

Magnetite as a Porphyry Copper Indicator Mineral in Till: a Test Using the Mount Polley Porphyry Copper-Gold Deposit, South-Central British Columbia (NTS 093A)

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Introduction

Magnetite (Fe₃O₄) is a common oxide mineral in a wide variety of igneous and metamorphic rocks, as well as in some ore-related hydrothermal systems. The composition of magnetite may be indicative of its environment including such factors as temperature, pressure, magma or fluid composition, and oxygen and sulphur fugacities (e.g., Buddington and Lindsley, 1964; Frost, 1991). Previous studies have demonstrated the utility of magnetite as a petrogenetic indicator because it can incorporate a wide variety of substituting cations such as Mn, Ni, Co, Zn, Al, Cr, Ti, V and Ga (e.g., Irvine, 1965, 1967; Dick and Bullen, 1984; Roeder, 1994; Barnes and Roeder, 2001). These studies predominantly focus on end-member compositions of spinel from igneous systems. More recent work has documented the variation in the trace-element composition of hydrothermal magnetite (Beaudoin and Dupuis, 2010; Nadoll et al., 2012, 2014; Dare et al., 2014).

In the Canadian Cordillera, Mesozoic calcalkaline and alkaline intrusive igneous rocks that are prospective for porphyry deposits may be overlain by a thick glacial sediment cover. Mineral exploration for porphyry deposits often utilizes bulk geochemical analysis of soil and stream sediments but results can be ambiguous due to the varied behaviour of ore-related elements during weathering and surface runoff. Therefore, a more robust geochemical indicator is required that would provide a direct vector to the actual bedrock source. Basal till represents a direct sample of the bedrock, which can be linked back to source via sediment

Keywords: magnetite, mineral chemistry, exploration, indicator mineral, till provenance, hydrothermal, porphyry deposits

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dispersal trains that are parallel to the ice-flow direction (Whiting and Faure, 1991; Levson, 2001).

The ubiquity of magnetite in porphyry systems and its resistance to weathering and glacial transport suggest that it may be a useful pathfinder mineral in basal till (Grigsby, 1990; Whiting and Faure, 1991). Ultimately, magnetite in till would provide a unique exploration vector for identifying mineralized porphyry systems up-ice and efficiently distinguish them from the vast number of barren felsic igneous intrusions in the Cordillera. To this end, a ground-truth test was performed using magnetite as an indicator mineral in till from the area surrounding the Mount Polley porphyry Cu-Au deposit. The purpose of the test was to determine if its geochemical signature can be applied to other locations in British Columbia without known porphyry deposits.

Geological Setting

The Mount Polley porphyry Cu-Au deposit occurs in the Quesnel terrane of the Intermontane Belt, which comprises Late Triassic to Early Jurassic volcanic arc rocks, in south-central BC (Figure 1). The Mount Polley intrusive complex is described by Logan and Mihalynuk (2005) as a subvolcanic composite stock, 4 by 5.5 km in size, composed of fine-grained porphyritic diorite and monzonite with dikes of plagioclase porphyry and syenite. The Bootjack stock, a coarse-grained syenite pluton, also occurs in the area but is separated from the Mount Polley stock by a 1 km wide belt of metavolcanic rocks. Porphyry Cu-Au mineralization in Quesnellia arc rocks occurs in several of these high level alkalic intrusive complexes, such as Mount Polley where mineralization is concentrated in various types of hydrothermal breccias (Logan and Mihalynuk, 2005).

As part of the Natural Resources of Canada's Targeted Geoscience Initiative 4 (TGI-4) program, the Geological



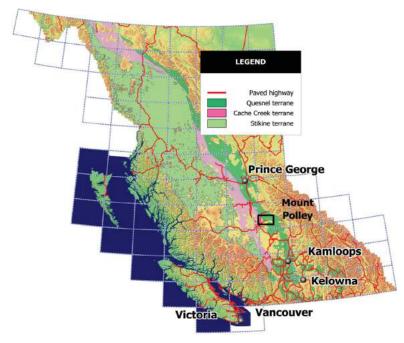


Figure 1. Location map of the Mount Polley study area in south-central British Columbia (courtesy of J.M. Logan).

Survey of Canada and the BC Geological Survey conducted a till sampling survey between 2011 and 2013 in the vicinity of the Mount Polley deposit, collecting 74 till samples covering an area of approximately 700 km² (Figure 2; Anderson et al., 2012; Plouffe et al., 2013b; Ferbey et al., 2014). Mineralized rocks were also sampled from bedrock exposed to recent glaciation and ice-flow indicators were measured from outcrop, allowing for reconstruction of the glacial history of the area. The dominant ice-flow direction in the Mount Polley area, which occurred at glacial maximum, was to the northwest and was preceded by ice flow to the west-southwest during an ice build-up stage (Hashmi et al., 2014).

Methodology

Sample Preparation

Large till samples (~10 kg) were submitted for heavy mineral separation. Bulk till samples were wet sieved to a <2 mm size fraction, which was first concentrated by density on a shaking table. The heavy minerals recovered on the shaking table were further concentrated in heavy liquids (methylene iodide) and sieved into three size fractions: 1–2 mm, 0.5–1 mm and 0.25–0.5 mm. Magnetite grains were separated from these heavy mineral concentrates by hand magnet and, for each sample, approximately 100 to 125 grains from the 0.25–0.5 mm fraction were randomly selected, mounted in epoxy and polished for analysis (Figure 3). Chips of bedrock samples from Mount Polley were also similarly prepared. Reflected-light microscopy was used to confirm mineral identification and visually assess

internal textures of individual grains prior to chemical analysis. Magnetite grains with appreciable alteration, fracturing or with a significant number of inclusions were excluded from analysis.

Scanning Electron Microscope

A subset of magnetite grains were examined with a Hitachi S-4800 field emission scanning electron microscope (SEM) at the University of Victoria (Victoria, BC) using an accelerating voltage of 16 kV and emission current of 20 nA. This method allows the user to readily identify different exsolution and alteration phases, as well as mineral inclusions present in some grains.

Electron Microprobe

Fifty magnetite grains per till sample were selected for elemental analysis. Concentrations of Al, Si, Ca, Ti, V, Cr, Mn, Fe and Ni were determined with a CAMECA SX 50 electron probe micro analyzer at the University of British Columbia (Vancouver, BC) using a 5 μ m

beam size, accelerating voltage of 25 kV and beam current of 20 nA. The Fe concentration in each magnetite grain is used as an internal standard for laser-ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS) trace-element analysis (see below).

Laser-Ablation Inductively Coupled Plasma— Mass Spectrometry

Analysis of Sc, Ti, V, Mn, Cr, Co, Ni, Cu, Zn, Ga, Nb, Mo, Sn, Ta and W in magnetite was performed by LA-ICP-MS at the University of Victoria using a 213 nm neodymium:yttrium-aluminum-garnet (Nd:YAG) ultraviolet laser operating at 50–55 Hz and interfaced to a Thermo Scientific XSERIES 2 Quadrupole ICP-MS. Spot and raster ablation methods were used with a beam size of 25–40 μ m depending on grain size and the internal texture present. National Institute of Standards and Technology standard reference material glasses were used for standardization with ⁵⁷Fe selected as the internal standard. Analyses showing apparent contamination in their spectra (e.g., by inclusions) were edited to remove contaminated sections, or were discarded where editing was not feasible.

Petrography

Petrographic analysis using reflected light microscopy identified a variety of habits, textures, inclusions and alteration types in magnetite from till (Figure 4). In general, magnetite grains vary from round, anhedral shapes to euhedral octahedrons and cubo-octahedrons, each reflecting the degree of sediment transport. Grain quality is also highly



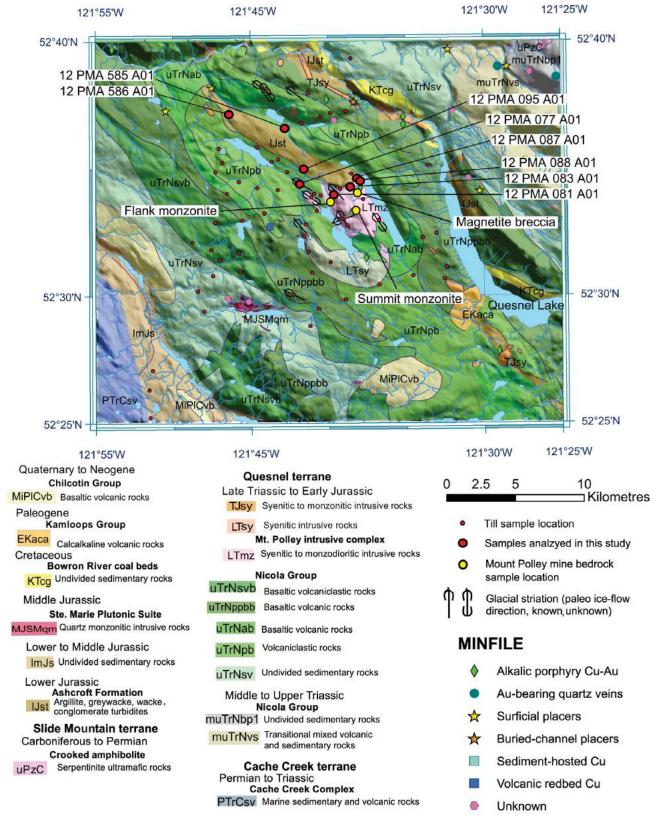


Figure 2. Geology of the Mount Polley area showing locations of till (red) and bedrock (yellow) samples used in this study (modified from Plouffe et al., 2013a), south-central British Columbia. MINFILE information from BC Geological Survey (2014).



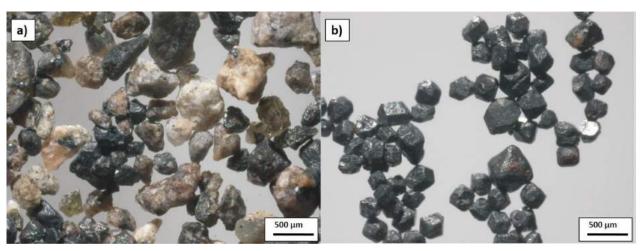


Figure 3. a) Initial magnetic fraction of heavy mineral concentrates from till sample 12 PMA 586 A01, Mount Polley, south-central British Columbia; b) magnetite grain selection following sample picking.

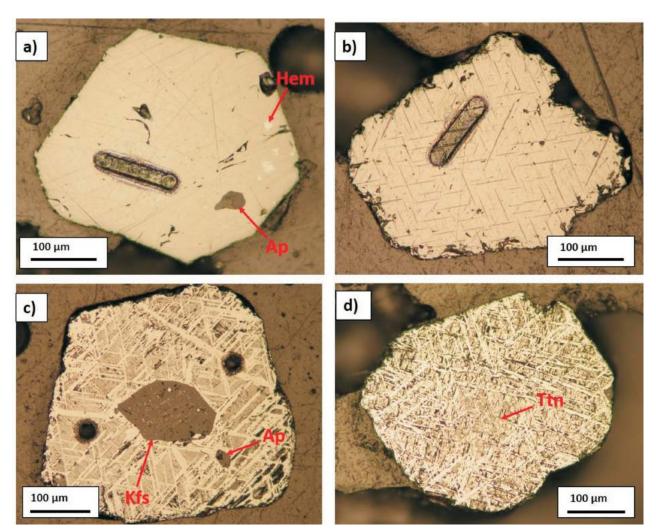


Figure 4. Petrographic varieties of magnetite from till in reflected light at 20 times magnification (from Mount Polley, British Columbia). **a)** Euhedral, homogeneous grain, 385 μm across with 100 μm long laser-ablation raster, apatite (Ap) inclusion and minor hematite (Hem) alteration patches near rim (12 PMA 081 A01-C3). **b)** Subhedral, 520 μm grain with coarse trellis lamellae and 110 μm long laser-ablation raster (12 PMA 077 A01-D1). **c)** Subhedral, 425 μm grain with both coarse (white) and fine (grey) trellis lamellae, potassium feldspar (Kfs) and apatite (Ap) inclusions and two 30 μm laser-ablation spots (12 PMA 088 A01-D4). **d)** Subrounded, heterogeneous grain, 450 μm across with both coarse and fine trellis lamellae, as well as blebby titanite (Ttn) predominantly concentrated in the core (12 PMA 087 A01-G6).



variable as some magnetite grains are highly fractured or strongly pitted, whereas others are relatively free of pits and appear texturally homogeneous. Mineral inclusions occur in some magnetite grains—apatite is the most common, followed by quartz, potassium feldspar and chalcopyrite in decreasing abundance (Figure 4a, c).

Exsolution is a predominant textural feature commonly manifested as trellis-type lamellae (Figure 4b) or, to a much lesser degree, parallel or sandwich-type lamellae (Haggerty, 1991). These are observed at a variety of scales from submicroscopic to thick, dense lamellae that occur throughout the entire grain. Some magnetite contains more than one exsolution phase (e.g., Figure 4c, d). A significant example is in sample 12 PMA 095 A01-C11 where thick lamellae are composed of ulvöspinel (Fe₂TiO₄) ± rutile (TiO₂), whereas the interstitial thin trellis has been replaced by an unknown secondary Si-Al-Mg phase (Figure 5). The exsolution in magnetite occurs as a direct result of subsolidus oxidation during cooling, increasing in intensity as the degree of oxidation increases (Haggerty, 1991).

Alteration is not prevalent but can occur as hematite along magnetite grain boundaries, fractures and lamellae, as well as in discrete patches. Few grains are completely altered to hematite. A large proportion of magnetite also contains significant amounts of intergrown titanite, which occurs as blebs, irregular stringers and within lamellae (Figure 4d).

Chemistry

Chemical analysis was completed for magnetites in eight till samples from various distances down-ice (northwest) from the Mount Polley deposit. Northwest also represents the dominant glacial transport direction of chalcopyrite grains in till from the Mount Polley mineralization (Hashmi

Usγo Si-Al-Mg

Figure 5. Back-scattered electron image of magnetite showing rutile (Rt) and coarse ulvöspinel (Usp) lamellae, and a Si-Al-Mg phase (possible alteration) along dark, fine trellis lamellae (12 PMA 095 A01-C11, Mount Polley, British Columbia).

et al., 2014). As expected, magnetite chemistry is highly variable reflecting the diverse bedrock sources of the till. In particular, titanium, which has strongly temperature-dependent substitution in magnetite (as a Fe_2TiO_4 component), varies from 0.04 to 12 wt. % (Figure 6). The covariation of Ti with Ni/Cr was proposed by Dare et al. (2014) to discriminate between igneous and hydrothermal magnetite. In general, the proportion of magnetite grains in till with the hydrothermal signature increases with proximity to the deposit (Figure 6).

Cations that commonly substitute in magnetite, such as divalent Mg and Mn as well as trivalent Al and Cr, exhibit a wide range of values from a few hundred parts per million (ppm) to as much as 4 to 4.5 wt. % for Mg and Mn and up to 5 and 7.5 wt. % for Al and Cr, respectively. Other divalent cations vary from below detection limits to 2400 ppm for Ni, 1100 ppm for Cu and 500 ppm for Co; however, Zn can be concentrated up to 18 000 ppm. High valence elements (i.e., Sn, Mo, Nb, Ta), as well as Ga and Sc have low concentrations (<100 ppm).

A large proportion of grains have significantly high Si and Ca concentrations up to 4 and 5.5 wt. %, respectively. A positive correlation between Si and Ca is observed in a trend leading to uncommonly high cation sums in magnetite when calculated to three cation per four oxygen atoms stoichiometry (Figure 7).

Discussion

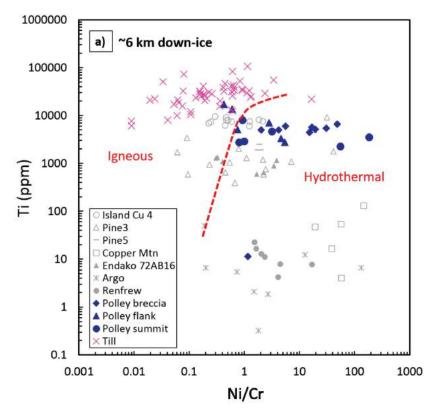
Distinguishing Hydrothermal Versus Igneous Magnetite

A fundamental goal of this study is to identify distinguishing characteristics of hydrothermal magnetite (associated

to mineralization event) versus igneous magnetite (not associated to mineralization event) in till. Previous studies have shown the importance of integrating both petrography and chemical analysis in developing a general classification of magnetite provenance (e.g., Grigsby, 1990; Mücke, 2003; Bouzari et al., 2011). Those studies, however, focused on igneous magnetite with little or no data for magnetite precipitated directly from hydrothermal fluids.

Initial petrographic analysis of magnetite provides a preliminary evaluation of provenance prior to chemical analysis. For example, the presence of exsolution lamellae in magnetite can be interpreted as likely indicative of an igneous source, where any Fe₂TiO₄ in solid solution with magnetite exsolves to ulvöspinel as a result of cooling and oxidation at magmatic temperatures (Buddington and Lindsley, 1964).





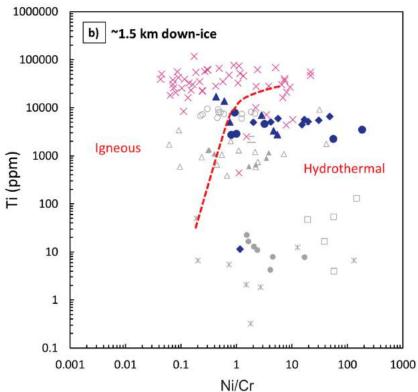


Figure 6. Concentrations of Ti (ppm) versus Ni/Cr in magnetite from till (pink X). Bedrock samples from Mount Polley (blue symbols) and various hydrothermal deposits in British Columbia (grey symbols) are also presented (Grondahl, 2014). **a)** Sample 12 PMA 585 A01 is located ~6 km down-ice from the Mount Polley deposit and **b)** sample 12 PMA 081 A01 is located ~1.5 km down-ice. Igneous and hydrothermal fields defined by Dare et al. (2014). Dashed line represents potential distinction of hydrothermal and igneous magnetite.



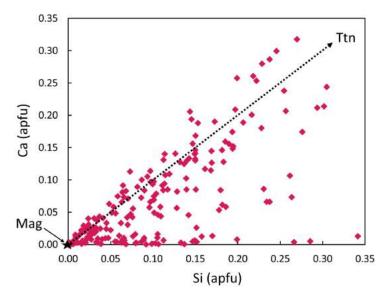


Figure 7. The Si and Ca contents in magnetite from till (Mount Polley, British Columbia) recalculated to atoms per formula unit (apfu), calculated assuming a three cation per four oxygen atoms stoichiometry. A positive correlation is consistent with mixing between magnetite (Mag) at the origin and titanite (Ttn), which contains one cation each Si and Ca (off axes). Several magnetite grains with high Si and low Ca may indicate some potential interference by quartz inclusions in these grains.

However, the absence of exsolution lamellae does not necessarily imply a non-igneous source since homogeneous magnetite can occur as phenocrysts in rapidly cooled volcanic rocks (Mücke, 2003) or as an accessory phase in felsic plutonic rocks, where the Ti content of magnetite is too low to exsolve (Grigsby, 1990). Thus, the integration of chemical analysis with petrography is essential.

A more recent chemical discrimination diagram suggested by Dare et al. (2014) provides a simple division of hydrothermal and igneous magnetite based on Ni/Cr and Ti concentrations. The general trend of increasing proportion of hydrothermal magnetite grains with decreasing distance from the deposit is favourable; however, the Ni/Cr versus Ti classification diagram fails to distinguish hydrothermal magnetite for various porphyry and skarn deposits in BC (Figure 6). Thus, consistent and accurate chemical discriminants for hydrothermal magnetite provenance have yet to be determined.

Anomalously high Si and Ca contents in some magnetite was also discovered by Dare et al. (2014), who attributed these values to substitution within the structure of hydrothermal magnetite. The results of this present study do not support this interpretation but instead suggest that high Si and Ca may be related to submicroscopic inclusions or reactions upon cooling to form titanite (Figure 4d). Such magnetites in this study appeared 'clean' in reflected light but show a submicroscopic turbid appearance in SEM images. This is consistent with the correlation of Si and Ca values along a mixing line between magnetite and titanite

(Figure 7) and is observed in a large proportion of magnetite grains. Further characterization by SEM of this phenomenon is required.

Magnetite as an Indicator Mineral

The trace-element signature of ore-related magnetite has been determined in a parallel study by Grondahl (2014) for Mount Polley and other porphyry deposits in BC. Those results indicate that individual ore deposits have unique trace-element signatures in hydrothermal magnetite that differ from magnetite in igneous rocks. Figure 8, for example, illustrates the potential for Ti and Sn concentrations in ore-magnetite to discriminate between individual deposits and possibly define a hydrothermal magnetite field for porphyry deposits in BC.

As a ground-truth test, magnetite composition as a function of distance to the Mount Polley deposit was examined. It was found that the proportion of magnetite grains with the Mount Polley chemical signature increases with proximity to the deposit and that the ore deposit 'signal' is detectable only to a maximum distance of

6 km down-ice from Mount Polley (Figure 8). Magnetite in till from greater distances down-ice (northwest) show no overlap with the Mount Polley data (not shown). This relationship between chemistry and proximity to deposit is similar to the geochemical dispersal train typically found in glaciated terrain, and could potentially be a valuable tool in exploring for these deposits.

Future Work

In principle, the method of using magnetite chemistry in till samples down-ice from the Mount Polley deposit as a pathfinder to the porphyry source is successful, however, this is complicated by the variety in composition of hydrothermal magnetite from several porphyry deposits in British Columbia. The implication of possible titanite exsolution on the chemistry of magnetite and its provenance also needs to be reconciled by further work. An empirical approach has been used to evaluate the similarity between Mount Polley ore magnetite and magnetite grains in till, but there also exists the potential to employ a more rigorous assessment of the magnetite trace-element concentrations (e.g., discriminant functions or multivariate analysis). Regardless, a method of more quantitative scoring needs to be developed in order to optimize the use of magnetite in basal till as an exploration tool.

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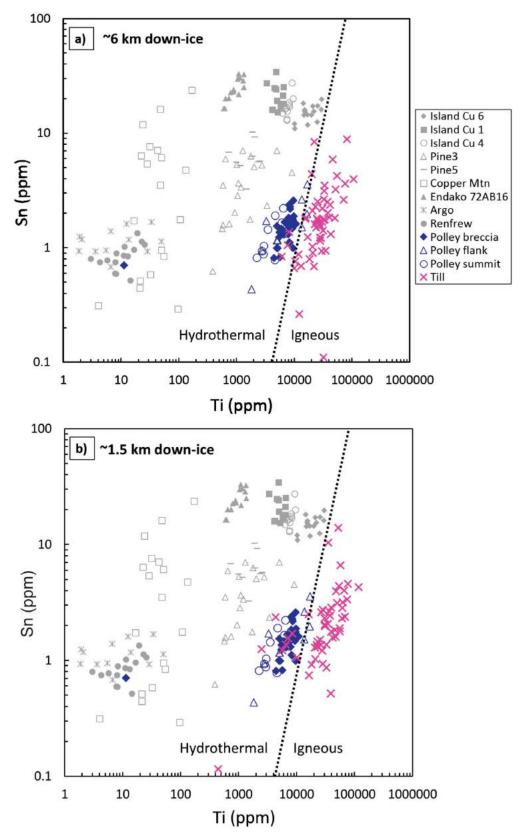


Figure 8. Concentrations of Sn versus Ti (ppm) in magnetite from till (pink X). Mount Polley ore magnetite (blue symbols) and various hydrothermal deposits in British Columbia (grey symbols) are also presented (Grondahl, 2014). **a)** Sample 12 PMA 585 A01 located ~6 km down-ice from the Mount Polley deposit and **b)** sample 12 PMA 081 A01 located ~1.5 km down-ice. Dashed line represents potential distinction of hydrothermal and igneous magnetite.



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