Trace element compositions of silicates and oxides as exploration guides to metamorphosed massive sulphide deposits: examples from Broken Hill, Australia, and Stollberg, Sweden


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Although the presence of indicator minerals has long been used as a guide in the exploration for various ore deposits on a regional scale (e.g. Spry 2000; McClenaghan 2005), the composition of these minerals has also helped to target sulphide mineralisation on a more local scale. Using major element compositions, an increase in the Mg/(Mg+Fe) ratio of ferromagnesian silicates, including garnet, biotite, tourmaline, chlorite, staurolite, cordierite, and amphibole, has been used to indicate proximity to metamorphosed ore deposits in low- to high-grade metamorphic terranes (e.g. Nesbitt 1986; Bryndzia & Scott 1987). More recently, trace element studies using various techniques (e.g. electron microprobe, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), proton-induced X-ray emission (PIXE)) have allowed the provenance of minerals and their composition in various ore deposits to be determined. Such techniques facilitate the measurement of many elements at concentrations as low as parts per billion (e.g. Jackson, 1992). Trace element studies of minerals spatially related to metallic mineral deposits include titanite in porphyry Cu deposits (Xu et al. 2014), magnetite in porphyry Cu-Mo, orogenic Au, skarn, iron oxide-copper-gold (IOCG), volcanogenic massive sulphide (VMS), and Ni-Cu-platinum-group element deposits (e.g. Dupuis & Beaudoin 2011; Nadoli et al. 2012, 2014), maghemite and hematite in IOCG deposits (e.g. Schmidt Mumm et al. 2012), garnet in skarn (e.g. Gaspar et al. 2008) and Broken Hill-type (BHT) deposits (Spry et al. 2007), and chromite (e.g. Pagé & Barnes 2009), and ilmenite (e.g. Dare et al. 2012) in magmatic sulphide deposits. Nine minerals (feldspar, calcite, garnet, pyroxene, amphibole, allanite, epidote-group minerals, titanite, and apatite) were analyzed by Ismail et al. (2014) in a study of the Hillside IOCG deposit, South Australia. The use of trace element studies of minerals to vector to metamorphosed massive sulphide has received minimal attention but has largely focused on garnet (e.g. Clark & Williams-Jones 2004; Layton-Matthews et al. 2013; O’Brien et al. 2013a, 2015a, b), garnet (Spry et al. 2007; Heimann et al. 2009, 2011), and tourmaline (Griffin et al. 1996), with the most detailed work being done on BHT deposits. The present contribution focuses on the trace element composition of garnet from BHT deposits and metamorphosed VMS, sedimentary exhalative (SEDEX), and non-sulphide zinc (NSZ) deposits, garnet from BHT deposits in the southern Curnamona Province, Australia (including the supergiant Broken Hill Pb-Zn-Ag deposit), and preliminary data for magnetite, garnet, and biotite from the Stollberg Zn-Pb-Ag and magnetite field, Sweden. The analytical methods used in this study are described in O’Brien et al. (2015a) and are not repeated here. The aim of study is to evaluate the use of trace elements of these minerals in guiding exploration, with a discussion of the physicochemical parameters that affect their trace element composition in metamorphosed metallic base metal deposits.

**TRACE ELEMENT COMPOSITIONS OF SILICATES AND OXIDES**

Gahnite

The major element chemistry of gahnite (AB2O4) is comprised of varying proportions of Zn2+, Fe2+, Mg2+ and lesser amounts of Mn2+ in the tetrahedral site (A), where Zn > (Fe + Mg), and dominantly Al3+ in the octahedral site (B), with minor amounts of Fe3+ also in the octahedral site. The most extensive gahnite horizons known occur in the Proterozoic Broken Hill domain of the southern Curnamona Province, New South Wales, Australia. Gahnite occurs in blue quartz-gahnite lode rocks and along strike from the Broken Hill Pb-Zn-Ag deposit as well as minor BHT deposits. These rocks form part of the so-called “lode horizon”, which occurs intermittently for >300 km throughout the Broken Hill domain, and also contains quartz garnetite and lesser amounts of garnetite and lode pegmatite. In addition to blue quartz-gahnite lode, garnite occurs in minor to trace amounts in sillimanite gneiss, lode pegmatite, tourmalinite, iron formation, quartzfeldspar-garnet gneiss, and amphibolite. O’Brien et al. (2015a) evaluated the composition of garnite from various rock types, including 11 minor BHT deposits and the main Broken Hill deposit. The aim of their study was to find a compositional fingerprint that could be used to distinguish gahnite associated with sulphides from those in rocks devoid of sulphides. Based on >500 major and trace element compositions of garnite from various rocks types, O’Brien et al. found that garnite from the Broken Hill deposit can be distinguished from that associated with unmineralized lode pegmatite and sillimanite gneiss using a principal component analysis and a plot of Zn/Fe versus Ni+Cr+V. Bivariate plots of Zn/Fe versus Ga,
Co, and Mn, or Ga versus Co showed that garnet from the Broken Hill deposit has a relatively restricted compositional range and that it overlaps with the composition of garnet from some minor BHT occurrences (Fig. 1). O’Brien et al. (2015b) further evaluated the same data set using a linear discriminant analysis and a relatively new statistical technique known as Random Forests to discriminate the composition of garnet in the Broken Hill deposit from those in minor BHT deposits (Fig. 2). The use of Random Forests was particularly valuable, more so than the linear discriminant analysis, in identifying compositional factors (i.e. the so-called “spinel elements”: Mg, Al, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, and Cd) that can be used for discrimination purposes.

Garnet in the Stollberg ore field (~12 Mt), Bergslagen district, Sweden, occurs in a variety of strongly altered (i.e. gedrite-albite, garnet-biotite, and garnet-pyroxene-carbonate alteration) rocks associated with massive Zn-Pb-Ag sulphides and magnetite deposits, and in unaltered to weakly altered 1.9 Ga bimodal felsic (dominated by rhyolitic ash-siltstone) and mafic rocks metamorphosed to the amphibolite facies. Sulphides are hosted by volcanic rocks and skarn, and occur as massive to semi-massive base metal lenses. Jansson et al. (2013) considered the deposits to be part of a synvolcanic, seafloor hydrothermal system, which was partly exhalative (iron oxide) and partly carbonate-replacive (sulphides + more iron oxides). Garnet in garnet-biotite alteration and high-grade sulphides is almandine-rich, whereas that in skarn and garnet-pyroxene alteration contains significantly higher proportions of the grossular and spessartine components (e.g. Jansson et al. 2013). In general, garnet contains elevated concentrations of Sc, Ti, V, Cr, Co, Zn, Ga, Ge, Y, and REEs, with Sc, Ga, and Ti being derived exclusively from a volcanoclastic (rather than a hydrothermal) component (Jansson et al. 2013). Overall, chondrite-normalized REE patterns of garnet in quartz garnetite at Broken Hill (Fig. 3) are similar to those for garnet in the Stollberg ore field (Fig. 4). Garnet in unaltered (or slightly altered) rhyolitic ash-siltstone at Stollberg typically shows no Eu anomaly and low concentrations of Zn, Ga, and V. In contrast, garnet in garnet-biotite and garnet-pyroxene alteration, which are strongly altered equivalents of rhyolitic ash-siltstone, shows a strong positive Eu anomaly and contains elevated concentrations of Zn and Ga, and low Ti contents. Garnet in gedrite-albite alteration, which likely represents part of a footwall feeder pipe to deposits on the eastern side of the Stollberg ore field, exhibits a relatively flat chondrite-normalized REE profile and contains elevated Sc and low concentrations of Cr, V, and Ti. Garnet in mafic dykes and marble contains the highest amounts of Cr, Co, V, and Ti.

**Magnetite**

Magnetite occurs in a variety of metamorphic, sedimentary, and igneous rocks, as accumulations in iron formations and as an accessory phase in a large variety of ore deposits (e.g. Dupuis & Beaudoin, 2011; Nadoll et al. 2012, 2014). Of all the accessory minerals associated with ore deposits, magnetite is the most studied because it occurs in so many different types
Fig. 2. Percentage of votes by Random Forests for compositions of gahnite from the Broken Hill deposit versus minor Broken Hill-type occurrences (Broken Hill domain). Predictions represent an average over ten 10-fold cross-validations (after O’Brien et al. 2015b).

Fig. 3. Chondrite-normalized rare earth element patterns of garnet in (A & B) quartz garnetite, and (C & D) metasomatic garnet in post-peak metamorphic quartz-garnet rock (Broken Hill, Australia) (modified from Spry et al. 2007).
of ores. Despite numerous studies being conducted on the trace element composition of magnetite associated with metallic mineral deposits, those involving magnetite in VMS deposits are limited in number (e.g. Singoyi et al. 2006; Dupuis & Beaudoin, 2011).

The lithological variability in the Stollberg ore field makes this location ideal to evaluate the physico-chemical parameters that affect the chemistry of magnetite in a district that contains exhalative and replacement base metal sulphide mineralisation metamorphosed to the amphibolite facies. The district has many of the same characteristics as a VMS district but it is atypical in that mineralisation has a high iron-oxide/sulphide ratio, it commonly occurs in limestone, and it lacks massive pyritic rocks. Trace element compositions of magnetite in high-grade ore, skarn, massive magnetite, and garnet-biotite alteration throughout the district show a wide range (Figs. 5 & 6). Such a broad compositional range is inconsistent with previous studies in other ore...
fields, which have suggested that magnetite chemistry can be used to define compositional fields for different ore deposit types (e.g. $\text{Al}/(\text{Zn}+\text{Ca})$ vs $\text{Cu}/(\text{Si}+\text{Ca})$ (Fig. 5); $\text{Ca}+\text{Al}+\text{Mn}$ vs $\text{Ti}+\text{V}$ (Fig. 6)) or can be used to approximate the temperature of the ore-forming fluid (e.g. Dupuis & Beaudoin 2011; Nadoll et al. 2014). Magnetite in garnet-biotite and gedrite-albite alteration spatially associated with the Dammberget deposit typically contains $>200$ ppm Ga, $>10$ ppm Sn, and has $\text{Ti}/\text{V}$ ratios of $>10$, whereas magnetite in garnet-biotite alteration associated with the smaller Cederkreutz deposit contains less Ga, Sn, and lower $\text{Ti}/\text{V}$ ratios. Magnetite in garnet-biotite alteration associated with the Gränsgruvan deposit contains $>10$ ppm Sn, 20 to 180 ppm Ga, and has $\text{Ti}/\text{V}$ ratios of 0.1 to 2. These and other trace element compositions of magnetite in altered host rocks show potential as exploration guides to ore in the Stollberg district.

**Biotite**

Biotite is a common mineral in metamorphic rocks and is locally intergrown with garnet and gahnite in both the Broken Hill and Stollberg deposits. Although trace elements of biotite have been obtained on rocks in metamorphic terranes (e.g. Yang & Rivers, 2000), their application as a vector to metamorphosed sulphide deposits has not previously been conducted. None-the-less the trace element composition of biotite intergrown with garnet and garnite in the Broken Hill deposit was evaluated by O’Brien et al. (2013b). The focus of the O’Brien et al. study was to gauge how trace elements partition among garnite, biotite, and garnet, with the view of determining how the concentration of “spinel elements” in garnite was affected by the composition of coexisting minerals. The compositions of biotite in garnite-bearing rocks from the Broken Hill deposit show solid solution between annite and phlogopite end-members, with $X_{\text{Mg}} = \text{Mg}/(\text{Mg}+\text{Fe})$ ranging from 0.29 to 0.60 and V/I$\text{Al}$ ranging from 0.41 to 1.30. Beryllium, Cr, Co, Ni, Ga, Cd, and to a lesser extent V strongly partition into garnite, whereas Li, Mg, Ti, Ge, Rh, Sr, Sn, Ba, Pb, Bi, Th, and REEs partition into biotite (Fig. 7).

Trace element compositions of biotite in various altered rocks in the Stollberg ore field were also evaluated. Preliminary studies show elevated concentrations of Cs and Tl in drillholes that cross-cut the Dammberget deposit over a distance of 100 m in its stratigraphic hanging wall, and appear to be the best indicators of proximity to ore (Fig. 8). It should be noted here that high bulk rock concentrations of Tl in the hanging walls of VMS deposits were reported by Large et al. (2001) and was considered by them to be a good guide to ore.

**DISCUSSION AND CONCLUSIONS**

Previous and ongoing studies suggest that various chemical plots and discrimination diagrams using the concentration of certain elements, or combinations of elements, are valuable for exploration purposes and for determining mineral provenance. For example, based on the major and trace element chemistry of garnite, the best guides to high-grade ore in the Broken Hill
domain involve the following chemical parameters: Zn/Fe = 2 to 4 versus Co = 10–110 ppm, Ga = 110–400 ppm, and Mn = 500–2,250 ppm; and Co = 25–100 ppm versus Ga 125–375 ppm (O’Brien et al. 2015a). In addition, garnet from the Broken Hill deposit is enriched in Zn (>400 ppm), Cr (>140 ppm), and Eu (up to 6 ppm and positive Eu anomalies), and depleted in Co, Ti, and Y compared to garnet in other garnet-rich rocks from other localities in the southern Curnamona Province. These values, as well as MnO contents of >15 wt% and Eu/Eu* >1, were only found in garnet from the Broken Hill deposit and appear to be good pathfinders to BHT mineralisation (Heimann et al. 2011). Garnet in massive sulphides and sulphide-bearing alteration assemblages in the Stollberg ore field can be distinguished from sulphide-poor or sulphide-free rocks of the same alteration type on the basis of a positive Eu anomaly, and the concentrations of Zn, Ga, and Ti. The compositions of magnetite and biotite in the Stollberg ore field also appear to show great promise as pathfinder minerals because the composition of magnetite in altered versus unaltered rocks, and larger versus smaller hydrothermal systems can be distinguished. The Tl and Cs content of biotite also appear to be more elevated in the hanging wall of sulphide mineralisation with proximity to ore (Fig. 8).

Although discrimination diagrams were developed by Dupuis & Beaudoin (2011) and O’Brien et al. (2013a) to assist in determining the provenance of magnetite and gahnite, respectively, they must be considered to be preliminary at best due to the limited number of compositional data that were used in both studies. In the discrimination diagrams used by O’Brien et al. (2013a), individual analyses were plotted; however for diagrams presented by Dupuis & Beaudoin (2011), fields that apparently characterize different types of ore

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**Fig. 7.** Distribution coefficients for coexisting gahnite and biotite in blue quartz-gahnite rock from the Broken Hill deposit. Note that gahnite preferentially incorporates Cr, Co, and Ga relative to biotite, whereas biotite preferentially incorporates Li, Mg, and Ti (after O’Brien et al. 2013a).

**Fig. 8.** Trace element composition (Mn, Zn, Ga, Y, Sn, Cs, and Tl) of biotite with depth along drillhole SSF 26, which intersects the Dammberget deposit, Stollberg ore field, Sweden. The stratigraphic bottom (i.e. gedrite-albite alteration) is at the top of the vertical section on the left.
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Deposits are based upon the average composition of magnetite from individual deposits, regardless of the number of data that were collected from that deposit. Such an approach, in the absence of error bars, is questionable, given that data from individual deposits from a specific ore type (e.g. sulphide mineralisation in the Stollberg ore field) can cover much of the diagram and plot in the fields of several different deposit types. Variability in trace element composition of a given mineral in metamorphosed massive base metal deposits is dependent upon several variables, including different physicochemical conditions during mineral growth, crystal-chemical controls (i.e. the major element chemistry of the mineral), pre-metamorphic alteration, the chemistry of precursor minerals, the partitioning of elements between coexisting minerals, fO2, f/S2, temperature, pressure, and host-rock geochemistry. The effect of most of these parameters on the trace element composition of oxides and silicates is unknown and, consequently, trying to assess the relative importance of these parameters is difficult at best, notwithstanding the possibility that some minerals may be subject to post-peak modification during retrograde metamorphism. For example, gahnite can break down to biotite, chlorite, and staurolite, all of which are known to contain elevated concentrations of Zn (e.g. Spry 2000), and both biotite and garnet can convert to chlorite.

Although considerably more work needs to be done on the minerals evaluated here (i.e. gahnite, magnetite, garnet, and biotite), the study of other silicates (e.g. tourmaline, staurolite, chlorite, titanite, amphibole, aluminosilicates, quartz, and pyroxene), and oxides (ilmenite, rutile, högbomite, and ecan-drewsite) is also warranted.

Given the complexity of the physicochemical parameters that affect mineral trace element chemistry, and the large amount of data that can be collected in a short amount of time using EMPA and LA-ICP-MS techniques, application of various types of statistical analyses of data are also important in refining or identifying new empirical parameters that can be used for targeting purposes (e.g. Dupuis & Beaudoin 2011; O’Brien et al. 2015a, b).

REFERENCES


