Ferromagnesian silicates and oxides as vectors to metamorphosed sediment-hosted Pb-Zn-Ag-(Cu-Au) deposits in the Cambrian Kanmantoo Group, South Australia

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Keywords
Trace elements of silicates and oxides, Metamorphosed SEDEX deposits, Exploration guides, Kanmantoo Group South Australia

Disciplines
Geochemistry | Geology | Mineral Physics

Comments

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1. Introduction

Sedimentary exhalative Cu-Pb-Zn-Ag deposits in clastic sediments of predominantly Proterozoic and Phanerozoic age constitute some of the world’s largest accumulations of base metals (e.g., Leach et al., 2005). Various geological, geochemical, mineralogical, and geophysical techniques have been used to explore for these deposits (e.g., Lavery et al., 1994; Duffett and Leaman, 1997; Large and McGoldrick, 1998; Large et al., 2000, 2001). For example, mineralogical guides to SEDEX deposits include compositional variations in pyrite (Mukherjee and Large, 2017) and carbonate with proximity to ore (Large and McGoldrick, 1998). In exploring for metamorphosed SEDEX deposits in...
low- to high-grade metamorphic terranes, variability in the Fe/(Fe + Mg) content of biotite, chlorite, staurolite, cordierite, and amphibole has been used to indicate proximity to ore as a result of the Fe component of the silicate having reacted with sulfur from the nearby sulfide deposit (e.g., Nesbitt and Kelly, 1980).

Utilizing the trace element compositions of oxides, silicates, and sulfides in exploring for various types of ore deposits has become common practice over the last 20 years, particularly as a result of improved technologies related to laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) (e.g., Schmidt Mumm et al., 2012; Wilkinson et al., 2015; Xu et al., 2015; Cook et al., 2016). In searching for metamorphosed base metal deposits (e.g., skarn, Broken Hill type (BHT) Pb-Zn-Ag, metamorphosed volcanogenic massive sulfide (VMS)), the trace and major element compositions of garnet (Spry et al., 2007; Gaspar et al., 2008; Heimann et al., 2013), magnetite (Makvandi et al., 2016), and garnhite (O’Brien et al., 2015), have been used as vectors to ore. However, applying both major and trace element mineral compositions as pathfinders to metamorphosed SEDEX Pb-Zn-Ag deposits has received relatively limited attention but includes using the composition of garnhite as a provenance indicator to distinguish among SEDEX, VMS, BHT, and non-sulfide zinc (NSZ) deposits (O’Brien et al., 2015), and silicates (garnet, biotite, chlorite, staurolite, muscovite) and magnetite as pathfinders to Cu-Au mineralization in metamorphosed clastic sedimentary rocks in the Cambrian Kanmantoo Group, South Australia (Pollock et al., 2018).

The Tapanappa Formation in the Kanmantoo Group hosts Cu-Au mineralization, with the largest deposit being Kanmantoo (34.5 Mt @ 0.6% Cu and 0.1 g/t Au, www.hillgroveresources.com.au/section/Projects/Kanmantoo), Fe-S deposits (e.g., Brukunga deposit) and pyritic schists, Pb-Zn-(Cu-Au) deposits, and Cu-Au deposits (Both, 1990; Toteff, 1999) (Fig. 1). The Angas deposit is the largest known Pb-Zn-Ag-(Cu-Au) occurrence in the Tapanappa Formation (3.04 Mt @ 8.0% Zn, 3.1% Pb, 0.3% Cu, 34 g Ag/t, and 0.5 g Au/t; www.portergeo.com.au/database/mineinfo.asp?mineid = mn1287). The Fe-S deposits are generally considered to be synsedimentary or syndiagenetic (Skinner, 1958; George, 1967; Seccombe et al., 1985; Both, 1990), whereas the genesis of the Cu-Au deposits has been the subject of debate with syngenetic (Seccombe et al., 1985; Spyri et al., 1988; Both, 1990; Toteff, 1999; Marshall and Spyri, 2000; Pollock et al., 2018), synmetamorphic (Solomon and Groves, 1994; Gum, 1998; Oliver et al., 1998), and post-paste metamorphic (Foden et al., 1999; Focke et al., 2009; Schmidt Mumm et al., 2009; Tedesco, 2009) models being proposed. Seccombe et al. (1985) and Pollock et al. (2018) suggested the discordant nature of the Kanmantoo deposit indicated that sulfides generally formed below the sea floor as stockwork, vein, or disseminated mineralization in sub-surface vents, whereas the generally concordant nature of Pb-Zn-Ag-(Cu-Au) occurrences indicated they formed on the sea floor. Although a syngenetic model is generally favored for the Pb-Zn-Ag-(Cu-Au) mineralization (e.g., Seccombe et al., 1985; Both et al., 1995; Gum, 1998; Toteff, 1999; Spyri et al., 2010), a structurally-controlled model was more recently proposed by Singer (2008; http://saexplorers.com.au/archive/2008/08 terramin.pdf) for the Angas deposit. The syngenetic model for the origin of the Pb-Zn-Ag-(Cu-Au) deposits is based on the alignment of sulfides parallel to bedding, the incorporation of sulfide inclusions in porphyroblasts that formed prior to D1, the spatial relationship of these deposits to a regional stratabase metamorphosed hydrothermal alteration zone composed of the assemblage quartz-biotite-garnet-andalusite ± staurolite, and the spatial association of various meta-exhalative rocks that are present at the same stratigraphic level as the base metal deposits (e.g., Toteff, 1999). Metals and sulfur were likely derived from the thick package of sediments in the Kanmantoo Group prior to deformation with hydrothermal fluids circulating within the sediments and focused along synsedimentary faults to form the base metal deposits and stratabase zones of regional hydrothermal alteration in a manner similar to that proposed by Seccombe et al. (1985), Toteff (1999), and Pollock et al. (2018).

Gum (1998), Toteff (1999), and Pollock et al. (2018) pointed out that most of the base metal deposits in the Kanmantoo-Strathalbyn corridor show a spatial association with a regional stratabound alteration zone that was subsequently metamorphosed, and meta-exhalative rocks, as defined by Rider (1971), including spessartine garnet-quartz rocks, quartz-magnetite rocks, garnetiferous iron formations, quartz-gahnite rocks, tourmalinates, and meta-chert.

The present contribution complements the recent major and trace element studies of Pollock et al. (2018) of ferromanganese silicates and magnetite spatially associated with the Kanmantoo Cu-Au deposit by evaluating the compositions of garnet, biotite, staurolite, chlorite, muscovite, garnhite and magnetite, proximal to Pb-Zn-Ag-(Cu-Au) deposits in the Tapanappa Formation (Angas, Wheat Ellen, St. Ives, Scotts Creek, Strathalbyn, and Aclare). The approach taken here compares the major and trace element compositions of ferromanganese silicates and oxides in ore and altered rocks spatially associated with the Pb-Zn-Ag-(Cu-Au) deposits and compares them to the compositions of these minerals in unaltered and unmineralized country rock schists analyzed by Hammerli et al. (2016). For comparative purposes, we also evaluate whether the composition of ferromanganese silicates and oxides associated with the Pb-Zn-Ag-(Cu-Au) deposits differ from the compositions of these same minerals in altered rocks spatially associated with the Kanmantoo Cu-Au deposit, which are reported in Pollock et al. (2018). The alteration zones vary in width from 10's of meters at Kanmantoo, to < 10 m surrounding the Pb-Zn-Ag-(Cu-Au) deposits.

The aims of this study are to determine 1. Whether geochemical fingerprints for ferromanganese silicates in exhalative and altered rocks genetically related to Pb-Zn-Ag-(Cu-Au) mineralization can be distinguished from those in rocks unrelated to sulfides; 2. If the compositions of ferromanganese silicates spatially associated with Pb-Zn-Ag-(Cu-Au) mineralization differ from those obtained by Pollock et al. (2018) that are spatially related to the Kanmantoo Cu-Au deposit; and 3. If the compositions of ferromanganese silicates can be used as vectors to Pb-Zn-Ag-(Cu-Au) occurrences in the Kanmantoo Group and metamorphosed SEDEX deposits in other terranes.

2. Regional geology

Early Cambrian tectonism along the southeastern part of the Mount Lofty Ranges initiated development of the Kanmantoo Trough, an extensional, fault-controlled basin (Parker, 1986; Belperio et al., 1998; Toteff, 1999). It was filled with Cambrian-age siliciclastic rift facies sediments and minor carbonates of the Kanmantoo Group, which extends for over 300 km along the eastern margin of the Mount Lofty Ranges through the Fleurieu Peninsula to Kangaroo Island. Most of the Kanmantoo Group consists of a sequence of quartz-feldspar-mica schists and quartz-feldspar rocks, which are metamorphosed mudstone and turbiditic sandstone (Belperio et al., 1998; Butt, 2006). The Kanmantoo Group is divided into two sub-groups, the lower Keynes Subgroup, which unconformably overlies the Proterozoic Normanville Group, and the Bollaparudda Subgroup (Jago et al., 2003). The succession of sediments is dominated by a repetitive sequence of massive sandstone (greywacke) beds grading up into siltstones.

Base metal mineralization in the Kanmantoo Group is primarily hosted in the Talisker and Tapanappa Formations. The former consists mainly of metasiltstones and minor calc-silicates, and includes the Nairne Pyrite Member, which hosts iron-sulfide deposits as well as minor Zn and Ag occurrences (e.g., Mt. Torrens, Brukunga, Talisker; Daily and Milnes, 1971; Gum, 1998). The Tapanappa Formation conformably overlies the Talisker Formation and is comprised of meta-graywacke, pyritic schist, lenses of sulfide-rich siltstones, and meta-exhalative units, including banded iron formation and manganese-rich garnet quartz rocks along with Cu-Au (e.g., Kanmantoo, Bremer, South Hill) and Pb-Zn-Ag-(Cu-Au) mineralization (e.g. Angas, Wheat Ellen, St. Ives, Strathalbyn, Scotts Creek, Aclare) (Seccombe et al., 1985; Belperio et al., 1998; O’Brien et al., 2015).
et al., 1998; Gum, 1998; Toteff, 1999). These deposits are restricted to a stratigraphic interval several hundred meters in width approximately 2 km above the base of the Tapanappa Formation (Flöttmann et al., 1998; Gum, 1998), primarily in an ~30 km long, discontinuous stratabound alteration zone composed of the assemblage quartz-biotite-garnet-andalusite ± staurolite (e.g., Seccombe et al., 1985; Toteff, 1999).

Deposition of the Kanmantoo Group occurred between 522 ± 2 Ma (Jenkins et al., 2002) and 514 ± 3 Ma (Foden et al., 2006). Sedi-
mentation in the Kanmantoo Trough ceased as a consequence of con-
vergent deformation of the Delamerian Orogeny, which occurred be-
tween 514 ± 3 and 490 ± 3 Ma (Foden et al., 2006). Rocks of the
Kanmantoo Group were subjected to at least three primary deformation events during the Delamerian Orogeny (Offler and Fleming, 1968; Fleming and White, 1984; Parker, 1986; Both, 1990; Mancktelow, 1990; Preiss, 1995; Oliver et al., 1998). The earliest deformation (D1) was associated with west-verging thrusts, low-angle schistosity (S1) fabrics, and major upright folds (F1). D1 was followed by two periods, D2 and D3, of tight to open, upright folds and weak crenulations, S2 and S3 (Offler and Fleming, 1968; Mancktelow, 1979, 1990; Flöttmann et al., 1998). Metamorphism reached the amphibolite facies (e.g. Offler and Fleming, 1968; Mancktelow, 1979, 1990; Sandiford et al., 1990), with a regional zonation from greenschist facies in the west to upper amphibolite facies and local zones of migmatite to the east. The base

Fig. 1. Geologic map of the Kanmantoo region showing the location of the Kanmantoo Cu-Au deposit and regional Pb-Zn-Ag and Cu-Au deposits, most of which are hosted in the Tapanappa Formation. Structural features, lithologies (including garnetiferous alteration zones), and known intrusives are shown. Inset shows the location of the Kanmantoo region in Australia (modified after Toteff, 1999; Chen and Liu, 1996).
metal deposits of the Tapanappa Formation are within metasedimentary rocks that reached the staurolite-andalusite-fibrolite zone (Dymoke and Sandiford, 1992). Schiller (2000) estimated peak metamorphic temperatures of 530–565 °C and 480–510 °C at the Kanmantoo Cu deposit based on phase equilibria and mineral geothermometry, respectively. He also estimated peak pressure conditions at 3–4 kb, which is consistent with pressures of 4.1 ± 0.3 kb at the Wheal Ellen, Aclare, Angas, and Brunguka deposits utilizing the sphalerite geobarometer (Spry et al., 1988; McElhinney, 1994). Peak metamorphism occurred pre to early D2 corresponding to the intrusion of syntectonic I- and S-type granites along the eastern margin of the Kanmantoo Group (Mancktelow, 1990; Sandiford et al., 1990; Toteff, 1999). Once convergent deformation ceased around 490 Ma (Foden et al., 2006), there was an abrupt transition to a bimodal magmatic association of A-type granites and mafic intrusions (e.g., Milnes et al., 1977; Turner, 1996; Foden et al., 1999).

3. Methodology

3.1. Sample selection

Samples were collected from diamond drill cores ANG-1, ANG-9, ANG-12, ANG-16, ANG-17, ANG-18, ANG-20, and ANG-29 from the Angas deposit, and WH002 and WH006 from the Wheal Ellen deposit. Surface samples were also obtained from the Wheal Ellen, St. Ives, Scotts Creek, and Aclare deposits. One hundred and seventy polished thin sections were examined at Iowa State University using an Olympus BX-60 dual reflected-transmitted light microscope. In addition, selected samples from the Strathalbyn deposit that were part of the study of Spry et al. (1988) have also been evaluated. The drill holes chosen from the Angas and Wheal Ellen deposits in some cases extended from unmineralized and unaltered country rocks, through the alteration envelope, and into massive sulfide mineralization. Other shorter drill holes just intersected the altered rocks and the massive sulfides.

Major element compositions of garnet, biotite, staurolite, chlorite, muscovite, garnihite, ilmenite, and magnetite were obtained using a JEOL JXA-8900 Electron Probe Microanalyzer at the University of Minnesota. Analyses were conducted using a 15 kV accelerating voltage with a 20 nA beam current, a 1–2 μm spot size, and mineral standards including hornblende (Si, Al, Mg, Ca), ilmenite (Ti, Fe), albite (Al, Na), spessartine (Al, Mn), pyrope (Si, Mg), K-feldspar (K), garnihite (Zn, Al), tugtupite (Cl), and apatite (F). Chlorite and biotite are reported as XFe, which is the molar proportion of total iron relative to iron and magnesium (i.e., XFe = Fe / (Fe + Mg)). Mineral abbreviations given in parentheses are from Whitney and Evans (2010).

Trace element data was pre-treated following the method of Croghan and Eggehy (2003) such that LA-ICP-MS results that include up to 40% censored data were substituted with the detection limit divided by the square root of 2. To unconstrain the data used for multivariate statistics and more easily recognize patterns in the dataset, a centered log-ratio transformation was applied using CoDaPack version 2.01.15 (Muriithi, 2015). Using a multivariate statistical approach, trace element data for garnet and biotite were discriminated through principal component analysis (PCA) using JMP Pro version 12.0.0. Principal component analysis is a statistical procedure that uses an orthogonal transformation to extract the major sources of variation (i.e., principal components are the eigenvectors of a variance-covariance matrix) in a multivariate set of data (Davis, 2002). In the present study, the PCA includes the elements Li, Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, Sr, Y, Sn, Cs, Th, Pb, and Cu.

4. Local geology of Pb-Zn-Ag-(Cu-Au) deposits

4.1. Angas deposit Pb-Zn-Ag

The Angas deposit was discovered by Aberfoyle Resources Limited in 1991, and subsequently mined by Terramin Australia Limited from 2008 to 2013. It lies on the eastern limb of the Strathalbyn Anticline, a regional, south-plunging F2 fold in the Tapanappa Formation within a sequence of interlayered biotite-feldspar-quartz schist, quartzite, and pelitic schists (Table 1). Most of the sulfide mineralization occurs in a pelitic interval that is at least 2 km long and up to 200 m wide, and is largely restricted to a quartz-biotite-muscovite-andalusite-garnet-staurolite ± garnihite ± fibrolite schist (Fig. 2a) with minor magnetite, plagioclase, and pyroxene.

Table 1

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Host rock sequence</th>
<th>Sulphide assemblage</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Wheal Ellen</td>
<td>Quartz-biotite chert, And-Grt-St ± Gln schist, metagraywacke, banded iron formation, quartz-garnet rock</td>
<td>Po - Sp ± Gln ± Ccp</td>
<td>Spry (1976), Both et al. (1995), Toteff (1999)</td>
</tr>
<tr>
<td>Strathalbyn</td>
<td>Quartz-biotite chert, And-Grt-St ± Gln schist, metagraywacke, banded iron formation, quartz-garnet rock</td>
<td>Po - Sp ± Gln ± Ccp</td>
<td>Both et al. (1995), Toteff (1999), Spry et al. (2000)</td>
</tr>
<tr>
<td>Scotts Creek/Wheel Margaret/Wheel Rose</td>
<td>Quartz-biotite chert, quartz-garnet rock</td>
<td>Gln - Sp ± Ccp ± Po ± Py ± Ttr</td>
<td>Askins (1968), Gum (1998), Toteff (1999)</td>
</tr>
<tr>
<td>Aclare</td>
<td>Metagraywacke, metasiltstone, andalusite schist, quartz garnetite</td>
<td>Sp + Gln ± Asp ± Mn + Po ± Py ± Ttr</td>
<td>Askins (1968), Gum (1998)</td>
</tr>
<tr>
<td>St. Ives/Wheel Harmony</td>
<td>Quartz-biotite chert, And-Grt-St ± Gln schist, metagraywacke</td>
<td>Po - Sp ± Gln ± Ccp</td>
<td>Gum (1990)</td>
</tr>
</tbody>
</table>
anthophyllite, and cordierite that is surrounded by a garnet-bearing pelitic halo (up to 3% garnet) (McElhinney, 1994; Toteff, 1999). These garnet-bearing schists are more common in the stratigraphic footwall of the deposit with massive garnetite being locally present in the main ore horizon, including the discovery outcrop (Fig. 2b). The southern extent of the garnet-rich rocks within the hinge of the Strathalbyn Anticline is currently unknown due to a lack of outcrop, but they have been identified in drill holes up to 1 km south of the Angas deposit. Schists that contain muscovite, pyrite, K-feldspar, and minor cordierite are locally present adjacent to the deposit and resemble pyritic schists elsewhere in the Kanmantoo Group (Spry et al., 1988). Rare dolerite dikes were identified in drill core, which appear to sub-parallel foliation.

Sulfide mineralization is of two main types, the so-called “western” and the sub-economic “eastern” mineralization of Toteff (1999). The western mineralization consists of the steep, easterly dipping semi-massive to massive so-called Rankine, Hanging Wall, and Garwood lodes, which extend to a depth of ~ 400 m. The deposit parallels bedding and a prominent S₂ schistosity, with fine disseminations of sulfides occurring parallel to bedding and coarser aggregates being aligned parallel to the schistosity. The main sulfides consist of pyrite,
pyrrhotite, sphalerite, and galena, and minor chalcopyrite, marcasite and arsenopyrite. Quartz-chlorite-gedrite-garnet-magnetite, andalusite-magnetite-garnet-biotite and quartz-tourmaline rocks with disseminated sulfides, locally occur in the western mineralization (Toteff, 1999), along with minor actinolite-magnetite-cordierite-quartz rocks (Fig. 2c). Rare calcsilicate-rich clastic horizons occur in the eastern mineralization and are composed of tremolite-actinolite, biotite, grossular, phlogopite, chlorite, quartz, and minor scapolite and epidote (Toteff, 1999). According to Toteff (1999), petrographic analysis suggests the rocks were originally pelites with a higher sedimentary carbonate content than the surrounding metasedimentary rocks. Note that while McElhinney (1994), Both et al. (1995) and Toteff (1999) considered the so-called clastic-hosted western mineralization to be syn-genetic, Toteff (1999) also regarded the minor, low-grade eastern mineralization to have had a post-peak “metamorphic/replacement component.”

The frequency of F2 folds decreases along strike from north to south away from the main Rankine mineralization. There also appears to be less intense folding in the footwall of the orebody. These observations indicate that micro- and macro-scale folding is more intense in the hanging wall with deformation possibly being localized by the high competency contrast between the massive sulfide ore lenses and more competent host greywacke. Small parasitic folds can be observed in drill core with the dominant regional S2 biotite foliation within the axial plane of F2 folds. Sulfides can occur in the axes of these folds but they can also occur in S1 inclusion trails in andalusite.

Laing (1998) described two types of mineralization based on textural relationships in the western mineralization. Type 1 consists of massive to banded, equigranular ore dominated by pyrite, sphalerite, and galena (Fig. 2d), whereas type 2 mineralization is remobilized with rounded ovoids of coarse-grained sphalerite that were cleaved or milled in a matrix of flattened grains of galena, rounded equigranular pyrite and quartz, and a marked increase in the proportion of pyrrhotite relative to base metal sulfides (Fig. 2e). The irregular sulfide breccia textures, or so-called “durchbewegt,” is typical of textures recorded from deformed stratiform base metal sulfide deposits (e.g. Vokes, 1973; Marshall and Gilligan, 1987).

4.2. Wheal Ellen Pb-Zn-Ag-(Cu-Au) deposit

Wheal Ellen lies about 6 km north of Strathalbyn on the eastern limb of a regional syncline and was worked between 1857 and 1911, producing 75,000 tons at grades of 10% Pb, 18% Zn, 150 g/t Ag, and 4 g/t Au (Spry et al., 1988; Gum, 1998; Toteff, 1999). Grades of 180 g/t Au were mined towards the oxidized, northern end of the deposit (Askins, 1968; Gum, 1998; Toteff, 1999). Base metals are zoned in the deposit with Zn-rich mineralization in the south and more Cu-rich mineralization in the north. Recent drilling by Hillgrove Resources crosscut
Table 2
Representative compositions of garnet, staurolite, and gahnite.

<table>
<thead>
<tr>
<th></th>
<th>Garnet</th>
<th></th>
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<th>Gahnite</th>
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significant polymetallic mineralization (http://www.hillgroveresources.com.au/article/SA_Exploration/Wheat_Ellen) including intercepts of 5 m @ 8.68% Zn, 5.89% Pb, 2.34 g/t Au in WHDD003, along with zones of Cu mineralization (1 m @ 2.55% Cu and 1 m @ 1.74% Cu in WHRC046). Metalic mineralization occurs in a tabular orebody, parallel to bedding and schistosity (S₁), in biotite schist, quartze-biotite-garnet-andalusite-staurolite ± chloride rock (Fig. 2f), quartz-feldspar-mica schist, quartz-gahnite-biotite-staurolite rock, and garnetite (Table 1; Seccombe et al., 1985; Gum, 1998; Spry et al., 1988; Toteff, 1999). Minor quartz-biotite-garnet rock, pyritic schist, cordierite-anthophyllite-garnet rock, and andalusite schists occur adjacent to or nearby the orebody, whereas a 1.5 m wide outcrop of banded iron formation occurs along strike from the deposit, ~50 m to the north (Fig. 2g, h). The orebody is 1.4 to 4.5 m wide, at least 230 m long, and forms to a depth of 110 m at the southern end (Gum, 1998; Toteff, 1999). The metallic mineralization consists of two main types: 1. Massive coarsely recrystallized pyrite, sphalerite, galena, and minor pyrrhotite and chalcopyrite primarily in biotite schist; and 2. Pyrite and chalcopyrite in quartz veins. Lesser amounts of tetrahedrite, marcasite, boulangerite, cobaltian arsenopyrite, magnesioferrite, and minor pyrrhotite and chalcopyrite primarily in biotite schist, which occur as copper carbonates in quartz-veined garnetiferous schist and as chalcopyrite in quartz veins and as remobilizates in fractures (Askins, 1968; Gum, 1998; Seccombe et al., 1985; Spry et al., 1988; Toteff, 1999).

4.3. Strathalbyn Pb-Zn-Cu-Au-(Au) deposit

The Strathalbyn mine, which operated from 1848 to 1858, occurs about 1 km north and along strike from the Angas deposit. The lenticular orebody, about 4 m thick, is copper-rich at the northern end and lead-zinc rich to the south, and produced about 2000–4000 tons @ 8–18.5% Pb, 12% Zn, and 220–480 g/t Ag (Brown, 1908; Seccombe et al., 1985; Gum, 1998). Metalic mineralization consists primarily of pyrite, chalcopyrite, sphalerite, marcasite, pyrrhotite, and galena with minor amounts of arsenopyrite and tetrahedrite (Askins, 1968; Seccombe et al., 1985; Gum, 1998). Sulfides are present as veins in quartz-garnet-mica ± garnite ± staurolite ± andalusite ± schist (Askins, 1968; Seccombe et al., 1985; Gum, 1998). The host rock is layered due to varying abundance of quartz, garnet, fibrolite (Fig. 3a), and garnite (Gum, 1998). Copper occurs as copper carbonates in quartz-veined garnetiferous schist and as chalcopyrite in quartz veins and as remobilizates in fractures (Gum, 1998; Toteff, 1999). The presence of massive galena and sphalerite in a garnite-garnet envelope within quartz-biotite-garnet-andalusite schists resembles that which occurs at the nearby Angas deposit.

4.4. Scotts Creek Pb-Zn deposit

The Scotts Creek mine consists of three orebodies situated on the western limb of an anticline that also contains the Aclare Pb-Zn deposit. The orebodies, which range from 1 to 4 m wide, were mined to a depth of 30 m over a length of 60 m, and produced about 3000 tons of ore @ 45% Pb and 2 kg/t Ag from the 1840s to 1889. They are hosted in a laminated quartz garnetite (Fig. 3b) and K-feldspar-garnet quartz rock within quartz-mica schist, and minor quartz-potassium feldspar-mica and biotite-andalusite schists (Gum, 1998; Smith, 1998; Toteff, 1999). Metalic mineralization consists of massive or, more commonly, disseminated layers of sphalerite, galena, chalcopyrite, pyrite, and tetrahedrite, and as minor galena-rich fracture fillings (Askins, 1968; Toteff, 1999). A garnet-calcisilicate unit, comprised of various amounts of garnet, actinolite, clinopyroxene, quartz, K-feldspar, cummingtonite, and up to 15% pyrrhotite, occurs in a carbonaceous meta-silstone stratigraphically above the laminated quartz garnetite, the latter of which has a strike length of at least 80 m. This carbonaceous meta-silstone was considered by Toteff (1999) to be the stratigraphic equivalent of a similar rock at the nearby Aclare Pb-Zn deposit, located approximately 2.5 km south of Scotts Creek (Toteff, 1999). Other rocks within 250 m of the Scotts Creek deposit include quartz-biotite ± andalusite ± sillimanite ± garnet ± staurolite ± garnite rocks, a plagioclase-rich quartzite, chloride-garnet- quartz ± cummingtonite schist, and garnet-biotite-cummingtonite ± magnetite quartzite that are either meta-exhalatives or stratabound altered rocks (Toteff, 1999).

4.5. Aclare Pb-Zn-Ag deposit

The Aclare deposit occurs in the nose of a regional south plunging antcline, and produced ~14,000 tons of supergene and primary ore, with the latter averaging ~6–9% Pb, 9–10% Zn, 0.3% Cu, 280–480 g/t Ag, and 2 g/t Ag (Chilman, 1982). The orebody has a tabular shape that ranges from 1 to 5 m wide, over a strike length of 90 m and to a depth of over 100 m (Askins, 1968). It is tightly folded and brecciated, and is locally remobilized into the axial planes of folds and fold hinges. The mineralization occurs in a quartz garnetite unit comprised of very fine-grained garnet laminations within a matrix of recrystallized quartz, and minor biotite and muscovite (Gum, 1998). The stratiform orebody consists of narrow (2 cm wide) folded layers of quartzite, quartz-mica schist, and quartz-garnetite (Table 1; Askins, 1968; Gum, 1998, Toteff, 1999). Carbonaceous silstone, andalusite schist (Fig. 3c), metacherts, plagioclase-biotite-garnet rocks, and minor calc-silicate rocks are also spatially related to the deposit (Toteff, 1999). Sulfide-rich layers contain coarse-grained sphalerite and galena with lesser amounts of arsenopyrite, pyrite, pyrrhotite, tetrahedrite, meneghinite, and boulangerite (Askins, 1968; Gum, 1998). Sulfide-poor layers consist of finer-grained, disseminated sulfides. Sphalerite and galena are also found in quartz veins, up to 30 cm wide (Toteff, 1999). Garnite is locally present in pyritic quartzite.

4.6. St. Ives/Wheel Harmony

The St. Ives Cu-Pb-Ag deposit, also known as Wheal Harmony, is stratiform and found in the hinge zone of a small syncline. Disseminated sulfides occur in quartz veins hosted in a quartz-biotite-garnet-staurolite-andalusite ± garnite schist (Fig. 3d, e, Table 1). Chalcopyrite, galena, sphalerite, pyrrhotite, ilmenite, garnite, and rare tourmaline (Fig. 3f) occur along with secondary chalcocite, cuprite, azurite, and malachite.

5. Results

Petrographic and mineralogical studies were done on ferromagnesian silicates and oxides in exhalative and altered rocks spatially associated with sulfides in the Pb-Zn-Ag-(Cu-Au) deposits. Over 2100 EMPA and 1100 LA-ICP-MS analyses were obtained. Table 2 includes

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(continued on next page)
representative major and trace element compositions of garnet, staurolite, and gahnite whereas those for biotite, chlorite, and muscovite are given in Table 3. Sample locations, and all major element and trace element compositions of minerals are available from the authors. Bollenhagen (1993) and Smith (1998) determined the major element compositions of garnet, biotite, staurolite, and muscovite in andalusite-staurolite zone rocks in the Kanmantoo Group in sulfide-free unaltered and altered quartz-mica schists, whereas Hammerli et al. (2016) obtained major and a limited number of trace element compositions of ferromagnesian silicates in schists metamorphosed to the andalusite-staurolite zone on the eastern side of the Kanmantoo Trough. These data, and those for major and trace element compositions of garnet, biotite, staurolite, chlorite, muscovite, and magnetite associated with the Kanmantoo Cu-Au mine from Pollock et al. (2018), and for major element compositions of garnet, staurolite, and gahnite from the Angas deposit from McElhinney (1994) are compared with mineral compositions obtained here.

5.1. Garnet

Garnets in unmineralized altered schist and unaltered country rock in the Kanmantoo Group contain 1.6–7.4 wt% MnO, 29.4–39.0 wt% FeO, and 0.3–2.3 wt% CaO (Bollenhagen, 1993; Smith, 1998; Hammerli et al., 2016), whereas garnets analyzed here from garnet-andalusite-biotite ± staurolite schist, quartz garnetite, and quartz-mica schist (with disseminated sulfides) spatially associated with the Pb-Zn-Ag-(Cu-Au) deposits. Compositions of garnet from the Kanmantoo Cu-Au deposit (Pollock et al., 2018) and country rock schist (Bollenhagen, 1993; Smith, 1998; Hammerli et al., 2016) are shown as separate ellipses. a. Ternary diagram of garnet end-member compositions. b. Fe (apfu) vs. Mn (apfu). c. Ca (apfu) vs. Mn (apfu).

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Fig. 4. Major element compositions of garnet from the Angas, Wheal Ellen, St. Ives, and Scotts Creek Pb-Zn-Ag-(Cu-Au) deposits. Compositions of garnet from the Kanmantoo Cu-Au deposit (Pollock et al., 2018) and country rock schist (Bollenhagen, 1993; Smith, 1998; Hammerli et al., 2016) are shown as separate ellipses. a. Ternary diagram of garnet end-member compositions. b. Fe (apfu) vs. Mn (apfu). c. Ca (apfu) vs. Mn (apfu).
Au) occurrences are more enriched in Mn (0.4–22.2 wt% MnO) (Fig. 4a, b), with the most Mn-rich garnet (> 40 mol% spessartine) being derived from quartz garnetite from the Scotts Creek deposit, gahnite-garnet bearing rocks from the Wheal Ellen deposit, and garnet-bearing rocks adjacent to the Angas deposit (Fig. 4a). It should be noted that garnet from the discordant orebodies, Kavanagh and Emily Star, at the Kanmantoo Cu-Au deposit are Fe-rich and relatively Mn-poor (up to 42 wt% FeO and 7 wt% MnO), compared to garnet associated with the concordant Nugent orebody in the same deposit that contains up to 20 wt% MnO (Pollock et al., 2018). Garnet in calcisilicates and carbonates associated with the eastern mineralization from the Angas deposit is unusual for garnet-bearing rocks spatially associated with sulfides in the Tapanappa Formation in that it contains up to 14.2 wt% CaO (i.e., > 40 mol% grossular). In comparison to garnet from the Wheal

Fig. 5. Trace element compositions (in ppm) of garnet from Angas, Wheal Ellen, and St. Ives. a. Zn vs. Gd. b. Ge vs. Gd. c. Co vs. V). d. Ti vs. V.

Fig. 6. Principal component analysis of garnet using Li, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, Ge, and Y. a. Score plot of component 1 and component 2 with percent variance shown on the X and Y axes, respectively. b. Loading plot showing the vector representation of data projected onto the score plot for each element.
Ellen and St. Ives deposits, garnet from altered rocks spatially associated with the Angas deposit are generally more enriched in Ca (Fig. 4c).

Trace element compositions of garnet in altered rocks spatially associated with the Pb-Zn-Ag-(Cu-Au) deposits have elevated amounts of Pb (up to 682 ppm, Fig. 5a), Zn (up to 535 ppm, Fig. 5a, b), Ge (up to 121 ppm, Fig. 5b), Co (up to 37 ppm, Fig. 5c), V (up to 205 ppm, with one outlier of 360 ppm, Fig. 5c, d), and Ti (up to 2080 ppm, Fig. 5d), compared to garnet in the Kanmantoo Cu-Au deposit and country rock garnet, which contain up to 12.4 ppm Pb, 170 ppm Zn, 10 ppm V, 16.8 ppm Ge, and 3.9 ppm V, respectively (Hammerli et al., 2016; Pollock et al., 2018). In general, garnets from altered rocks at the Angas deposit have the highest concentrations of Zn, Gd, Ge, V, and Ti (Fig. 5b-f), whereas those from the St. Ives deposit are notably enriched in Co (up to 31 ppm, Fig. 5c).

To explore compositional variations in garnet among the Angas, Wheal Ellen, and St. Ives deposits, a principal component analysis (PCA) was conducted for the elements Li, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, Ge, and Y. These elements were chosen since they were above the detection limits for the majority of the analyses. Garnet from the Angas deposit has the highest proportion of positive component 1 scores whereas those for garnet from St. Ives have negative component 1 scores (Fig. 6a). The compositions of garnet from Wheal Ellen overlap those from St. Ives, which are both dominated by negative component scores that are due to enrichments in Co, Fe, Y, and Ge (Fig. 6b).

Chondrite normalized rare-earth element (REE) values for garnet from Angas, Wheal Ellen, and St. Ives are shown in Fig. 7 a-c. The REE patterns are light rare earth element (LREE) depleted and heavy rare earth element (HREE) enriched. The enrichment in HREE is greater for garnet from Angas and Wheal Ellen, some of which are > 1000 for Ho to Lu, compared to garnet at St. Ives which are < 1000 (Fig. 7a-c). All garnets from the St. Ives and Wheal Ellen deposits, and most from Angas, show negative Eu anomalies (i.e., Eu/Eu+ < 1, where Eu/Eu+ = EuCN/([SmCN + GdCN]0.5)) and Eu/Eu+ = EuCN/([SmCN + GdCN]0.5; (Taylor and McLennan, 1985). However, some garnets from Angas show positive Eu anomalies of up to 2.8 (Fig. 7d). Approximately half the garnets from the Angas deposit and only two from the Wheal Ellen deposit show positive Ce anomalies, where Ce/Ce+ > 1; Ce/Ce+ = CeCN/([LaCN + PrCN]0.5, with the remainder from the Wheal Ellen and Angas deposits, along with all from St. Ives, having values of Ce/Ce+ < 1.

5.2. Biotite

Biotite, which is present in nearly all rocks spatially associated with the Pb-Zn-Ag-(Cu-Au) deposits, contains 8.94–22.0 wt% FeO and 4.70–16.9 wt% MgO, with XFe ratios (where XFe = Fe/(Fe + Mg)) ratios of 0.22–0.61 and 14Al values of 2.34–2.89. These compositions are similar to those for biotite in altered rocks spatially associated with the Kanmantoo Cu-Au deposit (13.8–25.9 wt% FeO, 6.39–13.2 wt% MgO, XFe ratios of 0.38–0.67, and 14Al values of 2.59–2.81; Pollock et al., 2018) with the exception of slightly broader XFe ratios and 14Al values for biotite associated with the Pb-Zn-Ag-(Cu-Au) deposits. The lowest
values of XFe (0.22–0.34) are from garnet-biotite schist immediately adjacent to massive ore in the Angas deposit (Fig. 8a). Compared to biotite in country rocks, biotite in the host rocks spatially associated with the Pb-Zn-Ag-(Cu-Au) occurrences have similar Alv values but have a broader range of XFe ratios (Bollenhagen, 1993; Hammerli et al., 2016).

Plots of Li vs. Co, Li vs. Cu, Zn vs. Mn, and Zn vs Pb are shown in Figs. 8b-d, and Fig. 9a, respectively. Biotite in altered rocks associated with the Angas deposit contains up to 410.8 ppm Li and is generally more enriched in Li than biotite (up to 105.1 ppm Li) in garnet-biotite, quartz-mica, and garnet-andalusite-biotite-staurolite schist adjacent to the Wheal Ellen deposit (Fig. 8b, c). Conversely, biotite in these same rocks from Wheal Ellen is generally more elevated in Co (up to 158.2 ppm), than biotite in altered rocks associated with the Angas deposit (up to 68.8 ppm Co; Fig. 8b). Copper is more enriched in altered rocks associated with the Wheal Ellen (up to 187.2 ppm) and St. Ives deposits (up to 23,823 ppm) than in altered rocks associated with the Angas deposit (18.8 ppm Cu; Fig. 8c). However, it is likely that the extraordinarily high values of Cu in biotite from the St. Ives deposit are due to minute inclusions of chalcopyrite in the lattice of biotite; such inclusions were not observed in high-magnification back-scattered electron images. Although there is overlap in Mn and Zn concentrations in biotite in altered rocks spatially associated with Angas, Wheal Ellen, and St. Ives deposits, the most Zn-rich biotites are from the Wheal Ellen deposit (up to 4079 ppm Zn; Fig. 8d) whereas the highest concentrations of Mn (up to 6667 ppm Mn) are from the Wheal Ellen and Angas deposits. Values of Pb are considerably higher in biotite from the St. Ives deposit than in samples from the Wheal Ellen and Angas deposits, which except for one outlier from the Wheal Ellen deposit of 3001 ppm (sample WH4–26), are generally < 350 ppm.

Biotite in altered rocks from the Angas, Wheal Ellen, and St. Ives deposits contains < 10 ppm Tl. However, biotite in five of twenty eight biotite-bearing samples from the Wheal Ellen deposit and seven of thirty one from the Angas deposit contains > 30 ppm. One exceptional sample from the Angas deposit (Ang-16) contains an average of 3.9 wt% Tl (Fig. 10).

A principal component analysis was performed using eleven trace elements (Sc, V, Co, Ni, Zn, Sr, Sn, Cs, Tl, Pb, and Cu) that are above

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**Fig. 8.** Composition of biotite in altered rocks from the Angas, Wheal Ellen, and St. Ives deposits. a. Alv (apfu) vs. Fe / (Fe + Mg). b. Li (ppm) vs. Co (ppm). c. Li (ppm) vs. Cu (ppm). d. Zn (ppm) vs. Mn (ppm). The compositions of biotite in country rock schist (Bollenhagen, 1993; Hammerli et al., 2016) and from the Kanmantoo Cu-Au deposit (Pollock et al., 2018) are shown as separate ellipses in a and d.
detection limits for biotite. Principal component 1 (PC1) accounts for 33.9% of the variation and PC2 accounts for 25.6% of the variation. The resulting score and loading plots (Fig. 9b-d) display compositional variation between biotite from the St. Ives, Wheal Ellen, and Angas deposits. Biotite compositions for altered rocks from the Wheal Ellen and Angas deposits overlap, whereas biotite from St. Ives plots separately due to an enrichment in Cu.

5.3. Gahnite

Gahnite occurs in at least ten locations in the Kanmantoo Group where it is spatially associated with the syngenetic Pb-Zn-Ag-(Cu-Au) deposits (e.g., Angas, Wheal Ellen, Strathalbyn, Aclare, St. Ives, Scotts Creek, Strathburn (located between Strathalbyn and Wheal Ellen), Guthries prospect, 4 km east of Mt. Torrens), locally in schists immediately north and south of the Kanmantoo Cu-Au deposit (Spry et al., 1988; Toteff, 1999; O’Brien et al., 2015), and in Monarto D prospect, 20 km east of Wheal Ellen. Gahnite is particularly abundant in quartz-biotite-muscovite-andalusite-garnet-staurolite ± gahnite ± fibrolite schists spatially associated with the Angas deposit, where its presence was key to the discovery of the deposit (Anderson, 1993), and in the Wheal Ellen deposit where it occurs in quartz-gahnite-garnet-biotite ± staurolite rocks. Although major element compositions of gahnite from Wheal Ellen, Strathalbyn, St. Ives, and Angas were reported previously by Spry et al. (1988), McElhinney (1994), Toteff (1999), and O’Brien et al. (2015), additional compositional data obtained here from these four Pb-Zn-Ag-(Cu-Au) deposits and the Aclare occurrence overlap compositions of gahnite in metamorphosed massive sulfide deposits found elsewhere in the world (i.e. 28–34 wt% ZnO, Fig. 11) (e.g., Spry and Scott, 1986; Heimann et al., 2005). Laser ablation-inductively couple plasma-mass spectrometry analysis of gahnite by Spry et al. (2017) from these deposits showed that gahnite is enriched in Cu (up to 39 ppm), and the first series transition elements, which include up to 3600 ppm Mn, up to 90 ppm Co, up to 320 ppm V, up to 1000 ppm Cr, and up to 217 ppm Ga.

5.4. Staurolite

Staurolite occurs in garnet-andalusite-biotite-staurolite schist spatially associated with both Cu-Au and Pb-Zn-Ag-(Cu-Au) deposits and in unmineralized aluminous schists (Oiffer and Fleming, 1968; McElhinney, 1994; Toteff, 1999; Schiller, 2000; Spry et al., 2017).
Staurolite spatially associated with the Angas deposit, occurs in rocks containing disseminated sulfides, mainly pyrrhotite with only trace amounts of sphalerite. From the data obtained herein, staurolite that coexists with gahnite and pyrrhotite in the Angas deposit have ZnO values of 5.11 to 5.33 wt%, whereas staurolite in gahnite-absent quartz-garnet-biotite-staurolite rocks has between 0.72 and 3.80 wt% ZnO (Fig. 12). McElhinney reported a wide range of compositions from the Angas deposit from 0.82 to 1.72 wt% ZnO in the upper host unit (UHU) and 4.4 to 6.3 wt% ZnO in the main host unit (MHU) (Fig. 12). Staurolite-bearing samples from the St. Ives deposit either occur in trace amounts in quartz-gahnite-muscovite rocks or in gahnite-absent biotite-andalusite-staurolite-muscovite rocks (Fig. 3e). Regardless of the presence or absence of gahnite, staurolite contains between 4.21 and 5.63 wt% ZnO. However, at Wheal Ellen, staurolite contains up to 4.71 wt% ZnO in gahnite-bearing quartz-garnet-biotite-muscovite-andalusite-staurolite schists and between 0.03 and 3.01 wt% ZnO in gahnite-absent varieties of these rocks (Fig. 2f).

Trace element concentrations of Co, V, Cr, Mn, Ti, and Cu are typically above detection limits for staurolite (Fig. 13a-c). Compositional differences occur between staurolite from the Pb-Zn-Ag-(Cu-Au)
deposits and the Kanmantoo Cu-Au deposit, the latter of which were reported in Pollock et al. (2018). For example, Co (23.4–344 ppm) and Cu (0.12–104.1 ppm) are elevated in staurolite from the Kanmantoo deposit relative to that from the Angas, Wheal Ellen, and St. Ives deposits, which contain 0.09–68.9 ppm Co and 0.07–10.9 ppm Cu. In contrast, staurolite from the Pb-Zn-Ag-(Cu-Au) deposits have greater amounts of V (38.9–485.0 ppm), Cr (12.8–533.2 ppm), Mn (11.9–4946 ppm), and Ti (75.5–3946 ppm) than staurolite in altered rocks associated with the Kanmantoo deposit, which contain 14.9–285 ppm V, 2.25–396.7 ppm Cr, 46–2070 ppm Mn, and 94.7–3438 ppm Ti (Pollock et al., 2018).

5.5. Chlorite

Chlorite in altered rocks associated with the Pb-Zn-Ag occurrences has a wide compositional range (Fig. 14a) with 4.03–34.8 wt% FeO and 4.95–29.2 wt% MgO compared to chlorite in altered rocks associated with the Kanmantoo deposit (24.4–29.8 wt% FeO, 11.5–14 wt% MgO; Fig. 14b; Pollock et al., 2018). Ratios of XFe for chlorite in altered rocks from the Angas and Wheal Ellen deposits range from 0.33 to 0.78.

Chlorite contains up to 3406 ppm Zn and up to 8922 ppm Mn in massive ore from the Angas and Wheal Ellen deposits (Fig. 14c), respectively, which are elevated compared to their concentrations (up to 1600 ppm Zn and 1780 ppm Mn) in chlorite associated with ore from the Kanmantoo deposit (Pollock et al., 2018). Other trace elements that are typically above detection limits in chlorite include Rb (up to 533 ppm), Sr (up to 299 ppm), and Sn (up to 66 ppm). The highest Pb value for chlorite (4519 ppm) is from a gahnite-bearing rock from the St. Ives deposit (sample SI-5), but a high Pb value (1500 ppm) also occurs in chlorite in sample WE-13 (garnet-andalusite-biotite schist) from a dump at the Wheal Ellen deposit.

Although chlorite in altered rocks associated with the Pb-Zn-Ag occurrences usually contains < 82 ppm Cu, chlorite in a quartz-garnet-gahnite rock from the St. Ives deposit (sample SI-5) contains up to 322 ppm Cu. Chlorite in this sample is also enriched in Bi (18.3–654.8 ppm), in contrast to chlorite from the Angas and Wheal Ellen deposits, which only contain up to 9.5 ppm Bi regardless of rock type. The highest Tl content for chlorite associated with the Kanmantoo Cu-Au deposit is 0.34 ppm Tl (Pollock et al., 2018), whereas considerably higher values of Tl occur in chlorite (i.e., 10s of ppm) from the Angas deposit, with one sample (Ang-24) of massive ore containing chlorite with an average value of 85 ppm Tl.

5.6. Muscovite

Muscovite was analyzed from massive ore (sample Angas-24) from the Angas deposit, gahnite-bearing (samples WE-1, WE-31), garnet-andalusite (sample WE-13) and biotite-muscovite schist (samples WH002-135.4, WH002-151.1) from Wheal Ellen, and gahnite-bearing rocks from St. Ives (SI-2, SI-7, SI-8, SI-9). Where spatially associated with gahnite or sulfides, muscovite is more elevated in Zn and Mn than in gahnite-free schists, with the former containing up to 217.2 ppm Zn and 278.1 ppm Mn (Fig. 15a). These values are high relative to the concentration of these elements in altered rocks spatially associated with the Kanmantoo deposit, which contain up to 57 ppm Zn and 64 ppm Mn (Pollock et al., 2018). Similarly, the Zn content of...
Fig. 13. Trace element compositions of staurolite in ppm from the Angas, St. Ives, and Wheal Ellen deposits. a. Co vs. V, b. Ti vs. Cu, and c. Cr vs. Mn.
muscovite reported by Hammerli et al. (2016) contains up to 77 ppm Zn and is lower than that reported in muscovite from these deposits. The concentrations of V and Cr are similar to those in muscovite in country rock and the Kanmantoo deposit. Muscovite from various rocks spatially associated with the Angas, Wheal Ellen, and St. Ives deposits contain 82.2–324.5 ppm V and 0.77–199.1 ppm Cr (Fig. 15b), and overlap compositions of muscovite from the Kanmantoo deposit (16–370 ppm V and 4–307 ppm Cr; Pollock et al., 2018). Although Cr was not analyzed by Hammerli et al. (2016), the V content of muscovite in unaltered country rock schists ranges from 187 to 298 ppm and overlaps the range V concentrations in unaltered rocks from the aforementioned sulfide deposits.

Other trace element concentrations that were above detection limits for muscovite in rocks from the Angas, Wheal Ellen and St. Ives deposits include Na (640.3–9794 ppm), Mg (1823–5614 ppm), Ca (18.7–1585 ppm), Ti (98.5–5640 ppm), Sr (4.49–204.9 ppm), and Ba (406–17,228 ppm), which are similar to that for muscovite reported by Pollock et al. (2018) from the Kanmantoo deposit (1177–15,832 ppm Na, 1164–5070 ppm Mg, 60–568 ppm Ca, 196–2540 ppm Ti, 10–496 ppm Sr, 700–15,828 ppm Ba). Thallium in muscovite is highest in altered rocks associated with the Angas and Wheal Ellen deposits (up to 58.1 ppm), whereas muscovite in altered rocks from St. Ives contains only up to 1.07 ppm Tl. This value is similar to the concentration of Tl in muscovite in altered rocks from the Kanmantoo deposit (up to 2.09 ppm; Pollock et al., 2018).

5.7. Ilmenite and magnetite

Ilmenite in a gahnite-bearing rock from St. Ives (SI-1) contains ~23 wt% ZnO and 7 wt% MnO, which approaches the composition of ecandrewsite (ZnTiO3). In contrast, ilmenite in gahnite-bearing and gahnite-absent mica schists from the Angas deposit only contains 0.3 wt% ZnO, but is enriched in Mn (1.7–8.4 wt% MnO). Although the low ZnO content of ilmenite from the Angas deposit is comparable to that reported by Pollock et al. (2018) from the Kanmantoo deposit (up to 0.1 wt% ZnO), ilmenite from the Angas deposit is more enriched in Mn than that in altered rocks from Kanmantoo (0.5 wt% MnO).
from the Kanmantoo deposit, those from Angas form an isolated field and have higher Al/Co ratios than magnetite from these two deposits and do not overlap any of the fields identified by Singoyi et al. (2006).

6. Discussion

6.1. Exploration guides

Spry et al. (2000) pointed out that meta-exhalites are commonly...
linked to seafloor base metal sulfide deposits in rift settings and, therefore, constitute potential exploration guides to ore. In the Tapanappa Formation, meta-exhalites include quartz-garnetite, garnet-quartz-cummingtonite schist, plagioclase rock, and iron formation, and are spatially associated with sulfides (e.g., Toteff, 1999). In addition, Spry (2000) and Spry et al. (2000) proposed that gahnite- and zincian staurolite-bearing rocks constitute pathfinders to metamorphosed ore deposits. Their presence in the Tapanappa Formation, along with the regional stratabound hydrothermal zone of altered rocks suggest such rocks should be the major target of exploration for Pb-Zn-Ag-(Cu-Au) deposits in the Tapanappa Formation. Because the stratabound hydrothermal zone of altered rocks extends intermittently for over 30 km in the Tapanappa Formation we have used compositional anomalies of silicates and oxides to guide exploration efforts on a more local scale.

### 6.1.1. Garnet composition

Major element studies of garnet in altered rocks associated with the Pb-Zn-Ag-(Cu-Au) deposits show that they are elevated in Mn, with up to 22, 20, 11 wt% MnO from Angas, Wheal Ellen, and St. Ives, respectively (Fig. 17a). Smith (1998) previously reported garnet with up to 28 wt% MnO from quartz-garnetite from the Scotts Creek Pb-Zn-Ag deposit, whereas Pollock et al. (2018) analyzed garnet with up to 20 wt% MnO from the stratiform Nugent orebody in the Kanmantoo Cu-Au deposit. These compositions are in contrast to the Fe-rich garnets (Fig. 17b) spatially associated with the discordant Kavanagh and Emily Star orebodies at Kanmantoo (solid purple circles); altered rocks and massive ore, Nugent drill hole 125 (solid dark blue circles); altered rocks and massive ore, Nugent drill hole 141 (solid dark blue diamonds). Kanmantoo Group: unaltered country rock schists (KG, solid orange circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
A downhole profile of garnet end-member compositions in Angas drill hole DDH-29, which intersects the western mineralization in the Angas deposit, goes from the UHU through the MHU, including the middle host unit, and to the lower host unit (LHU) of McElhinney (1994) (Fig. 18). Spessartine concentrations range from ~25–30, 35–40, and 25–50 mol% in the UHU, MHU, and LHU, respectively. This variation in garnet compositions across the western mineralization at Angas resembles that reported previously by McElhinney (1994) for garnet in Angas drill holes DDH-4, DDH-9, DDH-14, and DDH-18, which showed elevated Mn concentration in the UHU, MHU, and LHU. Of these drill holes, only DDH-14 intersected all three units. Like garnet compositions analyzed here from DDH-29, those in DDH-14 are also highest in Mn in the LHU (up to 35 mol% spessartine). The high Mn content of garnet associated with Pb-Zn-Ag-(Cu-Au) mineralization in the Kanmantoo Group is significant for exploration purposes as Mn-rich garnet rocks are spatially related to other metamorphosed base metal sulfide deposits, including the Broken Hill Pb-Zn-Ag deposit, Australia (Barnes et al., 1983; Spry and Wonder, 1989; Heimann et al., 2009), the Namaqualand Zn-Pb-Cu Province (Stumpfl, 1979), and the Huey deposit, Virginia (Gair and Slack, 1984).

Garnet in altered rocks associated with the Pb-Zn-Ag-(Cu-Au) occurrences generally have the highest Sc (Fig. 17c), V (Fig. 17d), and As (Fig. 17e) contents when compared to concentrations of these elements in garnet from the Kavanagh and Emily Star orebodies at Kanmantoo (Pollock et al., 2018), and, in the case of V, garnet from country rock schists from the eastern Kanmantoo Group (Hammerli et al., 2016). The Angas deposit contains garnet, which is particularly enriched in Sc (up to 245 ppm) and As (up to 33 ppm) compared to only 99 ppm Sc and 3.4 ppm As from these orebodies at Kanmantoo. At the Kanmantoo deposit, garnet in altered rocks contains up to 77 ppm Co and 20 ppm Ga (Pollock et al., 2018), which are mostly higher in garnet from the Pb-Zn-Ag-(Cu-Au) deposits (up to 28 ppm Co and 14 ppm Ga; Figs. 17f, g). Concentrations of Zn and Pb are, in general, higher (up to 535 ppm Zn and 682 ppm Pb) in garnet in altered rocks from the Pb-Zn-Ag-(Cu-Au) deposits relative to garnet in altered rocks from the Kavanagh and Emily Star orebodies (170 ppm Zn and 12 ppm Pb, Fig. 17i), and garnet from the country rock schists (17 ppm Zn and 0.2 ppm Pb) analyzed by Hammerli et al. (2016). However, there appears to be little distinction between the concentration of Cu in garnet in altered rocks from the Kanmantoo Cu-Au deposit and the Pb-Zn-Ag-(Cu-Au) deposits (i.e., < 60 ppm), although two samples from the Angas deposit contain > 250 ppm Cu (Fig. 17j).

Normalized REE patterns for garnet have been used in the past as potential guides in the exploration for metamorphosed massive sulfide deposits (e.g., Spry et al., 2006; Rozendaal and Stalder, 2001). For example, Spry et al. (2007) and Heimann et al. (2013) showed that positive Eu anomalies in garnet were common in rocks proximal to sulfide mineralization in the Proterozoic Willyama Complex, Australia, which hosts the Broken Hill-Pb-Zn-Ag deposit. In addition, Spry et al. (2015) reported similar positive Eu anomalies for garnet in rocks adjacent to sulfide mineralization in the Stollberg Zn-Pb-Ag-(Cu-Au) deposit, Sweden. Europium anomalies are affected by the temperature of the hydrothermal fluid, $f_{O_2}$, the ratio of detrital to hydrothermal components, the ratio of Eu$^{2+}$ to Eu$^{3+}$ in fluid, the REE content of the metamorphic fluid, the metamorphic fluid-rock ratio, and the fractionation between the precursor minerals and the premetamorphic hydrothermal fluid (e.g., Bau, 1991; Otamendi et al., 2002; Heimann et al., 2009; Moore et al., 2013). Normalized REE patterns obtained by Pollock et al. (2018) in garnet from altered rocks associated with the Kanmantoo Cu-Au deposit showed that about 25% of the garnets displayed positive Eu anomalies with the remaining garnets having negative or no Eu anomalies. Only 10% of REE patterns of garnet in massive ore, garnet-gahnite schist, and garnet-biotite schist adjacent to the Angas deposit show positive Eu anomalies. The rest of the patterns for garnet from Angas and all of the analyses from Wheal Ellen and St. Ives have negative Eu anomalies. It is likely that the negative Eu anomalies reflect a temperature of the ore-forming fluid of < 250°C (Sverjensky, 1984), which interacted with sediments with a high ratio of detrital to hydrothermal components. This is a likely scenario given the narrow width of the Wheal Ellen and Angas ore zones of ~ 4.5 m and 8 m, respectively. Such a high detrital to hydrothermal component ratio in precursor materials in iron formations was cited by Peter and Goodfellow (1996) to explain the negative Eu anomalies of these rocks in the Bathurst Pb-Zn mining district.

### 6.1.2. Biotite composition

The major element composition of biotite in and adjacent to base metal sulfides shows a broad range of Fe/(Fe + Mg) ratios (Fig. 9a), and concentrations of FeO (Fig. 19a) and MgO (Fig. 19b). It overlaps biotite compositions in unaltered rocks in the Kanmantoo Group, although some biotite in altered rocks associated with the Angas deposit show slightly lower Fe/(Fe + Mg) ratios and concentrations of FeO. Similarly, there appears to be no discernible difference between the
concentrations of Ga in biotite in altered rocks associated with Pb-Zn-Ag-(Cu-Au) and the Kanmantoo Cu-Au deposit (Fig. 19c).

However, there is an enrichment in the Mn content of biotite in the Angas and Wheal Ellen deposits (> 3000 ppm in some samples, Fig. 19d) and Nugent orebody (up to ~3000 ppm) relative to the discordant Kavanagh and Emily Star orebodies at Kanmantoo (< 1000 ppm; Pollock et al., 2018), and unaltered country rock schists (up to ~2600 ppm; Hammerli et al., 2016). The Zn content of biotite in some altered rocks associated with the Pb-Zn-Ag-(Cu-Au) and Kanmantoo deposits is hundreds to over 1000 ppm Zn (Fig. 19e), which
contrasts to low concentrations of Zn in biotite in country rock schists (up to 167 ppm Zn; Hammerli et al., 2016). Note that biotite with up to 0.81 wt% ZnO was reported by McElhinney (1994) in gahnite-bearing rocks spatially associated with the Angas deposit. The concentration of Pb in biotite in these schists is also low (up to 11 ppm; Hammerli et al., 2016) when compared to its concentration in altered rocks from St. Ives (up to 510 ppm), Angas (up to 140 ppm) and Wheal Ellen (up to 143 ppm), and the Kanmantoo deposit (110 ppm; Pollock et al., 2018) (Fig. 19f). The concentration of Li in biotite in altered rocks from the base metal sulfide deposits and unaltered country rock schists appear to be similar (i.e. up to ~100 ppm), except for biotite from the Angas deposit where Li concentrations between 100 and 300 ppm are common (Figs. 9c and 19g).

The Cu content of biotite differs among the various deposits (Fig. 19h) and is not a diagnostic indicator of proximity to sulfides, but values as high as 23,823 ppm and 21,784 ppm (Pollock et al., 2018) occur in biotite from the St. Ives and Kanmantoo deposits, respectively. These high values are likely due to small inclusions of chalcopyrite that were included in the ablation of these samples. Concentrations of Co in biotite in altered rocks are generally lower in the Pb-Zn-Ag-(Cu-Au) deposits than in the Kanmantoo deposit (Fig. 19i). Although only found in one sample from the Angas deposit, the Tl content of biotite in sample Ang-16 is 3.9 wt% Tl (Fig. 10), which is among the highest thallium content ever reported for biotite. Other analyses of biotite at Angas show only up to 211 ppm Tl. Although the presence of micro-inclusions of a Tl-bearing mineral in the biotite grain may be...
considered, micro-XRF analyses of the grains conducted at the U.S. Geological Survey (Denver) show that a high uniform concentration of Tl is present in biotite, consistent with stoichiometric lattice substitution. The Tl content of biotite from the St. Ives and Wheal Ellen deposits (up to 219 ppm Tl) is elevated relative to biotite in altered rocks from the Kanmantoo deposit (up to 6 ppm Tl; Pollock et al., 2018).

6.1.3. Staurolite composition

Toteff (1999) noted that staurolite in unmineralized aluminous schists contain ~0.1 wt% ZnO, whereas staurolite spatially associated with the Kanmantoo Cu-Au deposit contains up to 1.60 wt% ZnO (Schiller, 2000; Spry et al., 2017; Pollock et al., 2018). McElhinney (1994) pointed out that staurolite occurs in minor amounts in the garniferous pelitic unit surrounding the Angas deposit but is most common in the quartz-gahnite-garnet-biotite ± staurolite rocks hosting the ore. According to McElhinney (1994), staurolite from the footwall of garniferous rocks contains 0.82 to 1.7 wt% ZnO whereas that in the garniferous rocks in the hanging wall contains between 3.5 and 3.8 wt% ZnO. Those in the quartz-gahnite-garnet-biotite ± staurolite rocks hosting the ore contain 4.4 to 6.3 wt% ZnO. Such high Zn values in staurolite in the ore horizon were also confirmed by Toteff (1999) and this study where up to 5.0 wt% ZnO and 5.3 wt%, respectively, were obtained (Figs. 12 and 20a). Detailed compositional studies of staurolite by McElhinney (1994) from the Angas deposit showed that the Zn-end member of staurolite (zincostaurolite) was between ~25 and 40% in the MUH, and between 3 and 20% in the surrounding UHU.

Fig. 20. Composition of staurolite in altered rocks from Angas (AN), St. Ives (SI), and Wheal Ellen (WE) Pb-Zn-Ag-(Cu-Au) deposits, the Kavanagh and Emily Star (KE), and Nugent (NG) Cu-Au orebodies, Kanmantoo mine (Pollock et al., 2018). a. ZnO (wt%), b. MnO (wt%), c. Co (ppm), d. Ni (ppm), e. Cu (ppm), f. Pb (ppm). Angas deposit: quartz-gahnite-garnet-biotite-staurolite rock (solid red hexagons); garnet-andalusite-biotite-staurolite schist (solid red diamonds); garnet-biotite schist. St. Ives deposit: garnet-biotite-staurolite schist (solid green hexagons); quartz-gahnite-garnet-mica-staurolite rock (solid green rectangles). Wheal Ellen deposit: garnet-andalusite-biotite-staurolite schist (solid blue diamonds); massive sulfides (solid dark blue circles); quartz-mica schist (solid pale blue circles); pyritic schist (open blue squares). Kanmantoo Cu-Au ore: altered rocks and massive ore, Kavanagh and Emily Star orebodies (solid purple circles); altered rocks and massive ore, Nugent drill hole 125 (solid dark blue circles); altered rocks and massive ore, Nugent drill hole 141 (solid dark blue diamonds). Kanmantoo Group: unaltered country rock schists (solid orange circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
and LH1, suggesting to him that the Zn content of staurolite increased with base metal content of the host rock. High concentrations of Zn also occur in the Wheat Ellen (up to 4.8 wt% ZnO) and St. Ives (up to 5.7 wt % ZnO) deposits. Lower concentrations of Zn are found in country rock schist (~0.1 wt% ZnO; Toteff, 1999) and the Kanmantoo Cu-Au deposit (up to 1.60 wt% ZnO, with one outlier of 3.2 wt% ZnO; Pollock et al., 2018). Zincian staurolite is spatially associated with other metamorphosed massive sulfide deposits including the Bleikvassli Pb-Zn-Ag deposit, Norway (up to 9 wt% ZnO; Rosenberg et al., 2000), the Dry River South Zn-Pb-Cu-Ag-Au deposit, Australia (up to 7 wt% ZnO; Huston and Patterson, 1995) and the Koparpani Zn-Pb-Cu deposit, India (up to 7 wt% ZnO; Ghosh and Praveen, 2007).

The more-enriched Mn content of staurolite in altered rocks associated with the Pb-Zn-Ag-(Cu-Au) deposits (0.2 to 0.6 wt% MnO) relative to that in staurolite from the Kanmantoo deposit (up to 0.2 wt% MnO) suggests there is potential that Mn can also be used as a pathfinder element (Fig. 20b). Other elements including Co (Fig. 20c), Ni (Fig. 20d), Cu (Fig. 20e), and Pb (Fig. 20f) show no such potential given their overall low concentrations.

6.1.4. Chlorite and muscovite compositions

Chlorite in altered rocks associated with the Pb-Zn-Ag-(Cu-Au) deposits shows a wide range of Fe/(Fe + Mg) (Fig. 14a), FeO, and MgO compositions (Fig. 14b) similar to that reported by Pollock et al. (2018) for chlorite from the Kanmantoo Cu deposit. The composition of chlorite was not analyzed in country rock schists but it is of note that the Zn and Mn concentrations of chlorite and muscovite overlap but are generally higher in altered rocks associated with the Pb-Zn-Ag-(Cu-Au) deposits than in those associated with the Kanmantoo Cu deposit (Figs. 14c and 15a). The highest concentrations of Zn (> 2500 ppm Zn) and Mn (> 8000 ppm) in chlorite are from the Angas and Wheat Ellen deposits, respectively, whereas the highest Zn and Mn concentrations in muscovite are from the Wheat Ellen deposit and country rocks schists, respectively. Chlorite and muscovite in altered rocks associated with the Pb-Zn-Ag-(Cu-Au) occurrences are enriched in Pb (4519 ppm and 2290 ppm Pb, respectively) relative to chlorite (up to 10 ppm) and muscovite (up to 483 ppm) in altered rocks from the Kanmantoo deposit (Pollock et al., 2018).

6.1.5. Gahnite composition

The presence of gahnite has been utilized as an exploration tool for metamorphosed massive sulfide deposits, including Broken Hill-type, sedimentary exhalative, volcanogenic massive sulfide, and non-sulfide zinc deposits (e.g., O’Brien et al., 2015). Gahnite is useful as an indicator mineral whether it is found in situ or as detrital grains in glacial till, stream sediments, and aeolian or alluvial deposits since gahnite is a visually-distinctive, resistate mineral that is not easily broken down by weathering (McClenaghan, 2005). Electron microprobe analyses have shown that zirconic spinel associated with metamorphosed massive sulfide deposits in hydrothermally altered Fe-Al-rich metasedimentary and metavolcanic rocks contain 45–85 mol% of the gahnite (ZnAl₂O₄), 15–45 mol% hercynite (FeAl₂O₄), and 0–10 mol% spinel (MgAl₂O₄) molecules (Spry and Scott, 1986; Heimann et al., 2005). Compositions of gahnite from the Angas, St. Ives, Wheat Ellen, Strathalbyn, and Aclare deposits obtained here (28–34 wt% ZnO; 43–83 mol% gahnite) plot within the massive sulfide field defined by Heimann et al. (2005) and thus constitute an exploration guide in the Kanmantoo Group (Fig. 11).

6.1.6. Ilmenite and magnetite compositions

Ilmenite from the Angas deposit is enriched in manganese (1.7–8.4 wt% MnO) compared to ilmenite found in the Kanmantoo Cu-Au deposit (up to 0.5 wt% MnO) and very Zn-rich in the St. Ives deposit. The presence of magnetite and Mn- and Zn-bearing ilmenite, the former of which appears to be either in sulfides (e.g., Angas, Wheat Ellen) or spatially associated with sulfide deposits in iron formations (e.g., Wheat Ellen) constitute pathfinders to ore.

7. Conclusions

Exploration for syngenetic Pb-Zn-Ag-(Cu-Au) deposits in the Tapanappa Formation of the Kanmantoo Group, which involves petrological and mineralogical aspects, should focus on:

1. The stratobound, regionally metamorphosed hydrothermal alteration zone consisting of quartz-biotite-garnet-andalusite ± staurolite and garnet-andalusite-biotite-staurolite schist that extends intermittently for ~30 km in the Kanmantoo-Strathalbyn area.

2. Meta-exhalative rocks including quartz garnetite, garnet-quartz-cummingtonite schist, plagioclase rock, banded iron formation along with zincian staurolite- and gahnite-bearing rocks that occur on the local scale.

3. Garnet, staurolite and ilmenite that are enriched in the major elements Mn and Zn, as well as zinc spinel with 45–85 mol% of the gahnite molecule.

4. Garnet, biotite, chlorite, and muscovite that are enriched in Zn and Pb, along with elevated concentrations of Cu, Sc, V, and As in garnet, Cu, Li, Mn, and Ti in biotite, and Mn in staurolite, chlorite, and muscovite.

Positive Eu anomalies in garnet have been proposed as a potential indicator to ore in metamorphic terranes that host base and precious metal sulfide deposits elsewhere in the world. However, given that only ~10% of the chondrite normalized REE patterns for garnet from the Pb-Zn-Ag-(Cu-Au) deposits analyzed here have positive anomalies this feature should not be utilized on its own as an exploration tool in the Kanmantoo Group. The REE study shows that for narrow orebodies (~<10 m wide) positive Eu anomalies may be absent, in large part, due to the high ratio of detrital to hydrothermal components in the unmetamorphosed precursor materials.

In evaluating the composition of ferromagnesian silicates and oxides in the Tapanappa Formation, EMPA, SEM, and LA-ICP-MS techniques on polished thin sections from outcrop samples should be obtained along with the composition of the resistate minerals (garnet, gahnite, magnetite, and staurolite), which may be found in stream sediment or soil samples.

Supplementary data to this article are available from the corresponding author.

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References


McLennan, S., Ghasemzadeh-Barvarz, M., Beaudoin, G., Grunsky, E.C., McLennan, B.M., Duschenes, B., Coutroye, E., 2016. Principal component analysis of magmatite composition from volcanogenic massive sulfide deposits: case studies from the Ink Lake (Navanuva, Canada) and Halfmile Lake (New Brunswick, Canada) deposits. Ore Geol. Rev. 72, 60–85.


