



Evaluation of magnetite as an indicator mineral for porphyry Cu exploration: a case study using bedrock and stream sediments at the Casino porphyry Cu–Au–Mo deposit, Yukon, Canada

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Abstract: The trace element composition of detrital magnetite grains recovered from six local streams around the Casino high-grade porphyry Cu–Au–Mo deposit, west-central Yukon, is compared with igneous and magmatic-hydrothermal magnetite recovered from mineralized and unmineralized host rocks at the deposit. Linear discriminant analysis of 12 elements (Mg, Al, Ti, V, Mn, Co, Cr, Ni, Cu, Zn, Ga and Ge) and plots of Ti v. Ni/Cr are used to discriminate between magmatic-hydrothermal magnetite from the potassic alteration zone and igneous magnetite from granodiorite and quartz monzonite hosting the deposit. Magmatic-hydrothermal magnetite with a trace element composition similar to that from the potassic alteration zone at Casino is identifiable in stream sediments draining the deposit. Copper in magmatic-hydrothermal magnetite, present as minute inclusions of sulfide minerals such as chalcopyrite or substituted within the magnetite crystal lattice, is a strong indicator of Cu mineralization. We show that the chemical compositions of magnetite recovered from stream sediments can be used to explore for porphyry systems.

Keywords: geochemical exploration; magnetite; stream sediments; porphyry Cu

Supplementary material: Laser ablation data for major, minor and trace elements in magnetite from bedrock and stream sediment samples from Casino are available at <https://doi.org/10.6084/m9.figshare.c.5896900>

Thematic collection: This article is part of the Applications of Innovations in Geochemical Data Analysis collection available at: <https://www.lyellcollection.org/cc/applications-of-innovations-in-geochemical-data-analysis>

Received 6 October 2021; **revised** 15 March 2022; **accepted** 15 March 2022

Recent studies have focused on the trace element composition of magnetite from porphyry Cu deposits (Dupuis and Beaudoin 2011; Dare *et al.* 2012, 2014; Nadoll *et al.* 2012, 2015; Canil *et al.* 2016), iron-oxide copper gold deposits (Sillitoe 2003; Carew 2004; Ciobanu *et al.* 2015), Ni–Cu–PGE deposits (Boutroy *et al.* 2014; Duran *et al.* 2016; Ward *et al.* 2018), volcanogenic massive sulfide deposits (Dupuis and Beaudoin 2011; Makvandi *et al.* 2016a, b), and other deposit types to identify general trace element fingerprints that may reflect the presence of mineralization. Only a small number of studies have examined the chemical composition of magnetite recovered from glacial sediments proximal to mineral deposits (Beaudoin *et al.* 2009; McMartin *et al.* 2011; Sappin *et al.* 2014; Pisiak *et al.* 2017). We report on the potential for trace element signatures of magnetite in stream sediments to detect porphyry copper mineralization.

Stream sediment geochemistry has a long history of use in mineral exploration because of the relative ease of sample collection and because stream sediments represent a time-integrated signal of both mechanical and hydromorphic dispersion (e.g. Ottesen and Theobald 1994; Leybourne and Goodfellow 2003; Leybourne and Johannesson 2008). The mineralogy and chemistry of heavy

mineral concentrates recovered from in-stream sediments has only more recently received attention, especially compared to heavy minerals recovered from till (e.g. Hashmi *et al.* 2015; McClenaghan *et al.* 2017). Minerals derived from bedrock, colluvium and glacial sediments within a drainage basin can be concentrated up to three or four orders of magnitude in the heavy mineral fraction (specific gravity >3.2) from the active stream sediment sample (Ottesen and Theobald 1994). Some areas of Canada, including those in non-glaciated terrains, have no till cover making stream sediments an important sample medium in mineral exploration. To refine heavy mineral techniques for stream sediments, and to improve our understanding of magnetite geochemistry for mineral exploration, we have studied magnetite recovered from bedrock core samples of mineralized and hydrothermally altered rocks from the Casino porphyry Cu–Au–Mo deposit and unmineralized granodioritic and dioritic host rocks. Magnetite from these rocks was compared to magnetite recovered from streams draining the Casino deposit. The deposit, within the Yukon–Tanana terrane in west-central Yukon (Fig. 1), is potentially one of Canada's largest Cu–Au–Mo porphyry deposits. Current total measured and indicated resources are 2.173

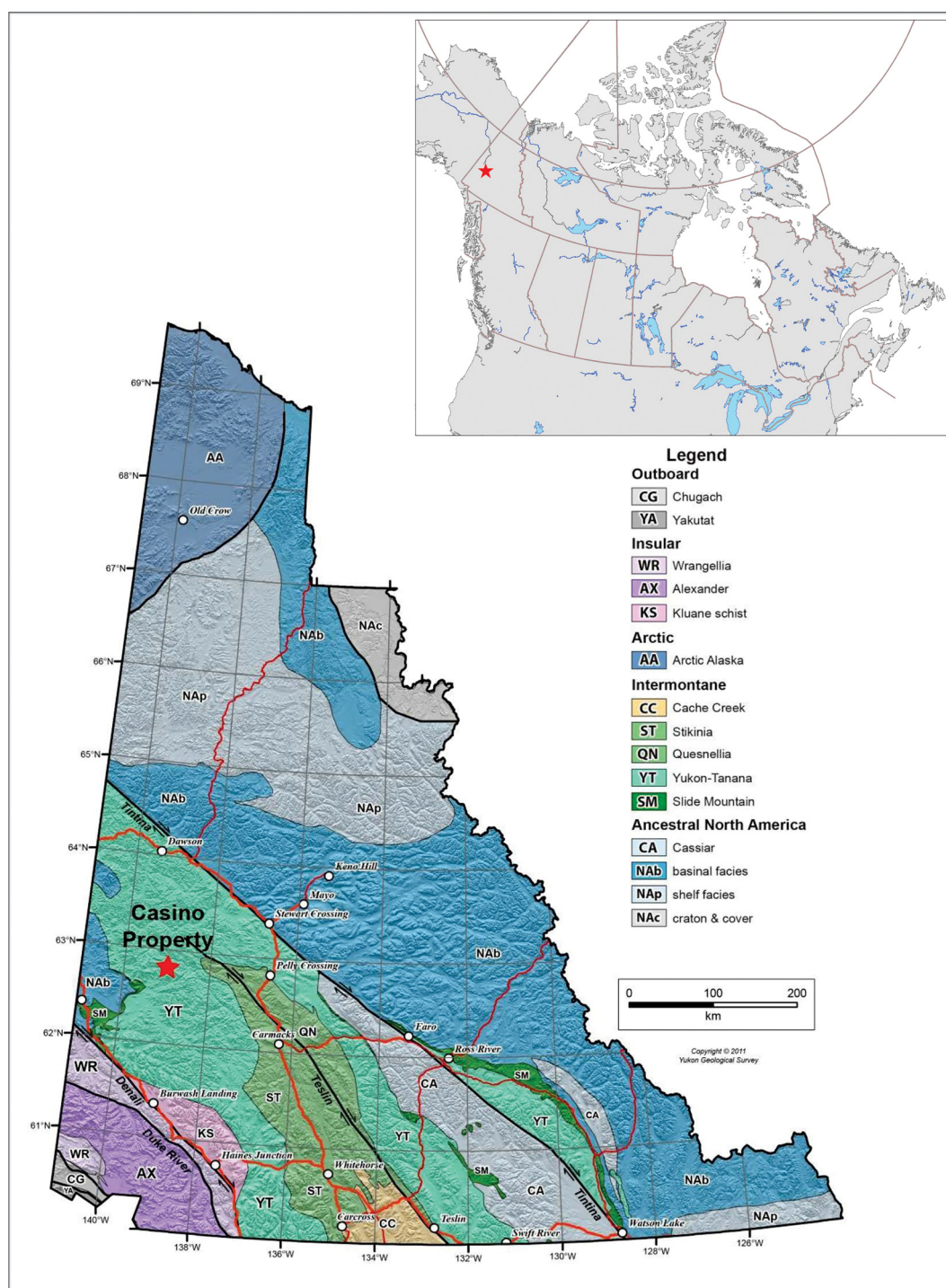


Fig. 1. Simplified tectonostratigraphic domain map of Yukon Territory showing the location of the Casino porphyry Cu-Mo-Au deposit within the Yukon-Tanana terrane in west-central Yukon (modified from Colpron and Nelson 2011).

billion tonnes grading 0.16% Cu, 0.18 g t⁻¹ Au, 0.17% Mo and 1.4 g t⁻¹ Ag (Casino Mining Corporation 2020).

The Casino deposit provides an ideal site for testing the potential of the trace element composition of magnetite in stream sediments as a vector to porphyry Cu mineralization because the deposit has only been minimally disturbed by exploration, is not yet mined, and has Cu-rich waters and sediments in local creeks draining the deposit (Archer and Main 1971; McClenaghan *et al.* 2018; McCurdy *et al.* 2019; Kidder *et al.* 2022). Here we use multivariate statistical analysis to interrogate laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) data. We determine trace element signatures of magnetite from two igneous sources and one magmatic-hydrothermal source around the Casino deposit, classify

detrital magnetite recovered from six streams by comparing trace element signatures with Casino deposit bedrock trace element signatures and apply this method of discriminating magnetite grains in streams to mineral exploration.

Geological background

Regional geology

The study area is underlain by the oldest part of Yukon-Tanana terrane (Fig. 1), consisting of multi-deformed and metamorphosed mostly amphibolite-facies siliciclastic rocks including quartzite,

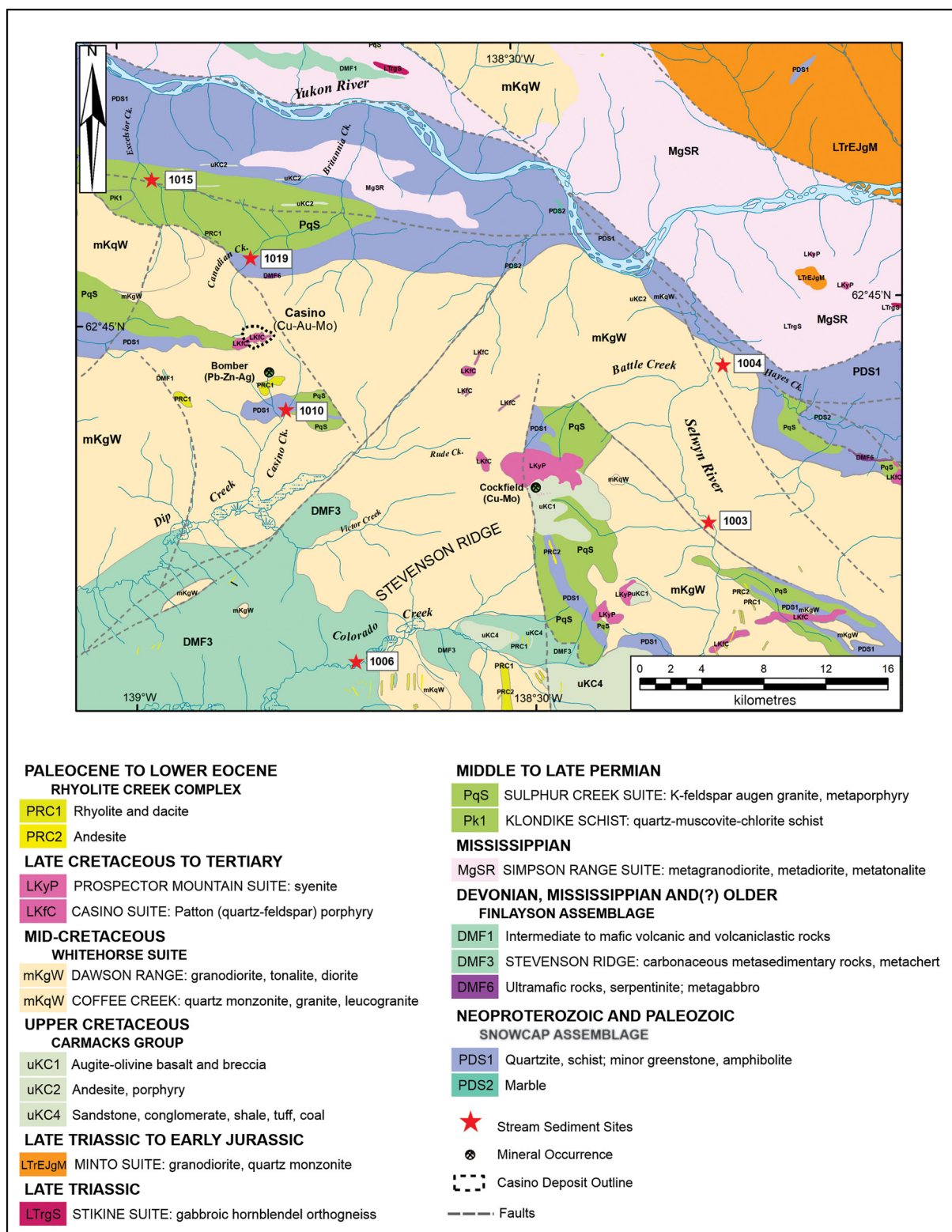


Fig. 2. Local Bedrock geology map of the Casino deposit area that shows the locations of mineral occurrences in the survey area (Yukon Geological Survey 2021a) and six stream sediment samples collected by the Geological Survey of Canada in 2017 (black stars) around the Casino deposit. Bedrock geology from Yukon Geological Survey (2017).

micaceous quartzite and psammitic quartz–muscovite–biotite ($\pm$ garnet) schist of the pre-Devonian Snowcap assemblage (Fig. 2). The main country rock spatially associated with the Casino deposit is the middle Cretaceous Dawson Range phase of the Whitehorse suite granitoids; these are nil to weakly foliated, comprising medium- to coarse-grained, white to beige, hornblende–biotite granodiorite and lesser granite, tonalite, quartz diorite and diorite. A second phase, the Coffee Creek granite, occurs as

unfoliated medium- to coarse-grained pink to beige biotite monzogranite, locally pegmatitic, containing smoky quartz phenocrysts. The Dawson Range and Coffee Creek phases generally occur as distinct plutons (Fig. 2; Godwin 1975; Ryan *et al.* 2013; Casselman and Brown 2017).

The Late Cretaceous Casino suite hosting the Casino Cu–Au–Mo porphyry and other intrusion-related mineralization in the region comprises sparse, small volume porphyritic quartz monzonite

plutons and associated breccia of the Patton porphyry (Fig. 2). Intrusions are fine- to medium-grained, and alkali feldspar-plagioclase-biotite-quartz-phyric (Ryan *et al.* 2013; Casselman and Brown 2017).

Deposit geology

The bedrock geology of the deposit is briefly summarized below from detailed descriptions by Archer and Main (1971); Godwin (1975, 1976); Bower *et al.* (1995); Casselman and Brown (2017) and the Yukon Geological Survey (2017). The Casino deposit is hosted in a Late Cretaceous Patton quartz monzonite porphyry along with associated breccia along the intrusion margins. During the Paleogene, the deposit was subjected to deep (up to 300 m) chemical weathering because of the porous nature of the breccias and strongly altered zones. The deep weathering profile is largely intact, with a well-formed zonation consisting of a leached cap, supergene oxide mineralization, supergene sulfide mineralization, and hypogene (primary) mineralization.

Alteration

Alteration minerals in the potassic alteration zone (Fig. 3) include K-feldspar, biotite, magnetite and quartz (Godwin 1975). Magnetite commonly forms braided veinlets in the potassic alteration zone (Godwin 1975; Casselman and Brown 2017). Phyllic alteration is peripheral to the inner potassic zone and locally overprints potassic alteration. Quartz, white mica and pyrite are dominant in the phyllic zone, which also includes muscovite (after biotite) and abundant tourmaline. Pyrite ranges from 5 to 10 vol% throughout the phyllic alteration zone and magnetite (and lesser hematite) extend from the potassic alteration zone into the phyllic alteration zone. Propylitic alteration forms a wide halo around the deposit in gradational contact with the inner potassic alteration (Huss *et al.* 2013). Epidote, chlorite and calcite are the common propylitic alteration minerals, with lesser clay, carbonate, pyrite, white mica and albite (Huss *et al.* 2013).

Mineralization

The leached cap is enriched in Au, depleted in Cu, and consists primarily of jarosite, limonite, goethite and hematite. The supergene oxide zone is Cu-rich and contains chalcantite, malachite and brochantite along with minor cuprite, azurite, tenorite, neotocite and trace molybdenite as coatings on fractures and in vugs (Casselman and Brown 2017). The supergene sulfide zone has Cu grades commonly nearly double those of the hypogene zone (Huss *et al.* 2013), with chalcocite, digenite or covellite commonly occurring along grain boundaries or fractures in chalcopyrite, bornite and tetrahedrite (Bower *et al.* 1995; Casselman and Brown 2017). Molybdenite is locally altered to ferrimolybdenite (Bower *et al.* 1995).

Hypogene mineralization is mainly contained within the contact breccia surrounding the Patton porphyry. Pyrite, chalcopyrite, molybdenite and trace sphalerite and bornite are finely disseminated throughout the potassic zone. Veins and disseminations of pyrite, chalcopyrite and molybdenite host increased gold, copper, molybdenum and tungsten contents in the phyllic alteration zone along the phyllic–potassic contact within the phyllic zone (Huss *et al.* 2013).

Surficial geology

The surficial geology of the Casino area is summarized from Huscroft (2002); Bond and Lipovsky (2011, 2012a, b), and McKillop *et al.* (2013). The area around the Casino deposit is largely unaffected by recent (Wisconsinan) glaciation. However, glacial sediments mapped on the east flank of Mount Cockfield

(20 km to the SE of the Casino deposit; Fig. 2) were deposited during the Reid and McConnell glaciations, during the Late Wisconsin McConnell glaciation (glacial maximum at 15 000 BP) and Reid glaciation (glacial maximum at 130 000 BP). During the Reid glaciation, alpine glaciers over Mount Cockfield extended west into the headwaters of Victor Creek and eastward into an unnamed tributary valley that drains eastward into the Selwyn River (Fig. 2). Minor evidence of pre-Reid (c. 3 Ma) glaciation has been identified near the headwaters of Canadian Creek, immediately NW of Patton Hill (Bond and Lipovsky 2011).

First- and second-order streams (e.g. Casino Creek; Fig. 2) are confined to narrow V-shaped valleys and contain mostly sub-angular to sub-rounded gravel to boulders of locally derived bedrock. Higher order streams occur in much broader valleys and are filled with more distally derived colluvium, loess carried from the Donjek and White River floodplains to the SW, and rounded gravel (e.g. Dip Creek, Colorado Creek; Fig. 2).

Sample collection, preparation, and analysis

Collection

Samples were collected at 22 sites around the Casino deposit. At each site, a bulk (c. 10 kg) stream sediment sample for recovery of indicator minerals and a water and stream silt sample for geochemical analysis were collected following GSC protocols described in Day *et al.* (2013). Bulk stream sediment samples were processed by Overburden Drilling Management Ltd. (ODM) to recover heavy (>3.2 specific gravity (SG)) and moderate-density (2.8–3.2 SG) mineral fractions and examine them for key indicator minerals, including tourmaline (Beckett-Brown *et al.* 2019), gold and sulfide minerals (McClenaghan *et al.* 2020) and magnetite.

Eleven bedrock samples were collected from drill core at varying depths from holes that had been previously drilled into the deposit. Surface sampling of competent bedrock at the Casino deposit was not possible because of the thick cover of colluvium or deeply weathered bedrock (McClenaghan *et al.* 2018). Drill hole locations of the three bedrock core samples used in this study are shown in Figure 3.

Preparation

Stream sediment samples plus three quality control samples (GSC in-house blanks) were processed at ODM. The <2.0 mm fraction of bulk samples were first passed across a shaking table to prepare a pre-concentrate. The pre-concentrate was then subjected to two heavy liquid separations and ferromagnetic separation to produce 2.8–3.2 specific gravity (SG) and >3.2 SG non-ferromagnetic heavy mineral concentrates for visual identification (binocular microscope) of indicator minerals. These fractions were examined by ODM, potential indicator minerals were counted and the 0.25–2.0 mm ferromagnetic fraction was set aside for future analysis. The masses of all fractions produced and abundances of indicator minerals in the routine and three ‘blank’ samples, along with a sample processing flow chart are reported in McClenaghan *et al.* (2020).

At ODM, 11 bedrock core samples were disaggregated using an electric pulse disaggregator to preserve natural grain sizes, textures and shapes of minerals (McClenaghan *et al.* 2020). Crushed vein quartz blanks were processed between each sample to reduce the potential for contamination between samples. Heavy mineral separation procedures were similar to those for sediment samples, except that bedrock samples were not passed across a shaking table. The masses of all fractions produced, abundances of indicator minerals for the bedrock samples and the sample processing flow chart are reported in McClenaghan *et al.* (2020). From these 11

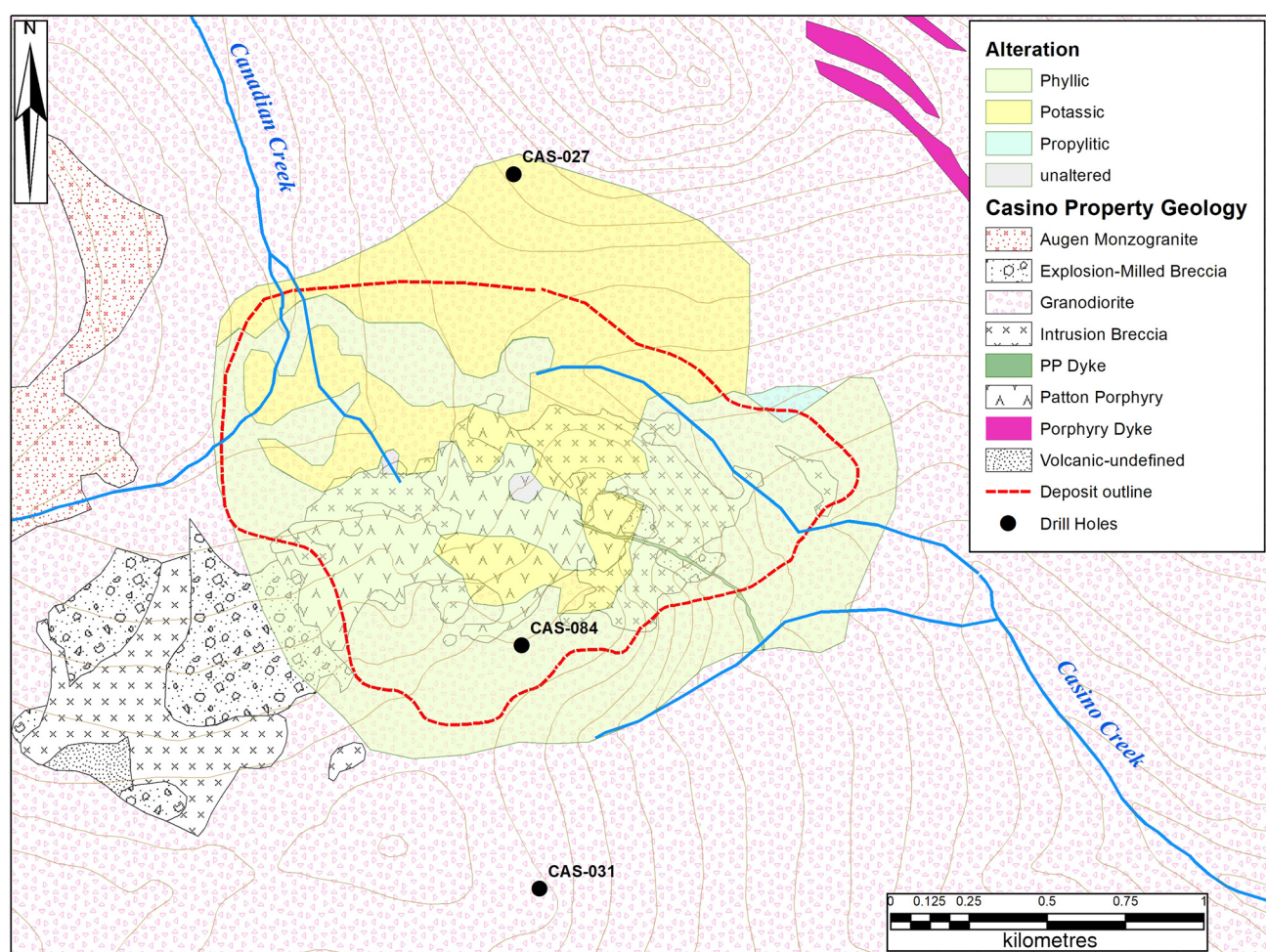


Fig. 3. Detailed bedrock geology and alteration assemblage map of the Casino deposit with surface locations of bedrock drilling core sites (modified from Casselman and Brown 2017).

samples, the 0.25–2.0 mm ferromagnetic fraction of three were selected for further investigation (Table 1).

Two circular 2.5 cm diameter epoxy grain mounts containing between 200 and 203 randomly selected magnetite grains (0.25–2.0 mm) from the ferromagnetic fraction were prepared from six stream sediment samples (see Fig. 2 for geographic locations). Two epoxy grain mounts were also prepared with 603 magnetite grains randomly selected from three disaggregated bedrock samples (18-MPB-004, 18-MYB-001 and 18-MYB-002). Polished thin sections were prepared from the 11 bedrock samples for petrographic studies

(Table 1). Thick sections (80 μ m) were prepared from three bedrock samples (18 MPB 004, 18-MYB-001 and 18 MYB 002).

Analysis

Polished thin sections were microscopically examined under reflected light to assess the abundance, size, and shape of magnetite and other opaque minerals. Magnetite grains were examined for evidence of alteration, exsolution textures, and grain boundary relationships. Under transmitted light, non-opaque minerals were

Table 1. Sample description summary

Sample number	Rock type	Alteration	Magnetite
18-MPB-001	Diorite	Weak potassic	Trace (0.01 g)
18-MPB-002	Granodiorite	Quartz-sericite	Trace (0.01 g)
18-MPB-003	Porphyry	Phyllic	Trace (0.01 g)
18-MPB-004*	Granodiorite	Weak potassic	10.6 g
18-MPB-005	Diorite	Sericite-chlorite (fractures)	(0.3 g)
18-MPB-006	Metasediment	Sericite	Trace (0.01 g)
18-MPB-007	Quartzite	Sericite	Trace (0.01 g)
18-MPB-008	Porphyry	Sericite	Trace (0.01 g)
18-MPB-009	Porphyry	Potassic/phyllic	0.1 g
18-MYB-001*	Quartz monzonite	Weak potassic	0.5 g
18-MYB-002*	Contact breccia	Potassic/phyllic	0.6 g

Sample number, rock type, alteration and amount of magnetite recovered from 11 bedrock samples. From these samples, three were chosen (*) for detailed investigation of magnetite chemistry.

identified and assessed for grain boundary relationships with magnetite and evidence of alteration.

A Field Electron and Ion Company (FEI) Quanta 650 field emission gun-environmental scanning electron microscope coupled with Mineral Liberation Analysis (MLA) software at the Queen's Facility for Isotope Research (QFIR) at Queen's University was used to create high-resolution backscattered electron (BSE) images of 11 thick sections and four epoxy grain mounts of the 0.25 to 2 mm ferromagnetic fraction from bedrock and stream samples. SEM analysis by energy dispersive spectrometry (EDS) was conducted under low vacuum and used to confirm the identification of magnetite made during visual examinations, identify and document mineralogy and mineral associations, and select magnetite grains for follow-up EPMA and LA-ICP-MS analysis. MLA images of three thick sections (18-MPB-004, 18-MYB-001, and 18-MYB-002) and four epoxy grain mounts (2019-1, -2, -3, and -4) were generated to identify iron oxide and selected minerals. The QFIR mineral chemistry library was used to create false-colour mineral maps and determine modal mineralogy (Layton-Matthews *et al.* 2017).

Major element compositions of igneous and magmatic-hydrothermal magnetite were determined by EPMA at the Geological Survey of Canada (GSC), Ottawa, Ontario. A JEOL 8230 EPMA equipped with five wavelength-dispersive spectrometers operated at an accelerating voltage of 20 kV, beam current of 20 nA and a focused spot of 10 µm. Relatively short counting times of 10 seconds on peak and 5 seconds on background, suitable for determining concentrations of major elements (McGee and Keil 2001), were used. Calibration standards were a mix of natural and synthetic minerals. Software used was Probe for EPMA and data were reduced using the method of Armstrong (1988).

Major and trace element abundances in magnetite were acquired by LA-ICP-MS at the GSC using a Photon Machines Analyte G2 laser ablation system, with a HelEx two-volume cell, and an Agilent 7700x quadrupole ICP-MS. Prior to analysis, the instruments were tuned on NIST-612 to achieve >9000 cps ppm⁻¹ 175 Lu (50 µm spot, *c.* 7 J cm⁻² at 10 Hz) and minimizing the production of oxides (<0.25% for ThO/Th) and maintaining a U/Th value of *c.* 1.0. Laser beam sizes of 15 or 25 µm (with a fluence of 4.5 J cm⁻²) were used to ablate nominally inclusion-free regions in the magnetite. The ablation aerosol was carried out of the HelEx cell using 1 L min⁻¹ of helium and mixed (via a Squid device) with *c.* 1 L min⁻¹ of argon prior to entering the ICP-MS. Measurements were conducted in time-resolved analysis mode on the ICP-MS, and data collection for each analysis included 40 s of background measurement (gas-blank) followed by 50 s of ablation and 40 s washout.

Analyses were calibrated using synthetic glass standard GSE-1G from the United States Geological Survey (USGS). Secondary standards consisted of USGS basaltic glass reference material BCR-2G and a matrix-matched magnetite standard from the Bushveld Complex, BC-28 (courtesy of Dany Savard, Université du Québec à Chicoutimi – see Barnes *et al.* 2004). Standards were inserted every 20 analyses for quality control. GLITTER® data reduction software (van Achterbergh *et al.* 2001) was used to inspect, evaluate, and select the best intervals of background and signal measurement for each analysis. Magnetite analyses were calibrated through internal standardization using the 'GeoReM preferred values' (Jochum *et al.* 2005) for elemental abundances in GSE-1G and the stoichiometric Fe content for magnetite (70.8 wt% Fe) as determined by EPMA. Most of the magnetite analyses are within 1–3% of the stoichiometric Fe value, with a maximum difference of *c.* 10%. Detection limits are determined in GLITTER® for each element via Poisson counting statistics, using the following equation:

$$LOD = 2.3\sqrt{2}(\text{gas blank cps})$$

where *LOD* is the limit of detection and *gas blank cps* refers to counts per second in the gas background signal containing zero analyte.

The LOD varies by element. As there is no fixed detection limit for any element in a sequence of analyses (Pettke *et al.* 2012), Table 2 reports minimum, maximum and median values for LOD. In cases where no counts are detected in the background during the interval selected, GLITTER® returns a LOD of zero and these are not used to calculate the median statistic. Repeated analyses of BC-28 and BCR-2G yielded precision and accuracy better than 5% for most elements.

Where possible, up to five ablation sites were selected on larger magnetite grains. Obvious mineral inclusions at the surface were avoided when identifying ablation sites, but heterogeneities in time-resolved spectra, caused by small inclusions intersected at depth by the laser were excluded from the integrated signal to avoid contamination. Where such heterogeneities resulted in >75% of unusable ablation signal, the analysis was discarded. In addition, all values greater than or equal to the 95th percentile for six of the most incompatible elements in magnetite (Si > Ca > Y > P > Pb > Zr) were trimmed from the dataset to reduce the effect of micro- or nano-inclusions intersected by the laser below the grain surfaces.

Statistical methods

LA-ICP-MS data were evaluated using univariate and multivariate statistical methods. Univariate statistics were generated using Microsoft Excel® and *R* for individual elements. Values below detection were set to half the LOD. Box and whisker plots for each element comparing concentrations in the three classes were generated in *R* to graphically compare medians, interquartile ranges and extrema. Values were log-transformed in *R* (Garrett 2018) to reduce effects of skewed data distributions. The Spearman rank method was used to estimate the correlation between pairs of elemental variables from bedrock samples because it is relatively robust against data outliers (Reimann *et al.* 2008). An approach based on the isometric log-ratio (ilr) transformation, resulting in symmetric coordinates (Reimann *et al.* 2017), was employed.

A set of 12 predictor variables selected using box-and-whisker plots and ribbon plots of the group centres of each variable were used to define discriminant functions for classifying magnetite analyses from unknown sources. Effects of data closure were reduced using an isometric logratio (ilr) transformation (Egozcue *et al.* 2003) before carrying out linear discriminant analysis (LDA) using the *lda* function from the MASS package in *R* (Ripley 2021). In order to build a linear discriminant model that includes missing and censored data, values were imputed using the method described by Hron *et al.* (2010) and the *impKNNa* function in the *R* package *robCompositions* (Templ *et al.* 2020; McCurdy 2021). A discrimination diagram prepared using the *R* function *decisionplot*, modified from Hahsler (2021), was used to categorize magnetite from three different sources using the LD1 and LD2 vectors (McCurdy 2021).

To test the LDA function, values were randomly assigned either into the training (75%) or the test (25%) set, and the LDA function developed with the training set used to predict group membership of samples in the test set. A confusion matrix was used to describe the performance of the classification model (or 'classifier') on the set of test data (Lopes 2017; McCurdy 2021).

Results

Petrography

Thin sections (*n* = 11) prepared from bedrock core samples of units hosting the Casino deposit were examined under a petrographic microscope to determine which lithologies contain magnetite grains present in sufficient quantities and sufficient size (>50 µm) for chemical analysis. Three samples (Fig. 4) met these criteria: 18-

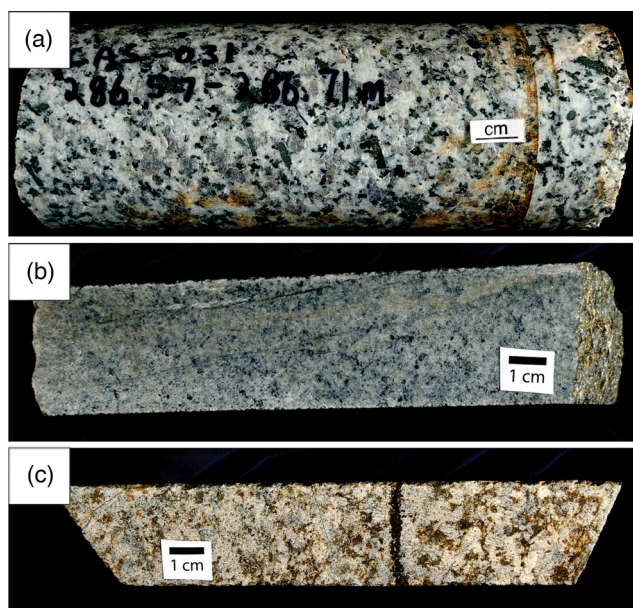


Fig. 4. Hand sample photographs of bedrock core samples from the Casino deposit. (a) Dawson Range suite granodiorite, (b) Casino suite quartz monzonite, (c) Casino suite contact breccia.

MPB-004 (granodiorite), 18-MYB-001 (quartz monzonite), and 18-MYB-002 (contact breccia); all three samples show evidence of hydrothermal alteration (Table 1).

Igneous magnetite in granodiorite (18-MPB-004)

Magnetite forms *c.* 1 vol% subhedral to euhedral individual crystals and larger glomerocrysts intergrown with biotite and hornblende, and, less commonly, potassium feldspar or plagioclase, in a groundmass of moderately sericitized plagioclase and potassium feldspar, quartz, biotite and hornblende. Accessory minerals include pyrite, calcite, and dolomite. Magnetite grains vary between 0.5 and 2 mm, and smaller grains (<0.5 mm) are disseminated throughout the sample. There are two varieties of igneous magnetite: (1) euhedral crystals with rare apatite inclusions within larger biotite and amphibole crystals (Figs 5a and 6c); and (2) subhedral magnetite grains with ragged boundaries hosting apatite, quartz, plagioclase and rare zircon, monazite and rare chalcopyrite inclusions (Figs 5b and 6a, b). Titanite and, less commonly, rutile and W-bearing rutile, have exsolved around the margins of larger magnetite grains (Fig. 6b) due to post-magmatic re-equilibration (Haggerty 1991). Grain boundaries have an eroded/ragged appearance (Fig. 5b). Minor martitization (pseudomorphic replacement of magnetite by hematite) appears as darker coloured patches and follows fractures and grain boundaries (Fig. 5b).

Hydrothermally altered igneous magnetite in quartz monzonite (18-MYB-001)

Magnetite is present as subhedral to euhedral glomerocrysts and individual grains up to 3 mm (Fig. 5c). Fine-grained crystals of magnetite (0.1–0.3 mm) with rims altered to hematite also occur in thin (0.5 mm) calcite–quartz–carbonate veins (Fig. 5d).

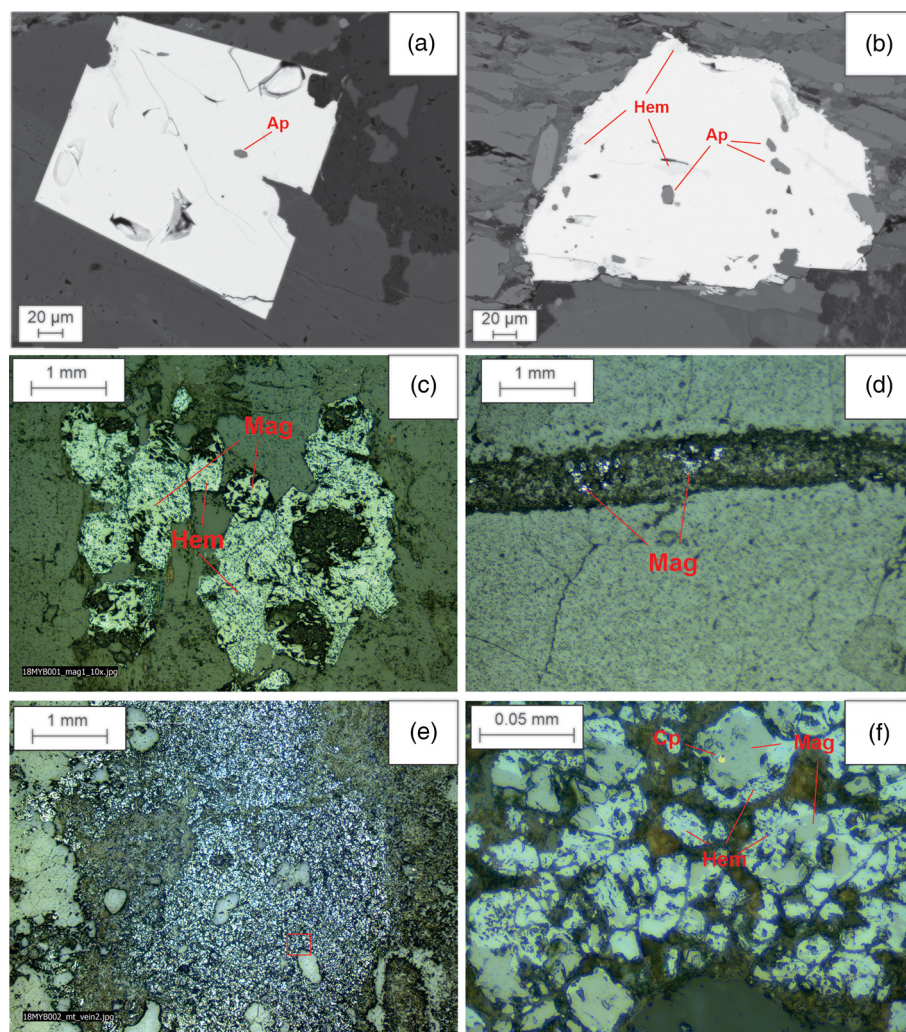


Fig. 5. BSE and reflected light images of magnetite textures in bedrock samples. Mineral abbreviations are after Whitney and Evans (2010). (a) BSE image of euhedral magnetite grain with small apatite inclusion (Ap) (sample 18-MPB-004), (b) BSE image of subhedral magnetite with numerous small apatite inclusions (Ap) and hematite (Hem) alteration along cracks and grain margins (sample 18-MPB-004), (c) subhedral magnetite (Mag) with hematite (Hem) alteration at cracks and grain margins (sample 18-MYB-001), (d) magnetite (Mag) in quartz-calcite stringer (sample 18-MYB-001), (e) vein of magnetite (bluish-grey) in a matrix of sericitized quartz and feldspar (sample 18-MYB-002), (f) Close-up of (e) (red outline) showing magnetite (Mag) with chalcopyrite (Cp) and hematite (Hem) (sample 18-MYB-002).

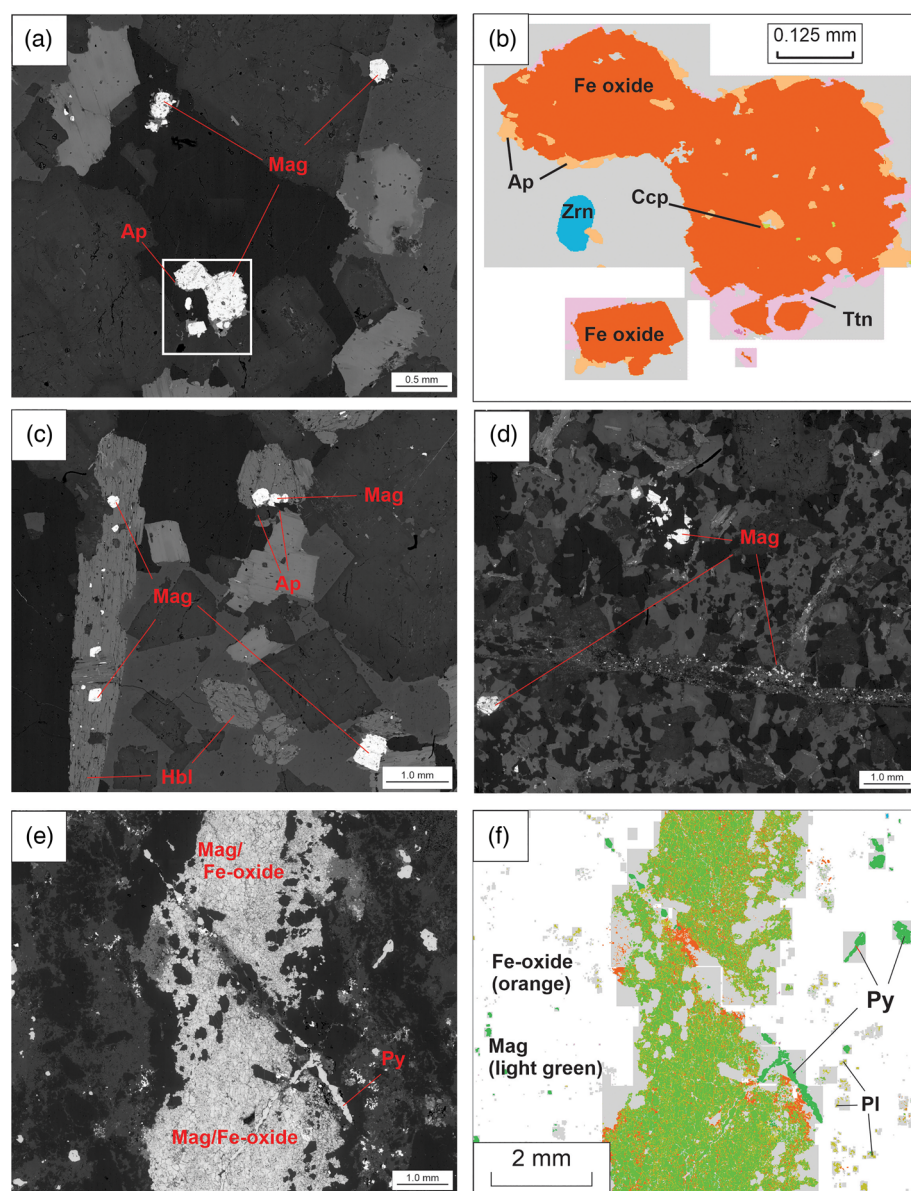


Fig. 6. BSE and SEM-MLA images of magnetite in bedrock core polished sections. (a) Euhedral magnetite (Mag) crystals with sharp boundaries and relatively few apatite (Ap) inclusions, commonly within larger biotite and hornblende crystals (sample 18-MPB-004), (b) false-colour image of the area in (a) outlined by a white square showing an iron oxide grain with apatite (Ap) and chalcopyrite (Ccp) inclusions and titanite (Ttn) exsolution (sample 18-MPB-004), (c) subhedral and euhedral magnetite (Mag) grains in hornblende (Hbl) containing abundant apatite (Ap) inclusions (sample 18-MYB-001), (d) subhedral to euhedral glomerocrysts and individual grains of magnetite (Mag) up to 3 mm along the long axes (sample 18-MYB-001), (e) 2–3 mm-wide veins consisting of small (0.05 mm) aggregated anhedral or subhedral grains (sample 18-MYB-002), (f) false colour image of (e) showing distribution of Fe-oxide and magnetite, pyrite (Py) and plagioclase feldspar (Pl) (sample 18 MYB 002).

Hydrothermal alteration around margins of larger magnetite grains gives them a porous, corroded appearance (Fig. 5c). In reflected light, martitization is prominent as mottling along grain boundaries and fractures. Inclusions are common, consisting mostly of apatite and biotite with lesser quartz and rare zircon. Ilmenite exsolution is present along grain boundaries and fractures within magnetite. Pyrite in veins and as discrete grains constitute 2–3 vol% of the sample, in a groundmass of feldspar, quartz, and fine- to medium-grained hornblende, biotite, chlorite and rare zircon and W-bearing rutile. Calcite-quartz-anhydrite veins bearing magnetite/hematite (Figs 5d and 6d) cross-cut pyrite veins. Larger phenocrysts of plagioclase exhibit incipient white mica alteration, whereas biotite and hornblende are incipiently hydrothermally altered to chlorite.

Magmatic-hydrothermal magnetite in contact breccia (18-MYB-002)

Magnetite, hematite, pyrite, and chalcopyrite in sample 18-MYB-002 comprise 3–5 vol% of the sample. Magnetite is present as 2–3 mm wide veins (Figs 5e and 6e, f) consisting of small (0.05 mm) aggregated anhedral or subhedral grains commonly forming 120° triple junctions, with biotite around grain margins (Fig. 5f).

Magmatic-hydrothermal magnetite has undergone partial or total martitization around grain boundaries and along fractures and is evident as lighter patches relative to darker magnetite (Fig. 5f) under reflected light. Samples of contact breccia are cross-cut by narrow (1 mm) pyrite-carbonate veinlets. Inclusions are mainly biotite, lesser quartz, plagioclase, chalcopyrite, and pyrite, with rare apatite, rutile and zircon. Ilmenite is present as inclusions and exsolution lamellae in magnetite rims. In this sample, potassic alteration has been overprinted by phyllic alteration, and biotite has been altered to chlorite.

LA-ICPMS results

Laser ablation spot analytical data were acquired from two polished thick sections (18-MPB-004 and 18-MYB-002), grains from three disaggregated bedrock samples (18-MPB-004, 18-MYB-001 and 18-MYB-002) and six stream sediment samples mounted in four polished grain mounts (Table 3). Data for multiple ablation sites on individual magnetite grains from stream sediments were averaged into a single value per grain in cases where all analyses were classified into the same group by LDA, but in cases where LDA classified multiple spots on grains into different groups, the data were not averaged. In the five cases where multiple analyses resulted in different LDA classes, the visual appearance of the grains

Table 2. *Detection limits*

Isotope	<i>n</i>	LOD Min (ppm)	LOD Max (ppm)	LOD Med (ppm)	Isotope	<i>n</i>	LOD Min (ppm)	LOD Max (ppm)	LOD Med (ppm)
²⁵ Mg	503	0.399	6.55	1.32	⁹⁰ Zr	368	0.0047	0.227	0.0163
²⁷ Al	503	0.335	3.31	0.729	⁹² Zr	359	0.0069	0.383	0.0261
²⁹ Si	503	45.65	519.78	105.29	⁹³ Nb	314	0.0030	0.0905	0.008
³¹ P	503	7.31	85.69	16.35	⁹⁵ Mo	403	0.0135	0.826	0.0531
³⁹ K	503	1.7	19.37	4.21	¹⁰⁹ Ag	495	0.0038	0.0843	0.0164
⁴² Ca	503	25.42	383.61	67.3	¹¹⁵ In	427	0.0019	0.0583	0.0074
⁴⁵ Sc	503	0.0433	0.689	0.13	¹¹⁸ Sn	503	0.0162	0.273	0.047
⁴⁷ Ti	490	0.102	3.66	0.397	¹²¹ Sb	501	0.0097	0.191	0.0467
⁵¹ V	502	0.0083	0.446	0.04	¹²⁵ Te	471	0.0312	5.34	0.162
⁵³ Cr	503	0.423	4.66	1.17	¹⁷⁸ Hf	348	0.0063	0.133	0.0242
⁵⁵ Mn	503	0.114	1.2	0.279	¹⁸¹ Ta	344	0.0019	0.098	0.0073
⁵⁹ Co	503	0.0115	0.213	0.0449	¹⁸² W	366	0.0073	0.198	0.0299
⁶⁰ Ni	503	0.0888	1.34	0.248	¹⁹⁷ Au	452	0.0030	0.135	0.0186
⁶⁵ Cu	503	0.0661	1.34	0.196	²⁰⁵ Tl	459	0.0018	0.0765	0.0090
⁶⁶ Zn	503	0.175	1.91	0.419	²⁰⁶ Pb	407	0.0103	0.273	0.0386
⁶⁹ Ga	502	0.0056	0.168	0.0269	²⁰⁷ Pb	366	0.0157	0.385	0.0709
⁷³ Ge	503	0.0994	1.62	0.275	²⁰⁸ Pb	368	0.009	0.259	0.0361
⁸⁸ Sr	376	0.0029	0.158	0.0104	²⁰⁹ Bi	465	0.0047	0.157	0.0205
⁸⁹ Y	358	0.0030	0.0501	0.0085	²³⁸ U	387	0.0018	0.0911	0.0082

Detection limits for LA-ICPMS analyses. Min, minimum value; Max, maximum value; Med, median value. When zero counts are detected in the background during the interval selected, GLITTER® will return a LOD of 0. These samples are not included in the statistical calculations for this table, and thus *n* can be <503.

Table 3. *Summary of ablation analyses*

Sample/site number	Grain mount/thick section	Number of grains	Number of grains ablated	Number of analyses	Analyses after trimming
18-MPB-004	2019-4	201	168	182	171
18-MYB-001	2019-3	200	102	113	91
18-MYB-002	2019-3, 2019-4	202	147	185	168
18 MPB 004 TS	Thick Section			47	42
18 MYB 002 TS	Thick Section			63	31
115J 2017 1003	2019-1	201	175	188	148
115J 2017 1004	2019-1	200	159	169	107
115J 2017 1006	2019-1	203	168	185	80
115J 2017 1010	2019-2	201	138	153	123
115J 2017 1015	2019-2	201	99	104	79
115J 2017 1019	2019-2	201	161	188	162

Summary of samples and numbers of grains and analyses from disaggregated ferromagnetic fractions of three bedrock samples, two bedrock thick sections (TS) and ferromagnetic fractions of six stream sediments analysed by laser ablation analysis.

Table 4. *Percentage of values below detection*

Isotope	% Below detection (<i>n</i> = 503)	Isotope	% Below detection	Isotope	% Below detection
²⁵ Mg	0	⁶⁵ Cu	55.67	¹²¹ Sb	31.41
²⁷ Al	0	⁶⁶ Zn	0	¹²⁵ Te	83.10
²⁹ Si	20.08	⁶⁹ Ga	0.20	¹⁷⁸ Hf	67.99
³¹ P	52.27	⁷³ Ge	0	¹⁸¹ Ta	43.94
³⁹ K	47.52	⁸⁸ Sr	18.29	¹⁸² W	38.77
⁴² Ca	52.29	⁸⁹ Y	23.46	¹⁹⁷ Au	85.29
⁴⁵ Sc	14.91	⁹⁰ Zr	38.17	²⁰⁵ Tl	61.63
⁴⁷ Ti	0	⁹² Zr	13.72	²⁰⁶ Pb	26.24
⁵¹ V	0	⁹³ Nb	31.41	²⁰⁷ Pb	30.62
⁵³ Cr	22.66	⁹⁵ Mo	34.79	²⁰⁸ Pb	26.44
⁵⁵ Mn	0	¹⁰⁹ Ag	69.58	²⁰⁹ Bi	59.05
⁵⁹ Co	0	¹¹⁵ In	47.71	²³⁸ U	20.68
⁶⁰ Ni	0	¹¹⁸ Sn	15.51		

Percent of analytical values reported as below detection (all analyses).

suggests that in all but one case, igneous magnetite has been overprinted by hydrothermal alteration. As a result, multiple analyses were included in the statistical analysis for these five grains.

A total of 590 analyses from bedrock samples and 900 analyses from stream samples were completed. To remove (or reduce) the effects of mineral inclusions on statistical results, samples with

Table 5. Sources of magnetite data

Location	Type	Magnetite	Age	Country	Host Rock	Data Source
Island Copper	Cu–Mo–Au porphyry	Magmatic-hydrothermal	165 Ma	Canada (BC)	Calc-alkaline	Canil and Lacourse (2020)
Pine	Cu–Au porphyry	Magmatic-hydrothermal	199 Ma	Canada (BC)	Calc-alkaline	Canil and Lacourse (2020)
Endako	Low-F Mo porphyry	Magmatic-hydrothermal	145–154 Ma	Canada (BC)	Calc-alkaline	Canil and Lacourse (2020)
Copper Mountain	Skarn	Massive	203 Ma	Canada (BC)	Alkaline	Canil and Lacourse (2020)
Mt. Polley	Cu–Au porphyry	Magmatic-hydrothermal	205 Ma	Canada (BC)	Alkaline (monzonite)	Canil and Lacourse (2020)
Argonaut/Iron Hill	Fe skarn	Massive	Jurassic	Canada (BC)	Massive magnetite	Canil <i>et al.</i> (2016)
Port Renfrew	Skarn	Massive	195 Ma	Canada (BC)	Massive magnetite	Canil <i>et al.</i> (2016)
Casino	Cu–Au–Mo porphyry	Igneous	74 Ma	Canada (YT)	Calc-alkaline (granodiorite)	McCurdy (2021)
Casino	Cu–Au–Mo porphyry	Magmatic-hydrothermal	74 Ma	Canada (YT)	Calc-alkaline (contact breccia)	McCurdy (2021)
Casino	Cu–Au–Mo porphyry	Altered igneous	74 Ma	Canada (YT)	Calc-alkaline (quartz monzonite)	McCurdy (2021)
Chuquicamata	Cu–Mo porphyry	Igneous	33 Ma	Chile	Calc-alkaline (granodiorite)	Sievwright (2018)
Elastite	Cu–Au porphyry	Magmatic-hydrothermal	92 Ma	Bulgaria	Calc-alkaline (granodiorite)	Sievwright (2018)
Clayton Peak Stock	Background	Igneous	35 Ma	United States (UT)	Calc-alkaline (diorite)	Sievwright (2018)
Alta Stock	Background	Magmatic-hydrothermal	33 Ma	United States (UT)	Calc-alkaline (granodiorite)	Sievwright (2018)
Lomas Bayas	Cu porphyry	Magmatic-hydrothermal	57.5 Ma	Chile	Calc-alkaline (granodiorite)	Sievwright (2018)
Little Cottonwood Stock	Background	Magmatic-hydrothermal	30 Ma	United States (UT)	Calc-alkaline (granodiorite)	Sievwright (2018)
Spar Lake	Sed.-hosted stratabound Cu	Hydrothermal	1450 Ma	United States (MT)	Quartzite	Nadoll <i>et al.</i> (2012)

Locations, descriptions and sources of magnetite data used to generate Figures 10 and 13.

determinations ≥ 95 th percentile for the 6 least compatible elements in magnetite, $\text{Si} > \text{Ca} > \text{Y} > \text{P} > \text{Pb} > \text{Zr}$, were trimmed (removed) from the dataset, reducing the number of analyses used for statistical analysis to 503 from bedrock samples and 699 from stream sediment samples (Table 3). All analytical results for Mg, Al, Ti, V, Mn, Co, Ni, Zn and Ge in the trimmed dataset of analyses from bedrock samples are above the LOD, and less than 25% of the analytical results are below detection for Si, Sc, Cr, Ga, Sr, Y, Zr, Sn and U. More than 25% of the analyses for all other elements are below detection (Table 4). Copper abundances are below LOD in igneous granodiorite (18-MPB-004) and quartz monzonite (18-MYB-001) but above LOD in magmatic-hydrothermal magnetite in contact breccia (18-MYB-002), whereas Cr values are below LOD in magmatic-hydrothermal magnetite and above detection in igneous samples.

Statistical results

Based on core log descriptions of geology and petrographic observations, bedrock magnetite grains were divided into three lithologic groups: magmatic-hydrothermal (contact breccia), altered igneous (quartz monzonite), and igneous (granodiorite) magnetite. Prior to undertaking LDA, median, minimum and maximum values, and Tukey boxplots for each variable were generated from subsets of the data based on each of the *a priori* groupings. Potentially useful variables include Mg, Al, Ti, V, Mn, Co, Ni, Ga, Ge and Zn. These variables were selected based on significant differences in median values between the three classes of data and $< 10\%$ of values being below the lower limit of detection. In instances where the spread of the central 50% of the data were similar between the three classes, these variables were deemed to not be useful discriminators and were dropped. In addition, Cr and Cu were included despite 23% and 56% of the values, respectively, being below the LOD, because of the unique presence of Cr in igneous magnetite and Cu in magmatic-hydrothermal magnetite (Fig. 7a–d). Missing and censored Cr ($23\% < \text{LOD}$), Cu ($56\% < \text{LOD}$), and Ga ($0.2\% < \text{LOD}$), values were imputed (McCurdy 2021).

A symmetric correlation matrix of Spearman correlation coefficients (Reimann *et al.* 2017) for 12 elements in magmatic-hydrothermal magnetite ($n = 199$; Fig. 8a) was chosen for LDA and shows a very strong positive correlation between Mn and Mg ($r = 0.84$) and Ga and Ni ($r = 0.85$), and a strong positive correlation between Ga and Zn ($r = 0.74$), Ga and Ge ($r = 0.66$), Ge and Ni ($r = 0.69$), Co and Ni ($r = 0.64$) and Co and Ga ($r = 0.64$). A strong negative correlation exists between Cu and Zn ($r = -0.64$). For 12 elements in igneous magnetite ($n = 213$; Fig. 8b), there is a strong positive correlation between Zn and Ga ($r = 0.66$). In altered igneous magnetite ($n = 91$), statistically significant positive correlations are observed between Al and Ti ($r = 0.80$), Co and Mn ($r = 0.84$), Ni and V ($r = 0.70$) and Co and Zn ($r = 0.70$; Fig. 8c). A strong negative correlation exists between Al and Mn ($r = -0.66$) and Mg and Zn ($r = -0.60$). With the exception of the strong negative correlation between Cu and Zn in magmatic-hydrothermal magnetite, neither Cu nor Cr exhibit significant correlations with the other elements.

The relative importance of each variable can be visualized in a ribbon plot (Reimann *et al.* 2008; Fig. 9) where the variables are plotted along the x-axis, and the group average for each respective variable on the y-axis. Variables are centred and scaled. Variables with high or low group means are relevant for distinguishing the three groups. Magmatic-hydrothermal magnetite is characterized by relatively high group means for Mg, Al, Ti and Mn, and relatively low means for Cr, Co, Cu and Ge. Igneous and altered igneous magnetite show similar behaviour; however, the group means for Cr, Mn and Co in altered igneous magnetite are relatively lower, and that of Ti is relatively higher in altered igneous magnetite (Fig. 9).

Table 6. *Magnetite in stream sediments*

Sample number	Magmatic-hydrothermal (LDA)	LDA and Ti v. Ni/Cr	Igneous (LDA)	Altered igneous (LDA)	Total igneous (LDA + Dare)	Total
1003	6 (4.2%)	3 (2.1%)	43	94	140 (97.9%)	143
1004	12 (11.7%)	3 (2.9%)	33	58	100 (97.1%)	103
1006*	5 (6.3%)	1 (0.0%)	52	22	78 (98.7%)	79
1010 [†]	8 (7.0%)	6 (5.2%)	98	9	109 (94.8%)	115
1015	12 (15.8%)	7 (9.2%)	61	3	69 (90.8%)	76
1019	50 (34.7%)	41 (28.5%)	66	28	103 (71.5%)	144
Total	93 (14.1%)	61 (9.2%)	353 (53.5%)	214 (32.4%)	599 (90.9%)	660

Numbers and percentages of magmatic-hydrothermal, igneous and altered igneous magnetite grains identified in six stream sediment samples, identified by linear discriminant analysis (LDA) and a combination of LDA and classification on a Ti v. Ni/Cr diagram.

*One glomerocrystic grain LDA-classified as igneous plots in the Dare diagram magmatic-hydrothermal field, lacks exsolution textures and apatite inclusions, and was classified as magmatic-hydrothermal.

[†]Two grains have Ti > 10 000 ppm, have exsolution textures and apatite inclusions and were classified as of igneous origin based on visual observation.

Zinc, close to zero for all groups, likely does not contribute useful information for discrimination.

Comparisons with different deposit types

Box and whisker plots compare the range in abundances of Ti, V, Al and Mn (Fig. 10a–d) in magnetite from different bedrock sources (Table 5). Illustrated are magmatic-hydrothermal magnetite from three skarns, one Cu-Au porphyry deposit hosted in alkaline rocks (Mt. Polley, B.C.), five calc-alkaline porphyry deposits located in the Canadian Cordillera, including Casino, igneous magnetite from the Casino deposit and Clayton Peak stock (Utah), magmatic-hydrothermal magnetite (based on Ti content) from the Chuquicamata (Chile) and Elatsite (Bulgaria) deposits and hydrothermal magnetite from the Spar Lake (Montana) sediment-hosted stratabound Cu deposit. Titanium, Al and Mn are generally higher in magmatic-hydrothermal magnetite samples from porphyry deposits in the Canadian Cordillera. Magmatic-hydrothermal magnetite from skarn is relatively low in Ti and V, except for Copper Mountain, and

hydrothermal magnetite from the Spar Lake sediment-hosted Cu deposit is relatively low in Al and Mn. The relationship between Ti and V is illustrated in Figure 10e, with relatively high Ti/V values in magmatic-hydrothermal samples from the Canadian Cordillera (except for Copper Mountain and Endako) compared with other magnetite sources. Relatively low Ti + V/Al + Mn ratios (>0.1 and <1) shown in Figure 10f characterize magmatic-hydrothermal sources from British Columbia and the Casino deposit, but higher ratios (>1) are seen in both Casino igneous samples and high-Ti magmatic-hydrothermal magnetite from the Chuquicamata, Elatsite and Clayton Peak Stock deposit locations. Magmatic-hydrothermal magnetite from skarn deposits (except Copper Mountain) is significantly lower (<0.01) than magnetite from other sources.

Ti v. Ni/Cr diagrams compared with LDA

A plot of Ti v. Ni/Cr can be used to discriminate between magnetite from magmatic-hydrothermal environments and igneous magnetite from felsic host rocks (such as I-type granites), which otherwise have

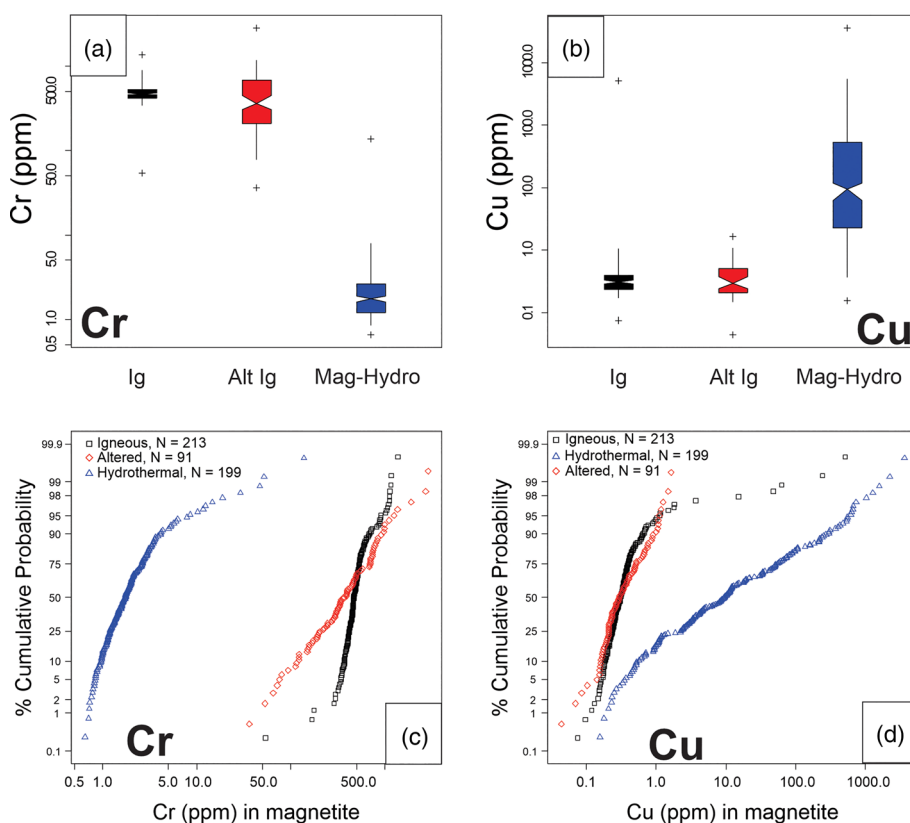


Fig. 7. Boxplots for Cr (a) and Cu (b) in igneous ('Ig'; black), altered igneous ('Alt Ig'; red), and magmatic-hydrothermal ('Mag-hydro'; blue) magnetite; (c) cumulative probability plot of Cr (c) and Cu (d), plotting igneous (black), altered igneous (red) and magmatic-hydrothermal values.

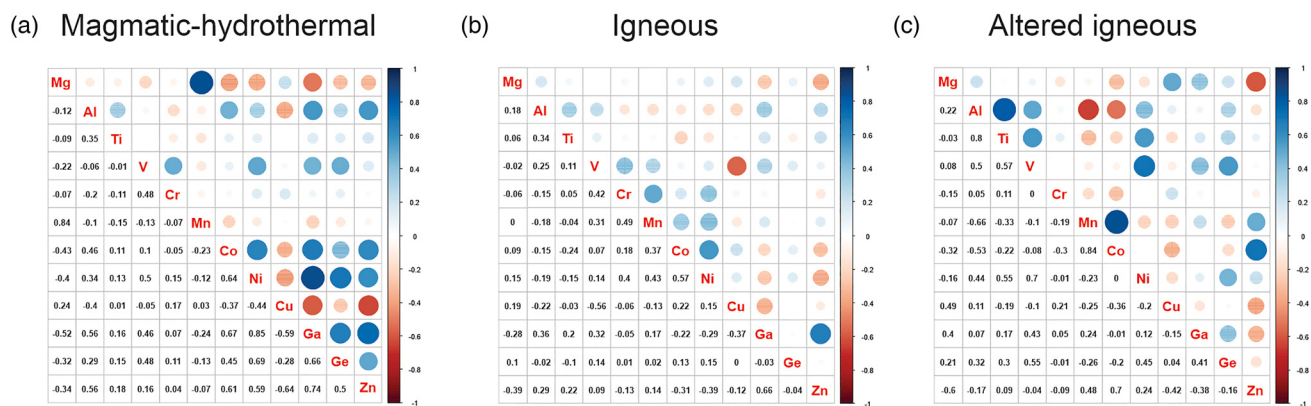


Fig. 8. Symmetric Spearman's rank correlation matrices for (a) magmatic-hydrothermal, (b) igneous, and (c) altered igneous elemental concentrations of 12 elements used for linear discriminant analysis.

similar trace element signatures (Dare *et al.* 2014). In silicate magmas, Ni/Cr values are ≤ 1 . However, in many magmatic-hydrothermal environments Ni/Cr values are typically ≥ 1 . To evaluate the efficacy of two different methods for separating magmatic-hydrothermal from igneous magnetite, a plot of Ti v. Ni/Cr was prepared using the same data used for the LDA (Fig. 11b). Both the LDA model and the Ti v. Ni/Cr plot of Dare *et al.* (2014) correctly classified over 99% of the igneous and magmatic-hydrothermal magnetite grains (Fig. 11a, b).

The R package mixtools (Benaglia *et al.* 2009) contains the function 'ellipse' that was used to plot ellipses on the diagrams from the means of x and y and their covariance matrix (function cov in R), which captures the shape and spread of their interrelationship. The function generates a specified number of points that define the default ellipse ($\alpha = 0.05$) to theoretically include 95% of the data. In addition, because Figure 11b is a log-log plot, the means and covariance of the $\log_{10}$ data are required.

Magnetite in stream sediments

Magnetite grains from six stream sediment sites were classified as igneous, hydrothermally altered igneous or magmatic-hydrothermal

using a linear discriminant model (Fig. 12a–f). Results in Table 6 illustrate that except for sample 1019 (Canadian Creek; Fig. 12f), the percentage of magmatic-hydrothermal magnetite grains in sediment samples do not exceed 16%. Plotting LDA-classified samples on a Ti v. Ni/Cr plot reduces these percentages further, so that except for sample 1019, <10% of the magnetite grains in stream sediment samples are classified as magmatic-hydrothermal. Subfields within the magmatic-hydrothermal discrimination field of Dare *et al.* (2014), hereafter referred to as the Dare diagram, are defined by ellipses (dashed lines) enclosing spaces representing 95% of the LDA-classified points from each of three Casino bedrock samples used to build the LDA model.

Six magnetite grains in sample 1003, from an unnamed creek draining Mt. Cockfield and the Cockfield porphyry Cu-Mo-Au occurrence (Yukon Geological Survey 2021a, b; Fig. 2), were LDA-classified as magmatic-hydrothermal (Fig. 12a). However, only three of these magnetite grains plot in the magmatic-hydrothermal discrimination field of the Dare diagram. Apatite inclusions and exsolution textures are absent in these grains and they are glomerocrystic. One grain analysis plots within and two grains, all with detectable Cu, plot just outside the Casino magmatic-hydrothermal subfield. Titanium exceeds 20 000 ppm in two of these grains.

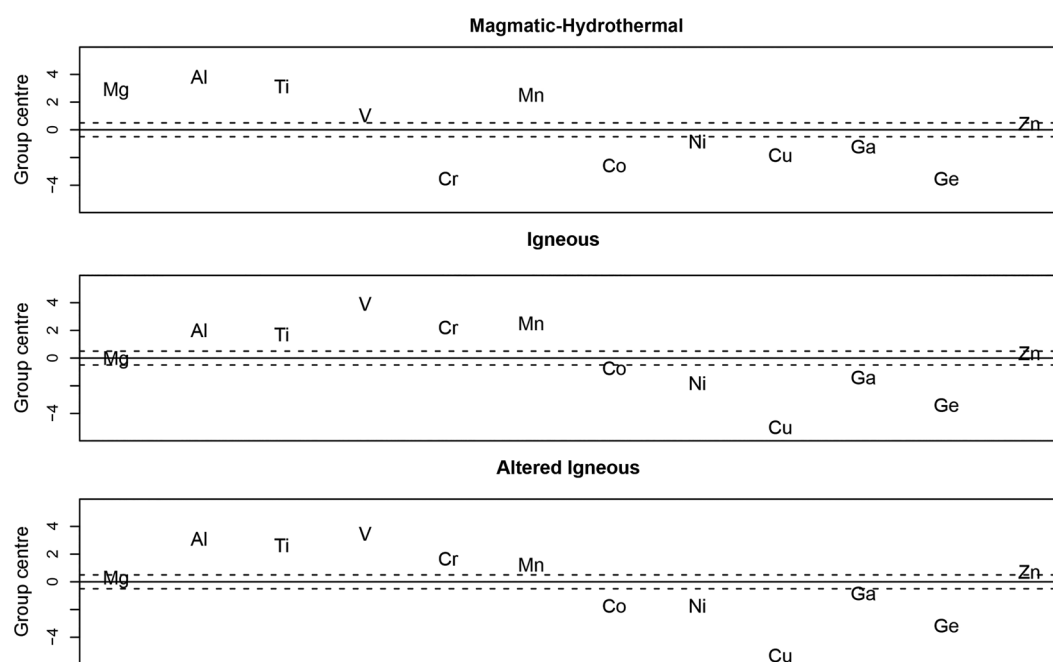


Fig. 9. Ribbon plots showing the group centres of each variable following the completion of a linear discrimination analysis with missing values of Cr and Cu replaced by imputed values.

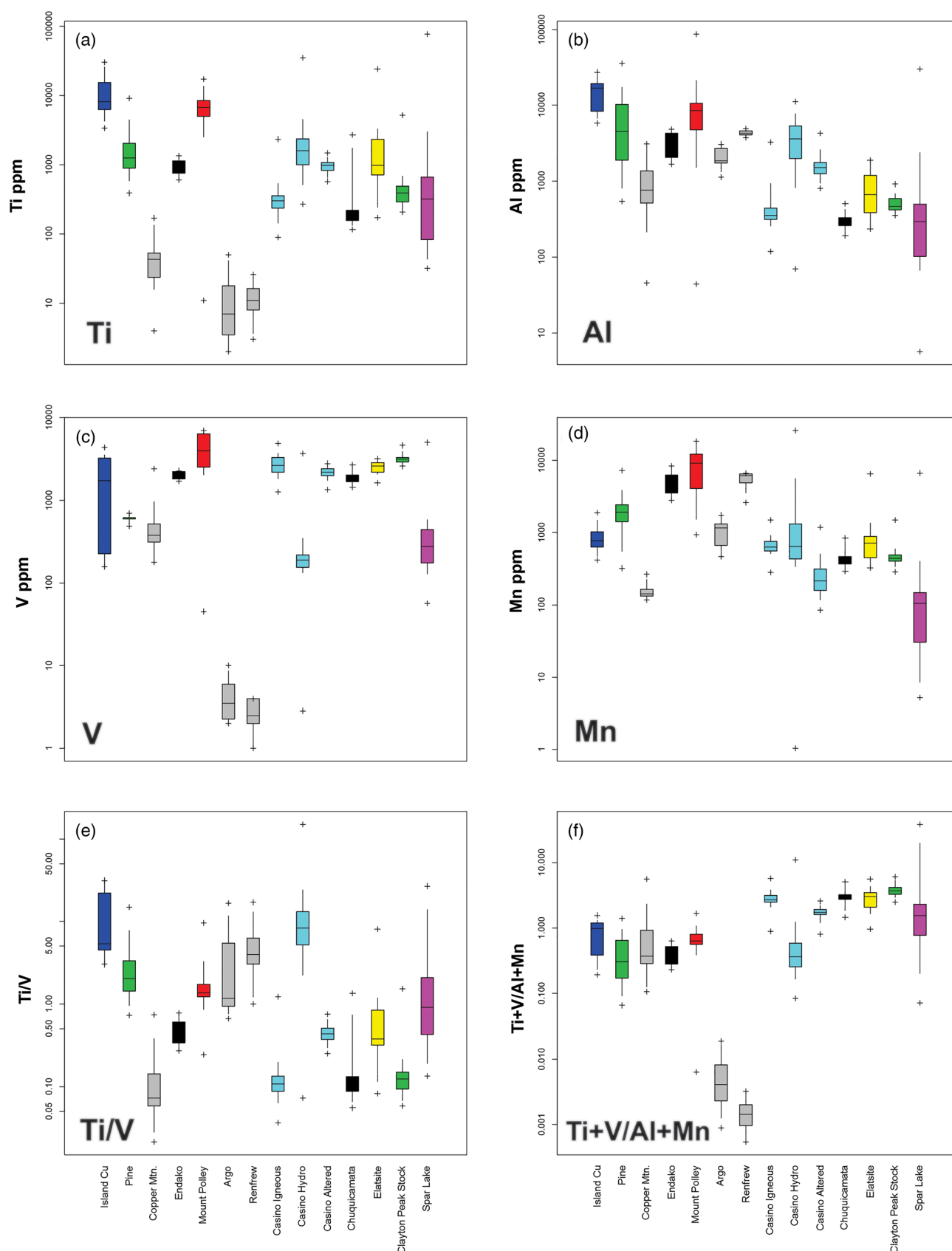


Fig. 10. Boxplots for Ti, Al, V, and Mn and Ti/V and $(\text{Ti} + \text{V})/(\text{Al} + \text{Mn})$ ratios for igneous and magmatic-hydrothermal magnetite from 12 deposit locations. Element ratios are used to compare multiple data sets. See Table 5 for data sources.

Twelve grains are classified as magmatic-hydrothermal by LDA in stream sample 1004 (Hayes Creek; Figs 2 and 12b). However, only three of these plot in the magmatic-hydrothermal field of the

Dare diagram and none are within the Casino magmatic-hydrothermal subfield. Apatite inclusions and exsolution textures are not apparent in these grains, however Cr abundances are

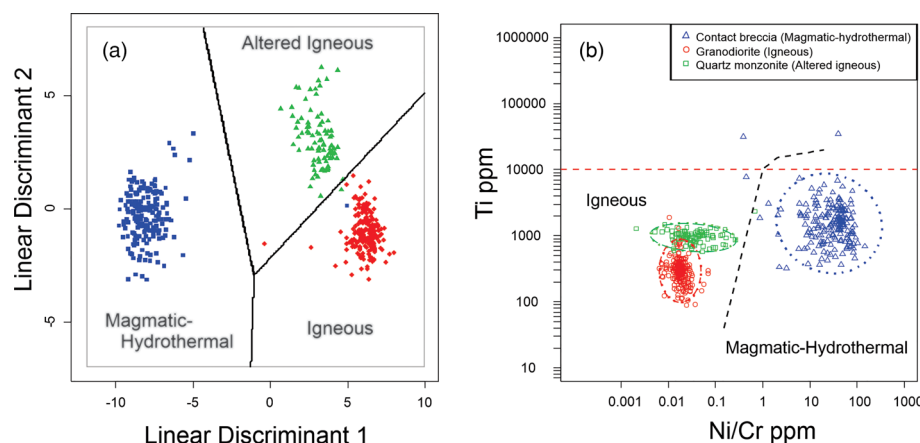


Fig. 11. (a) Territorial plot using the first (LD1) and second (LD2) linear discriminants to categorize magnetite sources based on variable levels of 12 elements in igneous, altered igneous, and magmatic-hydrothermal magnetite. Decision boundaries show group memberships for three magnetite sources estimated using element variables, including imputed values for Cr and Cu, (b) plot of Ti v. Ni/Cr plots (modified after Dare *et al.* 2014) with point attributes assigned by LDA classification. The LDA classification of the magnetite is reflected by the symbols representing igneous (red circles), altered igneous (green squares), and magmatic-hydrothermal (blue triangles). Ellipses enclose 95% of the data for each source. Three hydrothermal-magmatic grains with Ti >10 000 ppm are misclassified.

>200 ppm in all but one grain. In three grains, Ti values are >80 000 ppm.

Five grains are classified as magmatic-hydrothermal by LDA in stream sample 1006 (Colorado Creek; Figs 2 and 12c). All five grains plot in the igneous field of the Dare diagram; all exhibit trellis textures and two contain apatite inclusions. Titanium abundances range between 7 and 10 wt%. One grain classified by LDA as igneous magnetite plots in the magmatic-hydrothermal field, and the glomerocrystic appearance and absence of apatite inclusions and exsolution do not rule out a magmatic-hydrothermal source.

Eight grains are classified as magmatic-hydrothermal in stream sample 1010 from Casino Creek (Figs 2 and 12d). Two of these grains plot above the dashed red line marking 10 000 ppm Ti on the y-axis of the Dare diagram. These two grains have apatite inclusions and exsolution textures.

Eleven magnetite grains are classified by LDA as magmatic-hydrothermal in stream sample 1015 from Excelsior Creek (Figs 2 and 12e). One grain plots just within the Casino magmatic-hydrothermal subfield and has a glomerocrystic texture and lack of apatite inclusions characteristic of magmatic-hydrothermal magnetite from the Casino deposit; however, Cu is <LOD. Six grains plot outside the Casino magmatic-hydrothermal subfield but within the magmatic-hydrothermal field of the Dare diagram. Three of the four grains are classified by LDA as magmatic-hydrothermal but plot in the igneous field of the Dare diagram, do not have apatite inclusions but contain >10 000 ppm Cr.

Fifty grains (35%) were classified by LDA as magmatic-hydrothermal in stream sample 1019 from Canadian Creek (Figs 2 and 12f). Most of these grains (41) plot within or at the margin of the Casino magmatic-hydrothermal subfield of the Dare diagram, have glomerocrystic textures characteristic of magmatic-hydrothermal magnetite from the Casino deposit, and do not have apatite inclusions or exsolution textures.

Two samples, 1003 and 1004 (Fig. 12a, b) show a wide range of Ti contents, with many grains exceeding 10 000 ppm. Most of the grains in these two samples are LDA-classified as altered igneous (Table 6). The remaining four sediment samples (1006, 1010, 1015, and 1019) reflect a mainly igneous input, with most of the grains plotting in the Casino igneous (granodiorite) subfield. The relationship of LDA-classified altered igneous grains in stream sediments to the Casino altered igneous subfield is ambiguous, with no apparent relationship in samples 1004 and 1015 (Fig. 12b, e), a few grains in 1010 and 1019 (Fig. 12d, f), a grouping within the Casino altered igneous subfield in 1006 (Fig. 12c) and two clusters,

a high Ti (>10 000 ppm) and a low (<10 000 ppm) in sample 1003 (Fig. 12a).

Discussion

Factors affecting the composition of Casino magnetite

We examined textural and compositional characteristics of individual grains of magnetite in one hand specimen from each of three different bedrock types from the Casino deposit to identify magnetite from these sources in stream sediments. Except for V, Cr, and Co, concentrations of the remaining elements used for characterization (Mg, Al, Ti, Mn, Ni, Cu, Ga, Ge and Zn) are higher in magmatic-hydrothermal magnetite than in igneous magnetite. Parameters influencing element abundances in igneous magnetite include matrix (melt/fluid) composition, temperature, cooling rate, pressure, oxygen fugacity, sulfur fugacity, and silica activity (Buddington and Lindsley 1964; Frost and Lindsley 1991; Ghiorso and Sack 1991; Haggerty 1991; Toplis and Carroll 1995). These also apply to lower temperature magmatic hydrothermal conditions (Nadoll *et al.* 2014) and are assumed to have affected the compositions of igneous and magmatic-hydrothermal magnetite from the Casino deposit.

Igneous and magmatic-hydrothermal magnetite from the Casino deposit have distinctive textures characteristic of each source. Samples of igneous magnetite from relatively unaltered granodiorite (Fig. 5a, b) and partially altered quartz monzonite contain euhedral to subhedral apatite inclusions within or at the margins of magnetite grains; apatite inclusions are common in magnetite from igneous sources (Piccoli and Candela 2002; Mao *et al.* 2016; Pisiak *et al.* 2017). The low solubility of P₂O₅ in silicate melts (Watson 1980) from which the two rock types formed results in early apatite crystallization that preceded magnetite formation (Piccoli and Candela 2002; Mao *et al.* 2016). Trellis textures were not observed in magnetite from either igneous sample. These observations, supported by median Ti contents of magnetite (Table 7), suggest that both the Casino granodiorite (median Ti = 299 ppm) and quartz monzonite (median Ti = 975 ppm) crystallized from a relatively low-Ti magma (cf. Nadoll *et al.* 2014; Pisiak *et al.* 2017; Huang *et al.* 2019).

The texture of sub-solidus (<600°C) magmatic-hydrothermal magnetite from the potassic alteration zone is a distinctive pattern of recrystallized <0.05 mm magnetite grains with 120° triple junctions bordered by biotite (Fig. 5f) similar to that described by Canil *et al.*

Table 7. Summary statistics

Isotope	Granodiorite (igneous) <i>N</i> = 213			Quartz monzonite (altered igneous) <i>N</i> = 91			Contact breccia (hydrothermal) <i>N</i> = 199		
	Min	Max	Med	Min	Max	Med	Min	Max	Med
²⁵ Mg	14.21	527.79	40.76	19.89	502.3	69.57	17.04	62 689.54	862.64
²⁷ Al	119.02	3246.41	353.38	807.93	4304.98	1525.19	69.88	11 133.16	3589.98
²⁹ Si	bd	2838.83	114.84	bd	7116.83	198.06	bd	14 493.35	6371.64
³¹ P	bd	363.38	bd	bd	120.84	bd	bd	315.13	117.73
³⁹ K	bd	42.69	bd	bd	178.55	bd	bd	5305.10	232.68
⁴² Ca	bd	1764.89	bd	bd	9234.9	bd	bd	8212.08	418.3
⁴⁵ Sc	bd	13.67	0.18	1.12	8.94	3.4	bd	9.69	3.16
⁴⁷ Ti	88.71	2333.64	298.84	573.65	1482.31	975.05	270.14	34 684.03	1600.99
⁵¹ V	1260.79	4862.77	2630.19	1345.42	2792.03	2186.9	2.84	3693.89	188.8
⁵³ Cr	53.87	1370.68	466.95	36.24	2870.84	364.14	bd	137.63	bd
⁵⁵ Mn	279.72	1491.93	630.33	83.98	1185.84	215.93	1.04	25 945.49	645.21
⁵⁹ Co	17.32	142.43	23.67	1.24	28.26	13.13	1.40	5150.60	5.19
⁶⁰ Ni	6.01	36.58	8.59	6.01	16.21	11.92	9.43	61.75	28.41
⁶⁵ Cu	bd	510.7	bd	bd	1.48	bd	bd	3630.59	8.62
⁶⁶ Zn	35.04	544.74	68.21	27.69	459.28	175.42	1.15	558.11	87.39
⁶⁹ Ga	2.58	42.82	13.06	7.29	87.88	32.21	bd	39.55	19.44
⁷³ Ge	0.61	4.75	1.75	1.15	7.76	2.82	0.51	5.73	1.96
⁸⁸ Sr	bd	3.99	0.013	bd	129.53	0.10	bd	55.11	1.33
⁸⁹ Y	bd	0.80	0.01	bd	4.03	0.03	bd	11.47	1.68
⁹⁰ Zr	bd	2.93	bd	bd	8.25	0.03	bd	5.62	0.19
⁹² Zr	bd	2.59	0.05	bd	5.98	0.08	bd	4.02	0.22
⁹³ Nb	bd	3.29	0	bd	4.67	0.05	bd	8.59	0.12
⁹⁵ Mo	bd	236.05	0.04	bd	0.65	0.079	bd	5.86	0.13
¹⁰⁹ Ag	bd	1.46	bd	bd	0.30	bd	bd	1.886	bd
¹¹⁵ In	bd	0.35	bd	bd	0.09	0.01	bd	0.13	0.01
¹¹⁸ Sn	bd	2.45	0.06	0.25	4.46	0.95	0.10	15.86	0.73
¹²¹ Sb	bd	2.11	bd	bd	20.78	0.10	bd	42.38	2.39
¹²⁵ Te	bd	0.49	bd	bd	0.58	bd	bd	2.01	bd
¹⁷⁸ Hf	bd	0.26	bd	bd	0.17	0	bd	0.47	0
¹⁸¹ Ta	bd	0.5	bd	bd	0.12	0	bd	0.83	0.0586
¹⁸² W	bd	1.06	bd	bd	0.65	0.01	bd	1298.69	26.97
¹⁹⁷ Au	bd	0.12	bd	bd	0.04	bd	bd	0.261	bd
²⁰⁵ Tl	bd	1.98	bd	bd	0.06	bd	bd	0.675	0.01
²⁰⁶ Pb	bd	17.44	0.01	bd	16.03	0.08	bd	27.85	1.11
²⁰⁷ Pb	bd	15.32	0	bd	16.57	0.09	bd	27.42	1.05
²⁰⁸ Pb	bd	79.57	0.02	bd	17.68	0.07	bd	27.29	1.05
²⁰⁹ Bi	bd	5.39	bd	bd	0.14	bd	bd	2.25	0.03
²³⁸ U	bd	3.57	0.01	bd	3.75	0.05	0.002	38.62	2.14

Summary statistics for igneous, altered igneous and hydrothermal magnetite based on LA-ICP-MS analyses from two polished thick sections and three disaggregated bedrock samples from the Casino deposit. Min, minimum value; Max, maximum value; Med, median value; bd, below detection.

(2016); Sievwright (2018), and Huang *et al.* (2019). This recrystallization texture is distinctive to the magmatic-hydrothermal magnetite in the Casino bedrock sample from the potassic alteration zone and readily recognized in samples of magnetite recovered from streams draining the deposit, which were classified as magmatic-hydrothermal by LDA.

Magnetite in Casino bedrock samples from the two igneous sources have lower Ti and Al abundances than those in the magmatic hydrothermal source (Fig. 10a, b). This is contrary to the observations of other studies, who ascribe their results to higher temperatures of formation for igneous magnetite (Dupuis and Beaudoin 2011; Dare *et al.* 2014; Nadoll *et al.* 2014; Canil *et al.* 2016; Pisiak *et al.* 2017). However, Nadoll *et al.* (2014) suggested that it is important to consider the evolution of the host rock because sub-solidus re-equilibration during cooling of plutonic rocks can deplete minor and trace elements, including Ti. Additionally, under specific conditions of T - fO_2 - fS_2 , minor and trace elements can partition into sulfide and silicate minerals, reducing minor and trace elements in magnetite (Nadoll *et al.* 2014).

Compared with magnetite from other sources, igneous magnetite associated with the Casino deposit has several unique features that include Mg, Al, Ti, Cr, Co, Ni, Zn and Ga median values up to an order of magnitude lower than the median contents reported elsewhere (Table 8; Nadoll *et al.* 2014). This is partly because the statistics for igneous magnetite reported by Nadoll *et al.* (2014) include high-Ti mafic igneous samples as well as magnetite from intermediate and felsic igneous sources. However, sub-solidus re-equilibration of felsic plutonic rocks during cooling results in low-Ti magnetite that is also depleted in Mg and Al (Grigsby 1990; Frost and Lindsley 1991). Magnetite in felsic igneous rocks can approach end member Fe_3O_4 due to extensive sub-solidus re-equilibration (Frost and Lindsley 1991). This process likely influenced magnetite compositions in felsic plutonic rocks associated with the Casino deposit. We conclude that values of Mg, Ti and Al, and possibly other elements, that are relatively low in Casino igneous magnetite samples compared with the Casino magmatic-hydrothermal magnetite sample are the result of sub-solidus re-equilibration and element partitioning within rocks associated with the Casino

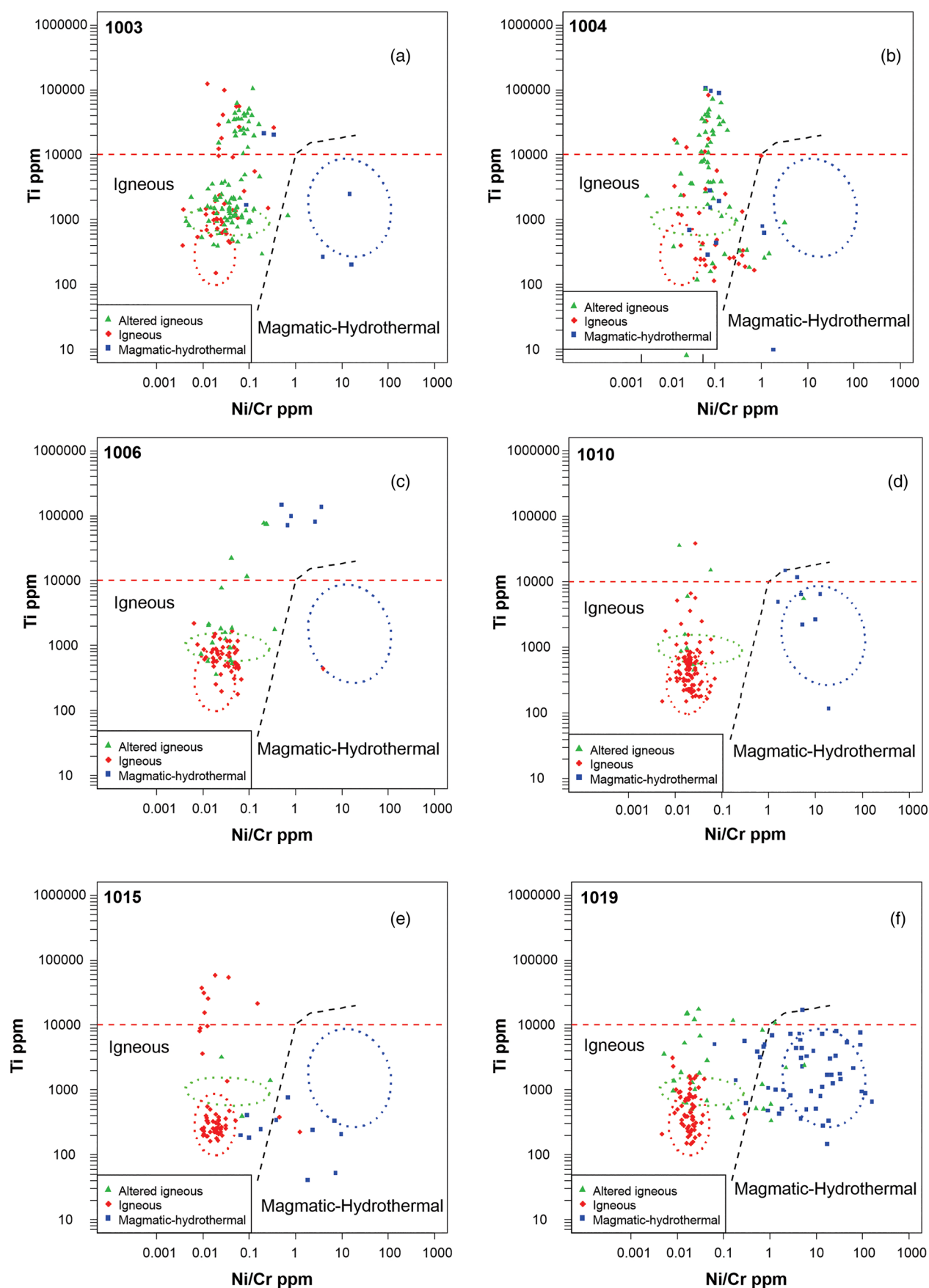


Fig. 12. Ti v. Ni/Cr discriminant plots for magnetite recovered from six streams in the study area. Plots identify various magnetite types in stream sediments: igneous magnetite in granodiorite (red) and quartz monzonite (green), and magmatic-hydrothermal magnetite in contact breccia (blue) (modified from *Dare et al. 2014*). Point attributes (colour and shape) are based on LDA classifications.

Table 8. Summary statistics

Porphyry-igneous (Nadoll <i>et al.</i> 2014)					Casino Cu porphyry-igneous				
Element	<i>n</i>	Min	Max	Med	Element	No.	Min	Max	Med
Mg, ppm	65	103	3940	478	Mg	213	14.21	527.79	40.76
Al, ppm	75	459	9720	2260	Al	213	119.02	3246.41	353.38
Ti, ppm	94	191	97 800	1650	Ti	213	88.71	2333.64	298.84
V, ppm	96	367	6660	1970	V	213	1260.79	4862.77	2630.19
Cr, ppm	14	194	3290	544	Cr	213	53.87	1370.68	466.95
Mn, ppm	99	115	10 500	464	Mn	213	279.72	1491.93	630.33
Co, ppm	62	4.95	131	45.6	Co	213	17.32	142.43	23.67
Ni, ppm	28	21.7	448	77.8	Ni	213	6.01	36.58	8.59
Zn, ppm	54	48	2430	456	Zn	213	35.04	544.74	68.21
Ga, ppm	72	15.1	108	59.4	Ga	213	2.58	42.82	13.06
Sn, ppm	10	2.3	67.6	7.78	Sn	213	bd	2.45	0.06

Porphyry-hydrothermal (Nadoll <i>et al.</i> 2014)					Casino Cu Porphyry - Magmatic-Hydrothermal				
Element	<i>n</i>	Min	Max	Med	Element	No.	Min	Max	Med
Mg, ppm	583	110	32 200	840	Mg	199	17.04	62 689.54	862.64
Al, ppm	750	384	15 900	2300	Al	199	69.88	11 133.16	3589.98
Ti, ppm	733	176	37 900	1930	Ti	199	270.14	7685.05	1600.99
V, ppm	715	57.8	18 200	1470	V	199	2.84	34 684.03	188.80
Cr, ppm	78	270	2240	370	Cr	199	bd	137.63	bd
Mn, ppm	748	77.2	19 300	1000	Mn	199	1.04	25 945.49	645.21
Co, ppm	143	8.47	760	380	Co	199	1.40	5150.60	5.19
Ni, ppm	183	15.9	1090	400	Ni	199	9.43	61.75	28.41
Zn, ppm	563	20.1	6210	530	Zn	199	1.15	558.11	87.39
Ga, ppm	86	12.9	151	47.7	Ga	199	bd	39.55	19.44
Sn, ppm	14	2.53	70.1	7.78	Sn	199	0.10	15.86	0.73

Summary statistics comparing selected igneous magnetite analyses reported by Nadoll *et al.* (2014) and igneous magnetite from the Casino deposit. Med, median value.

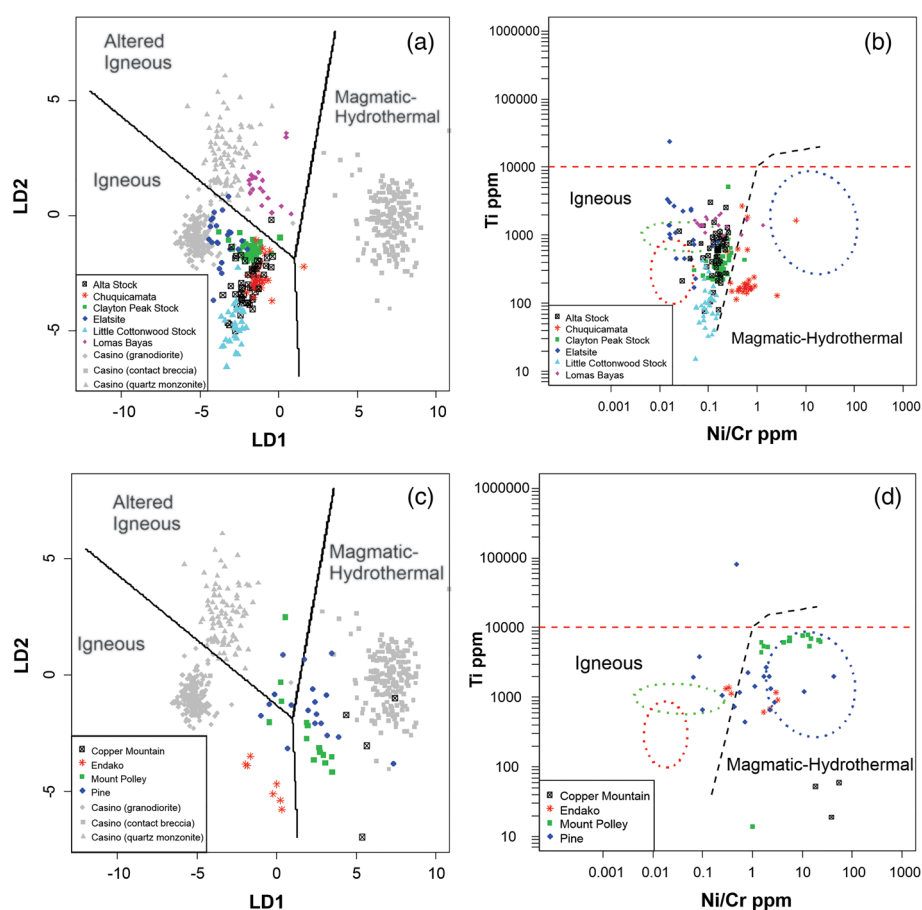


Fig. 13. LDA territorial plots (a), (c) and Ti v. Ni/Cr plots (b), (d) comparing magnetite data from four porphyry deposits in British Columbia (a, b) and six locations from Utah, Chile and Bulgaria (c), (d). See Table 5 for additional location information. In (a) and (c), Casino results can be seen as light grey symbols, and in (b) and (d) as ellipses include 95% of the data for each Casino igneous magnetite type.

deposit. Applying the geothermometer of Canil and Lacourse (2020) to our Casino data results in an average igneous magnetite crystallization temperature of 610°C, a relatively low temperature that suggests slow cooling and ample time for re-equilibration (Wen *et al.* 2017).

Ranges of individual element compositions within a single sample of magmatic-hydrothermal magnetite from the Casino deposit can vary by several orders of magnitude, such as Ti and V (Table 7; Fig. 10). Short growth histories, low temperatures and multiple fluid input and precipitation events could explain much of the heterogeneity for the trace elements in magmatic-hydrothermal magnetite (Canil *et al.* 2016). A crystallization temperature of 340°C determined for this group of magnetite, as determined using the Canil and Lacourse (2020) geothermometer, is consistent with subsolidus conditions and supports a magmatic-hydrothermal origin.

Comparing methods for classifying igneous and magmatic-hydrothermal magnetite

A number of authors have proposed ways to differentiate between igneous and magmatic-hydrothermal magnetite (Dare *et al.* 2014; Nadoll *et al.* 2014, 2015; Knipping *et al.* 2015; Canil *et al.* 2016; Pisiak *et al.* 2017; Wen *et al.* 2017; Sievwright 2018; Huang *et al.* 2019). Dare *et al.* (2014) used Ni/Cr values to distinguish magmatic-hydrothermal from igneous magnetite, noting that in many environments Ni/Cr is typically ≥ 1 . Dare *et al.* (2014) attributed this to the higher solubility of Ni compared to Cr in fluids. Plotting Casino samples on the Ti v. Ni/Cr diagram indicates that Ni/Cr values successfully discriminate between Casino magmatic-hydrothermal and igneous magnetite (Fig. 11a, b). However, Knipping *et al.* (2015) and Huang *et al.* (2019) reported that Ti v. Ni/Cr diagrams were not very useful for discriminating between magmatic-hydrothermal and igneous magnetite, noting that low Cr (high Ni/Cr) is not necessarily an indicator of magmatic-hydrothermal origin. Canil and Lacourse (2020) report that the lack of Cr in magmatic-hydrothermal magnetite may be temperature-dependent, based on experimental data and observations by Watenphul *et al.* (2014) and Wen *et al.* (2017), and that a Ti v. Ni/Cr diagram may not be suitable for discriminating between igneous and magmatic-hydrothermal magnetite in all cases. Sievwright (2018) did not find Ti v. Ni/Cr diagrams effective and used Ti content to distinguish between magmatic-hydrothermal and igneous magnetite, with magmatic-hydrothermal magnetite classified as $<1\%$ Ti and magnetite $>1\%$ Ti classified as igneous. This classification is not suitable for magnetite from the Casino deposit, with median Ti values of 299 ppm in igneous magnetite, 975 ppm in altered igneous magnetite and 1600 ppm in magmatic-hydrothermal magnetite (Table 7, Fig. 10a). We used our LDA model to classify magnetite from six sources (Table 5) identified by Sievwright (2018) as magmatic-hydrothermal and all but one analysis corresponds with magnetite either from an igneous or an altered igneous source (Fig. 13a). Except for magnetite from the Chuquicamata deposit, samples from the other five locations plot in the igneous field of the Ti v. Ni/Cr diagram (Fig. 13b). These five sources examined by Sievwright (2018) and classified as magmatic-hydrothermal have average Cr values ranging between 310 (Lomo Bayas, Chile) and 1535 ppm (Elatsite). The median Cr value of Casino magmatic-hydrothermal magnetite is below LOD. The differences in Cr values would explain why the Sievwright (2018) samples do not plot in the Casino LDA model magmatic-hydrothermal field. Relatively high Ti values in the Sievwright (2018) samples suggest that the source of fluids from which the magmatic-hydrothermal magnetite crystallized may have been derived from a more mafic magma than that from which Casino magmatic-hydrothermal magnetite was derived. This leads to the

conclusion that Casino data and most of the Sievwright (2018) data are incompatible for most statistical applications because variations in the conditions of formation have resulted in quite different magmatic-hydrothermal magnetite compositions.

Pisiak *et al.* (2017) reported that compositional ranges in magmatic-hydrothermal magnetite were too variable to accurately classify with simple binary diagrams and proposed a discrimination model based on a multivariate statistical method to characterize the composition of magnetite. They used LDA to classify magnetite from various porphyry deposits and barren igneous rocks using Mg, Ti, Al, V, Mn, Co and Ni and successfully applied their model to identify magmatic-hydrothermal magnetite in till samples. Using a linear discriminant analysis based on 12 variables (Mg, Al, Ti, V, Mn, Co, Ni, Ga, Ge, Cu and Cr) in magnetite samples from known sources, we adapted this model to identify magmatic-hydrothermal magnetite from the potassic alteration zone of the Casino deposit recovered from stream sediments, and by incorporating the Ti v. Ni/Cr plot (Dare *et al.* 2014) with our model, are able to characterize and identify two additional types of magnetite from igneous sources.

We tested our LDA model with data from deposits in British Columbia (Canil *et al.* 2016; Pisiak *et al.* 2017; Canil and Lacourse 2020). Subsets of variables common to both datasets (Mg, Al, Ti, V, Cr, Mn and Ni) were used to build and test our model. Pine, Copper Mountain and most of the Mount Polley samples are correctly classified as magmatic-hydrothermal magnetite, whereas Endako samples are classified as igneous or altered igneous magnetite (Fig. 13c). Most of the samples plot in the magmatic-hydrothermal field of the Ti v. Ni/Cr plot, although samples with relatively high Cr abundances from Endako and Pine plot in the igneous field (Fig. 13d).

A universal method of identifying magnetite from different locations remains elusive given the many factors that can determine the nature of igneous and magmatic-hydrothermal magnetite. Bivariate diagrams using single elements and ratios are effective in many cases, but as we have shown above, they may not reliably classify magnetite under different conditions of formation or post-magmatic alteration that result in modified element contents. Multivariate classification models such as LDA are based on accurate identification of the sources of magnetite used to build the model, using textural characteristics and high-resolution in-situ analyses, but again, do not always accurately classify magnetite from other locations. Laser ablation data using different instrument set-ups and methods of calibration can also affect results of comparing or combining data from different sources. To reduce differences and aid comparison, analytical methods need to be similar or identical, and in particular, should use similar primary reference materials and matrix-matched quality control standards for comparison. We feel that our methods can be applied to exploration for porphyry deposits in different areas; however, care must be taken if data from other locations are used to build the LDA model. As more data become available from different locations in the near future, machine learning will likely have applications in this area of research.

Applications and implications for mineral exploration

The texture of magmatic-hydrothermal magnetite in veins (Fig. 5e) consists of small to medium-sized (<0.25 mm) grains that recrystallized during cooling (Fig. 5f). Presumably these grains weather out of bedrock as glomerocrysts that may disaggregate along grain boundaries during fluvial transport. Our study, limited to grains >0.25 mm, did not consider the composition of finer-sized magnetite grains. Future study should investigate smaller size fractions of magnetite (<0.25 mm) recovered from stream sediments and analysed by LA-ICPMS.

The minimum number of magnetite grains from a single stream sediment sample mounted for LA-ICPMS analysis for this study was 200. For multivariate analysis, at least 10 observations for each independent variable are recommended (Peduzzi *et al.* 1996). In our study, twelve variables were selected for LDA, with 76 to 144 ablated magnetite grains per stream sediment sample (Table 6). This number of analyses per sample was sufficient to identify magmatic-hydrothermal magnetite downstream of Casino but also in other regional streams. However, we agree with Pisiak *et al.* (2017), who set the number of analyses per till sample at 50, that the optimum number of grains per sample should be further investigated. Up to 50% or more of our analytical results were discarded for various reasons (Table 3). We determined that 200 grains are a reasonable number to analyse, given the relative scarcity of magmatic-hydrothermal grains in stream sediment samples, the possibility of grains other than magnetite present in samples, and contamination of results by mineral inclusions or rock fragments.

Our methodology can be applied to different types of detrital materials that contain magnetite in addition to stream sediments, including till, colluvium, and desert lag deposits. Dupuis and Beaudoin (2011); Dare *et al.* (2014); Nadoll *et al.* (2014); Canil *et al.* (2016) and Huang *et al.* (2019) compared different types of magmatic-hydrothermal deposits from many different locations around the world; this is useful for outlining broad similarities and differences between magmatic-hydrothermal magnetite from banded iron formation, skarn, veins, porphyry-type and other sources. However, none of these studies report the composition of magnetite in detrital sediments in the region of mineralization. This knowledge gap was filled by Makvandi *et al.* (2016a, b), Pisiak *et al.* (2017), and Ward *et al.* (2018) who demonstrated that magnetite in tills and soils could be used as vectors to VMS, porphyry Cu and Ni–Cu–PGE mineralization. Our study further shows that in an unglaciated landscape, magnetite from streams draining a known porphyry Cu deposit can be used to vector to mineralization. Combined, these studies show that different types of detrital materials that contain magnetite, such as till and stream sediments and potentially colluvium, and desert lag deposits could be used as sampling media for mineral exploration based on magnetite composition.

Porphyry Cu systems are widely distributed along convergent plate boundaries (Sillitoe 2010). In the Canadian Cordillera, porphyry deposits occur in association with two distinct intrusive suites, calc-alkalic and alkalic, formed during two separate periods; Late Triassic to Middle Jurassic, and Late Cretaceous to Eocene (McMillan *et al.* 1996). The Casino deposit formed during the younger period, along with the Granisle, Bell, and Fish Lake deposits in central British Columbia (McMillan *et al.* 1996). The three contemporaneous calc-alkaline deposits located in a glaciated part of central British Columbia are good candidates to test the Casino model as they are easily accessible and in areas for which bedrock and surficial maps are available. By compiling magnetite data from many deposits, the methodology outlined here can be refined and applied to different styles of porphyry mineralization using a variety of detrital materials. Another candidate for testing reproducibility of results is the Cash porphyry Cu–Mo deposit, located 80 km NW of Carmacks, Yukon in the unglaciated portion of the Dawson Range (Yukon Geological Survey 2021b). Alluvial drift covers part of the mineralized zone and thin residual soil covers the remainder. Conventional stream sediment sampling for pathfinder elements (Cu, Mo) did not detect the mineralization (Roberts and Brabec 1970), but no studies on magnetite provenance or chemistry have been done on this deposit. Additionally, undiscovered porphyry Cu deposits are predicted to exist in this geological environment (mainly Jurassic calc-alkaline igneous rocks in accreted and syn-accretionary terranes of mixed island-arc and continental arc affinities; Mihalasky *et al.* 2011). Successful

application of the methodology outlined here would support the use of magnetite recovered from streams for porphyry Cu exploration.

Conclusions

Magnetite originating from granodioritic host rocks and from the potassic alteration zone of the Casino deposit can be identified in local stream sediments. A combination of linear discriminant analysis based on 12 variables (Mg, Al, Ti, V, Mn, Co, Ni, Ga, Ge, Cu, Cr and Zn) in samples from known sources with a Ti v. Ni/Cr plot (Dare *et al.* 2014) effectively classifies igneous and magmatic-hydrothermal magnetite from the Casino deposit. Further refinement of the methodology, identifying Cu contents above the detection limits of LA-ICP-MS in magmatic-hydrothermal magnetite, is effective in classifying magnetite grains from a mineralized source. The presence or absence of apatite inclusions and trellis textures are useful for identifying magnetite from other igneous and magmatic-hydrothermal sources, as are relative abundances of Ti and Cr in igneous sources and Cu in magmatic-hydrothermal magnetite. Alteration, oxidation, exsolution, and re-equilibration processes can each affect the petrographic characteristics and chemical composition of both igneous and magmatic-hydrothermal magnetite, and must be accounted for when attempting to classify grains and establish provenance.

Analysis of different size fractions of magnetite grains recovered from stream sediments is recommended: an examination of the chemical composition of magnetite grains that are <0.25 mm could improve the efficiency of this exploration method. Further work is required to establish an optimum grain size for recovery and chemical analysis. We recommend that a minimum of 200 magnetite grains from each stream site be analysed by LA-ICPMS for robust multi-variate analysis.

Comparing and combining magnetite mineral chemistry data from different locations must be carried out with extreme care. Factors such as bulk rock and fluid composition, temperature, fugacity, pressure, and cooling history affect the composition of magnetite and can vary even within hand samples. Different instrument parameters and calibration methods could affect LA-ICPMS analytical results and must be taken into consideration when using data from other locations.

Petrographic and compositional characterization of magnetite from potential bedrock sources is key to tracing the bedrock source of magnetite in streams. Applying this knowledge to mineral exploration using magnetite in stream and other detrital sediments could be further refined by characterizing magnetite from all potential bedrock sources in a survey area. These strategies would be of practical use in the exploration for porphyry systems in Canada, especially when combined with abundance data for other indicator minerals present in the same stream sediment samples.

Acknowledgements We thank D. Canil, Alain Plouffe and one anonymous reviewer for their rigorous and thoughtful reviews. This study was funded by the Geological Survey of Canada as part of its Targeted Geoscience Initiative 5 (TGI-5) program and by Queen's University as part of a M.Sc. thesis by the first author. We gratefully acknowledge the support of Western Copper and Gold, and the Casino Mining Corporation, and in particular, Mary Mioska, Senior Environmental Manager, Western Copper and Gold Corporation, for her assistance with this project. Kathy Spalding ('Over the Top' expediting services) and Bob Younker (Casino Camp Manager) provided logistical support and Adrienne and Luc Turcotte for sharing their knowledge of the camp and surrounding area. Andy Robertson is thanked for his considerable navigational skills and helicopter flying ability. We thank Katherine Venance, Igor Bilot, Patricia Hunt, Agatha Dobosz, Heather Seeley (Wolfbear Geological), Alexandre Voinot, and Marissa Valentino for assistance with lab analysis and Dante Canil and Chris Beckett-Brown for sharing geological insights and information. Natural Resources of Canada contribution number 20210356.

Author contributions MWM: conceptualization (lead), data curation (lead), investigation (lead), methodology (lead), visualization (lead), writing –

original draft (lead); **JMP**: supervision (supporting), validation (supporting), writing – review & editing (supporting); **MBM**: funding acquisition (lead), project administration (equal), resources (lead), supervision (equal), writing – review & editing (supporting); **MGG**: investigation (supporting), supervision (supporting), validation (supporting); **DL-M**: conceptualization (supporting), funding acquisition (equal), project administration (equal), resources (equal), supervision (equal), validation (equal), writing – review & editing (equal); **MIL**: resources (lead), supervision (lead), validation (lead), writing – review & editing (lead); **RGG**: methodology (supporting), software (lead), validation (supporting), writing – review & editing (supporting); **DCP**: data curation (equal), formal analysis (supporting), methodology (supporting), resources (supporting), software (supporting), validation (equal); **SEJ**: methodology (supporting), resources (supporting), software (supporting), validation (supporting); **SC**: resources (supporting), validation (supporting), visualization (supporting)

Funding This research received funding from Natural Resources of Canada (contribution number 20210356).

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability All data generated or analysed during this study are included in this published article (and its [supplementary information files](#)).

Scientific editing by Scott Wood

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