Trace element chemistry of indicator silicates and oxides as vectors to metamorphosed sediment-hosted Pb-Zn-Ag and Cu-Au deposits in the Cambrian Kanmantoo Group, South Australia

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The presence of resistate indicator minerals (e.g. garnet, gahnite, magnetite, Cr diopside, ilmenite, olivine, and gold) in surficial sediments (e.g. glacial, eolian, stream, alluvial, beach, and residual soils) and bedrock have been used to explore for various types of mineral deposits, including porphyry Cu, lode gold, magmatic Ni-Cu-PGE, metamorphosed volcanogenic massive sulphide (VMS), rare metals, and iron oxide-copper-gold (IOCG) (Averill, 2001, 2007; McClenaghan, 2005, 2013). Optical- and electron- (e.g. scanning electron microscope coupled with QEMSCAN® or MLA™ software, electron microprobe analysis (EMPA), and mass spectrometry (e.g. laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)) based techniques are used to identify indicator minerals, with EMPA and LA-ICP-MS techniques being able to determine their major and trace element compositions (e.g. Layton-Matthews et al., 2013). Laser ablation-inductively coupled plasma-mass spectrometry allows for the measurement of many elements at concentrations as low as parts per billion (e.g. Jackson et al., 1992).

In the past, individual studies using trace elements to vector to mineral deposits have generally only included one or two minerals (e.g. hematite and magnetite (Schmidt Mumm et al., 2012)); however, there are exceptions. Ismail et al. (2014) analyzed multiple minerals (feldspar, calcite, garnet, pyroxene, amphibole, allanite, epidote-group minerals, titanite, and apatite) in a study of the Hillside IOCG deposit, South Australia. In addition, Spry et al. (2015) analyzed garnet, biotite, and magnetite in the metamorphosed Stollberg Zn-Pb-Ag and magnetite field, Sweden. Trace element studies have been utilized to explore for metamorphosed massive sulphide deposits, including tourmaline (Griffin et al., 1996), sulphide minerals (George et al., 2016), garnet (Spry et al., 2007; Heimann et al., 2011), and gahnite (O'Brien et al., 2015a,b). However, these studies focused mostly on minerals spatially associated with Broken Hill-type Pb-Zn-Ag (BHT) deposits. By contrast, there are relatively few trace element studies of minerals associated with metamorphosed VMS and sedimentary-exhalative deposits, two of which were done by Makvandi et al. (2016a,b) for magnetite in various metamorphosed VMS deposits. Here, we have analyzed the trace and major element compositions of common rock-forming silicates (garnet, biotite, staurolite, chlorite, and muscovite) and oxides (gahnite, ilmenite, and magnetite) in sediment-hosted massive sulphide Cu-Au (Kanmantoo, South Australia) and Pb-Zn-Ag deposits (Wheal Ellen, Angas, Scotts Creek, Aclare, Strathalbyn, and St. Ives, South Australia), which were metamorphosed to amphibolite facies. Minerals were analyzed by EMP and LA-ICP-MS methods, the details of which are given in O'Brien et al. (2015a) and are not repeated here. The aim of study is to evaluate the use of trace elements of multiple minerals to guide exploration in the Kanmantoo area and metamorphosed sediment-hosted sulphide deposits, in general.

GEOLOGICAL SETTING

The Cu-Au and Pb-Zn-Ag deposits occur in a structurally thickened package (~7–8 km) of metamorphosed pelitic and psammitic (including metaturbidite) sediments of the Cambrian Kanmantoo Group, South Australia, within an extensional fault-controlled back-arc basin (Kanmantoo Trough). Up to five deformation events have affected the deposits, with peak metamorphic conditions (amphibolite facies) coinciding with the second deformation event (e.g. Spry et al., 1988). The Cu-Au and Pb-Zn-Ag deposits occur in the Tapanappa Formation, primarily in a stratigraphic interval, several hundred metres wide, in garnet-andalusite-biotite±staurolite schist that we consider to be a regional, stratabound, metamorphosed hydrothermal alteration zone. This zone extends intermittently for more than 30 km, from about 10 km north of Kanmantoo toward Strathalbyn, and has been, in the past, a major focus of exploration for base metal sulphides in the Kanmantoo Group (Fig. 1).
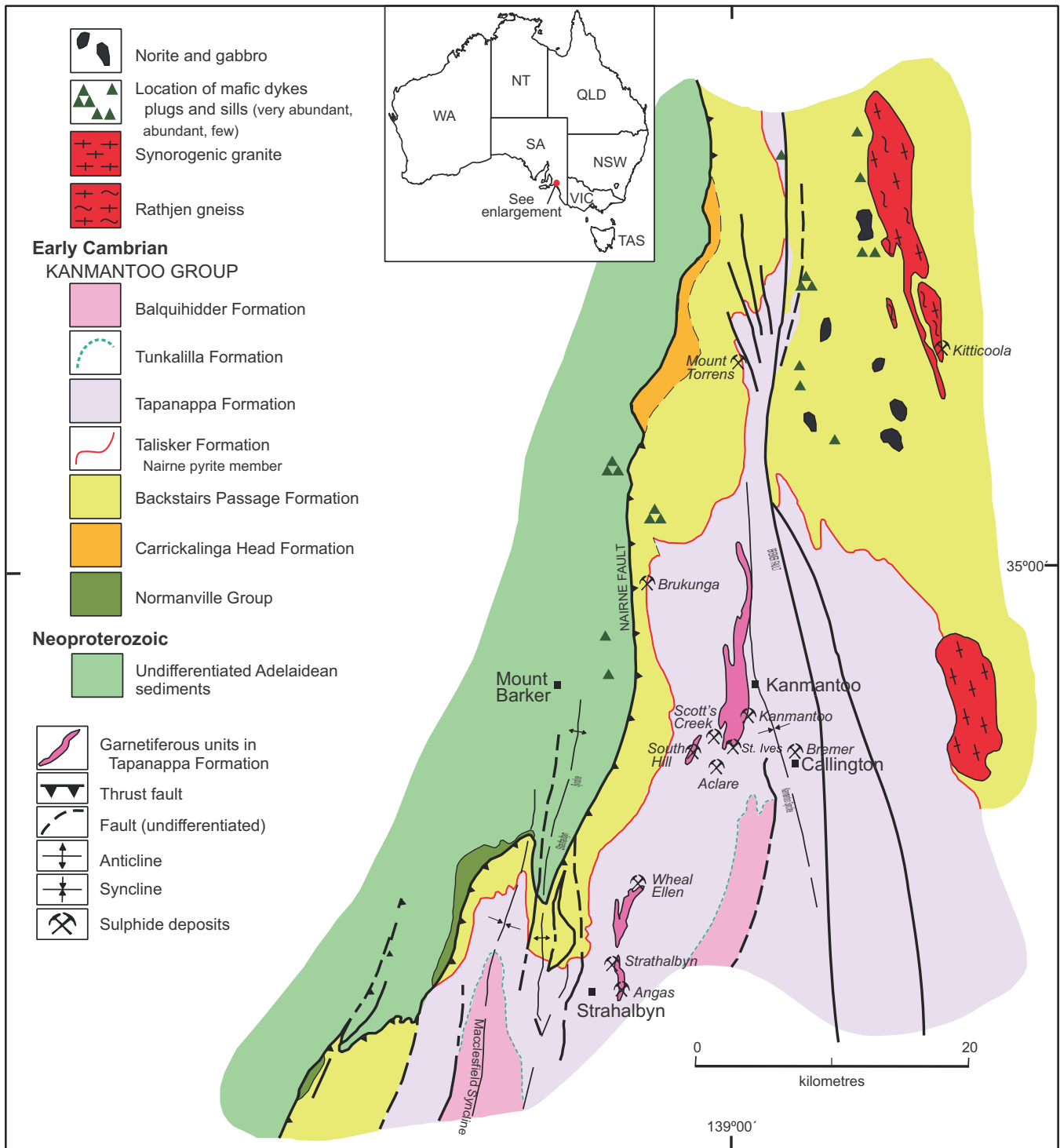
Figure 1. Geological map of the Kanmantoo region showing the location of Cu-Au and Pb-Zn-Ag deposits in the Kanmantoo Group, South Australia (modified after Toteff, 1999).

Rock types associated with sulphide mineralisation include quartz-mica schist, quartz-biotite-garnet-andalusite±chlorite± staurolite±magnetite rock, and biotite-garnet-chlorite rock, the last of which is the immediate host for much of the sulphides. Minor rock types include exhalite (e.g. quartz garnetite, garnet-quartz-cummingtonite schist, plagioclase rock, banded iron formation: Toteff, 1999), gahnite-bearing mica schist, pyritic schist, and calc-silicate rocks. The Kanmantoo Cu-Au deposit (34.5 Mt @ 0.6% Cu and 0.1 g/t Au; http://www.hillgroveresources.com.au/section/Projects/Kanmantoo), which is the largest Cu-Au deposit in the Kanmantoo Group, is characterized by discordant and pipe-like orebodies (e.g. Kavanagh, Spitfire, and Emily), and concordant mineralisation (Nugent). The Pb-Zn-Ag deposits are mostly concor-
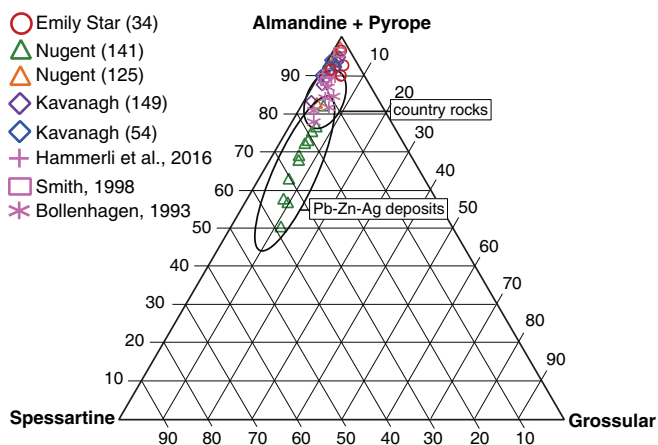
Figure 2. Ternary plot of garnet compositions from the Kanmantoo deposit (Emily Star, Kavanagh, and Nugent orebodies) and country rock schist (Bollenhagen, 1993; Smith, 1998; Hammerli et al., 2016) shown by an ellipse. The compositional field of garnet associated with Pb-Zn-Ag deposits is shown as a separate ellipse.

dant to bedding, with both Cu-Au and Pb-Zn-Ag types exhibiting local remobilization of sulphides. The discovery of gahnite- and spessartine garnet-bearing rocks were key to finding the Angas Pb-Zn-Ag deposit (3.04 Mt @ 8.0% Zn, 3.1% Pb, 0.3% Cu, 34 g/t Ag, and 0.5 g/t Au; http://www.portergeo.com.au/database/mineinfo.asp?mineid=mn1287), the largest known Pb-Zn-Ag occurrence in the Kanmantoo Group. The metallic minerals of the Cu-Au deposits consist mostly of chalcopyrite, pyrrhotite, magnetite, Bi minerals, and pyrite, whereas those associated with Pb-Zn-Ag deposits are primarily sphalerite, pyrite, galena, chalcopyrite, pyrrhotite, and cobaltian arsenopyrite. A zone of chalcopyrite-magnetite-rich rocks at the Wheal Ellen Pb-Zn-Ag deposit, which shows a metallic mineral assemblage almost identical to the most common assemblage at Kanmantoo, suggests a genetic link between the Pb-Zn-Ag deposits and Cu-Au mineralisation. The presence of both Cu and Pb-Zn-Ag zones at the Strathalbyn deposit also supports this concept.

MINERAL CHEMISTRY

Garnet

Although Fe-rich (Mn-poor) garnet is common in most orebodies at Kanmantoo (2–4 wt% MnO), country rock mica schists and unmineralized altered rocks in the Kanmantoo Group contain slightly higher concentrations of Mn (~3–7 wt% MnO) (Bollenhagen, 1993; Smith1998; Hammerli et al., 2016), whereas the composition of garnet is more Mn-rich in and proximal to Pb-Zn-Ag mineralisation (up to 30 wt% MnO), and the concordant Nugent orebody (up to 18 wt% MnO) at Kanmantoo (Fig. 2). Furthermore, the Zn concentration of garnet associated with Pb-Zn-Ag mineralisation is high (100–252 ppm Zn) relative to that spatially associated with the Kanmantoo Cu-Au deposit and the
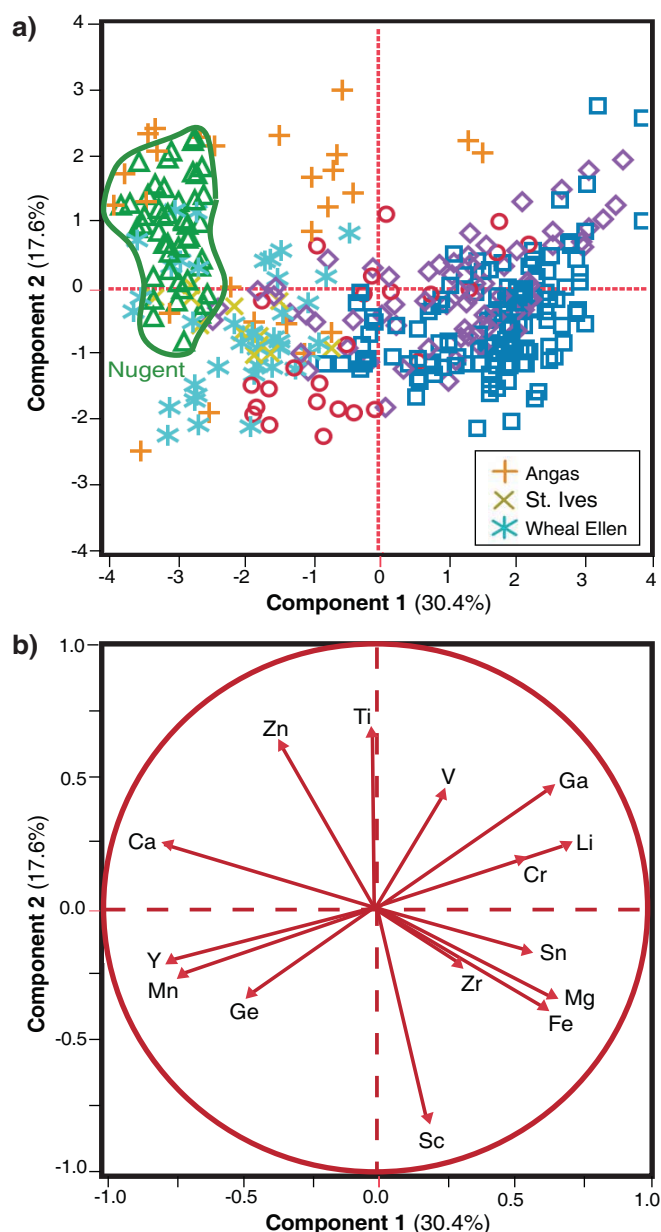

Figure 3. Principal component analysis of garnet using 15 elements, Ca, Cr, Fe, Ga, Ge, Li, Mg, Mn, Sc, Sn, Ti, V, Y, Zn, and Zr. **a)** Score plot of the first two principal components with percent variance for component 1 and 2 on the x and y axis, respectively. **b)** Loading plot showing the vector representation of data projected onto the score plot for each element. Symbols same as shown in Figure 2 for Kanmantoo orebodies.

country rocks (<26 ppm Zn). A principal component analysis of garnet from Pb-Zn-Ag deposits overlaps that of the Nugent orebody at Kanmantoo (Fig. 3), which is spatially associated with laminated quartz-garnet rocks.

Gahnite

Gahnite is spatially associated with the Pb-Zn-Ag deposits (e.g. Angas, Wheal Ellen, Strathalbyn, Aclare, and St. Ives) but it also locally occurs in schists imme-
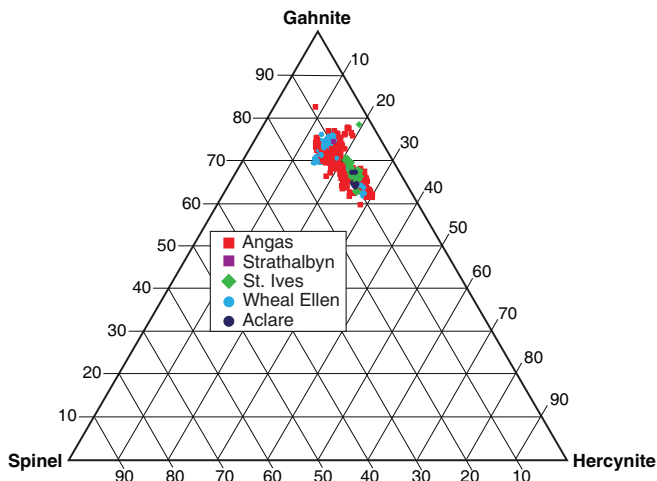
Figure 4. Ternary plot of gahnite compositions from the Aclare, Angas, St. Ives, Strathalbyn and Wheal Ellen Pb-Zn-Ag deposits, in terms of the gahnite-hercynite-spinel *sensu stricto* spinel endmembers.

Figure 5. Histogram of Zn content of staurolite. Some data for Angas are from McElhinney (1994).

Figure 6. Plot of Sn/Ga (ppm) vs. Al/Co (ppm) used for provenance of hydrothermal ore deposits (after Singoyi et al., 2006). Please note that the symbols used in this figure are different than those used in the other figures.

diately north and south of the Kanmantoo deposit (Toteff, 1999). Gahnite in the Pb-Zn-Ag occurrences has major element compositions (Zn, Mg, and Fe) that overlap compositions of gahnite in metamorphosed massive sulphide deposits found elsewhere in the world (i.e. 28–34 wt% ZnO) (Fig. 4). Gahnite is enriched in Cu (up to 39 ppm), and the first series transition elements, which include up to 3,600 ppm Mn, up to 90 ppm Co, up to 320 ppm V, up to 1,000 ppm Cr, and up to 217 ppm Ga. The trace element compositions of gahnite from Pb-Zn-Ag deposits generally overlap with each other but those from St. Ives are more enriched in Co.

Staurolite

The Zn and Mn contents of staurolite are also high in the Pb-Zn-Ag deposits (up to 6.3 wt% ZnO and up to ~5,000 ppm Mn) relative to those associated with staurolite in the Kanmantoo deposit (up to 1.6 wt% ZnO (with one outlier of 3.2 wt% ZnO), 344 ppm Co, 285 ppm V, and 2070 ppm Mn) (Fig. 5).

Biotite

Biotite in the Cu-Au and Pb-Zn-Ag deposits has compositions generally close to the phlogopite-annite boundary. Biotite in the Pb-Zn-Ag deposits is unusually enriched in various trace elements, including up to 2,600 ppm Mn, 6,400 ppm Cu, and 1,200 ppm Zn in the St. Ives deposit, and up to 1,200 ppm Zn, 5,400 ppm Mn, and 5 wt% Tl in the Angas deposit. The Tl content of biotite is amongst the highest yet reported for biotite in nature. These elemental concentrations are in contrast to those associated with biotite in the Kanmantoo deposit, which are less enriched in metallic trace elements (e.g. <200 ppm MnO and ZnO, and <2 ppm Tl).
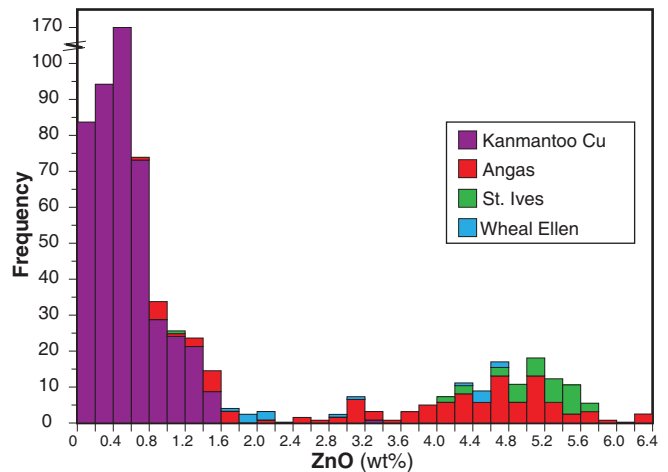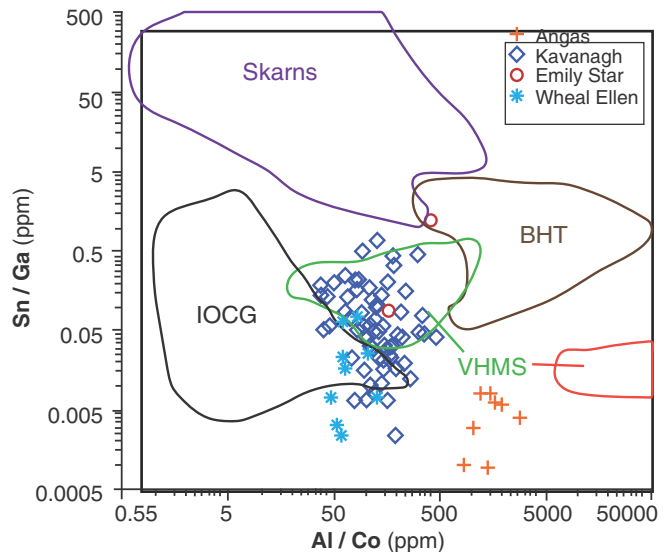
Chlorite

Mg-rich chlorite in sulphide mineralization at Kanmantoo contains up to 2,300 ppm Mn and 1600 ppm Zn, whereas Fe-rich chlorite contains up to 628 ppm Mn and 202 ppm Zn. Chlorite in Emily Star is characterized by an enrichment in Cu (up to 593 ppm) relative to all other samples that typically contain <10 ppm Cu. The reason for this is unclear. Chlorite spatially associated with Pb-Zn-Ag sulphides contains up to 8922 ppm Mn, 6970 ppm Zn and 321 ppm Cu.

Muscovite

Trace element compositions of muscovite in unaltered country rocks and altered rocks spatially associated with the Kanmantoo deposit contain up to 724 ppm V, 973 ppm Sr, 482 ppm Pb, ppm Cu, 212 ppm Zn, and

31,023 ppm Ba, whereas those associated with the Pb-Zn-Ag deposits contain up to 324 ppm V, 204 ppm Sr, 721 ppm Pb, 101 ppm Cu, 661 ppm Zn, and 17,227 ppm Ba. Muscovite from country rocks elsewhere in the Kanmantoo Group contain lower amounts of these elements (up to 298 ppm V, 125 ppm Sr, 32 ppm Pb, 70 ppm Cu, 51 ppm Zn, and 3,072 ppm Ba: Hammerli et al., 2016).

Ilmenite

Ilmenite in the Kanmantoo deposit is essentially end-member $FeTiO_3$, with up to 0.5 wt% MnO and 0.1 wt% ZnO, differing greatly from that at St. Ives, which contains up to 22.9 wt% ZnO, close to ecandrewsite ($ZnTiO_3$). Ilmenite in the Angas deposit is enriched in Mn, with concentrations ranging from 1.7 to 8.4 wt% MnO, and up to 0.5 wt% ZnO.

Magnetite

Magnetite is intergrown with chlorite, chalcopyrite, and pyrrhotite in the Kanmantoo Cu-Au deposit. Concentrations of select elements in magnetite in the Kanmantoo Cu-Au and Pb-Zn-Ag deposits, respectively, contain up to 7070 and 5394 ppm Al, 4520 and 1195 ppm Ti, 5085 and 4506 ppm V, 1285 and 1775 ppm Cr, 23200 and 983 ppm Cu, 12715 and 509 ppm Zn, and 252 and 607 ppm Ga. A plot of Sn/Ga vs. Al/Co was developed by Singoyi et al. (2006) to assess the provenance of hydrothermal magnetite from skarn, IOCG, Broken Hill-type Pb-Zn-Ag, and VMS deposits. Although there is no designated field for sediment-hosted deposits, it should be noted that most magnetite from the Kanmantoo and Pb-Zn-Ag deposits generally overlap the compositions of magnetite associated with VMS deposits (Fig. 6).

DISCUSSION AND CONCLUSIONS

The enrichment of Zn, Mn, Co, V, Cr, and Cu in gahnite, Mn and Zn in garnet and ilmenite, and Zn, Mn, Cu, and Tl in biotite in Pb-Zn-Ag and Cu-Au deposits relative to those found in the same minerals in unmineralized rocks, constitutes a potential pathfinder to metamorphosed sediment-hosted massive sulphide deposits in the Kanmantoo Group. The enrichment of Co in gahnite at St. Ives may not be surprising since Co is enriched in sulphides in the Kanmantoo Group (e.g. pyrite in pyritic schists, and cobaltian arsenopyrite at Wheal Ellen). Like those obtained here, garnet, gahnite, and biotite in BHT deposits contain elevated concentrations of Mn and Zn. Common rock-forming minerals, such as biotite, muscovite, chlorite, ilmenite, garnet, magnetite, gahnite and staurolite, some of which are resistate minerals, serve as potential chemical vectors in the exploration for SEDEX deposits in the Kanmantoo Group and in other metamorphic terranes.

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