Sediment-Hosted Base Metal Deposits

- P384A -
Sediment-hosted base metal deposits

AMIRA/ARC project P384A

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— Ross Large and Peter McGoldrick
Introduction

This interim report contains the results of a study of the lithogeochemistry of some sedimentary rocks from the Lawn Hill Platform in the Century area. The analytical data was provided from the AGSO Rockchem database, and the interpretation is based on our lithogeochemical vector research previously presented in P384/P384A reports.

This report is being distributed prior to the final project meeting because of the significance of the results to exploration for Century style Zn–Pb–Ag deposits.

Also included as an appendix to this report is a paper by Large and McGoldrick to be published shortly in the Journal of Geochemical Exploration. It is included here because it provides important background to the Century lithogeochemical study. The published paper is a modified version of the report presented to sponsors of P384 in October 1993 (Report 3: 63-91).

Ross Large
Director, CODES
Lithogeochemical study of a select group of sediments from the Century area, Lawn Hill Platform

Ross Large
Centre for Ore Deposit Research

1. INTRODUCTION

Previous studies in AMIRA project P384 have outlined the existence of extensive lithogeochemical halos within the sediments surrounding the Lady Loretta and HYC stratiform Zn-Pb-Ag deposits (Large and McGoldrick, 1993). These studies have led to the development of six geochemical vectors that increase towards ore both across strike and along strike:

- **SEDEX Metal Index** = \( Zn + 100Pb + 100\Pi \)
- **SEDEX Alteration Index** = \( \frac{(FeO + 10MnO)100}{(FeO + 10MnO + MgO)} \)
- **Al Mark 3** = \( \frac{(FeO + 10MnO)100}{(FeO + 10MnO + MgO + Al_2O_3)} \)
- **Manganese content of dolomite** \( MnO_d = \frac{MnO \times 30.41}{CaO} \)
- **Manganese content of siderite** \( MnO_s = \frac{MnO \times 62.01}{FeO_{carb}} \)
- **Carbon and oxygen isotopes of carbonates** \( \delta^{18}O, \delta^{13}C \)

Subsequent studies by McGoldrick (1994, 1995) have shown that these vectors are also applicable to the Mt Isa and Hilton Pb-Zn deposits, but show poorly developed or opposite trends for small uneconomic Proterozoic Pb-Zn deposits such as Walford Creek and Kamarga.

Up until now no data has been available for the Century deposit, and therefore it has not been possible to test the alteration indices and vectors on the remaining world-class deposit in northern Australia.

In January 1998 AGSO released some new geochemical whole rock and trace element analyses, as part of their expanded Rockchem database, for a group of sediments from the Lawn Hill Platform close to the Century deposit. This data provides an opportunity to test the lithogeochemical vectors on sediments from the Lawn Hill Formation. This is an important test of our previously developed alteration vector approach to exploration for three reasons:

(i) The samples are from close to Century and enable us to test for a Century halo.

(ii) The samples are from a dominantly siliciclastic host-rock sequence which contrasts with the dolomitic sequences studied previously.

(iii) The data set is an exploration style geochemical set of samples taken to be representative of a range of sedimentary rock types in the Lawn Hill Formation.
2. SAMPLE LOCATIONS AND STRATIGRAPHY

The AGSO data set of Lawn Hill Formation geochemistry comprises 165 sediment samples collected from six drill holes in the Century area. The drill holes are listed below and their locations are shown in Figure 1.

<table>
<thead>
<tr>
<th>Drill hole no.</th>
<th>Number of samples</th>
<th>Stratigraphy</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH 195</td>
<td>67</td>
<td>Pmh1 and Termite Range Fm</td>
</tr>
<tr>
<td>LH 198</td>
<td>38</td>
<td>Pmh4 Upper Footwall</td>
</tr>
<tr>
<td>LH 203</td>
<td>22</td>
<td>Pmh2 and Pmh3</td>
</tr>
<tr>
<td>LH 205</td>
<td>19</td>
<td>Lower Pmh4</td>
</tr>
<tr>
<td>LH 206</td>
<td>4</td>
<td>?</td>
</tr>
<tr>
<td>LH 210</td>
<td>11</td>
<td>Pmh6</td>
</tr>
</tbody>
</table>

A listing of the whole rock and trace element geochemical data is available direct from AGSO. Part of the data set has been analysed for CO₂, however none of the samples have been analysed for thallium.

3. LOCAL GEOLOGY

The Stratiform Century Zn-Pb-Ag deposits is hosted in unit Pmh4 of the Lawn Hill Formation. Details on the geology of the deposit are found in Waltho and Andrews (1993), Broadbent (1995) and Broadbent et al. (in press) and will not be repeated here.

A list of the features of the sedimentary units Pmh1 to Pmh6 are provided in Table 1 after Broadbent et al. (in press). The samples from the AGSO data base are from units Pmh1, Pmh2, Pmh3, Pmh4, Pmh6 and the Termite Range Formation (Fig. 2). The stratigraphically equivalent sediments to the Century Zn-Pb mineralisation (upper part of Pmh4) are not represented in the data set. The samples analysed in the data set are described variously as shale (73 samples), arenite (51), sandstone (9), mudstone (18), argillite (11) or tuff (5).

![Figure 1: Location of drill holes in the Century area sampled for the AGSO Rockchem database.](image)

4. TREATMENT AND INTERPRETATION OF THE DATA

The procedure used to interpret the dataset is similar to that proposed in previous AMIRA reports (e.g., Large and McGoldrick, 1993, 1995; Large, 1994) However, because CO₂ analyses were not available for all samples then a modification of the usual procedure was developed.

The first priority was to determine whether siderite and/or dolomite was present in any of the sediments and then to divide the dataset into three groups.
based on the type and presence of carbonates:

Group 1: Dolomitic sediments (>3 wt% dolomite)

Group 2: Sideritic sediments (>3 wt% siderite)

Group 3: Shales (carbonate poor sediments)

The procedure to achieve these groups is shown in Figure 3. Based on this procedure the division of the database is shown graphically in Figure 4.

4.1 Carbonate types and content

Sixty-nine samples from the data set are shown to contain significant siderite (>3 wt%), a further 39 samples contain significant dolomite and the remaining 55 samples are classified as shales with a variable but generally low dolomite content.

The high carbonate content of many of the sediments in the Lawn Hill Formation and Termite Range Formation is surprising as these rocks have been described by previous authors as siliciclastics. However histograms based on the geochemistry indicate that the dolomitic sediments generally contain from 3 to 30 wt% dolomite, with a second grouping containing over 93 wt% dolomite. The sideritic sediments average between 3 and 20 wt% siderite with outliers at 25% and 45%.

The linear trends of increasing iron and manganese with LOI (loss on ignition = carbonate %) indicates that most of the dolomite is a ferroan dolomite variety, and that the siderite contains significant manganese (Figs 5, 6).

4.2 Application of the alteration index

Our previous research on the lithogeochemical halo at Lady Loretta (Large and McGoldrick, 1993) resulted in the development of an alteration index to assist in mapping alteration surrounding SEDEX deposits and to provide a vector to ore;
<table>
<thead>
<tr>
<th>Formation Unit</th>
<th>Lithology</th>
<th>Sedimentary Features</th>
<th>Volcaniclastic Component</th>
<th>Paleoenvironment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lawn Hill Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pmh6</strong></td>
<td>Laminated siltstones, thinly bedded sandstones</td>
<td>(!) Sandstone storm layers</td>
<td></td>
<td>Outer shelf</td>
</tr>
<tr>
<td><strong>Pmh5</strong> (Widdallion Sandstone Member)</td>
<td>Thick-thin bedded arkosic sandstones, minor siltstone and shale</td>
<td>Abundant mass-flow features: grain-flow sandstones with dewatering structures and shale rip-up clasts; classical Bouma turbidite intervals, debris flow deposits</td>
<td>Thin tuffaceous mudstones with variable pyroclastic (ash shard) and detrital grains; zircon age of 1595 ± 6 Ma^a</td>
<td>Deep turbidite basin</td>
</tr>
<tr>
<td><strong>Pmh4</strong></td>
<td>Shales, siltstones, minor sandstone</td>
<td>Thin basal sand-streaked shales display fine HCS; silt-mud coupletes are subly graded with small shale rip-up flakes suggesting dilute turbidites</td>
<td>Thin tuffaceous mudstones with variable pyroclastic (ash shard) and detrital grains; zircon age of 1595 ± 6 Ma^a</td>
<td>Shelf (just above storm wave base) deepening to basinal</td>
</tr>
<tr>
<td><strong>Pmh3</strong> (Bulmung Sandstone Member)</td>
<td>Bedded to laminated volcanic sandstones</td>
<td>Coarsening - upward sandstone bodies (&lt; 4m thick) characterised by HCS^b</td>
<td>Epiclastic, angular volcanic quartz and ash shards</td>
<td>Mid - inner shelf (above storm wave base)</td>
</tr>
<tr>
<td><strong>Pmh2</strong></td>
<td>Massive to bedded, green pervasively altered fine sandstone-siltstones; mudstone-clast conglomerates</td>
<td>Sandstones/siltstones often internally chaotic with slump folds, and shale rip-up clasts/flakes suggest mass-flow origins; open framework mudstone-clast conglomerates have characteristics of debris flow units, clast-supported conglomerates may have a similar origin</td>
<td>Green sandstones/siltstones composed predominantly of pyroclastic generated ash shards; however, detrital crystal component and shale intraclasts confirm redeposition of juvenile volcanic component; pervasive green alteration reflects original high proportion of volcanic glass</td>
<td>Mid-shelf</td>
</tr>
<tr>
<td><strong>Pmh1</strong></td>
<td>Carbonaceous silty shales, thinly bedded sandstones, laminated shales</td>
<td>Thin sandstones exhibit classical Bouma turbidite intervals</td>
<td>Laminated shales become more tuffaceous towards top of unit</td>
<td>Outer shelf or slope</td>
</tr>
<tr>
<td>Termite Range Formation</td>
<td>Thick-thin bedded subarkosic-subgreywacke sandstone, shales</td>
<td>Abundant mass flow structures: thicker sandstones display high concentration features (internally massive, shale rip-up clasts, dewatering structures, aggradational stacking); thinner sandstones exhibit classical Bouma turbidite intervals</td>
<td>Minor tuffaceous mudstones with variable pyroclastic (ash shard) and detrital grains; zircon age of 1630 ± 10 Ma(^2) from base</td>
<td>Deep turbidite basin</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Riversleigh Siltstone</td>
<td>Lower succession of thin bedded quartzitic-subarkosic sandstones, silty shales, dolomitic siltstones; upper succession of carbonaceous silty shales with thin-thick bedded lithic sandstones</td>
<td>HCS in lower sandstones, some desiccation structures in dolomitic siltstones; upper sandstones display mass-flow structures with classical Bouma turbidite intervals</td>
<td></td>
<td>Shelf, deepening to deep turbidite basin</td>
</tr>
<tr>
<td>Shady Bore Quartzite</td>
<td>Mature quartzites, dolomitic siltstones</td>
<td>Bimodal cross-beds, wave ripples in sandstones; desiccation structures (mudflake breccias, shrinkage cracks) in dolomitic siltstones</td>
<td></td>
<td>High energy, shallow marine shoreline; intermittent desiccation</td>
</tr>
</tbody>
</table>

\(^1\) Approximate stratigraphic thicknesses are given in Figures 2 and 6; all stratigraphic contacts are apparently conformable, at least on the local field scale
\(^2\) Terminology of Sweet and Hutton (1982)
\(^3\) Hummocky cross-stratification
\(^4\) From Page et al., (1994)
\(^5\) From S. Andrews (after Page, personal communication; this volume)
Figure 3: Flow chart of the procedure used to divide the AGSO database into dolomitic, sideritic and shale samples.

Figure 4: Fields for dolomitic sediments, sideritic sediments and shales on an FeO_{carb} versus loss on ignition (LOI) plot.
Figure 5: The complete AGSO data set from Century divided into the three
chemofacies.

Figure 6: Variation in MnO content with LOI showing that the sideritic sediments
have variable MnO values from 0 to 2.5 wt% while the dolomitic sediments and
shales contain less than 0.5% MnO.
SEDEX \( A1 = \frac{(FeO + 10Mn)100}{(FeO + 10MnO + MgO)} \)

The index relies on the changes in whole rock chemistry accompanying carbonate alteration associated with Zn-Pb-Ag mineralisation; FeO and MnO are enriched during development of Fe-Mn carbonate phases, while MgO is depleted due to replacement by FeO and/or MnO in the carbonate structure. The index varies from values of 0 to 40 in background dolomitic sediments upwards to values of 80 to 100 in sediments directly associated with mineralisation. A trend of increasing SEDEX A1 with increasing zinc mineralisation was proposed to characterise the sedimentary units hosting stratiform Zn-Pb-Ag mineralisation (Fig. 7).

A plot of the Century database sediments is shown in Figure 8. The strongly dolomitic samples plot in the background field, but all the sideritic sediments, the shales and the remaining dolomitic sediments show anomalous SEDEX A1 values from 50 to 95. The sideritic sediments give particularly anomalous values (70 to 95), although their zinc contents are less than 500 ppm.

AI Mark 3 was developed as a modification of SEDEX A1 in order to eliminate the anomalous values recorded by some “barren” shales (see Large, 1994). By applying the modified alteration index (Fig. 9) it is apparent that most of the dolomitic sediments and shale samples are drawn back to the background field. However at least 50% of the sideritic sediments continue to display anomalously high alteration index values (30 to 80) suggesting proximity to a major stratiform Zn-Pb-Ag deposit.

### 4.3 Pyrite content of sediments

Elevated pyrite content of sediments will lead to increased alteration index values which may, or may not, be related to the environment of Zn-Pb mineralisation. In the Century data set it is apparent (Fig. 10) that the pyritic samples with greater than 10,000ppm (1 wt%) sulphur form a tight cluster of dolomitic sediments with \( A13 \) varying from 20 to 40. The sideritic sediments with \( A13 \) values greater than 40 are pyrite poor, with less than 1 wt% S.

### 4.4 Manganese content of carbonates

Our previous research at both Lady Loxton and HYC has shown that the MnO content of carbonate (ferroan dolomite and siderite) increases systematically both along strike and across strike towards the ore. The most direct way to determine the MnO content of carbonate is by calculation from the whole rock data using the following equations:

\[
\text{MnO content of dolomite MnO}_d = \frac{\text{MnO} \times 30.41}{\text{CaO}} \quad \ldots \ldots \quad (1)
\]

\[
\text{MnO content of siderite MnO}_s = \frac{\text{MnO} \times 62.01}{\text{FeO}_{\text{carb}}} \quad \ldots \ldots \quad (2)
\]

The alternative method of microprobe analysis is slow and expensive. Plots of Al Mark 3 against MnO content of carbonate (Fig. 11) have been previously devised to divide regional or drill hole data sets into priority groups (e.g., Large and McGoldrick, 1994). Three priority boxes have been developed for this plot based on our Lady Loretta and HYC research (Large, 1994, p.48).

**Priority 1:**

\[ A13 > 50, \text{MnO}_d > 1\% \]

to very close to ore

**Priority 2:**

\[ A13 > 40, \text{MnO}_d > 0.5\% \]

to close to ore

**Priority 3:**

\[ A13 > 30, \text{MnO}_d > 0.2\% \]
	potential distal horizon for SEDEX Zn/Pb

It is apparent from the data in Figure 11, that 8% of the Century samples plot in Priority 1 (very close to ore), 5.5% in Priority 2 (close to ore) and 11% in Priority 3 (distal ore horizon). In Figure 12 a comparison between the Century and Lady Loretta data shows that the Century sideritic sediments have a similar \( A13 \) and MnO pattern to the sediments from the Lady Loretta siderite halo. The only
Figure 7: Trend of SEDEX Al versus Zinc for the Lady Loretta deposit - showing the classic pattern of increasing SEDEX Al with increasing zinc from background to ore. This pattern is characteristic of the immediate halo to a stratiform Zn-Pb-Ag deposit.

Figure 8: Pattern of SEDEX Al versus Zn for the Century data set, showing the anomalous alteration index for all sideritic and shale samples, but a typically low content of zinc.
Figure 9: Modified alteration index (Al Mark 3) for the Century data set showing that about 50% of the sideritic sediments give anomalous Al₃ values (>30), whereas most of the dolomitic sediments and shales fall within the background.

Figure 10: Sulphur versus Al₃ plot showing that the dolomitic sediments are typically pyritic (>10,000ppm S) while the sideritic sediments and shales are generally pyrite poor (<10,000ppm S).
Figure 11: Trend of MnO in carbonate with alteration index for the Century data showing that 24.5% of the data plots within the priority fields P1 to P3, indicative of proximity to a

Figure 12: Comparison of the trend of Century sideritic sediments from this study with rocks from the sideritic halo at Lady Loretta from Large & McGoldrick (1993) and Large (1994).
difference is that the Century siderites are generally more manganiferous (3-20 wt% MnO) than the Lady Loretta siderites (1-3 wt% MnO).

5. COMPOSITION OF SIDERITE IN THE ORE ZONE AT CENTURY

An envelope of siderite development surrounds the Century deposit (Broadbent et al., in press), extending 100 m into the hangingwall sediments and 20 to 30 m into the footwall (Fig. 13). Broadbent et al. (in press) provide a summary of the composition of siderite within the upper Pmh4 unit including the ore zone. They report that siderite becomes progressively enriched in manganese in proximity to the mineralised sequence; in a similar fashion to that reported previously by Large and McGoldrick (1993) for Lady Loretta siderite halo.

At Century, Broadbent et al. (in press) observed the following mole % Mn variations in siderite for Pmh4 (our recalculated MnO₃ values are shown for comparison).

Table 2: Range of manganese content of siderite at Century reported by Broadbent et al. (in press)

<table>
<thead>
<tr>
<th>Unit</th>
<th>Mole % Mn in siderite</th>
<th>MnO₃ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hangingwall sequence</td>
<td>15.8 to 20.1</td>
<td>9.8 to 12.5</td>
</tr>
<tr>
<td>Mineralised sequence</td>
<td>11.4 to 22.7</td>
<td>7.1 to 14.1</td>
</tr>
<tr>
<td>Upper Footwall</td>
<td>2.1 to 9.6</td>
<td>1.3 to 5.9</td>
</tr>
<tr>
<td>Lower Footwall</td>
<td>1.0 to 2.4</td>
<td>0.6 to 1.5</td>
</tr>
</tbody>
</table>

A progressive increase in the wt% MnO in siderite (MnO₃) from 0.6 to over 7.1 wt% is apparent from the data passing stratigraphically upwards from the lower Footwall shales to the Mineralised Sequences in unit Pmh4. The MnO₃ remains high within the Hangingwall siltstone-shale sequence.

Figure 13: Extent of siderite halo surrounding the Century Zn-Pb-Ag deposit (from Broadbent et al., in press).
6. DRILL HOLE LITHOGEOCHEMICAL PROFILES

Downhole profiles of AI Mark 3, MnO₄⁻/ß, carbonate content and Zn are shown in Figures 13 to 17 for the five drill holes sampled in the AGSO data set.

6.1 DDH LH 195 (Fig. 14)

This hole, which was collared 2.5 km south west of the Century deposit, intersected Lawn Hill Formation Pmh1 (black shales) from 0 to 105 m followed by Termite Range Formation (arenites) from 105 to approx. 190 m.

The whole rock analyses indicate that the Pmh1 black shales are generally sideritic in character containing from 5 to 50 wt% siderite. This contrasts with the Termite Range Formation arenites which contain no siderite but have a widely variable dolomite content (Fig. 14) from less than 1% dolomite to over 90% dolomite. The interval from 127 to 135 m downhole contains near pure dolomite (>95% CaMg (CO₃)₂).

The alteration index (AI₃) and MnO content of siderite (Fig. 14) in Pmh1 show anomalous values indicative of proximity to stratiform Zn-Pb-Ag mineralisation. The systematic increase in MnO content of siderite up stratigraphy (100 m to 80 m downhole) from 0.1 wt% MnO to 4.5 wt% MnO identifies the base of Pmh1 as a favourable interval for Zn-Pb mineralisation. This pattern is identical to that exhibited by the footwall sediment at both Lady Loretta and HYC. These MnO values are also similar to those recorded by Broadbent et al. (in press) for the Upper Footwall Sequence, Pmh4, at Century.

6.2 DDH LH 198 (Fig. 15)

This hole is collared 1.4 km north of the Century deposit, and 7 km northwest of the Termite Range Fault. Over the interval 40 to 80 m, the hole intersected shale and siltstone of the Upper footwall sequence Pmh4, i.e., the footwall stratigraphy to the Century mineralised sequence. Except for the upper-most sample (which is possibly effected by oxidation) no siderite was detected in the sediments. All samples exhibit low AI₃, MnO₄ and Zn values.

There is no evidence in the data that the sediments intersected in this hole have been affected by hydrothermal Pb-Zn bearing fluids similar to those that formed the Century deposit. From this data the background values for Pmh4 are considered to be: AI mark 3 = 20 to 35, MnO₄ = 0.5 to 1.5 wt% and Zn = 10 to 300 ppm.

6.3 DDH LH 203 (Fig. 16)

This hole, collared 900 m west of the Century deposit, intersected mudstones and sandstones of units Pmh2 and Pmh3. The sediments exhibit a siderite content from 2 to 12 wt%. The MnO content of siderite increases from 2 to 8 wt% up stratigraphy and AI Mark 3 shows anomalous values particularly in the upper parts of the hole (30-45 m). The gradual increase in MnO in siderite is paralleled by a systematic increase in Zn up-hole from 10 to 400 ppm. This trend may relate to the Century mineralisation in the overlying Pmh4 unit, or alternatively can be interpreted to suggest the potential for a mineralised interval at the top of Pmh3.

6.4 DDH LH 205 (Fig. 17)

Collared 500 m west of Century this hole intersects 20 m (from 70 to 90 m downhole) of the lower Pmh4 unit (Footwall Black Carbonaceous Shale Sequence). The shales over this interval contains from 5 to 10 wt% siderite, but exhibits low AI Mark 3, MnO₄ and Zn values. Because of the limited sampling in this hole, no conclusions can be drawn about the Century deposit halo.

6.5 DDH LH 210 (Fig. 18)

This hole was drilled into an synclinal structure of Pmh6, 21 km south of Century. Siderite is developed throughout the argillites intersected in the hole (20 - 130 m) varying in content from 5 to 17 wt%. Although Zn content is low throughout the hole, the AI Mark 3 and MnO₄ show a systematic increase up-hole. In fact the MnO content of siderite exhibits a dramatic pattern, increasing from 0.5 to 18 wt% up stratigraphy. Based on our experience at Lady Loretta and HYC, this indicates strong potential for stratiform Zn-Pb mineralisation in the upper part of Pmh6 in close proximity to DDH LH 210. These very high MnO₄ values (7-18 wt% MnO) are similar to those found in the ore zone at Century (Table 2).
Figure 14: Downhole lithogeochemical plots for DDH LH 195, Century area. Note the systematic increase in MnO content of siderite, up-hole, from 100 to 90 m at the base of Pmh 1. This indicates the potential for the lower Pmh 1 shales to host stratiform Zn-Pb-Ag mineralisation elsewhere in the basin.
Figure 15: Downhole lithogeochemical plots for DDH LH 198. The lack of siderite in this hole and the low Al₃ and MnOₓ values at indicate that this hole is outside the Century halo, and probably represents background values for this part of the stratigraphy.
Figure 16: Downhole lithgeochemistry plots for DDH LH 203. The systematic up-hole increase in MnO content of siderite indicates that the upper part of Pmh 3 may host stratiform Zn-Pb-Ag mineralisation.
Figure 17: Downhole lithogeochemistry plots for DDH LH 205. The sideritic nature of these lower Pmh 4 shales indicates that they lie within the sideritic halo to the Century deposit.
Figure 18: Downhole lithgeochemistry plots for DDH LH 210.
A comparison of data from DDH LH 203, 900 m west of Century, with DDH LH 210 (Fig. 19) indicates a very similar pattern in the Al₃-MnO₃ trend for both drill holes, supporting the likelihood of stratiform mineralisation at this stratigraphic level in the Lawn Hill Formation.

6.6 Summary of drill hole patterns

The ubiquitous occurrence of siderite throughout the stratigraphy intersected in these holes, and the highly anomalous alteration indices and MnO content of carbonate, can be explained in one of two possible ways:

1. The siderite and manganese halo to the Century deposit is very extensive, being developed in a variable manner throughout the sediments from the base of Pmh1 to the top of Pmh6. This conclusion is contrary to statements by Broadbent et al., (in press), who suggest that the Century siderite halo extends only 100 m vertically above and 20 to 30 m below the mineralised sequence (within Pmh4); or

2. There is more than one mineralised horizon in the Lawn Hill Platform. In addition to the upper part of Pmh4, this study indicates that stratiform Zn-Pb mineralisation may occur at three other stratigraphic levels (Fig. 20):

- the base of Pmh1 (indicated by DDH LH 195);
- the top of Pmh3 (indicated by DDH LH 203);
- the upper part of Pmh6 (indicated by DDH LH 210).

The author favours the second alternative.

Figure 19: Comparison of siderite geochemistry vectors for samples from DDH LH 203 (900 m west of Century) with those from DDH LH 210 (21 km south of Century). This data suggests the possibility of a separate stratiform Pb-Zn-Ag ore system in proximity to DDH LH 210. The range of MnO₃ for the Century ore zone and footwall alteration on Pmh 4 are indicated by the arrows for comparison.
7. GENETIC CONSIDERATIONS

Broadbent et al., (in press) consider that the Century deposit formed during basin inversion at a depth of 800 to 3000 m? by reaction between an Fe-Mg-Zn-Mn connate fluid with organic-rich shales of Pmh4 to form a laminated sulfide deposit by pore infill and replacement. Early siderite development caused porosity occlusion in the hangingwall sequence and progressively confined the ore-fluid to the host Pmh4 stratigraphy (Broadbent et al., in press).

This model has been used to produce the diagrammatic representation of siderite development at various stratigraphic levels of the Lawn Hill district (Fig. 20) based on the Rockchem sediment geochemistry. Alternative models for Century of exhalative Pb-Zn mineralisation with associated Mn-carbonate halos, such as proposed for HYC (Large et al., 1995), cannot be evaluated from the available data. However the application of vectors based on carbonate composition, MnO_d/a or alteration index do not depend on a particular genetic model, but are based on empirical observations of the chemical changes in sediments surrounding large stratiform Pb-Zn-Ag deposits.

8. CONCLUSIONS

Evaluation of the AGSO Rockchem database of 165 samples collected from units Pmh1 to Pmh6 in the Lawn Hill Formation, using the alteration vector approach developed previously in this AMIRA project, indicates the following;

1. There is little doubt that Century exhibits a manganiferous siderite halo similar to that defined previously at Lady Loretta.

2. The whole rock alteration indices and vectors developed for Lady Loretta and HYC work equally well for Century.

3. In contrast to Lady Loretta and HYC there does not appear to be a widespread primary zinc halo at Century.

4. Even though the Lawn Hill Formation is dominantly siliclastic, with little pyrite development, the Century deposit has been ‘found’ using the alteration vector approach recommended in previous AMIRA P384 reports.

5. An equally exciting outcome of this analysis is that three other stratigraphic levels of the Lawn Hill Formation may have potential for stratiform Zn-Pb-Ag mineralisation:
   - the base of Pmh1,
   - the top of Pmh3,
   - the upper part of Pmh6.

6. The elevated values of both Alteration Index and MnO content of siderite in sediments from
Pmhe intersected in DDH LH 210, 21 km south of Century, indicate the potential for a separate hydrothermal Zn-Pb system in proximity to this drill hole.

9. ACKNOWLEDGEMENTS

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10 REFERENCES


Lithogeochemical halos and geochemical vectors to stratiform sediment hosted Zn-Pb-Ag deposits. Part 1: Lady Loretta Deposit, Queensland

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ABSTRACT

Stratiform sediment hosted Zn-Pb-Ag deposits, often referred to as SEDEX deposits, represent an economically important class of ore, that have received relatively little attention in terms of defining lithogeochemical halos and geochemical vectors useful to exploration. This study concentrates on the Lady Loretta deposit which is a typical example of the class of Proterozoic deposits SEDEX in Northern Australia. We examined the major and trace element chemistry of carbonate-bearing sediments surrounding the deposit and defined a series of halos which extend for several hundred meters across strike and up to 1.5 km along strike. The stratiform ore lens is surrounded by an inner siderite halo (Carr, 1984), followed by an outer ankerite/ferroan dolomite halo which merges with low iron dolomitic sediments representative of the regional background compositions. Carbonate within the inner siderite halo varies in composition from siderite to pistomitesite (Fe$_{0.6}$Mg$_{0.4}$CO$_3$), whereas carbonate in the outer ankerite halo varies from ferroan dolomite to ankerite (Ca$_{0.5}$Mg$_{0.5}$Fe$_{0.02}$CO$_3$).

Element dispersion around the stratiform ore lens is variable with Pb, Cu, Ba and Sr showing very little dispersion (<50 m across strike), Zn and Fe showing moderate dispersion (<100 m) and Mn and Ti showing broad dispersion (<200 m). Within the siderite halo Cu, Mg and Na show marked depletion compared to the surrounding sediments. The magnitude of element dispersion and change in carbonate chemistry around the Lady Loretta orebody has enabled the development of three geochemical vectors applicable to exploration. Whole rock analyses are used to calculate the three vector quantities as follows:

1. SEDEX metal index

\[ \text{Zn} + 100\text{Pb} + 100\text{Tl} \]

2. SEDEX alteration index

\[ \frac{(\text{FeO} + 10\text{MnO})\times100}{(\text{FeO} + 10\text{MnO} + \text{MgO})} \]

3. Manganese content of dolomite

\[ \frac{\text{MnO}_d = \text{MnO} \times 30.41}{\text{CaO}} \]

All three vectors increase in ore both across strike and along strike. The manganese content of dolomite (MnO$_d$) exhibits the most systematic pattern increasing from background values of about 0.2 wt% to a maximum of around 0.6 wt% at the boundary between the ankerite and siderite halos. Siderite within the inner halo contains considerably more Mn with MnO values of 0.4 to 4.0 wt%.

It is suggested here that the basket of indices defined at Lady Loretta (Zn, Tl, metal index, alteration index, MnO$_d$ and MnO$_j$) is applicable in the exploration for stratiform Zn-Pb-Ag deposits in dolomite-rich sedimentary basins generally. The indices defined can firstly assist in the identification of sedimentary units favourable for SEDEX mineralisation, and secondly provide vectors along these units to ore.
The alteration index and MnO₂, however, should only be used for exploration of dolomitic sequences; they are not recommended for exploration in clastic sequences devoid of carbonates.

INTRODUCTION

Considerable research has been undertaken over the past twenty-five years to characterise the mineralogy and chemistry of halos surrounding volcanic hosted massive sulphide (VHMS) deposits. (Ishikawa et al., 1976; Frankin et al., 1981; Date et al., 1983; Urabe et al., 1983; Ashley et al., 1988; Galley, 1995). The development of alteration indices (e.g. Ishikawa et al., 1976) related to hydrothermal fluid/rock interaction surrounding massive sulphide deposits have proved very useful in mapping alteration zones and providing vectors to ore to assist mineral exploration.

Although there are several studies of sediment geochemistry and geochemical halos surrounding sediment-hosted Zn-Pb-Ag deposits (e.g. Lambert and Scott, 1973; Gwozd and Krebs, 1977; Large DE, 1981; Stumpfi, 1979; Carr, 1984) there has been little published work on the development of quantifiable lithogeochemical vectors useful for mineral exploration. The purpose of this paper is to describe research on the Lady Loretta stratiform Zn-Pb-Ag deposit in northern Australia aimed at developing a consistent lithogeochemical halo model, including quantifiable vectors to ore, that can be applied in mineral exploration.

LADY LORETTA Zn-Pb-Ag DEPOSIT

The Lady Loretta deposit is hosted by late Palaeoproterozoic sediments of the McNamara Group (Hutton et al., 1981) in NW Queensland about 115 km NNW of Mt Isa (Fig. 1). The deposit was selected for this study because it is a small (8.3 Mt at 18.4% Zn, 8.5% Pb and 125g/t Ag) but high grade example of the northern Australian Proterozoic stratiform Zn-Pb-Ag deposits, and drill core through the complete stratigraphic section was available both proximal and distal (up to 2.5 km from ore) to the deposit. The orebody occurs within the upper third of Lady Loretta Formation, one of nine units that constitute the McNamara Group (Hutton et al., 1981). Zircons from tuffaceous sediments a few tens of meters below the deposit have been dated at about 1647 Ma (Page and Sweet, in press).

The stratiform orebody occurs in the hinge zone of a north-east trending syncline, known as the Small Syncline (Figs 2, 3) which is separated by a high-strain zone (the 'Syncline Dividing Fault') from a larger structure termed the Big Syncline. Both are subsidiary structures within a larger, regional structure, the Lady Loretta Syncline (Hutton et al., 1981). The Lady Loretta Syncline, including the base metal mineralisation, is truncated to the north west by the Carlton Fault (Fig. 2). In the Big Syncline, the ore sequence is represented by pyritic, baritic and, sometimes, hematitic sediments, with generally low
Figure 2: Geology of the Lady Loretta district (modified from Hancock and Purvis, 1990). B-B' is the section line shown in figure 3.

base metal tenor. Mineralisation in the Small Syncline comprises a sulphide lens up to 50 m thick (in the keel of the syncline) composed of sphalerite, galena, pyrite, chalcopyrite, quartz, siderite, tetrahedrite and freibergite (Hancock and Purvis, 1990; Aheimer, 1994). The ores commonly show fine layering parallel to sedimentary layering in the host sediments, however, much of the ore has been recrystallised during deformation and now has a tectonic fabric (Aheimer, 1994; McGoldrick et al., 1996). The highest grade (>30 wt% Zn+Pb) parts of the orebody comprise massive laminated ore immediately overlying highly pyritic sediments (Fig. 4). Lower grade parts of the orebody contain more sediment interbeds. These comprise black carbonaceous shales and grey and brown siltstones and shales containing variable amounts of siderite. Siderite grains are sutured and intimately intergrown with the detrital minerals (mainly white mica and quartz). Siderite is the dominant carbonate in these rocks. The lateral facies equivalent of Zn-Pb-Ag ore is a barite-chert unit containing ore-grade Zn, but low Pb. This unit is present in the upper parts of the eastern and western fold limbs in the northern part of the deposit.

Host rock sediments
The hangingwall and footwall host rocks to the deposit are fine grained clastic and chemical sedimentary rocks and the lithostratigraphic subdivision used herein, for this part of the Lady Loretta Formation, is from Dunster (1997). The Lower Carbonate Unit (Fig. 4) is about 200 m thick and consists of thin bedded to laminated, variably dolomitic siltstone, claystone and carbonaceous shale, with minor dolostone and sandstone (Dunster, 1997). In the Small Syncline the unit becomes more pyritic and sideritic up section. The lower carbonate unit is overlain by the Pyritic Unit which is from 25 to 80 m thick and comprises interbedded silty shale, dolomitic and sideritic siltstone, shaley fine grained sandstone, carbonaceous shale and ubiquitous bedded fine grain pyrite. In this unit the amount of pyrite increases
systematically up sequence to more than 70 modal percent within a few meters of the contact with ore (Carr, 1984). In the Small Syncline siderite is the principal carbonate mineral in the Pyritic Unit.

The Ore Sequence in the Small Syncline has been structurally thickened to a maximum of about 50 m, but original stratigraphic thickness was probably about 20 m. In the Big Syncline, the Ore Sequence lithologies are very similar to those of the Pyritic Unit. Ore grade base metals are present in only one drill core (out of sixteen) that intersected the Ore Sequence in the Big Syncline.

The hangingwall rocks in the Small Syncline are called the Cyclic Unit (Hancock and Purvis, 1990; Dunster, 1997). This unit averages about 120 m in thickness and consist of carbonaceous shales, dolomitic and sideritic siltstones, claystones, sandstones, and bedded pyrite which decreases in abundance up section. As its name suggests, there is a cyclic arrangement of sandstone, siltstone, pyrite and carbonaceous shale beds in this unit (Carr. 1981; McGoldrick et al., 1996; Dunster, 1997).

The Upper Clastic Unit (Fig. 4), a lithologically variable, more than 200 m thick, coarsening upwards package transitional to the overlying Shady Bore Quartzite, is not present in the Small Syncline, but crops out in the Big Syncline where it comprises slightly dolomitic siltstone and sandstone.
Previous studies of halo geochemistry

Carr (1984) undertook a study of the primary geochemical and mineralogical dispersion about the Lady Loretta deposit, which formed the starting point for this investigation. There were three principal findings from Carr's study that are relevant to our research. Firstly the lead-zinc deposit is surrounded by a halo of pyrite-rich layers within the dolomite and carbonate host rocks. The proportion of pyrite-rich layers was shown to increase progressively from about 2% at 150 m stratigraphically below the ore to >90% in the top 10 m of the footwall sediments. Hanging wall rocks contain up to 20% pyrite layers for at least 100 m above the ores. Secondly, Carr (1984) recognised a distinct siderite halo surrounding the orebody, extending 50 m above and up to 75 m below the deposit. He reported that sideritic sediments gave way to dolomitic sediments beyond the halo (Fig. 3). Thirdly, he demonstrated that zinc displayed the maximum primary dispersion around the deposit, extending as a halo up to 100 m into the footwall and 50 m into the hanging wall, with a lateral extent in the Big Syncline of some 1.5 km along strike. Other elements (Hg, Pb, Ag, Cd, Ba) exhibited dispersion halos which were less extensive than zinc.

**SAMPLING AND ANALYTICAL STRATEGY**

A total of 108 rock samples were collected from a series of surface and underground drill holes in the Small Syncline (84 samples) and Big Syncline (24 samples). Sampling was mainly focused on the hanging wall and footwall to the ore sequence, in order to provide a wide stratigraphic coverage. Every effort was made to collect samples with a low sulphide content (i.e., pyritic and base metal sulphide-rich layers were avoided). The sample interval covered about 350 m of true stratigraphic thickness. The material analysed comprised pieces of quarter or one half core, ten to twenty centimeters long, that were cleaned, coarse crushed in a jaw crusher, then milled to a fine powder in a WC ring mill. Wherever possible, individual samples for analysis were from a single lithology or recognisable depositional unit (e.g., a complete graded siltstone/shale unit).
The samples were analysed by XRF at the University of Tasmania for the following suite of major and minor elements:

Majors: SiO$_2$, Al$_2$O$_3$, FeO, MnO, MgO, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$

Minors: Zn, Pb, Ba, Cu, Ni, As, Sb, Ti, Rb, Sr, Cr, V, Zr, Y, U, Th and Br.

Thallium is not normally determined by XRF, and considerable effort was put into developing a reliable and sensitive method for measuring this element (McGoldrick and Robinson, 1994). For routine geochemical exploration purposes, inductively coupled plasma - mass spectrometry is a more cost-effective and sensitive technique for measuring Tl (Potts, 1993). Total C was measured by high temperature combustion using a Carlo Erber elemental analyser. A second C measurement (inorganic C) was made on samples pre-ignited at 450°C, and organic C was assumed to be the difference between the total C and the inorganic C values. This technique provides reliable data for dolomitic and ankeritic samples, but, because siderite begins to decompose at about 450°C, it underestimates organic C, and overestimates organic C in sideritic samples (Krom and Berner, 1983).

Complete geochemical data can be provided on request from the second author.

**CARBONATE COMPOSITION AND SIDERITE HALO**

Due to the simple mineralogy of the sediments at Lady Loretta (quartz, muscovite, carbonate and pyrite) it was possible to gain an indication of the variability in the composition of the sedimentary carbonate using whole rock chemical relationships. This was supplemented by microprobe analysis and staining techniques where appropriate. Two groups of sediment can be distinguished on plots of whole rock CaO, FeO, MnO against CO$_2$ (Fig. 5). The groups correspond to samples with siderite of dolomite as the principal carbonate phase (rocks contain either dolomite or siderite but rarely both together). The relationships in Fig. 5 show that the carbonates are not simply pure dolomite and siderite, but that the dolomite contains variable Fe and Mn while the siderite is enriched in Mn and Mg. Fig. 5(a) gives a clear distinction between the sideritic and dolomitic sediments due to the paucity of CaO in the former. From the whole rock MnO/CO$_2$ relationships in Figure 5c it is apparent that the carbonate in the siderite halo, has a higher Mn content than the dolomite outside the halo. By extrapolation it is
possible to estimate that the siderite in the sideritic sediment has a mean value of 1.6 wt% MnO compared to 0.6 wt% MnO for dolomite in the dolomitic sediments. Microprobe analyses outlined below have confirmed this result.

**Microprobe analysis of carbonates**

Microprobe analyses of sedimentary carbonates throughout the sequence were carried out to check the interpretations based on whole rock analyses and to study fine scale variations in carbonate chemistry. This proved to be a difficult and time consuming exercise due to the fine grain sizes of the carbonate minerals and complex intergrowths with muscovite and quartz on a scale of 2-10 microns. However, a total of 134 carbonate grains were successfully analysed from nine separate samples. Selected carbonate analyses are given in Table 1, and the complete results are plotted in Figure 6. The data in Figure 6a indicate that carbonate within the siderite halo varies in composition from siderite (dominantly FeCO$_3$) to pistomesite (Fe$_{0.6}$Mg$_{0.4}$CO$_3$), whereas carbonate outside the siderite halo varies from pure dolomite (Ca$_{0.5}$Mg$_{0.5}$CO$_3$) to ankerite (Ca$_{0.5}$Mg$_{0.5}$Fe$_{0.3}$CO$_3$). The MnCO$_3$ content of the dolomite varies from 0.1 to 2.0 mole %, whereas the siderite varies from 1.0 to 20.0 mole % MnCO$_3$ (Fig. 6b). Carr (1984) reported up to 14 mole % ZnCO$_3$ in siderite at Lady Loretta, and this result is supported by our study (Fig. 6c). It is noteworthy that only carbonates with greater than 70 mole % FeCO$_3$ (Fig. 6c) show significant zinc substitution (> 0.2 mole % ZnCO$_3$), whereas the complete spectrum of carbonate compositions (dolomite, ankerite, pistomesite, siderite) exhibit manganese substitution (of > 0.2 mole % MnCO$_3$) into the carbonate structure.

**Siderite and ankerite halos**

The extent of the siderite halo at Lady Loretta was established using the whole rock analyses, in particular the relationship between CaO and CO$_2$ (Fig. 5a). Within the halo, siderite occurs as a very fine grained phase varying from <2% up to 70% of the sediment, and it appears to replace, or exist as an alternative phase, to the dolomite present outside the halo. Based on our sampling and analysis, the siderite halo extends at least 50 m into both the hangingwall and footwall of the ore deposit. Both our studies and those of Carr (1984) indicate that the siderite halo penetrates deeper into the footwall below the thickest concentration of Pb-Zn ore, and thins laterally towards the extremities of the ore lens.

In core, sideritic intervals often have a distinct brown colouration, however, it can be difficult to identify the siderite/dolomite boundary in core, due to the fact that the dolomite is also Fe-rich (ankerite to ferroan dolomite) and develops a brown strain on

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>P155-5</th>
<th>L31</th>
<th>L27</th>
<th>Ni00i</th>
<th>P2ii</th>
<th>P4</th>
</tr>
</thead>
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<tr>
<td>Wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>49.97</td>
<td>50.77</td>
<td>51.13</td>
<td>0.59</td>
<td>2.5</td>
<td>0.07</td>
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<tr>
<td>MgCO$_3$</td>
<td>43.03</td>
<td>31.35</td>
<td>30.41</td>
<td>33.65</td>
<td>15.52</td>
<td>1.19</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>6.62</td>
<td>16.85</td>
<td>17.24</td>
<td>63.75</td>
<td>78.92</td>
<td>88.16</td>
</tr>
<tr>
<td>MnCO$_3$</td>
<td>0.36</td>
<td>0.56</td>
<td>1.03</td>
<td>1.86</td>
<td>2.68</td>
<td>3.30</td>
</tr>
<tr>
<td>ZnCO$_3$</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.07</td>
<td>0.20</td>
<td>6.92</td>
</tr>
</tbody>
</table>

| Mole %     |        |     |     |       |      |    |
| CaCO$_3$   | 46.48  | 49.28| 49.61| 0.61  | 2.74 | 0.08|
| MgCO$_3$   | 47.86  | 36.12| 35.03| 41.06 | 20.11| 1.63|
| FeCO$_3$   | 5.36   | 14.13| 14.45| 56.62 | 74.43| 88.52|
| MnCO$_3$   | 0.29   | 9.47 | 0.87 | 1.66  | 2.54 | 3.34|
| ZnCO$_3$   | 0.01   | 0.01 | 0.04 | 0.05  | 9.18 | 6.43|
| Total      | 100.00 | 100.00| 100.00| 100.00| 100.00| 100.00|

<table>
<thead>
<tr>
<th>Mineral</th>
<th>dolomite</th>
<th>ankerite</th>
<th>ankerite</th>
<th>pistomesite</th>
<th>sideropside</th>
<th>siderite</th>
</tr>
</thead>
</table>

Table 1: Selected microprobe analyses of carbonates from the Lady Loretta host sediments. These six analyses were selected from the total data base of 134 analyses.
oxidation. Toward the outer boundary of the siderite halo, sideritic sediments are interbedded with dolomitic and ankeritic sediments, however on the micro scale the dolomite and siderite are mutually exclusive (Hancock and Purvis, 1990). Microprobe analyses of carbonates in dolomitic sediments adjacent to the siderite halo reveal high Fe in these dolomites (e.g., sample L31, Table 1), indicative of ankeritic compositions. The whole rock and microprobe analyses indicate the presence of mixed ankerite-dolomite assemblages in the footwall sediments up to 100 m beyond the siderite halo. Beyond 100 m (ferroan-)dolomite is the principal carbonate phase.

Our work has shown that the best geochemical discriminator for sideritic siltstones versus ferroan dolomitic or ankeritic siltstones is the whole rock CaO analysis (Figs. 5a, 7). As shown in Figure 7a, the dolomitic siltstones contain greater than 1% CaO, while the sideritic siltstones contain less than 1% CaO. In fact, there are two orders of magnitude difference between the median sideritic siltstone (0.1% CaO) and the median dolomitic siltstone (10% CaO). Another significant factor revealed by Figure 7 is that the dolomitic siltstones (outside the siderite halo) have much lower zinc contents (20-200 ppm Zn, median 50 ppm) compared with sediments within the siderite halo (70 ppm to 10% Zn, median 300 ppm). In other words, the siderite halo at Lady Loretta also appears to represent a zinc halo. Based on the microprobe data from Carr (1984) and this study (Fig. 6c), it is most probable that much of the zinc, within the siderite halo (outside the ore boundaries) is due to substitution of zinc into the siderite structure, rather than the presence of sphalerite dispersed in the sediments. This conclusion is supported by the positive correlation between Zn and CO₂ for sediments in the siderite halo (Fig. 7b).

In summary, the orebody at Lady Loretta is surrounded by a zincian siderite halo, up to 50 m thick, which gives way to an ankerite/ferroan dolomite halo (a further 50-100 m thick) followed by low iron dolomitic sediments.
ELEMENT DISPERSION AROUND THE OREBODY

In order to study major and minor element dispersion about the ore deposit, the Small Syncline data set has been plotted in a series of graphs showing stratigraphic distance from the ore position against elemental variation. Samples have been collected up to 265 m into the footwall and 60 m into the hangingwall. Consequently, although our data set is adequate for the study of footwall dispersion, it is limited on the hangingwall side. It was not possible to obtain fresh (unoxidised) core samples, greater than about 50 m stratigraphically above the ore position, due to the tight synclinal structure at Lady Loretta.

Elements which show similar behaviour, relative to the ore position are discussed in their groups below:

Calcium, magnesium and sodium
All three elements show significant depletion in the footwall siderite zone (Fig. 8). This is due to the change in carbonate composition from ferricon dolomite to siderite approaching the ore position. Calcium shows the greatest depletion of about two orders of magnitude. On the other hand potassium shows no trend toward the ore (Fig. 8d). This is probably due to the reasonably consistent argillaceous component (muscovite) of the sediments over the 350 m interval surrounding the ore position, both within and outside the siderite halo.

Zinc, lead, copper, iron, barium and strontium
All six elements display enrichment around the ore position (Figs 9, 10). Zinc shows the greatest dispersion, up to 150 m into the footwall and 80 m into the hangingwall. Outside the siderite halo, the dolomitic siltstones generally contain 20 to 80 ppm zinc, while within the halo they vary erratically from 80 ppm to over 1 wt% Zn. Iron is concentrated in the siderite halo, within 50 m of the ore horizon, where whole rock values vary from about 4 wt% to over 10 wt% FeO. In the footwall dolomite zone there is a gradual and steady increase in FeO from 255 m below the ore position to the boundary of the siderite halo (Fig. 9). Lead, copper, barium and strontium exhibit limited dispersion of less than 50 m into the footwall and hangingwall. The greater dispersion of zinc and iron is likely to be due to their substitution into the respective carbonate minerals (dolomite, ankerite and siderite) that constitute the halo zones. Based on the whole rock and microprobe analyses Pb, Cu, Ba and Sr do not appear to show significant substitution into the carbonates.

Manganese and thallium
Both Mn and Tl exhibit broad dispersion of up to 200 m into the footwall sediments and greater than 60 m into the hangingwall. This data (Fig. 10) indicates that Mn and Tl are dispersed well beyond the siderite halo into the footwall dolomitic sediments. Deep into the footwall (> 200 m below the ore position) the sediments contain < 0.1 wt% MnO and less than 1 ppm Tl (the limit of detection by
Figure 8: Variation in major elements CaO, MgO, Na₂O and K₂O in sedimentary host rocks, relative to stratigraphic distance from the orebody. For convenience, samples from within the orebody are plotted at zero meters on the y-axis (labelled 'ore horizon').
Figure 9: Variation in Zn, Pb, Cu and FeO with stratigraphic distance from the orebody.
Figure 10: Variation in MnO, Tl, Ba and Sr with stratigraphic distance from the orebody.
Figure 11: Positive correlation between Tl and K₂O suggesting substitution of Tl for K in the muscovite component of the sideritic sediments.

XRF. Although the Mn and Tl values are erratic throughout the footwall ankeritic and sideritic halo zones, there is a general increase in both elements towards the ore position. As demonstrated previously (Fig. 6), increasing Mn is related to substitution into ankerite and siderite within sediments approaching the ore position. Thallium on the other hand, correlates positively with whole rock K₂O (Fig. 11) suggesting substitution into the muscovite component of the sediments.

**Summary of element dispersion**

Based on the degree of across strata dispersion it is possible to group the halo indicator elements discussed above into four classes:

- **Class 1:** tight dispersion (less than 50 m from ore): Pb, Cu, Ba, Sr
- **Class 2:** broad dispersion (up to 100 m from ore): Zn, Fe
- **Class 3:** very broad dispersion (up to 200 m from ore): Mn, Tl
- **Class 4:** broad depletion (up to 50 m from ore): Ca, Mg, Na

The lithogeochemical data from the Big Syncline (collected 500 m to 1500 m south of the deposit) indicates that the across-strata dispersion summarised above, applies equally to along strata dispersion, but over a greater distance. For example, Mn and Tl dispersion extends the full length of the structure, up to 1500 m from the deposit, along the favourable stratigraphy.

**DEVELOPMENT OF GEOCHEMICAL VECTORS TO ORE**

There are three characteristics that we considered important in the development of geochemical vectors useful for exploration for stratiform sediment-hosted massive sulphide deposits (SEDEX deposits).

1. The geochemical parameter should aid in the identification of potential host-rock units for stratiform Zn-Pb-Ag deposits. To do this the parameter must increase, across strata, to pinpoint the most favourable unit or units in the stratigraphic column of a basin.

2. The geochemical parameter should act as a vector toward the ore deposit; once the favourable unit is identified, the index should increase along the unit toward ore.

3. The geochemical parameter should be character-
istic of the environment for stratiform Zn-Pb-Ag deposits only. In other words, the parameter or a combination of parameters, should be able to distinguish the target sought (in this case SEDEX Zn-Pb-Ag) from other less favourable styles of Zn-Pb deposits in sedimentary basins, such as MVT deposits, granite related vein deposits, and structurally controlled Pb-Zn deposits.

The approach adopted here is to develop a series of indices (called the basket of indices) characteristic of stratiform Zn-Pb deposits, which when combined together provide a quantitative vector to ore. Three indices are discussed below, based on the Lady Loretta study. Further indices have been developed from research on the HYC deposit, which are presented in an accompanying paper (Large et al., in prep). The basket of indices are yet to be tested on the full range of Zn-Pb deposit styles found in sedimentary basins as required in criterion (3) above.

A metal index for SEDEX Zn-Pb-Ag deposits

The most obvious index to use as a vector to ore is based on the major metal components of the orebody, zinc and lead. At Lady Loretta, lead exhibits little dispersion outside the ore lens, and zinc shows broad dispersion both across strata and along the ore horizon. As a compliment to lead and zinc, thallium exhibits very broad dispersion and provides the ingredient to develop a regional vector. By combining these three metals together it is possible to develop a metal index that increases toward ore throughout the full extent of the deposit halo. The metal index chosen for this purpose is:

\[
\text{SEDEX Metal Index} = \text{Zn} + 100 \text{ Pb} + 100 \text{ Ti}
\]

with Pb, Ti and Zn measured in ppm.

This metal index increases in a regular fashion over a distance of 200 m towards ore in the footwall of the Lady Loretta deposit. (Fig. 12a). The pattern in the hanging wall of the deposit is not as clear due to limited sampling.

An alteration index for SEDEX Zn-Pb-Ag deposits

In view of the successful use of the alteration index developed by Ishikawa et al. (1976) for volcanic-hosted massive sulphide deposits, it was decided to attempt to develop a similar index for sediment-hosted Pb-Zn deposits, based on the Lady Loretta data set.

The basis of an alteration index is to determine the key elements enriched during alteration and the key elements depleted during alteration and to combine them in an index that varies from 0 to 100.

Thus, Alteration Index =

\[
\frac{(\text{key enriched elements}) \times 100}{(\text{enriched + depleted elements})}
\]

The Ishikawa alteration index was developed to quantify the key alteration reactions that occur in volcanics surrounding VHMS deposits; in particular the replacement of plagioclase and volcanic glass by sericite and chlorite. These reactions involve depletion of Na₂O and CaO in the volcanic rock (due to felspar and glass destruction) and the enrichment of MgO and K₂O (due to chlorite and sericite deposition).

In this case:

\[
\text{Ishikawa Alteration Index} = \frac{(\text{MgO} + \text{K}_2\text{O}) \times 100}{(\text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO})}
\]

(Ishikawa et al., 1976).

Based on the Lady Loretta data set, MnO and FeO were selected as the key enriched elements and MgO was selected as the key depleted element. Other combinations using CaO as a depleted element and/or Ba as an enriched element were tried, but found to be less useful in terms of producing an index which gave a systematic variation from 0 to 100. The selected index is defined as:
Figure 12(a): Variation in SEDEX metal index with stratigraphic position showing a regular increase toward the ore position (zero meters on the y-axis). (b) Variation in SEDEX alteration index with stratigraphic position showing a general increase toward the ore position.

SEDEX Zn-Pb-Ag Alteration index =

\[
\frac{(\text{FeO} + 10\text{MnO}) \times 100}{(\text{FeO} + 10\text{MnO} + \text{MgO})}
\]

MnO is factored by 10 to bring its base value up to the magnitude of the other elements used; FeO and MgO.

From a plot of SEDEX Zn-Pb-Ag Alteration Index (SEDEX Al) against stratigraphic distance (Fig. 12b) it is evident that the SEDEX Al increases fairly systematically from a background of about 30 to a maximum of 95 approaching the orebody from the footwall side. In the hangingwall sediments, the alteration index varies from 50 to 90 within 50 m of the orebody.

A surprisingly good relationship emerges from a plot of SEDEX Al against Zn for the Lady Loretta Small Syncline data (Fig. 13). This relationship indicates that zinc enrichment in the halo sediments is accompanied by a change in alteration index, thus reflecting changing chemistry in the composition of the carbonate minerals. In other words, the hydrothermal processes that have led to zinc deposition either directly, or indirectly, caused changes in MnO, FeO and MgO accompanying modification of the chemistry of the precipitated carbonate minerals dolomite,ankerite and siderite. This pattern of zinc and alteration index has major implications for mineral exploration, as will be outlined later.

It could be argued that the positive correlation between SEDEX Al and Zn shown in Figure 13, indicates that zinc alone is a better index or vector to ore. However the combination of zinc with SEDEX Al satisfies the third criteria previously outlined for a suitable vector, i.e. the positive relationship displayed in Figure 13 characterises the environment for SEDEX deposits. Increasing Zn and SEDEX Al provide a vector to the target SEDEX ore type. Increasing zinc alone may provide a target in a secondary, less favoured, ore type. Furthermore, anomalous Zn, unrelated to known SEDEX mineralisation, is a common feature of Palaeanoproterozoic sequences in northern Australia.
Figure 13: Positive trend of increasing SEDEX Alteration index with zinc content for sediments in the Small Syncline at Lady Loretta. The field for background dolomitic sediments in the Lawn Hill Platform is based on unpublished data from the second author.

MANGANESE CONTENT OF CARBONATE AS A VECTOR

In an earlier section it has been shown that Mn substitutes into the carbonate minerals in the siderite and ferroan dolomite halos surrounding the Lady Loretta Pb-Zn orebody (Fig. 5d) and that the overall MnO content of the sediments increases, somewhat erratically, towards the orebody from the footwall side (Fig. 10).

This erratic variation in whole rock MnO is largely due to the variation in the amount of carbonate (host to the manganese) in the various sedimentary facies in the halo. Because dolomite and siderite are the only major carbonate minerals present in the samples, and because they are virtually mutually exclusive of each other, it is possible to eliminate the effect of variable sediment carbonate content by re-calculating sample MnO (to 100% carbonate) using the following relationships:

MnO content of dolomite:

\[ MnO_d = \frac{MnO_{wr} \times 30.41}{CaO_{wr}} \]  

\[ \text{MnO content of siderite:} \]

\[ MnO_s = \frac{MnO_{wr} \times 62.67}{FeO^*} \]  

where FeO* = (whole rock FeO) - (FeO present in pyrite), and MnOwr and CaOwr are the whole rock values.

It is strongly recommended that the MnOd formulae only be used for rocks with >1 wt% CaO, as rocks with <1 wt% CaO are virtually devoid of significant dolomite.

Using equations 1 and 2, the MnO content of carbonates from the Lady Loretta Small Syncline have been calculated and are plotted in Figure 14. MnOd shows a very systematic increase in the footwall sediments towards ore from a background value of 0.2 wt% to a maximum of 0.6 wt% at the dolomite/siderite boundary. MnOd has considerably higher values generally in the range 0.4 to 4.0 wt% MnO in siderite (Fig. 14); however, some samples close to, or within, the ore-bearing sediments contain values of greater than 4 wt% MnO. Compared to the other two indices (metal index and SEDEX AI), the MnOd index shows the most systematic and smooth variation.
Figure 14: Variation in wt % MnO in carbonate, calculated from the whole rock data, using the equations discussed in the text. Note the systematic increase in MnO content of dolomite from deep in the footwall sediments up toward the ore position.

towards the orebody from the footwall side over the entire stratigraphic interval of 265 m sampled.

In order to check the whole rock calculations of Mn content of carbonate minerals a program of microprobe analyses of selected samples of dolomitic and sideritic sediments from Lady Loretta was undertaken. Although considerable variability of Mn substitution was found in any given sample, the mean MnO content of all microprobe carbonate analyses was close to the calculated MnO$_d$ value, especially when a large number of probe analyses were involved (>10 per sample). A comparison of the mean microprobe analysis and the calculated MnO$_d$ for each sample is shown in Figure 15. In all but one case the calculated MnO$_d$ values are lower than the mean microprobe values. This is probably due to the fact that the calculated values do not take into account substitution of Fe and Mg in the dolomite structure and Mg and Zn into the siderite structure.

Figure 15: Plot of calculated MnO$_d$ for selected sediment samples against the mean wt % MnO in dolomite from microprobe analyses. There is a good correlation between the two measurement techniques with the microprobe MnO values generally exceeding the calculated MnO values by about 30%.
HALO MODEL FOR LADY LORETTA

By combining the element dispersion and mineral chemistry data outlined here and in Carr (1984) with the known geology of the deposit from Hancock and Purvis (1990) and McGoldrick et al. (1996), it has been possible to develop a primary halo model for Lady Loretta (Fig. 15). This is a pre-folding reconstruction which utilises the Small Syncline and Big Syncline geochemical data base. The major features of the halo model are:

(1) An inner siderite halo which surrounds the orebody extending at least 50 m across strike and about 1 km along strike as a narrow sheath enclosing the favourable unit. Mn and Zn are enriched within the siderite halo due to substitution into the siderite structure. CaO, MgO and Na2O are strongly depleted within this zone.

(2) An intermediate ankerite and ferroan dolomite halo surrounds the siderite halo and extends a further 100 m into the footwall and hangingwall sediments. Mn, Ti and Fe are generally elevated throughout the ankerite halo, while CaO and MgO exhibit normal background values.

(3) An outer dolomite zone which shows no anomalous characteristics except for marginally elevated manganese content of dolomite (MnO_d), that increases toward the orebody.

CONCLUSIONS AND APPLICATION TO EXPLORATION

This study has identified a group of geochemical parameters which are useful in (a) defining the favourable sedimentary unit hosting stratiform Zn-Pb-Ag ore at Lady Loretta and (b) providing a vector to ore, both across strike and along strike.

Identification of favourable sedimentary units

Parameters useful in the identification of a potential ore-bearing host unit in the Lady Loretta Formation at a distance of at least 1 km from ore are:

(1) SEDEX AI > 40
(2) MnO content of dolomite, MnO_d > 0.2 wt%
(3) Thallium > 4 ppm
(4) Zn > 70 ppm
(5) SEDEX metal index > 3000.

Coincidence of all five parameters is considered to indicate a high priority for stratiform Zn-Pb-Ag mineralisation within the sedimentary unit elsewhere in the basin. Note that SEDEX AI and MnO_d depend on changes in chemistry of carbonate within the sediments related to mineralisation. These parameters should only be applied in sedimentary packages with greater than 2 wt% carbonate, and are not recommended for application in clastic packages devoid of carbonate.

Vectors to ore

Based on this study, the following vectors are recommended for the discovery of Proterozoic Zn-Pb-Ag deposits in the Northern Australia dolomite-rich sedimentary basins.

(1) Change in carbonate composition from dolomite to ankerite to siderite within the sediments. The change dolomite to ankerite occurs within 150 m across strike, while the change to siderite occurs within 50 m across strike of the orebody. Along strike variations are an order of magnitude greater in distance.

(2) MnO content of dolomite (MnO_d) increases systematically from 0.2 wt% to 1 wt% over 300 m approaching the orebody from the footwall side.

(3) SEDEX Alteration Index, defined by SEDEX AI increases for 30 to >90 over at least 300 m approaching the ore across strike.

(4) Zinc content of sediments increases erratically from 100 ppm to 1 wt% over 100 m in the footwall and hangingwall.

(5) Thallium content of sediments increases erratically from <4 ppm to 100 ppm over a distance of 200 m approaching the ore position across strike.
Figure 16: Halo model (pre-folding) for the Lady Loretta deposit based on geochemical data from the Small Syncline and Big Syncline.

(6) SEDEX metal index $(Zn + 100Pb + 100Ti)$ increases from 1000 to over 10,000 towards ore both across strike and along strike.

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