Introduction

The Paris silver deposit, Northern Eyre Peninsula (Fig. 1), is hosted by rocks of the ~1,600 Ma Gawler Range Volcanics (GRV) deposited upon the Katunga dolomitic marble of the Paleoproterozoic Hutchison Group (Fig. 2). Together with several other prospects, Paris occurs in the Uno Province, a region of Ag-base metal mineralization located along the Uno Fault, marking the southern boundary of the GRV. Mineralization is hosted within intensely clay-altered polymict volcanic breccias and an upper, oxidised zone of the Katunga dolomite. Paris contains an inferred resource of 8.8 million tonnes at 116 g/t Ag for a total of 33 Moz Ag (Inv Res 2015).

The dolomite is intruded by a series of narrow, NW-trending granitic dikes, which although yet to be dated, are considered temporally related to the Kimban orogeny. Genetic relationships between mineralisation and these intrusions remains inadequately constrained. In addition, the dolomite is host to rare gingo sil veins and narrow, discontinuous, deformed magnetite- and sulphide-bearing veins, which contain comparable assemblages to sulphide-rich clasts in the breccias. An oxidised interface is present between the dolomite and the breccias, potentially representing the pre-eruption paleosurface. This zone, in addition to the upper, altered dolomite form the base of the ore zone at Paris. At depth, magnesian skarn assemblages, dominated by forsterite but also containing spinel and retrograde assemblages of chlorite, pyrite and secondary carbonates (calcite and kainite), prevail across the footwall to the silver deposit.

Ore assemblages in both dolomite and breccia clasts are characterized by galena, arsenopyrite, pyrite, sphalerite and chalcopyrite. Silver is primarily present as acanthite and native silver; however, significant amounts of refractory silver have been measured in pyrite, galena, arsenopyrite and sphalerite. Pyrite demonstrates significant variation in trace element chemistry between different sulphide-assemblages, dominated by forsterite but also containing spinel and retrograde assemblages of chlorite, pyrite and secondary carbonates (calcite and kainite), prevail across the footwall to the silver deposit.

Sulphide trace elements

The sulphide minerals at Paris are host to elevated concentrations of several trace elements, with Ag being of most economic interest. Table 1 indicates the highest average concentration of Ag can be found in pyrite and sphalerite in the breccias, and galena in the gingo sil.

Ag can be present both as discrete inclusions in solid solution within the host mineral, which can be distinguished by the LA-ICP-MS spectra. The pyrite from the breccia (Fig 3a), with rough spectra with peaks and troughs indicates for Ag and Sb indicates the presence of discrete Ag-Sb inclusions in the pyrite grain. Conversely, the smooth spectra for sphalerite and galena (Fig 3b, c, d) indicate Ag is likely to be present in solid solution. It is also possible for Ag to be present in homogeneously distributed nano-inclusions.

<table>
<thead>
<tr>
<th>Breccia</th>
<th>Arsenopyrite</th>
<th>Galena</th>
<th>Sphalerite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11492</td>
<td>163</td>
<td>1894</td>
</tr>
<tr>
<td>Wins</td>
<td>115</td>
<td>16</td>
<td>340</td>
</tr>
<tr>
<td>Gingo</td>
<td>N/A</td>
<td>N/A</td>
<td>1071</td>
</tr>
</tbody>
</table>

Table 1. Average Ag (ppm) values for different sulphides by lithology.

Coupled substitution

Ag is largely insoluble in galena via simple 2Ag⁺ ↔ Pb²⁺ substitution, as one of the Ag atoms must be placed in an interstitial position in the galena lattice (George et al. 2015). Coupled substitution is necessary for galena accommodate large concentrations of Ag, most commonly Sb and Bi.

Figure 4 demonstrates the correlation between Ag and Sb for galena from the breccia (fig. 4a), and Ag and Bi for galena from the gingo sil, and the proposed coupled substitution mechanism.

Conclusions

- The sulphides pyrite, sphalerite and galena host significant concentrations of Ag.
- Ag is present both as inclusions and in solid solution within sulphides.
- Galena from different lithologies demonstrate different coupled substitution mechanisms for Ag.