman and Crispin, 2010), the diffusion distance (x) at 700°C calculated for divalent (Fe, Co, Ni, Mn with $D = 10^{-16} \text{ m}^2/\text{s}$) and higher valence cations (Ti, Al with $D = 10^{-20} \text{ m}^2/\text{s}$) varies between 200 to 20 microns, respectively, over a period of $t = 10$ years. These diffusion distances of tens of microns approach the grain size of many hydrothermal magnetite grains in our samples (Fig. 2, Table 1) and will be an order of magnitude shorter for lower

temperatures inferred for some porphyry deposits (Richards, 2014). The calculation shows that short growth histories, low temperatures and the likelihood of multiple fluid/precipitation events could explain much of the heterogeneity for the trace elements in hydrothermal magnetite that we observe on the scale of a hand sample (Fig. 4). Such attributes may obfuscate using simple bivariate plots of multivalent elements to accurately discriminate magnetite from various different hydrothermal settings. Nevertheless, it is clear that Ti, Al, Ni and Cr show promise to at least discriminate hydrothermal magnetite during exploration (Fig. 10c). A more rigorous multi-element discriminant function may help matters, in concert with more experimental controls on the trace element substitution in hydrothermal magnetite. Ultimately these approaches could be rigorously tested by a well-constrained study of magnetite in till systematically sampled in proximity to known porphyry Cu systems (e.g. Pisiak et al. 2014) [as has been done for other types of deposits \(Sappin et al., 2014; Makvandi et al., in press\).](#)

6. Summary

Our study shows an exceptionally wide range of trace element compositions for hydrothermal magnetite from porphyry Cu deposits in British Columbia. A consistent distinction of igneous from hydrothermal magnetite is in Ti and Al content. Inferences based on experimental data suggest temperatures of below 700°C for formation of most hydrothermal magnetite from British Columbia porphyry deposits. Other trace elements in hydrothermal magnetite from the deposits may show variations due to either oxygen fugacity (V) or fluid redox potential, acidity or chlorinity (Cu, Mn, Sn, Mo, Sc).

The Cu and Mn contents of fluids in equilibrium with hydrothermal magnetite from the deposits in British Columbia, calculated from experimental partitioning data, are similar to those measured in quartz hosted fluid inclusions in other porphyry deposits, and show they may have been in equilibrium with brines. Overall, the chalcophile elements in magnetite show extreme range and heterogeneity that is not easily assigned a specific parameter given the paucity of experimental work on metal substitutions in hydrothermal magnetite. Specifically variations in Cu, Sn, Mo and Co may be related to the plethora of fluid compositions generated in the history of a deposit (Seo et al. 2012). In till exploration using magnetite as an indicator mineral for porphyry deposits, low concentrations of Ti and Al (< 10,000 and 4000 ppm, respectively) and high Ni/Cr (> 1 – Dare et al. 2014) may serve as the most suitable compositional criteria for classifying hydrothermal ore-related grains from those derived from igneous source rocks.

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Figure Captions

Figure 1 – Regional geology of the northern Cordillera of British Columbia (Massey et al. 2005), and showing the names and locations of porphyry Cu deposits (triangles) and skarns (circles) sampled for hydrothermal magnetite in this study.

Figure 2 – Reflected light images showing magnetite textures in samples from this study. Mineral abbreviations are after Whitney and Evans (2010). (a) Massive magnetite (Mag) with small pyrite stringer (Py), and hematite (Hem) alteration at cracks and grain boundaries in sample AT110. (b) Magnetite stringer in matrix of altered feldspar in sample ICu6. (c) Disseminated grains of magnetite (Mag) in a matrix of quartz and altered feldspar in sample AT109. Note laser ablation pit. (d) Massive magnetite (Mag) with chalcopyrite (Ccp) and quartz (Qz) in sample Pine3.

Figure 3 – Comparison of mean trace element concentrations determined by EMP and LA ICPMS in massive and homogeneous magnetite samples Argo and LHG, from the Argo and Copper Mountain deposits, respectively (Table 2). Also shown is the estimated minimum detection limit for the electron microprobe (D.L.) using operating conditions of this study.

Figure 4 – Covariation of Al with: (a) Ti, (b) V, and (c) Mn in magnetite from this study. Also plotted in (a) are the Al and Ti contents of magnetite crystallized in experiments on dacite and granodiorite bulk composition at 700-800°C and fO_2 's of NNO+2 to NNO+4.8,

where NNO is the nickel-nickel oxide oxygen buffer (Dall Agnol et al. 1999; Muir et al. 2014; Bogaerts et al. 2006; Proteau and Scaillet, 2003). The dashed line in (a) is an estimated upper limit for Ti in hydrothermal magnetite, bound by the lowest Ti in igneous magnetite from experiments at 700°C, and the highest Ti in the Island Copper samples forming at up to 720°C (see text).

Figure 5 – ‘Box-and-whisker’ plots of (a) Ti, (b) V, and (c) Mn in magnetite ordered by deposit. The box encompasses the median (line) and is bounded by the upper and lower quartiles, with the lines showing 95% of all data for that sample. Outliers are shown by open circles. Orange boxes at far right are LAICPMS and EMP data for magnetite classified as ‘hydrothermal’ from the porphyry Cu deposits in the southwestern USA and Ertzberg/Grasberg Indonesia, respectively (Nadoll et al. 2014; 2015).

Figure 6 - ‘Box-and-whisker’ plots of (a) Co, (b) Ni, and (c) Cu in magnetite ordered by deposit with symbols as in Figure 5. Note heterogeneity in Cu within samples, and extreme values from Mount Polley flank.

Figure 7 - ‘Box-and-whisker’ plots of (a) Sn (b) Mo, and (c) Sc in magnetite ordered by deposit with symbols as in Figure 5. Note the positive correlation for these elements with one another. There is no trace element data for these elements available for Ertzberg/Grasberg.

Figure 8 – Principle component plots of (a) element loadings and (b) sample scores of magnetite in deposits from this study and igneous grains in till (Pisiak et al. 2014), plotted on the first and second principal axes, which account for 38.6% and 21.4% of the total variation, respectively.

Figure 9 – Calculated Cu/Fe and Mn/Fe for fluids in equilibrium with hydrothermal magnetite at 650°C from each deposit in this study. The calculation uses either the median (solid diamond) or mean (open symbol) Cu/Fe and Mn/Fe in magnetite from each deposit, with fluid-magnetite partition coefficients for Cu-Fe and Mn-Fe between magnetite and fluid measured at 650°C from Ilton and Eugster (1989). The Cu/Fe and Mn/Fe in the fluids are minima, as lower assumed temperatures of formation would shift calculated metal ratios to higher values. For comparison are the Cu/Fe and Mn/Fe measured in vapour and brine of quartz-hosted inclusions in three well-studied porphyry Cu deposits (Ulrich et al. 1999; Landtwing et al. 2005; Seo et al. 2012). Note similar Cu/Fe in fluids in equilibrium with magnetite to the brines measured in fluid inclusions.

Figure 10 – Comparison of mean compositions of magnetite in porphyry (solid circle) and skarn (star) deposits in this study with three different proposed classification schemes (note change in scale and identity of the axes): (a) Magnetite from this study compared with the fields for skarn and porphyry deposits from Dupuis and Beadoin (2011), (b) A similar plot with the fields for skarn and porphyry deposits from Nadoll et al. (2015), (c) A plot of Ti and Ni/Cr dividing hydrothermal from igneous magnetite (Dare et al. 2014).

784 **Appendix – Detailed Sample Descriptions**

785 ***ICu 6b – Island Copper:*** Sample showing Type I and II veins of Arancibia and Clark
 786 (1996) where magnetite and quartz+magnetite veinlets are observed up to 3 mm wide.

787 Magnetite is altered to hematite along edges/fractures. Minor pyrite and chalcopyrite less
 788 than 100 µm present are present as disseminated grains and as inclusions in magnetite.

789 Chalcopyrite up to 600 µm in size is observed in a larger magnetite veinlet.

790 ***ICu U1 – Island Copper:*** Sample showing Type I veins of Arancibia and Clark (1996) with
 791 closely-spaced magnetite ± pyrite veinlets less than 100 µm wide. Magnetite is also

792 observed as larger subhedral grains up to 300 µm, and smaller sub- to anhedral grains less
 793 than 20 µm. Disseminated chalcopyrite occurs as grains between 10 and 100 µm.

794 ***ICu 4 – Island Copper:*** Sample showing Type III veins of Arancibia and Clark (1996) with
 795 magnetite (± chalcopyrite ± pyrite) + amphibole in a vein up to 350 µm wide. Disseminated
 796 subhedral magnetite ± chalcopyrite smaller than 100 µm.

797 ***Pine 3 – Pine:*** Magnetite is observed in a vein up to 1 mm wide, with smaller (< 50 µm)
 798 chalcopyrite and pyrite; magnetite is commonly altered to hematite. Magnetite (with some
 799 lighter hematization along grain edges) and chalcopyrite as < 300 µm grains also occur in
 800 quartz veins and disseminated in the host rock.

801 ***Pine 5 - Pine:*** Magnetite is observed as large grains in an approximately 1 mm wide quartz
 802 vein with some alteration to hematite along edges/fractures, and a widely spaced,
 803 discontinuous trellis of thin (< 5 µm) darker ilmenite exsolution in the larger magnetite
 804 grains. Magnetite ± chalcopyrite ± pyrite also occurs as smaller (< 100 µm) disseminated
 805 grains in the host rock.

806 **2AB-16 – Endako:** Magnetite occurs as sub- to euhedral 100 µm sized crystals in a narrow
 807 vein. Grain boundaries are irregularly altered to hematite.

808 **LHG - Copper Mountain:** This sample is from skarn peripheral to the Cu-Au
 809 mineralization. Magnetite is massive and observed in a fractured/brecciated form. Pyrite
 810 occurs as subhedral grains up to 2 mm, smaller disseminated grains and blebs, and as
 811 fracture fill in magnetite. Chalcopyrite occurs as fracture fill in magnetite and pyrite, and as
 812 disseminated grains.

813 **Magnetite Breccia (AT110) – Mt. Polley:** Massive magnetite is a matrix amongst clasts of
 814 brecciated potassic altered monzonite. Magnetite is altered to hematite along grain
 815 edges/fractures. Lesser secondary pyrite occurs as grains and veinlets/fracture fills in
 816 magnetite. Disseminated magnetite and pyrite grains 25-100 µm in diameter occur in the
 817 monzonite clasts.

818 **Flank (AT109) – Mt. Polley:** Magnetite is observed as disseminated subhedral grains
 819 approximately 20-50 µm diameter, and in some cases in more massive agglomerations.
 820 Hematite is commonly observed as shatter/trellis exsolution.

821 **Summit (AT111) – Mt. Polley:** Magnetite is observed as disseminated grains up to 200 µm
 822 diameter and as aggregates of smaller (approximately 25 µm) grains. Magnetite can be
 823 texturally complex with alteration/intergrowths to lighter hematite and darker ilmenite. In
 824 some cases pyrite and chalcopyrite (<50 µm) occur as disseminated grains and inclusions in
 825 oxides.

826 **Argo – Argo/Iron Hill:** The sample studied (Argo) is massive magnetite with no other
 827 phases present.

828 **Renf – Port Renfrew:** The sample studied (Renfrew) is massive magnetite.