RELIENCE, FLINDERS RANGES: MINERALOGY, GEOCHEMISTRY AND ZINC DISPERSION AROUND A NONSULFIDE OREBODY

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INTRODUCTION
The Reliance zinc deposit is situated in the northern Flinders Ranges, South Australia (Figure 1). It is one of a series of nonsulfide zinc resources in this region, some of them among the highest grade zinc orebodies in the world (Groves et al. 2002). Like the nearby Beltana mine, which ceased operations in 2003, it is a predominantly willemite (Zn$_2$SiO$_4$) deposit, with alteration to smithsonite (ZnCO$_3$) in the oxidized zone (Whitehead 1967, Groves et al. 2002, Groves et al. 2003). Unlike Beltana, parts of the Reliance deposit are “blind”, covered by thick, transported regolith (Groves et al. 2002; Figure 2). In addition, the site is dominated by a large (> 250 m deep) central karst in the Late Proterozoic carbonate host rock. This presents a challenge to traditional prospecting techniques, with no surface expression and gravity surveys dominated by the low-density karst (Groves et al. 2002).

Previous geochemical surveys by Perilya Ltd. show elevated zinc concentrations in near surface material over the orebody, in both transported and in situ regolith (Pengelly 2003). This indicates that the elevated Zn concentrations could be either residual or the result of dispersion through transported cover. The study of metal distribution in regolith can lead to improved exploration techniques. The aims of this project are thus to understand:

- The distribution of zinc in regolith, both at surface and at depth;
- How the zinc exists in the regolith and the orebody (i.e., mineralogy, fractionation); and,
- The processes that have led to the elevated concentrations of zinc in the regolith and dispersion from the orebody.

\textbf{Figure 1:} Location of the Reliance prospect and sampling sites.
PREVIOUS WORK
There have been several studies of nearby nonsulfide zinc deposits at Beltana, Third Plain and Aroona (Whitehead 1967, Grub 1971, Muller 1972, Groves 2001, Groves et al. 2003). All have focussed on the origin of these deposits and the debate regarding supergene versus hypogene formation (see Heyl & Bozion 1962).

Early interpretations of the Beltana deposit suggested a supergene origin from the replacement of a Mississippi Valley-type massive sulfide ore (Muller 1972). Grub (1971) argued that Beltana was of hypogene origin, and related to salt diapirs. Reliance has little associated sulfide, or evidence of a sulfide precursor, indicating a likely hypogene origin similar to Beltana (Groves et al. 2002, Brugger et al. 2003, Groves et al. 2003).

The geology of the Reliance deposit has been well constrained by an extensive drilling program, operated by lease-holders Perilya. The total resource has been estimated at 355,000 tonnes at an average 30 wt. % Zn (Groves et al. 2002). Regolith mapping of the Reliance area confirmed the presence of transported colluvial cover over the orebody, but also identified areas of outcropping saprolite (slightly to moderately weathered dolomite) to the south-east of the prospect (Pengelly 2003).

METHODS
Regolith was sampled from eleven surface locations (5-15 cm depth) on a northwest-southeast transect along the strike of the deposit, with a transverse section over the central karst, plus samples at 30-50 cm depth at two locations (R4 and R8), and one drill-hole (Figure 1). The bulk geochemistry of the samples was analysed by X-Ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at Geoscience Australia. The mineralogy was determined by X-Ray diffraction (XRD) analysis at The Australian National University, including amorphous material by the addition of 20 wt. % zincite (ZnO), after checking for its absence. The modal abundance of minerals and amorphous material was quantified using SIROQUANT™ software.

RESULTS AND DISCUSSION
Surface samples
The measured zinc concentrations for surface material are given in Table 1 and depicted with Cd, As, Pb and Mn concentrations in Figure 3. Zinc concentrations range from 50 to 5,678 ppm, with maximum values to the south-east of the orebody (Figure 1) in the in situ weathered dolomite mapped by Pengelly (2003). There was no correlation with shallow depth. There is a clear correlation between the concentrations of Zn and Cd, As, Pb and Mn, which are associated with the orebody (Figure 3), but no correlation between Zn and Fe. These results suggest that these elements are residual, however, we cannot exclude the possibility that they were
dispersed by hydromorphic or other processes.

**Table 1:** Zn concentrations in surface regolith samples at Reliance deposit (locations on Figure 1).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>R1A</th>
<th>R1B</th>
<th>R2</th>
<th>R3</th>
<th>R4A</th>
<th>R4B</th>
<th>R4C</th>
<th>R4D</th>
<th>R5</th>
<th>R6</th>
<th>R7</th>
<th>R8A</th>
<th>R8B</th>
<th>R8C</th>
<th>R9</th>
<th>R10</th>
<th>R11</th>
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</thead>
<tbody>
<tr>
<td>Zn ppm</td>
<td>872</td>
<td>731</td>
<td>864</td>
<td>5678</td>
<td>2894</td>
<td>3803</td>
<td>2363</td>
<td>1881</td>
<td>1119</td>
<td>227</td>
<td>238</td>
<td>273</td>
<td>130</td>
<td>493</td>
<td>50</td>
<td>66</td>
<td>76</td>
</tr>
</tbody>
</table>

Note: Samples A and B (for R1, R4 and R8) are fine grained (< 1 mm) and bulk, respectively. R4D and R8C are at 30-40 cm depth. R4C is a duplicate surface sample.

**Figure 3:** Correlations of Cd, As, Pb and Mn with Zn for surface regolith samples from the Reliance deposit.

Figure 4 shows the locations and mineral phases identified by XRD. The southeast part of the transect (R1-R5) is dominated by amorphous material, quartz and carbonates, mainly calcite. In contrast, the northwest part of the transect (R6-R11) is dominated by amorphous material and quartz, with little or no carbonate. No Zn minerals were detected in the surface samples. The mineralogy corresponds to the distribution of Zn observed in this and previous studies (Perilya geochromical survey), with carbonate-bearing samples corresponding to elevated Zn concentrations and carbonate-absent samples with lower Zn concentrations (Figure 4). This suggests that Zn is associated with carbonates and *in situ* regolith. In addition, the carbonate-absent samples are associated with transported regolith mapped by Pengelly (2003).

**Drill-hole samples**

Zinc concentrations vary from 0 to 82 wt. % and reflect the mineralisation and lithology (Figure 5). In contrast to the surface results, there is little or no correlation between Zn and Cd, As, Pb, Mn or Fe. This is probably a result of sampling bias, i.e., a “nugget effect” of discrete mineral grains in the samples.

Figure 5 shows the minerals identified in the drill-hole samples and their estimated modal abundances. Dolomite is the predominant mineral, except where willemite, smithsonite and quartz predominate in mineralised and sandy lithologies. Zinc is present as the minerals willemite and smithsonite (Figure 5); chalcopyrite \( \text{Zn}_4\text{Fe}^{2+0.5}\text{Mn}^{2+0.5}\text{Mn}^{4+3}\text{O}_7\cdot3(\text{H}_2\text{O}) \) was also identified but its abundance could not be
estimated from the XRD patterns because it is not present in the SIROQUANT™ database. The modal abundances of the Zn minerals do not account for the measured Zn concentrations, so that up to more than 50 wt. % of the Zn exists in the amorphous material. Zinc is likely to be substituted into dolomite, as suggested by Groves (2001); however, it could be present as adsorbed species on carbonates (Gatehouse et al. 1977, Zachara et al. 1988), iron oxyhydroxide and clay minerals. There is some correlation between clay minerals and elevated Zn concentration (Figure 5), suggesting that sorption is possible but also that Zn-rich clays such as saucnite could be present. If Zn is present in dolomite, then it would be a likely source of Zn during weathering. Note that weathered dolomite is observed in saprolite associated with the deposit.

Figure 4: Mineralogy and contoured Zn concentrations in near surface regolith material at the Reliance deposit.

Zinc dispersion may be by physical (alluvial, colluvial), chemical (dissolution, precipitation) or biological processes, although the modern vegetation at Reliance—sparse and low shrubs—indicates that the latter is not significant at present. The solubility of phases in the ore limits the extent of chemical dispersion. Willemite is likely to be refractory, however, the Zn-rich amorphous fraction may be less refractory. Current and past groundwater flow may be important dispersing agents. Based on the distribution of in situ versus transported regolith and the distribution of regolith Zn, physical dispersion from Zn-rich dolomite from weathered outcrops, most likely by colluvial processes, appears to be of greatest importance in the surface regolith samples. There is limited evidence of dispersion through the transported cover. This has implications for prospecting, including the sampling of material and the interpretation of geochemistry, and reinforces the importance of understanding the origin of overburden material. It also impacts on our understanding of the dispersion of Zn in the regolith, showing which processes are likely to be of the most importance.

SUMMARY
Preliminary work suggests that Zn substitution into dolomite, adsorption to carbonates and Zn-clays are the main reservoirs of Zn in the periphery of the Reliance orebody, however, the amorphous fraction requires further investigation. Surface regolith material contained no identified Zn minerals. Zinc distribution in these samples is correlated with both calcite and Mn, though not with Fe, suggesting adsorption primarily to carbonates. The coincidence of calcite- and Zn-rich samples with in situ weathered dolomite suggests that the surface Zn is either residual or the result of physical dispersion from Zn-bearing outcrops.
Further work will include sequential extractions to identify the fractions of regolith with which Zn is associated, e.g., acid extractable (carbonates) and reducible (oxyhydroxides). In addition, we will use Scanning Electron Microscopy/Energy Dispersive X-ray Analysis (EDXA) to identify minor and trace minerals that contain Zn. Present groundwater conditions, including composition and flow, will be analysed to determine their capacity to disperse Zn.

**Figure 5:** Modal abundances identified by XRD, wt. % Zn determined by XRF, and drill hole depth, from Reliance deposit. Note: Sample 160-02 contains chalcophanite and coronadite and sample 160-13 contains unknown minerals (possibly siderite), which are not in the SIROQUANT™ database.

**REFERENCES**


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