The use of magnetite as a geochemical indicator in the exploration for magmatic Ni-Cu-PGE sulfide deposits: a case study from Munali, Zambia

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Abstract

Magmatic sulfide deposits hosted by mafic-ultramafic intrusions are the most important source of Ni and PGE on Earth. Exploration strategies rely on geophysics to identify the host intrusions, and surface geochemistry to identify anomalous concentrations of Cu, Ni, Co, Cr, As and other associated elements. The use of geochemical indicator minerals in overburden is used widely in diamond exploration and mineral chemistry in fresh rock is increasingly used to identify proxies for mineralisation in magmatic-hydrothermal systems. However, no indicator mineral techniques are routinely applied to magmatic sulfides. Magnetite represents an ideal indicator mineral for this mineralisation style due to its ubiquity in such deposits, its resistance to weathering, its recoverability from soil samples, and its chemical variability under differing conditions of formation. We use the Munali Ni sulfide deposit to test the use of magnetite as an indicator mineral. Magnetite from mafic, ultramafic, and magmatic sulfide lithologies in fresh rock at Munali show discernible differences in the most compatible elements (V, Ni, Cr). We propose a new Cr/V versus Ni discrimination diagram for magnetite that can be used to indicate fractionation of the parent magma (Cr/V increases from ultramafic to mafic), and the presence of co-existing sulfides (Ni contents >300ppm). The signatures of these three elements at Munali are comparable to sulfide-related magnetites from other deposits, supporting the broad applicability of the discrimination diagram.

Samples taken from overburden directly on top of the Munali deposit replicate signatures in the fresh bedrock, strongly advocating the use of magnetite as an exploration indicator mineral. Samples from areas without any geophysical or geochemical anomalies show weak mineralisation signatures, whereas magnetite samples taken from prospects with such anomalies display mineralisation signatures. Magnetite is thus a viable geochemical indicator mineral for magmatic sulfide mineralisation in early stage exploration.
Keywords: Magnetite, LA-ICP-MS, magmatic sulfides, Ni-Cu-PGE, indicator minerals
**Introduction**

Indicator mineral chemistry has been a successful early stage exploration technique for many years. The key features of successful indicator minerals are that they have a much higher abundance than the main commodity; they survive in weathering processes; and have distinctive geochemical signatures (Layton-Matthews et al. 2014). This approach is well established in diamond exploration, where indicator minerals (e.g. ilmenite, olivine, Cr-diopside, garnet) are present in much higher quantities than diamonds in overburden; and their abundance, co-occurrence and chemistry have been used to identify the presence and fertility of kimberlites (Gurney 1984; Fipke et al. 1995). Early stage geochemical exploration for base and precious metals, conversely, has traditionally relied primarily on bulk elevations of certain elements in overburden and transported (e.g. stream) samples (Cameron and Hattori 2005), alongside geophysical anomalies (Balch 2005). Recently, however, there has been a drive to develop indicator mineral geochemistry for base metal deposits in fresh rock (e.g. Mao et al. 2016); most significantly for porphyry Cu-Au deposits in arc-related magmatic rocks, where plagioclase, apatite, and magnetite have all been shown to be useful in identifying key processes that determine fertility (Williamson et al. 2016; Bouzari et al. 2016; Pisiak et al. 2017).

Magmatic Ni-Cu-platinum group element (PGE) deposits are the world’s most important source of Ni and PGEs, accounting for ~56% of the world’s Ni production and over 96% of Pt, Pd, and the other PGE production (Mudd and Jowitt 2014). Such deposits are hosted in ultramafic/mafic intrusions that have undergone sulfide saturation and the separation of an immiscible sulfide liquid from the silicate magma, which scavenged chalcophile elements like Ni, Cu, and the PGE (Barnes et al. 2017). Exploration for these deposits has traditionally relied on geophysics; primarily gravity and magnetic surveys to identify the host
ultramafic/mafic complexes; and overburden geochemistry to identify elevated levels of elements like Cu, Ni, Co, As, and Cr (Rose et al. 1979; Cameron and Hattori 2005). Olivine is used as a fresh rock indicator mineral, with its relative enrichment or depletion in Ni content used to indicate sulfide undersaturated, or saturated conditions of formation (e.g., Li and Naldrett 1999), olivine breaks down too easily to be used as an effective indicator mineral in overburden. At present, no minerals are routinely used as indicator minerals in early-stage exploration for magmatic Ni-Cu-PGE sulfides.

Iron-oxides are common accessory minerals across hydrothermal, metamorphic and magmatic ore deposits and magnetite is amongst the most abundant Fe-oxide phase within the continental crust. Magnetite possesses the key properties of a successful indicator mineral, including the ability to incorporate a number of foreign cations (Nadoll et al. 2014), resistance to weathering/erosion, magnetic properties for easy identification and sampling, and it is widespread in many geological settings. Recent advances in the field of Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) analysis have been able to further constrain magnetite’s petrological significance based on its chemistry (Dupuis and Beaudoin 2011; Nadoll and Koenig 2011; Nadoll et al. 2014; Boutroy et al. 2014; Dare et al. 2014; Chen et al. 2014; Chung et al. 2015; Liu et al. 2015; Zhao and Zhou 2015). Dupuis and Beaudoin (2011) have shown that magnetite formed from different deposit types can be fingerprinted using trace element chemistry and Pisiak et al. (2017) have shown that magnetite chemistry has significant potential to discriminate between mineralised and barren porphyry sources in overburden sampling.

In mafic-ultramafic systems, magnetite can form via fractional crystallisation of a silicate magma, secondary hydrothermal processes (e.g., serpentinisation), or from the fractionation
of Ni-Cu-PGE-bearing sulphide liquids (Dare et al. 2012; 2014; Boutory et al. 2014; Duran et al. 2016). Recent LA-ICP-MS studies of magnetite associated with magmatic Ni-Cu-PGE sulfide has been useful in determining magma and co-existing sulfide compositions, source conditions, fractionation histories and the distinction of magmatic versus hydrothermal origins (Dupuis and Beaudoin 2011; Nadoll et al. 2014; Boutroy et al. 2014; Dare et al. 2014; Liu et al. 2015).

In this paper, we build on this to test the application of magnetite as a geochemical indicator mineral for magmatic Ni-Cu-PGE sulfide mineralisation for the first time. As a case study, we use the Munali Ni sulfide deposit and mine in southern Zambia due to there being: (1) a well characterised multi-stage, magmatic and sulfide history, each with associated magnetite in an economic deposit (Holwell et al. 2017), thus providing a solid framework of local magmatic and mineralised signatures in fresh rock to compare with overburden; (2) topographical and vegetation constraints that limit surface outcrop in places and thus it is an example of where early stage exploration requires surface geochemistry; (3) the presence of a number of prospective locations, based on magnetic (and in some cases surface geochemical) anomalies, that can be used to test whether prospective geochemical signatures in magnetite are replicated proximal to other prospects. Different generations of magnetite are texturally, then geochemically classified, with petrogenesis discussed, and we propose a new discrimination diagram that can become a powerful tool in surface geochemical exploration for Ni-Cu-PGE sulfide deposits.

The Munali Ni sulfide deposit

The mafic-ultramafic Munali Intrusive Complex (MIC) is located in the Zambezi Supracrustal Sequence (ZSS) within the medium-high metamorphic grade Zambezi Belt,
southern Zambia (Evans 2011; Holwell et al. 2017a; Fig. 1A). The ZSS comprises a
Neoproterozoic package of metasediments and metavolcanics (Johnson et al. 2007), which
defines the east-west striking orogenic belt extending from Central Zambia to northern
Zimbabwe (Hanson et al. 1994). During the Neoproterozoic, the southern margins of the
Congo Craton were subject to rifting and intraplate magmatism from ~880 to ~820 Ma
(Johnson et al. 2007), likely as part of the breakup of the supercontinent Rodinia (John et al.
2003). During this period, magmatism intruded rift sediments that included the multi-stage
emplacement of the MIC (862-858 Ma; Holwell et al. 2017a).

The MIC was emplaced along a major NW-SE trending crustal lineament (the Munali Fault,
Fig. 1A), proximal to the margins of the southern Congo Craton, into ZSS sediments that
comprise marbles, quartzites, and pelites of the Nega Formation (Johnson et al. 2007;
Holwell et al. 2017a). Basement material in the Munali Hills region (Fig. 1) comprises the
1106 ± 19 Ma Mpande Gneiss, a complex of gneisses and granites (Hanson et al. 1988),
succeeded by the 1090 ± 1.3 Ma Munali Hills Granite (Katongo et al. 2004). The MIC
displays a very strong magnetic anomaly, with additional anomalies present along the Munali
Fault and the northern fault splay (Fig. 1A), marking the presence of a number of proven and
inferred intrusions of a similar genesis (Howe and Holwell. 2016).

The MIC comprises a number of magmatic stages, all of which contain magnetite, but only
some also contain magmatic sulfides. The Central Gabbro Unit (CGU), the earliest stage, was
emplaced at 862 Ma and does not contain any Ni-sulfide mineralisation. This was followed
by the mineralised, Marginal Ultramafic-mafic Breccia Unit (MUBU) emplaced at 858 Ma
(Fig. 1; Holwell et al. 2017a). The CGU comprises heterogeneously textured magnetite-
bearing gabbro, whereas the MUBU is a chaotic megabreccia unit containing clasts of
poikilitic gabbro, ultramafic olivinites (referred to as such rather than dunites, due to the
oxide being magnetite, rather than chromite), olivine-magnetite rocks, phoscorites, and dykes
of olivine dolerite, all in a groundmass of sulfide-magnetite-carbonate-apatite (Holwell et al.,
2017a). The magmatic sulfide assemblage is pyrrhotite >>=pentlandite>chalcopyrite+pyrite
and there is evidence of a number of sulfide-magnetite (± carbonate ± apatite) generations
within the MUBU (Blanks et al. 2017). Dominant magnetite-bearing rocks at Munali include
gabbros of the CGU, poikilitic gabbros, olivinites, and phoscorites of the MUBU, and the
dolerite dykes. Magnetite is also present as an essential component within all of the sulfide
assemblages: in the massive breccia fill and late stage sulfide-carbonate veins of the MUBU.

Materials and methods

Twelve samples of quarter core were selected from a suite of samples from diamond drill
holes that intercepted the MUBU and CGU of the MIC, comprising a range of representative
magnetite styles. All drillcores sampled were drilled through the southern MUBU in the MIC
(Fig. 1B). Five detrital magnetite samples (OB01-05) were collected from the soil overburden
on top of the MIC, and proximal to other regional magnetic/geochemical anomalies (Fig. 1B).
Locations of soil samples are shown in Figure 1B. Magnetite from soil samples was separated
using a magnet and mounted in resin and made into polished blocks. All size fractions were
retained from this method, and the size of grains ranged up to 500 µm.

Mineralogical, petrological, and textural analysis of oxides and associated sulphides was
undertaken on twelve polished thin sections and five mounted detrital magnetite samples.
Second generation automated mineralogy was conducted at ZEISS’ Natural Resources
Laboratory in Cambridge, UK. Mineralogic Mining software was used to quantitatively
classify mineralogy, major element chemistry, and magnetite textures. The technique maps
the samples and quantifies EDS spectra allowing quantitative phase identification and element deportment (Holwell et al. 2017b). Spot analyses were undertaken to be used for LA-ICP-MS normalisation. Full analytical conditions and methodology is detailed in Supplementary Material A1.

Magnetite in all samples was then subject to LA-ICP-MS analysis. The methodology and list of trace elements analysed was conducted in accordance to recent studies of LA-ICP-MS performed on magnetite (e.g., Dare et al. 2014; Boutroy et al. 2014). A natural magnetite standard from the Bushveld Complex (BC-28) provided by S-J. Barnes (Université de Québec à Chicoutimi, Canada) was used to monitor data quality and ensure internal data consistency. Laser Ablation-ICP-MS was conducted at the University of Leicester using a New Wave Research-ESI 213 nm laser coupled with a ThermoScientific iCAP-Qc quadrupole ICP mass spectrometer. Full analytical conditions and methodology are detailed in Supplementary Material A1.

Petrology and classification of magnetite styles

The mineralogical mapping of thin sections allowed full textural and petrological classification of a number of magnetite styles. These can split into four textural categories: (1) igneous magnetite in mafic and ultramafic rocks; and in syn-MUBU dolerite dykes; (2) magnetite related to massive sulfides that forms the matrix in the MUBU; (3) magnetite formed as reaction rinds; and (4) late stage magnetite in carbonate-sulfide injections and veins in the MUBU. The textural characteristics described below are summarised in Table 1.

Igneous magnetite in mafic/ultramafic rocks

This textural category comprises magnetite that is considered a normal rock-forming constituent. All of the magnetite of this style that we analysed can be considered Ti-poor,
containing <1 wt% Ti based on EDX analysis. The CGU, and the poikilitic gabbro clasts in
the MUBU, are mineralogically similar, though differ texturally (Fig. 2A,B), comprising a
silicate assemblage of plagioclase and clinopyroxene with up to 20 modal % magnetite and
lesser ilmenite. The finer-grained CGU can be characterised by interstitial grains of magnetite
(Fig. 2A). Very minor pyrrhotite is present (Fig. 2Ai), but there is no appreciable Ni-Cu-
PGE mineralisation and these rocks are considered unmineralised, or barren in this sense. In
the poikilitic gabbro, magnetite is present as large oikocrysts (<20 mm) with accompanying
plagioclase chadacrysts (Fig. 2B). No inclusions (sulfide or otherwise), were observed within
magnetite in either the CGU or the poikilitic gabbro, though both contain abundant ilmenite
occurring as two textures: (1) coarse-grained ilmenite blebs intergrown with magnetite (Fig.
2Aiii, 2Bii); and, (2) fine laths of exsolved ilmenite commonly in trellis patterns (Fig. 2Aiii,
2Bii). The poikilitic gabbro contains a minor primary sulphide assemblage (<1% modal
mineralogy; pyrrhotite>>pentlandite>chalcopyrite; Fig. 2Bi), and thus is considered to be
weakly mineralised.

Magnetite is a ubiquitous and often abundant constituent of the ultramafic rocks of the
MUBU (Fig. 2C). Olivinites grade into olivine-magnetite rocks and phoscorites (olivine-
magnetite-apatite) and contain large cumulus olivine crystals up to several centimetres in
diameter, and interstitial magnetite and apatite. Magnetite is present as large sub-angular
grains (<1 cm) containing frequent ilmenite lamellae (Fig. 2Cii). Nickel-Cu sulfides are
sporadic, but occur as large interstitial blebs in textural equilibrium with interstitial magnetite
and apatite (Fig. 2C) and as such these rocks are considered mineralised.

The latest intrusive stage is the emplacement of dolerite dykes, which comprise a silicate
assemblage of plagioclase with actinolite pseudomorphs of clinopyroxene phenocrysts and
totally altered and serpentinised olivine phenocrysts (Fig. 2D). Minor, disseminated magnetite is present in addition to coarser magnetite grains (<3 mm) occurring in textural equilibrium with ilmenite in equal abundance (Fig. 2Dii). Very minor pyrrhotite is present (Fig. 2Dii), but these are considered, like the CGU, to be barren of Ni-Cu-PGE mineralisation.

Magnetite within massive sulfide assemblages
Magnetite is always present within pyrrhotite-pentlandite-chalcopyrite-pyrite blebs and accumulations, comprising typically ~5, but up to 20, modal %, of the sulfide assemblage that makes up the breccia matrix of the MUBU. Magnetite is spatially associated with massive sulphide, and as such, is believed to have formed via the direct fractionation of a sulphide liquid (Fig. 3A). Whilst texturally associated with sulphide, it is important to note that some magnetite in this association may in fact be xenocrysts from mafic-ultramafic phases disaggregated during brecciation (c.f. Fig. 13D of Holwell et al. 2017a). Magnetite is present as large (<1.5 cm) sub-angular grains that exhibit no preference to any single sulfide mineral (Fig. 3A).

Magnetite in late stage carbonate-sulfide veins
Carbonate-associated magnetite is present intergrown with primary calcite and dolomite and sulfide in late stage veins/injections within the MUBU (Fig. 3B). Sub-angular magnetite grains marginal to sulphide are common, though less abundant than sulphide, making up ~5 modal % of the mineralogy. Generally, ilmenite is uncommon though the largest magnetite grains (<3 mm) exhibit minor ilmenite association (Fig. 3Bii).

Reaction rind magnetite
Reaction-rind magnetite can be divided into two subcategories based on adjacent material: (1) at sulphide-silicate boundaries, often seen around the margins of sulphide-enclosed mafic and...
ultramafic xenoliths within the MUBU and at the boundary between massive and semi-
massive sulfide veins and mafic/ultramafic host rocks (Fig. 3C); and (2) silicate-silicate
reaction rinds between mafic lithologies, predominantly between poikilitic gabbro and
dolerite intrusions (Fig. 3D). The sulphide-silicate reaction rinds are the more dominant of
the two sub-categories, typically forming 1-2 cm thick rims made up of 100% magnetite
against adjacent silicate rocks (Fig. 3C). Rinds form irrespective of silicate rock composition.
Silicate-silicate magnetite reaction rinds comprise 1-1.5 cm thick rims (Fig. 3D). Magnetite
tends to exhibit a euhedral morphology (Fig. 3D) defining the contact between the silicate
rocks.

Magnetite geochemistry

Laser-Ablation-ICP-MS data is reported for all textural magnetite styles. Full LA-ICP-MS
datasets can be found in Supplementary Material A2. Multi-element plots (Fig. 4) have been
devised for the four textural magnetite classifications and lithological subdivisions for
elements above detection (Si, Y, Pb, Zr, Hf, Al, Ge, W, Sc, Ta, Nb, Cu, Sn, Ga, Mg, Ti, Zn,
Co, V, Ni and Cr). Elements are plotted in order of compatibility into magnetite (left to right;
Dare et al., 2014). The LA-ICP-MS data shown in Figure 4 has been normalised to the
composition of bulk continental crust (Rudnick and Gao 2003) to compare the compositions
of source magmas (Dare et al. 2012; Boutroy et al. 2014). Figure 5 illustrates a time-resolved
analysis (TRA) profile for a typical laser track across a composite magnetite-ilmenite grain to
clearly illustrate the elements that are relatively enriched in magnetite (Fe, Cr, V, Co, Ni, and
Ga; Fig 5A), compared to ilmenite (Ti, Al, Ta, Y, W, Cu, Nb, Pb; Fig 5B). Whilst every
effort was made to only include parts of each analysis that ablated magnetite, some ilmenite
will have been homogenised into the LA data (this is seen in the LA-ICP-MS data indicating
up to 10 wt% Ti, whereas the EDS analysis gave a maximum of 1 wt%). As such, variations
in each of the plots shown in Figure 4 in the latter set of elements are likely due to variable
contents of ilmenite included. This is seen in the variation in Ti (ilmenite controlled) in Fig.
4C versus Ga (magnetite controlled).

Magnetite is variably enriched in Sn, Ga, Mg, Ti, Co, V, Ni, and Cr relative to bulk
continental crust in most styles (Fig. 4), whereas Si, Y, Pb, Zr, Hf, Ta, Nb, and Cu are
relatively depleted, which is expected given their relative incompatibility into magnetite. The
concentration of highly compatible elements in magnetite (Cr, Ti, and V) across all styles are
typically an order of magnitude higher than incompatible elements (e.g., Si, Y, Pb, and Zr).
Chromium, an element commonly enriched in mafic-ultramafic systems, is remarkably
depleted at Munali and no chromite is found within the ultramafic rocks (Holwell et al.
2017a). However, the Cr concentrations in magnetite from the MIC (60-2600 ppm) are not
significantly lower than those reported for magnetite in other mafic-ultramafic intrusions
(e.g., 24-5668 ppm; Dare et al. 2012).

Igneous magnetite in mafic/ultramafic rocks
The geochemical profiles for all the analysed igneous magnetites are comparable, with some
notable exceptions that distinguish some of the separate phases. For example, the poikilitic
gabbro demonstrates Cr enrichments and Y and Ta depletions compared to the rest of the
Munali mafic rocks (Fig. 4A). The dolerite dykes have the lowest Zn concentrations of any of
the mafic rocks. Chromium concentrations are higher in mafic lithologies (<505 ppm) than in
ultramafic rocks (<72 ppm). Both the mafic and ultramafic magnetites at Munali demonstrate
variable enrichment in Al, Sc, Sn, Ga, Mg, Ti, Zn, Co, V, Ni, and Cr, with element
abundances consistently higher in mafic relative to ultramafic rocks (Fig. 4). The sulfide-
bearing poikilitic gabbro has higher Ni contents than the sulfide-poor mafic lithologies (~10x
and ~2x bulk continental crust, respectively), higher Cr and lower V, and lower Ta and Nb contents (Fig. 4A).

Magnetite within massive sulfide assemblage

All magnetite analysed that was associated with massive sulfides (Fig. 3A) share geochemical similarities, suggestive of a common origin, though they display subtle differences in Zr, Hf, Ta, Zn, W, Cu, and Cr (Fig. 4C) and exhibit the highest Cr values of any style (up to 3132 ppm). Notably, magnetite in igneous rocks that contain sulfides (poikilitic gabbro, ultramafics) share similar profiles with magnetite in massive sulfides that make up the matrix of the MUBU; most notably with consistent Ni contents around 10 times higher than bulk continental crust (~600 ppm). Furthermore, whilst of different generations, both the poikilitic gabbro and the ultramafic rocks contain interstitial sulfides, yet magnetite chemistry is comparable between these. Thus chemically, all magnetite associated with either massive sulfide, or rocks containing disseminated sulfide show similar characteristics. Therefore, irrespective of generation, there appears to be a common signature, which reflects the co-existence of sulfides. There are, however, some clear differences in the overall profile with a notable depletion in Ta-Nb in massive sulfide-associated magnetite relative to the igneous phase magnetite (Fig. 4C), with the exception of the sulfide-bearing poikilitic gabbro.

Magnetite in late stage carbonate-sulfide veins/injections

Similarities are observed between magnetite in carbonate-sulfide veins and those from the massive sulfides. Geochemical profiles of magnetite in the sulfide-carbonate veins are comparable with those in the massive sulfides (Fig. 4C) and poikilitic gabbro (Fig. 4A);
sharing similar enrichments in Ni. The carbonate-associated magnetites differ slightly from
the massive sulfide magnetites in having higher Nb, and lower Cr contents (Fig. 4C).

Reaction rind magnetite
There are some significant differences between the two textural sub-classifications of
reaction rinds, with sulfide-silicate reaction rinds notably more enriched in Zr, Hf, Sc, Cu,
Mg, Zn, and Cr compared to silicate-silicate rinds (Fig 4D). Overall, the geochemical profiles
are distinct not just from each other, but from both the igneous phase magnetite and sulfide-
associated magnetite; however, the sulfide-silicate reaction rind magnetite shares a similar V-
Ni-Cr signature to the massive sulfides.

Cr/V versus Ni discrimination diagram for magnetite
Although it has been shown that late stage hydrothermal re-equilibration of hydrothermal
magnetite can modify textures and compositions (Hu et al., 2014; 2015), the most compatible
elements in magnetite (e.g., V, Cr, Ni, and Co) are relatively immobile (Hu et al., 2014), and
thus the contents and ratios of these elements can be a very robust indicator of provenance,
unaffected by hydrothermal overprints.

Chromium, V, and Ni have been selected for use as discriminant criteria for the following
reasons: (1) good degrees of data reliability; (2) they are compatible in magnetite with limited
influence by ilmenite crystallisation (Fig. 5), and also have minimal mobility during
hydrothermal alteration (Hu et al., 2014); (3) they show clear differences in profiles between
different textural types that reflect lithology and/or the presence of sulfide (Fig. 4); and (4) Ni
is a useful element in tracing sulfide-saturation of a magma. Using these elements, we
propose a new discrimination diagram that can be used in exploration as a way of
distinguishing magnetite from different lithologies and those associated with sulfide mineralisation (Fig. 6).

The ratio between Cr and V concentrations is an efficient lithological discriminant, dividing igneous textural types into two distinct geochemical fields, with Cr/V in ultramafic rocks <0.022. Alone however, Cr/V ratios are ineffective in distinguishing magnetite in mineralised and barren rocks, but Ni shows a clear cut off at 300 ppm; with all magnetite above this in rocks with magmatic sulfides, the reasons for which will be discussed later. Therefore we present plots of Cr/V versus Ni (Fig. 6) where three geochemical (c.f. textural) classifications can be recognised:

1. High Ni and Cr/V ore-related magnetite (including: poikilitic gabbro from the igneous phase textural association; magnetite associated with massive sulfide; and magnetite associated with carbonate-sulfide);

2. High Ni and low Cr/V ultramafic magnetite (including all ultramafic rocks in the igneous phase textural class); and

3. Low Ni and high Cr/V barren igneous phase magnetite (including all non-mineralised mafic rocks from the igneous phase textural class; and the silicate-silicate reaction rind textural classification).

The silicate-silicate reaction rind samples sit within the barren igneous field on the Ni diagram (Fig. 6), but the sulfide-silicate reaction rinds sit very close to the boundary of barren and mineralised and are the closest group to the ore-related field, with a relatively high Cr/V ratio as well (Fig. 6).

Detrital magnetite petrology and geochemistry
Detrital magnetite was sampled from overburden above the Munali deposit, and three other areas within the Munali Hills region (Fig. 1B). Figure 7 illustrates some of the typical morphologies and sizes of the detrital grains recovered from overburden in these areas. In samples taken from the northeastern part of the study area (OB1-3), the grains typically have a subrounded morphology and are somewhat pitted (Fig. 7A,B) compared with those taken directly above the MIC, which are more angular (Fig. 7C,D); most likely reflective of the transport distance from their source. Irrespective of the shape, ilmenite exsolution lamellae are preserved (e.g., Fig. 7B). Figure 7D shows the track of the laser during a typical line analysis over one such grain (c.f. Fig. 5).

As both mineralised and barren magnetite geochemical signatures for the main magnetite-bearing bedrock lithologies at Munali have been established, detrital magnetite can be compared using the Cr/V versus Ni discriminant diagram (Fig. 8). Magnetite collected from soil directly on top of the MUBU in the MIC (OB04; Fig. 8A) displays Cr-V-Ni relationships almost identical to the mineralised fields from the primary rocks. This is critical as these data demonstrate that:

1. Magnetite sampled directly on top of known sources of economic grade mineralisation preserves mineralised signatures;
2. Magnetite chemistry of the original host rock is preserved in detrital grains; and
3. Cr, V, and Ni are sufficiently immobile to efficiently preserve the chemistry of known source origins.

A second sample taken from soil over the MIC (OB05; Fig. 8B) shows a wider spread in compositions, but most of the grains overlap with the fields from the fresh rocks. An exception is the four grains that have Cr/V ratios consistent with the ultramafic rocks, but contain ‘barren’ levels of Ni. In fact, none of the detrital grains match the ultramafic
signature in terms of Ni content, but many plot in the low \(Cr/V\) ultramafic field with ‘barren’ Ni signatures. This may indicate Ni is somewhat mobile during weathering and that these grains may have experienced more weathering/transport from their source. As such, the 300 ppm Ni cut-off in bedrock may be lowered slightly with the degree of weathering.

One other sample returned magnetite compositions consistent with a Munali sulfide signature. Sample OB01 was collected close to the Termite prospect, a large magnetic anomaly on the southern edge of a soil and termite mound geochemical anomaly (Figs. 1A, 8C). This sample exhibited two clear populations: one that overlaps the Munali mineralised field very closely; and one that displays a linear trend with low Ni and mafic \(Cr/V\) ratios. The former indicates that magnetite in the Termite area has signatures of mineralisation, analogous to Munali; the significance of which is discussed below. The latter indicates the presence of another generation of magnetite that is either not present, or was not sampled, in the MIC.

Two samples were taken from along strike from Munali, with OB02 (Fig. 8D) taken from an area with no magnetic or geochemical anomaly, and OB03 (Fig. 8E) taken from above the Chibuku magnetic anomaly. Both samples show evidence of the linear low-Ni population, and also a few points that plot above the ‘mineralised’ Ni concentration (Fig. 8D,E), though in terms of the proportion of overall grains, there are fewer mineralisation indicators than the other three samples. Chibuku is a mafic-ultramafic intrusion with indications of mineralisation potential from Cu/Pd ratios (Howe and Holwell 2016), that does not crop out, but is proven to be present at \(~200\) m depth from a single exploration drillhole. It would not be expected that any indicator minerals would be present from an intrusion present at such
depth, although given the very limited drilling, some parts of it may be closer to the surface, which may be a source for the mineralised signatures in the overburden.

**Discussion**

The Munali area provides an excellent test ground to assess the applicability of magnetite as an indicator mineral. Firstly, there are a number of generations of magnetite that are abundant in the MIC, which have discernible geochemical characteristics; most importantly, between magnetite associated with sulfides, and those in barren rocks. Secondly, the Ni, Cr, and V concentrations of magnetite can be used to identify such signatures in soil effectively. The following discussion firstly briefly addresses the processes that determine the variability in magnetite chemistry at Munali, and then focusses on the application of this to exploration.

*Origin of different styles and chemical signatures of magnetite*

There are three separate origins of the magmatic magnetite in our study: (1) that formed from the fractional crystallisation of a silicate liquid; (2) that formed from the crystallisation of a sulfide melt; and (3) that formed during silicate-silicate or –sulfide interaction. Each of these has distinct geochemical signatures indicative of the different modes and conditions of formation as would be expected (Dupuis and Beaudoin 2011; Nadoll et al. 2014; Boutroy et al. 2014; Dare et al. 2011, 2014).

Dare et al. (2014) showed that the relationship between Ti and Ni/Cr ratio in magnetite could be used to distinguish a magmatic or hydrothermal origin. Our data, plotted on a Ni/Cr versus Ti plot, together with the fields of Dare et al. (2014) in Figure 9A, shows that magnetite in all but the ultramafic magnetites plot in the magmatic field. The textural evidence is clearly in favour of a magmatic origin for the ultramafics (Fig. 2) and the high Ni/Cr ratio reflects the
low Cr and high Ni content of the ultramafic (phoscoritic) magnetites (Fig. 4B), and is not necessarily an indicator of a hydrothermal origin. Phoscorites contain low levels of Cr (<82 ppm), and magnetites from other phoscorites have typically low Cr and Ni (<0.02 wt% of oxides) and high MgO (2.5-8 wt%) and Al₂O₃ (0.5-3.8 wt%) contents (Krasnova et al. 2004). The magnetite from the ultramafics we have analysed contain on average 70 ppm Cr, 2.2 wt% MgO, and 2.2 wt% Al₂O₃. The exception is the Ni content in the Munali ultramafic magnetites is high. Phoscorites rarely contain appreciable magmatic sulfides, so the presence of Ni-sulfides co-existing with the magnetite may account for the high Ni contents (see below). The amount of fractionation of a silicate magma affects the V content of magnetite, with early, more primitive magnetite being more enriched in V (Dare et al. 2014). Thus, the Cr/V ratio can be used as proxy for fractionation and this is seen by the difference between the more primitive ultramafic (lower Cr/V) and more evolved mafic (higher Cr/V) rocks in Figure 6.

Up to 30% magnetite can crystallise directly from a sulphide liquid (Naldrett 1969; Fonseca et al. 2008; Boutroy et al. 2014). All lithophile elements are compatible into Fe-oxide as a result of their relative incompatibility into sulphide (Dare et al. 2011; Boutroy et al. 2014) and thus are concentrated in the oxide, and excluded from the sulfide on cooling. The concentration of chalcophile elements in magnetite, however, is responsive to co-crystallising sulphide (Dare et al. 2014). As such, although genetically the igneous phase and sulfide-associated magnetites differ in terms of texture and lithophile contents, the chalcophile contents of both textural styles are affected by the presence of sulfide. This is seen in the consistent Ni relationships in sulfide-bearing and sulfide-barren samples (Fig. 6).
Copper concentrations within magnetite have been suggested as a proxy for sulphide mineralisation (e.g., Dare et al. 2014), as Cu, along with other chalcophile elements, including Ni, should be concentrated into the sulfide liquid, thus being depleted in any co-existing phase (analogous to Ni depletion in olivine formed from a sulfide-saturated magma; Li and Naldrett 1999). Whilst the ilmenite effect on Cu analysis precludes any rigorous testing of this on magnetite, it is interesting to note that whilst magnetites in massive sulfides have some of the lowest Cu contents (Fig 4). The expected depletion of Ni in sulfide-associated magnetite does not occur and requires some explanation. We suggest that enriched Ni contents in magnetites formed from the fractionation of a sulfide liquid may be the result of initial concentration of Ni into the sulfide liquid, which attains Ni concentrations in the wt % range, rather than, for comparison, a few hundreds of ppm in a silicate melt. The subsequent formation of magnetite from a Ni-enriched sulfide liquid as opposed to a Ni-poor silicate liquid produces magnetite with relatively higher Ni contents (though still with the overwhelming bulk of Ni partitioning into sulfide). Thus the enrichment in Ni in magnetite over Cu is effectively a measure of the $D_{\text{sulfide/magnetite}}$ during sulfide-magnetite crystallisation. Essentially, Cu and Ni will partition into sulfide liquid, but as that fractionates to Ni-rich monosulfide solid solution (mss), Cu-rich intermediate solid solution (iss), and magnetite, virtually all the Cu will stay in sulfide, but some Ni will partition into the magnetite formed in this way. Importantly, this feature means that elevated Ni signatures in magnetite indicate co-existing magmatic sulfide formation, and Cu is an unreliable measure of the presence of sulfide.

The origin of the reaction rinds between the massive sulfides and silicate clasts within the MUBU was discussed by Holwell et al. (2017a), who proposed they were analogous to chromite reaction-rinds observed in komatiite-hosted sulphide deposits formed by
dis-equilibrium between sulfide and silicate melts (Groves et al. 1977; Dowling et al. 2004).

At Munali, this process formed magnetite rather than chromite in the absence of appreciable Cr (Holwell et al. 2017a). The sulfide-silicate reaction rind compositions sit neatly midway between the ore-related and barren mafic fields on the Cr/V versus Ni plot (Fig. 6) and thus conceivably represent signatures inherited from a mixture of sulfide and silicate sources. Silicate-silicate rinds are most commonly observed between dolerite and poikilitic gabbro, and have compositions that sit within the barren mafic field and thus reflect the mafic nature of the two rock types they separate.

The detrital grains in our study also show at least one chemically distinct population of magnetite that do not have a magmatic equivalent within the Munali system. Whilst these could be sourced from a distinct magmatic event that is not present within the MIC, it is pertinent to explore the possibility that these grains have a very different source. Firstly, it has been established that magnetite can undergo significant dissolution and reprecipitation (DRP) processes under hydrothermal conditions (Hu et al. 2015). There is obvious rounding and pitting in some of the detrital grains we studied (Fig. 7A,B), but this is most likely due to mechanical weathering and erosion. The high temperature oxy-exsolution of ilmenite lamellae are preserved in the detrital grains (Fig. 7B), but there is perhaps some evidence of the secondary textural generations of magnetite observed as characteristic of DRP (Fig. 7B; c.f. Hu et al. 2015).

The Ni-poor geochemical population (Fig. 8) are present in samples in the northwest of the study (samples OB1-3; Fig 8C-D) and are characterised by extremely low Ni contents (<30 ppm) and a positive correlation between Ni and Cr/V ratio (Fig. 8). Hydrothermal magnetite from both skarns and Late Proterozoic ironstones have been recorded to have Ni contents
typically around 10, and Cr/V ratios <1 (Zhao and Zhou, 2015; Chung et al. 2015); consistent
with the low-Ni population in Figure 8C-E. Therefore, we suggest that to the northwest of
Munali, there is likely to be a bedrock source of hydrothermal magnetite, and that grains
sourced from this may have undergone some DRP (Fig. 7B).

Application to exploration

Magnetite is a ubiquitous accessory mineral in magmatic sulfide assemblages and a common
igneous phase in many related mafic rocks, with distinctive chemistries due to different
conditions of formation. It is resistant to weathering and is easily recovered during
overburden sampling due to its magnetic properties. As such, it has great potential to be used
as an indicator mineral in exploration. Our study demonstrates three critical relationships that
provide proof of concept for the use of magnetite as a geochemical indicator mineral in early
stage exploration for Ni-Cu-PGE sulfide deposits.

1. The Cr/V versus Ni discrimination diagram provides a powerful tool for determining
magnetite formed from mineralised and barren systems;

2. The comparison shown in Figure 9 illustrates how Cr, V, and Ni at our case study area
is consistent with other deposits worldwide. Thus, our discrimination diagram is
widely applicable; and

3. The transfer of geochemical signatures from bedrock sources into overburden shows
that using the Cr/V versus Ni discrimination diagram for soil samples is robust and
the signatures are representative of the source.

Dupuis and Beaudoin (2011) showed that Cr+Ni versus Si+Mg discrimination diagrams can
effectively discriminate magnetite formed in different ore deposit types; distinguishing Ni-
Cu-PGE deposits from a range of other magmatic and hydrothermal deposit types. Where our
study advances this is in the proposal of the Cr/V versus Ni discrimination diagram that can discriminate fractionation effects and the co-existence of sulfides within this environment.

Both Cu and Ni have the potential to be discriminators of sulfide saturated and undersaturated rocks. However, there are problems with using Cu, related to its compatibility in ilmenite (Fig. 5). Co-crystallising ilmenite will render the surrounding magnetite Ti-poor (Nadoll et al. 2014) and thus the relative amount of co-existing ilmenite will control the Cu content of the magnetite, which presents a restricting factor in the use of Cu as a proxy for mineralisation.

We conclude that Ni is more reliable due to: (1) the higher compatibility of Ni in magnetite resulting in its presence in concentrations comfortably above detection limits; (2) Ti-rich magnetite and ilmenite are more likely to incorporate Cu than Ti-poor magnetite, potentially introducing a biasing component, especially in analysis of magnetite with ilmenite exsolution lamella; and (3) Cu is a more mobile element in the surficial environment and can thus be remobilised during weathering. That said, there is some evidence from the lack of ultramafic signatures with Ni >300 ppm in the overburden at Munali (Fig 7B) that may indicate some loss of Ni in the surficial environment.

Our work has some specific implications for the prospectivity of the Munali Hills region. The fewer number of grains with mineralised signatures from soil samples in the centre of the study area is consistent with no evidence of major intrusions close to the surface in those areas. However, the Termite prospect has magnetite in soil that has Cr-V-Ni signatures indicative of magmatic sulfide mineralisation. As such, coupled with the known Cu and Ni soil geochemical and magnetic anomalies in this area, this would be consistent with a significant indication of magmatic sulfide mineralisation at Termite. This illustrates how
magnetite indicator mineral chemistry within a soil sampling program can add further confidence to early stage prospectivity and fertility assessments.

The determination of mineralised/barren and mafic/ultramafic fields on the Cr/V versus Ni discrimination diagram we present is based on the ability to define the fields with available bedrock material. It would always be optimal to have a control on the likely local signatures, however, in greenfields exploration areas, this may not be possible. Our discrimination quadrants are based on the signatures present in the case study area we used, and are necessarily restricted by any particular local signatures. The sulfide composition at Munali is consistent with most Ni-sulfide deposits, and is an Fe-rich, mss-like orebody (Holwell et al. 2017a). Magnetite associated with mineralisation at Munali is plotted onto diagrams devised by Boutroy et al. (2014) to assess the composition of the sulphide liquid (Fig. 9B,C). This confirms that magnetite associated with the main sulphides at Munali is consistent with the chemical signature of Fe-rich, as opposed to Cu-rich sulfides (Holwell et al. 2017a). It also implies that the interstitial sulfides in the ultramafic rocks (which are temporally earlier) are slightly more evolved; consistent with a multi-stage history in the MIC (Holwell et al. 2017a).

One of the most significant conclusions to be drawn from the relationship shown in Figure 9B,C is that the Cr, Ni, and V contents of the sulfide-associated Munali magnetite are similar to those from other sulfide deposits. This means that the fields in the Cr/V versus Ni discrimination diagram should be widely applicable to any magmatic sulfide deposit. Given that hydrothermal magnetite generally has very low Ni contents (Zhao and Zhou, 2015; Chung et al., 2015), we would suggest that any analyses plotting below around 30 ppm Ni may be considered to have a likely hydrothermal origin as discussed above. However, use of
the Ti v Ni/Cr discrimination diagram proposed by Dare et al. (2014) is an effective
determinant of hydrothermal versus magmatic origins, and the key application of our Cr/V
versus Ni diagram is to identify mineralised magmatic signatures.

It is worth noting that some Ni-Cu-PGE reef deposits are hosted within cumulates where
chromite is the oxide present, and not magnetite, and the Merensky Reef, Platreef and UG2
PGE deposits in the Bushveld Complex, for example, do not contain any cumulus magnetite
(Naldrett et al. 2011; McDonald and Holwell 2011). However, magnetite is a ubiquitous
(though often minor) component of magmatic sulfide assemblages, and therefore whilst in
some cases, the Cr/V distinction for lithologies may be not be applicable due to the lack of
igneous phase magnetite, the presence of Ni-enriched magnetite derived from sulfide
assemblages (for which the sulfide will have degraded during weathering) can still be used as
an effective indicator for mineralisation.

Summary

One of the greatest challenges in exploration is the recognition of mineralisation at greater
and greater distances from the primary source (Nadoll et al. 2014). Our proof of concept
study clearly shows the potential to use magnetite as a geochemical indicator mineral in
surface sampling to identify magmatic Ni-Cu-PGE sulfide mineralisation. We have shown
this to be effective directly above and within at least ~1 km of magnetic anomalies/surface
outcrops, however, there are various parameters not considered in this work, including,
though not exclusive to, prevailing wind directions, heterogeneous weathering regimes,
surface water flow directions and the potential for bidirectional transport of magnetite grains
away from the primary source. Further development of the application of magnetite to early
stage exploration will necessarily need to consider these factors. Nevertheless, magnetite can
be considered to be an ideal indicator mineral for magmatic sulfide fertility in that it is abundant, chemically variable, with distinctive signatures related to the presence, or absence, of sulfides.

Acknowledgments

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Figure captions

**Fig 1** A: Regional gravity map of the Munali area showing the major crustal lineaments of the NW-SE Munali Fault, and its WNW-ESE northern splay; along with several magnetic anomalies located along them, including the Munali Intrusive Complex (MIC), the Chibuku intrusion and the Termite prospect (modified from Evans 2005). Inset: location of Munali within Zambia. B: geological map of the Munali Hills area showing the location of the MIC and the five soil samples (OB01-05) used in this pilot study. Grid system is in UTM, projection WGS84.

**Fig 2** Textural association of magnetite in igneous rocks of the MIC illustrated through Mineralogic phase mapping, backscattered SEM imaging and thin section transmitted light. A: Central Gabbro Unit microgabbro: (i) Mineralogic colour coded oxides and sulfides on transmitted light image; (ii, iv) Mineralogic phase map on transmitted light image showing magnetite-ilmenite textures and very minor pyrrhotite; (iii) backscattered SEM image showing magnetite-ilmenite textures. B: poikilitic gabbro: (i) Mineralogic colour coded oxides and sulfides on transmitted light image; (ii) backscattered SEM image showing magnetite-ilmenite textures; (iii) transmitted light image showing magnetite oikocryst with plagioclase chadocrysts. C: coarse grained ultramafic phosphorite with interstitial sulfide-oxide-apatite blebs: (i) Mineralogic colour coded oxides,apatite, sulfides and zircon on transmitted light image; (ii) backscattered SEM image of magnetite-ilmenite textures with included zircon; (iii) transmitted light image showing magnetite in association with apatite in serpentinised olivine. D: olivine dolerite dyke: (i, iii) Mineralogic colour coded oxides and sulfides on transmitted light image; (ii) Mineralogic phase map showing magnetite-ilmenite textures and very minor pyrrhotite. Abbreviations: mt=magnetite, ilm=ilmenite, po=pyrrhotite, pn=pentlandite, plag=plagioclase, ol=olivine.

**Fig 3** Textural association of magnetite in MUBU sulfide rocks, and as reaction rims in the MIC illustrated through Mineralogic phase mapping, backscattered SEM imaging and thin section transmitted light. A: typical massive sulfide with magnetite: (i,ii,iv) Mineralogic phase maps showing
pyrrhotite-pentlandite loop textures, minor chalcopyrite and large magnetite-ilmenite blebs; (iii)
backscattered SEM image of magnetite-ilmenite texture. B: sulfide-carbonate-magnetite vein: (i,ii,iv)
Mineralogic phase map of sulfides and oxides on transmitted light image showing sulfide oxide
textures with euhedral carbonate crystals; (iii) backscattered SEM image of magnetite-ilmenite
texture. C: core sample showing magnetite reaction rind between semi-massive sulfide and adjacent
CGU gabbro. D: transmitted light image of magnetite reaction rind between dolerite and poikilitic
gabbro. Abbreviations: mt=magnetite, ilm=ilmenite, po=pyrrhotite, pn=pentlandite, cpy=chalcopyrite,
py=pyrite, cal=calcite.

Fig 4 Bulk continental crust-normalised multi-element plots from LA-ICP-MS of magnetite
(normalisation values from Rudnick and Gao 2003). A: Magnetite from mafic igneous rocks; B:
magnetite from ultramafic rocks; C: magnetite from sulfide-dominant lithologies in the MUBU; D:
magnetite in reaction rinds.

Fig 5 Time resolved analysis (TRA) spectra of a single laser traverse across magnetite (mt) and
ilmenite (ilm). A: response of elements compatible in magnetite; and conversely B: response of
elements compatible in ilmenite.

Fig 6 Plot of Cr/V versus Ni for all magnetite analyses from the MIC, defining four discriminating
fields based on fractionation (Cr/V) and the presence of sulfide (Ni).

Fig 7 Reflected light photomicrographs of detrital magnetite grains mounted in resin showing (A-C) -
variable morphology. A: pitted and rounded morphology from erosion and transport from a sample
away from any outcropping igneous rocks; B: rounded grain with ilmenite exsolution lamellae; C:
relatively fresh and angular grain from soil directly above the Voyager gossan at Munali, reflective of
little transport. D: the track of the laser ablation analysis in a typical line analysis across a magnetite
grain that
Detrital magnetite chemistry of soil samples from the Munali Hills area plotted on Cr/V versus Ni discrimination diagram. Fields are from the Munali bedrock samples shown in Figure 6, and are: UM = ultramafic; M = mafic; and S = sulfide-bearing. Grid system is in UTM, projection WGS84.

Comparison of the MIC magnetite with other discriminant fields. A: all MIC magnetite plotted on the Ni/Cr versus Ti magmatic-hydrothermal discrimination diagram of Dare et al. (2014); B and C: All sulfide-bearing MIC magnetite plotted on the Cr versus V and Ni sulfide evolution discrimination diagrams of Boutroy et al. (2014).
Table 1. Summary of the textural classifications of magnetite in bedrock samples from Munali.

<table>
<thead>
<tr>
<th>Textural classification</th>
<th>Host rock</th>
<th>Modal abundance magnetite</th>
<th>Associated mineralogy</th>
<th>Sulfide abundance</th>
<th>Textural characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Igneous rocks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGU</td>
<td>gabbro</td>
<td>&lt;20%</td>
<td>plagioclase, clinopyroxene, plagioclase, ilmenite</td>
<td>none</td>
<td>oikocrystic magnetite with ilmenite</td>
</tr>
<tr>
<td>Poikilitic gabbro</td>
<td>gabbro</td>
<td>&lt;20%</td>
<td>clinopyroxene, olivine, very minor</td>
<td></td>
<td>oikocrystic magnetite with ilmenite</td>
</tr>
<tr>
<td>Ultramafic</td>
<td>phoscorites, olivinites</td>
<td>&lt;50%</td>
<td>apatite altered plagioclase, clinopyroxene, sporadic</td>
<td></td>
<td>interstitial magnetite with apatite and sulfide</td>
</tr>
<tr>
<td>Olivine dolerite</td>
<td>fine grained basalt/dolerite</td>
<td>&lt;2%</td>
<td>minor olivine</td>
<td>none</td>
<td>disseminated magnetite</td>
</tr>
<tr>
<td>Syn-breciation MUBU sulfides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MUBU sulfides</td>
<td>massive sulfide</td>
<td>&lt;20%</td>
<td>pyrrhotite, pentlandite, chalcopyrite</td>
<td>major</td>
<td>magnetite part of fractionated sulfide blebs/patches</td>
</tr>
<tr>
<td>Late stage MUBU sulfides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MUBU sulfide-carbonate</td>
<td>carbonate-sulfide veins</td>
<td>5%</td>
<td>dolomite, calcite, sulfides</td>
<td>major</td>
<td>magnetite part of fractionated sulfide blebs/patches</td>
</tr>
<tr>
<td>Reaction rinds</td>
<td>sulfide-gabbro/ultramafic, massive sulfide</td>
<td>&lt;100%</td>
<td>n/a</td>
<td>in adjacent rock</td>
<td>massive magnetite rind ~1 cm</td>
</tr>
<tr>
<td>Sulfide-silicate</td>
<td>dolerite-gabbro</td>
<td>&lt;100%</td>
<td>n/a</td>
<td>none</td>
<td>massive magnetite rind ~1 cm</td>
</tr>
<tr>
<td>Silicate-silicate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>
Supplementary material A1: SEM and LA-ICP-MS methodology

Supplementary material A2: Table A2. LA-ICP-MS data of magnetite from the MIC and overburden samples.
Fig 4

A

B

C

D

--- CGU
--- Poliklitic gabbro
--- Dolerite

--- Olivinite
--- Phoscorite

--- Massive sulfides
--- Carbonate-sulfide

--- Sulfide-silicate rinds
--- Silicate-silicate rinds
Fig 6

![Graph Showing the Distribution of Various Rocks and Minerals](image)

- Mafic rocks:
  - CGU
  - Pollitized gabbro
  - Dolomite
- Ultramafic rocks:
  - Olivine
  - Phoscorite
- MUBU sulfides:
  - Massive sulfide
  - Carbonate-sulfide
- Reaction rims:
  - Sulfide-silicate
  - Silicate-silicate

Legend:
- Ultramafic
- Mafic
- Mineralised
- Barren

Axes:
- Cr/N
- Ni (ppm)
Fig 8

Termite magnetic and geochemical anomaly at surface

Chibuku Magnetic Anomaly at depth

Munali Intrusive Complex

FIGURES

A. OB04

B. OB05

C. OB01

D. OB02

E. OB03

Ni (ppm) vs Cr/V

Mineralised Barren
Fig 9
Supplementary data A1: SEM and LA-ICP-MS analytical methodology

SEM analysis

Second generation automated mineralogy was conducted at ZEISS’ Natural Resources Laboratory in Cambridge, UK, where Mineralogic Mining software was used to quantitatively classify mineralogy, major element chemistry and magnetite textures through quantitative EDX mapping and spot analysis for stoichiometric collection for LA-ICP-MS normalisation (e.g. Holwell et al., 2017b). A ZEISS Sigma 300 field emission gun Scanning Electron Microscope (SEM) was used, with GEMINI column electron optics, coupled with two Solid State Drift (SSD) Bruker 6 | 30 Energy Dispersive X-ray (EDX) Spectroscopy detectors. Counts for EDX detection were consistently above 3000 (in accordance with ZEISS’ QA/QC) with mineral classifications based on stoichiometric values (wt.%). The analyses where taken at 10 µm steps where at each analysis point an EDX spectrum is acquired, has a peak deconvolution, PB-ZAF matrix correction and full spectrum chemical quantification applied, giving the wt% contribution of the elements present for each analysed pixel. These quantified compositions with the chemical data are then passed through a mineral list to classify the analysed locations using a best match method. Standardless Energy-dispersive X-ray spectroscopy calibrations were performed every hour on a Cu standard to perform an EDX energy calibration to the Cu Kα (8.040). Brightness and contrast calibrations were undertaken every 60 minutes to remove any brightness and contrast drift from the Back Scatter Detector (BSD). Analytical operating conditions of 25 keV, using the 60 µm aperture, with the high current mode provided a measured I Probe of 2.6 nA with an analytical working distance of 8.5 mm. Large area photomicrographs were created using the ZEISS Imager Z2M microscope with a motorized 130x85 STEP scanning stage for all seventeen samples (RL and TL). Images were captured with a high resolution AxioCamMR3.
Thin section photomicrographs and Mineralogic maps were layered and visualised using the ZEISS Atlas correlative software.

**LA-ICP-MS analysis**

*Data reduction*

Reduction of magnetite standard data was carried out using Iolite. Data reduction for samples of unknown concentrations was conducted offline using Excel. In both cases, $^{57}$Fe values collected from quantitative EDX analysis were used as the normalisation element to ensure internal data consistency. Stages to offline data processing were: (1) blank correction; (2) internal normalisation using an internal reference isotope to correct for variations in the efficiency of the laser-ablation process (based on $^{57}$Fe Bushveld magnetite standard averaged measured laser concentrations), and (3) a concentration calculation and conversion to ppm.

Corrections (calculated using measured concentrations from the magnetite standard BC-28) were applied to account for variations in the tuning and instrument readings on a daily basis, in addition to correcting for the consistent overestimation of isotope concentrations induced by standardising with a high abundance element ($^{57}$Fe).

*Offline data processing for LA-ICP-MS data, in Excel*

The Thermo Fisher Qtegra software (software used to collect data analysis) outputs raw data as either an accumulated intensity per element (for the entire region of interest; this was modified based on grain size if grains were too small for a 60 second analysis), or an average intensity per element for the region of interest, or as the intensity per sweep during analyses. There are four stages to processing laser data offline:
Stage 1 – Blank correction. Raw counts per second (cps) intensity data are initially corrected for an average gas blank by subtraction. In addition, five second gas blanks were left at the start of the analysis to correct for background interference and false readings (readings which are similar/the same during gas blank and when the laser is switched on) though were removed during data reduction.

Stages 2 and 3 – Internal normalisation. It is necessary to use an internal reference isotope standard to correct for variations in the efficiency of the laser ablation process (magnetite standard from the Bushveld Complex), and for any matrix effects induced by variations in the type and quantity of the material entering the plasma torch. Prior to LA-ICP-MS analysis, it is therefore necessary to know the accurate content of normalisation elements. $^{57}$Fe was used as the normalisation element based on EDX stoichiometric data for samples collected using ZEISS’ Mineralogic software. As normalisation values will vary from sample to sample, it is necessary to normalise samples to separate values. Internal normalisation was calculated using equation 1, though note at this stage, only reference isotopes are effected.

Equation 1.

\[
\text{Normalised } ^{57}\text{Fe intensities} = \frac{\text{Average magnetite standard gas blank corrected } ^{57}\text{Fe intensities}}{\left( \frac{^{57}\text{Fe values for mt standard}}{^{57}\text{Fe stoichiometric value for sample}} \right)}
\]

As the ablation process affects different samples differently, a further normalisation, or standardisation, corrects all of the intensity data to the same intensity of $^{57}$Fe. Using the magnetite standard the calculation is given in equation 2.
Equation 2.
Corrected intensity of any other element =
Normalised intensities for $^{57}$Fe in sample
x
($^{57}$Fe average values for mt standard gas blank corrected/normalised $^{57}$Fe intensities for a sample)

Note that errors in the values for the internal reference isotope ($^{57}$Fe) will affect the quality of the final data.

Stage 4 – Concentration calculation. Calculation of the element concentrations. Magnetite standard values are used to construct the element calibration lines, and the line is fitted through the zero intercept. Concentrations are reported in ppm.

Equation 3.
Concentration of any element =
Intensities of individual element in sample (from stages 2 and 3)
x
(Mt standard acceptance values for that element/Average measured mt standard value for element)

Correction of isotope overestimations
Following data normalisation and conversion of intensities into ppm, a correction value is applied. Using an element in high abundance for data normalisation ($^{57}$Fe) leads to a consistent overestimation of isotope concentrations, resulting in poor data accuracy. To improve this, isotope estimations were corrected using known measured magnetite standard values in conjunction with magnetite standard acceptance values. Note, data corrections were calculated for each isotope per-day of analysis to account for variation in instrument tuning.
A correction factor for each isotope was calculated using the following equation:

\[
\text{Correction factor} = \frac{\text{Certified magnetite standard value}}{\text{Average measured magnetite standard value}}
\]

Once a correction value was calculated, the following equation was used to correct LA-ICP-MS ppm data:

\[
\text{Corrected concentrations} = \frac{\text{Correction factor for isotope/value (ppm) for element in sample}}{}
\]

**Data accuracy**

Overestimations were corrected using magnetite standard measured values, though as a result initial measures of accuracy are no longer representative. Instead, percentage errors (calculated from magnetite standard 2σ values in Iolite; Table 4) are presented. Importantly, this study aims to find comparative differences between magnetite-style chemistry, and as such, poor data accuracy as a result of isotope overestimation does not impact data interpretation given the applied corrections, high degrees of elemental precision (for critical elements; Ni, V and Cr) and acceptable percentage errors. Isotopes which yield the best percentage error and precision were selected for use.

**Technique development and data uncertainty**

Instrument calibration is a restrictive factor in obtaining quantitative data. Whilst a methodology established by Dare et al., (2014) was followed, various problems were encountered during both analysis and data reduction. Typically during LA-ICP-MS analysis, a certified reference material is used (e.g. NIST glass) for laser calibration. However, in the case of this study, an external reference material (natural magnetite standard) was used for several reasons: (1) NIST is a glass and as such, behaves differently to magnetite during the
ablation process and (2) calibrations using NIST relies on Si values as the normalisation
element, which is not possible for magnetite given low Si abundances.

Laser spots were insufficient in acquiring data for all elements based on data collection time,
often appearing below detection. This issue was resolved using laser tracks, though added a
constraint to the smallest grains that could be analysed. It is important to note that whilst laser
tracks ablate the surface of grains; it is unknown what material lies underneath and may
potentially introduce erroneous readings.

Iron values were used as the normalisation element as it was the only element consistently
detected during EDX analysis. As discussed, high element concentrations introduce problems
during data reduction. Using a different technique to collect normalising values (e.g. electron
microprobe as opposed to EDX values) in lower abundances is recommended for use in
further analytical work, though crucially, elements valuable for data interpretation cannot be
used as they are needed for data reduction.
Supplementary data A2