CHAPTER NINE - LEAD ISOTOPE STUDIES

9.0 Introduction

A model of the hydrothermal processes involved in the formation of Nifty mineralisation requires an understanding of the source and characteristics of fluids involved in the mineralising event. An insight into the source of the hydrothermal fluids can be gained from Pb isotope ratios of 1) mineralisation at the Nifty Cu deposit, 2) other mineralised occurrences in the Paterson Orogen, and 3) isotope signature of potential Pb sources.

The rationale for using Pb isotope data at Nifty assumes that Cu and Pb were precipitated synchronously. This assumption needs to be stated explicitly, as the Pb at Nifty Cu deposit is concentrated in 53 Silicified Pyritic Shale altered zones and not in the chalcopyrite-rich intervals. 52 is a discord alteration texture associated with chalcopyrite mineralisation and occurs preferentially in the lowermost hanging-wall beds, pyrite marker bed and uppermost footwall beds. Galena occurs as 1) pseudomorphs of frambooidal pyrite, 2) anhedral to subhedral grains in quartz + anhedral pyrite + sphalerite + chalcopyrite, and 3) as pseudomorphs of pyrite blebs. The association of galena with syn-mineralisation alterations and D5 deformation suggests precipitation during the main mineralisation event. In chalcopyrite-rich intervals of the Nifty carbonate member geochemical analyses indicate only trace amounts of Pb (<10ppm). This chapter presents Pb isotope results from the Nifty Cu deposit and other mineralised occurrences within the Paterson Orogen. Pb isotope signatures of potential Pb sources are then examined. Pb isotope evolution models developed for the Paterson Orogen are then presented and discussed. Using data from potential Pb source and mineralised occurrences a new model is proposed that accounts for the new data.

9.1 Pb isotope systematics

The radiogenic decay of $^{206}$Th, $^{235}$U and $^{238}$U results in the end-member isotopes $^{208}$Pb, $^{207}$Pb and $^{206}$Pb. A fourth isotope of Pb, $^{204}$Pb, is weakly radioactive with a half-life of $1.4 \times 10^{11}$ years but because of its long half-life $^{204}$Pb can be considered stable and therefore used as a reference isotope. The decay of the parent elements to the daughter isotopes can be mathematically modelled using three equations (Equations 1-3):

$$
\frac{\text{206 Pb}}{\text{208 Pb}} = \text{206 Pb}_{0} \times (1 - e^{-\lambda T})
$$

$$
\frac{\text{207 Pb}}{\text{204 Pb}} = \text{207 Pb}_{0} \times \left(1 - e^{-\lambda T/137.88}\right)
$$

$$
\frac{\text{204 Pb}}{\text{208 Pb}} = \text{204 Pb}_{0} \times \left(e^{\lambda T} - e^{\lambda T/137.88}\right)
$$

143
Where, $t$ = time at which Pb was leached from source and incorporated into galena, $T$ = age of source rocks, $\mu$ = the present $^{238}\text{U}/^{206}\text{Pb}$, $\mu(13.88) = ^{238}\text{U}/^{206}\text{Pb}$, $W_{\mu} = ^{235}\text{Th}/^{206}\text{Pb}$, $137.88 = $ present day $^{238}\text{U}/^{235}\text{U}$, $\lambda_1$, $\lambda_2$, and $\lambda_3$ are the decay constants of $^{238}\text{U}$, $^{235}\text{U}$, and $^{235}\text{Th}$ respectively and these constant are defined as $\lambda_1 = 0.155125 \times 10^{-9}$ yr$^{-1}$, $\lambda_2 = 0.98485 \times 10^{-7}$ yr$^{-1}$, $\lambda_3 = 0.040475 \times 10^{-9}$ yr$^{-1}$, and $^{206}\text{Pb}/^{208}\text{Pb}$, $^{206}\text{Pb}/^{208}\text{Pb}$ initial Pb isotope composition.

A fourth equation (4) is used to calculate a secondary isochron and relate the slope of a line in $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$ space to the decay of $^{238}\text{U}$ and $^{235}\text{U}$ between time $t$ and $T$. The calculation uses a known point of either the initial ratio ($T$) or the present day ratio ($t$).

$$ \frac{^{207}\text{Pb}}{^{204}\text{Pb}} = \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \lambda_3 \left( \frac{e^{1.3788T} - e^{1.3788t}}{e^{1.3788T} - e^{1.3788t}} \right) $$

(4)


9.2 Sampling and Analytical Methods

This study presents 1) ten new Pb isotope analyses on galena from the pyrite marker bed at the Nifty Cu deposit, 2) three new galena results from the Greenvilla pyrite, and Rainbow stratiform Cu prospects and 3) four new K-feldspar results from the Rudall Complex and the Gregory Granitic Complex. Galena from Nifty, Greenvilla and Rainbow were hand picked from diamond drill. K-feldspar separates were obtained from Rudall Complex and Gregory Granitic Complex samples with U-Pb zircon SHRIMP ages (Nelson, 1995; 1996). All K-feldspar separates were provided by the Geological Survey of Western Australia (GSWA). K-feldspar separates were selected so that Pb-Pb ratios could be constrained for samples with well defined age dates and therefore their selection was based on these being minimal spread of data in U-Pb concordia plots (Nelson, 1995, 1996) and no unusual features in petrographic descriptions or analytical notes.

Pb isotopic analyses were undertaken at Curtin University by Br. D. Nelson. About 5 µg of galena was dissolved in concentrated HNO$_3$ and purified by electropolishing using micro-electrode position techniques. Analyses were conducted using a VG954 mass spectrometer and data was corrected for mass fractionation by reference to NBS-981 and the 95% confidence intervals are 0.1%, 0.15% and 0.2% for the ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ respectively.
9.3 Results

9.3.1 Nifty Cu Deposit

Table 9.1 lists galena Pb isotope results from the samples collected from the S2 altered zones in pyrite marker bed and these results are shown in Figure 9.1A-B. Ten samples were collected and analysed as part of this study and to this data were added three results from the Geological Survey of Western Australia (GSWA, written comm.); and a single result from Smith (1996). The location of diamond drill holes from which samples were collected is shown in Figure 5.2.

<table>
<thead>
<tr>
<th>DTH</th>
<th>Depth (m)</th>
<th>Pb206Pb/Pb207Pb</th>
<th>Pb206Pb/Pb208Pb</th>
<th>Description</th>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>TND9</td>
<td>243.5</td>
<td>17.370</td>
<td>15.665</td>
<td>37.823</td>
<td>gn bble with S2</td>
</tr>
<tr>
<td>TND17</td>
<td>240.0</td>
<td>17.318</td>
<td>15.670</td>
<td>38.241</td>
<td>gn + sph bble</td>
</tr>
<tr>
<td>TND27</td>
<td>255.0</td>
<td>17.275</td>
<td>15.657</td>
<td>37.518</td>
<td>gn in ch-ve</td>
</tr>
<tr>
<td>TIRD628</td>
<td>187.5</td>
<td>17.254</td>
<td>15.642</td>
<td>37.165</td>
<td>gn bble</td>
</tr>
<tr>
<td>TIRD645</td>
<td>265.5</td>
<td>17.356</td>
<td>15.655</td>
<td>37.798</td>
<td>gn in S2 lense</td>
</tr>
<tr>
<td>TIRD645</td>
<td>266.7</td>
<td>17.337</td>
<td>15.625</td>
<td>37.705</td>
<td>gn bble</td>
</tr>
<tr>
<td>TIRD645</td>
<td>262.2</td>
<td>17.352</td>
<td>15.647</td>
<td>37.759</td>
<td>gn in S2 lense</td>
</tr>
<tr>
<td>TIRD750</td>
<td>258.0</td>
<td>17.365</td>
<td>15.649</td>
<td>37.873</td>
<td>gn bble</td>
</tr>
<tr>
<td>TIRD750</td>
<td>253.1</td>
<td>17.366</td>
<td>15.651</td>
<td>37.789</td>
<td>gn bble</td>
</tr>
<tr>
<td>TIRD754</td>
<td>199.1</td>
<td>17.372</td>
<td>15.621</td>
<td>37.695</td>
<td>gn selvage on py grain</td>
</tr>
</tbody>
</table>

Table 9.1: The results of Pb isotope analyses on galenas from the Nifty copper deposit. Abbreviations; DTH - diamond drill hole, gn - galena, ch - carbonate, chl - chlorite, py - pyrite, sph - sphalerite, ve - vein, para - parallel, GSWA - Geological Survey of Western Australia.

Nifty galena Pb isotope data plot (Fig. 9.1A-B) as two groups with the largest group of data plotting along a linear 206Pb/207Pb fractionation trend with 206Pb/207Pb ratios between 17.316-17.390, 206Pb/208Pb ratios between 15.67-15.621, and 206Pb/208Pb ratios between 37.885-38.241. A second group of two samples (TIRD27, 535.8m and TND9, 241.5m) plot with lower 206Pb/207Pb ratios close to samples from Warnabary. The TIRD27 sample is from a dolomite vein in carbonaceous slate in a diamond drill hole drilled several kilometres from the main Nifty Cu deposit, the second sample (TND9, 241.5m) was collected and analysed by the GSWA and no information on the form or relationships of the galenas are available. To validate the original result from TND9 another sample was collected from two metres further down hole (TND9, 243.5m). The result from this analysis does not plot in the Warnabary field but is consistent with the majority of Nifty data. With the exception of the two data points discussed above, the new data presented as part of this study overlaps with existing galena Pb isotope results (Smith, 1996; GSWA, written comm., 1997). The GSWA sample from TMD8 (209.9m) occurs in a
Figure 5, A-B: A. Galena $^{206}\text{Pb} / ^{204}\text{Pb}$ vs $^{207}\text{Pb} / ^{204}\text{Pb}$ data from Thrustell Group deposits and prospects plot on as groups on a linear trend with Warrabary at the least radiogenic, and Maroochydore at the most radiogenic end. B. Galena $^{206}\text{Pb} / ^{204}\text{Pb}$ vs $^{208}\text{Pb} / ^{204}\text{Pb}$. Locations of the deposits and prospects are shown in Figure 2.1. The Cumming and Richards (1975) growth curve is included for reference. Data from McKnight (1992), Reed (1996), Smith (1996), Froud (1997), GSWA (written comm., 1997).
banded sequence of dolomite mudstone and the distal alteration texture. SJ-Hydrothermal Quartz-
Dolomite.

9.4 Throssell Group Pb isotope Signatures

Within the Throssell Group detailed Pb isotope studies have been conducted on the Warrabay Pb-Zn
prospect (Smith, 1996) and Maroochydore Cu deposit (McKnight, 1992; Reed, 1996) (Fig. 2.11). In
addition to these mineralised occurrences reconnaissance Pb isotope data exist for Rainbow (Nelson,
written comm., 1997; Smith, 1996), Grevillea, and Goosewacker (Proud, 1997). Pb isotope ratio data
(Fig. 9.1A-B) from Throssell Group mineralised occurrences plot as a linear trend with Warrabay and a
single Rainbow result at the least radiogenic end of the trend and Maroochydore at the most
radiogenic end.

9.4.1 Maroochydore Cu Deposit

Three studies have examined the Pb isotopic composition (Fig. 9.1A-B) of Maroochydore Cu prospect
(McKnight, 1992; Reed, 1996) and these detailed studies have been in addition to reconnaissance data
collected as part regional mapping projects conducted by the Geological Survey of Western Australia.
McKnight (1992) examined the initial isotopic ratio of Pb and to constrain the timing of copper
mineralisation at Maroochydore (Fig. 9.1A-B). Seven samples of hand-picked galena grains or galenas
dissolved from polished thin sections from the Cu horizon and footwall were analysed at Curtin
University of Technology (McKnight, 1992). Reed (1996) conducted a second study on the Pb isotopic
component of Maroochydore and the Paterson Orogen (Fig. 9.1A-B) using galena data of McKnight
(1992), GSWA, and new data from pyrite, chalcopyrite, and whole rock data samples. Whole rock and
pyrite results are discussed in a later section. Four results from the GSWA are combined with data from
McKnight (1992) and Reed (1996). Galena Pb isotope data plot with average 206Pb/207Pb, 208Pb/207Pb, and
204Pb/207Pb ratios 18.007, 15.471, and 38.229 respectively (Fig. 9.1A-B). This data forms the most
radiogenic end of the Throssell mineralisation trend.

9.4.2. Warrabay Pb-Zn Prospect

Smith (1996) examined the Pb isotope characteristic of mineralisation and potential sources of
Warrabay Pb. Isotopic data (Fig. 9.1A-B) consists of 3 galena results from Geological Survey of
Western Australia (Nelson, written comm., 1997) and 4 galena samples from grey stage syn-
mineralisation veins (Smith, 1996). Pb isotope data was analysed at CSIRO and Curtin University
laboratories and these data plot are within error. Warrabay galena data plot (Fig. 9.1A-B) within error
of each other with 206Pb/207Pb ratios ~17.2, 208Pb/207Pb ratios ~15.58, and 204Pb/207Pb ratios of ~37.57.
Warrabay data forms the least radiogenic endpoint of the Throssell mineralisation trend.
9.4.3 Rainbow Ca Prospect

Rainbow galena Pb isotope data is shown in Figure 9.1A-B and listed in Table 9.2. Data from the Rainbow area is from 1) the Geological Survey of Western Australia (GSWA, written comm.), 2) Smith (1996) and 3) single sample collected as part of this study. All samples were analysed at Curtin University of Technology. In addition to Pb isotope compositions on galena, several whole rock samples from Rainbow have also been analysed and these results are presented and discussed in a following section.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>(^{206}\text{Pb}/^{207}\text{Pb}</th>
<th>(^{207}\text{Pb}/^{206}\text{Pb}</th>
<th>(^{208}\text{Pb}/^{206}\text{Pb}</th>
<th>\text{Pb} Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRD 6</td>
<td>216.7</td>
<td>17.031</td>
<td>15.507</td>
<td>37.369</td>
<td>G3 bedding parallel quartz-chlorite-sulphide vein</td>
</tr>
<tr>
<td>Holly</td>
<td>17.517</td>
<td>15.591</td>
<td>38.170</td>
<td>G2A, written comm.</td>
<td></td>
</tr>
<tr>
<td>TRD 7</td>
<td>609.8</td>
<td>17.741</td>
<td>15.618</td>
<td>38.642</td>
<td>G4, attacted ch-sm-co-cpy</td>
</tr>
</tbody>
</table>

**Goosewacker prospect**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>(^{206}\text{Pb}/^{207}\text{Pb}</th>
<th>(^{207}\text{Pb}/^{206}\text{Pb}</th>
<th>(^{208}\text{Pb}/^{206}\text{Pb}</th>
<th>\text{Pb} Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>THR7665</td>
<td>262.9</td>
<td>17.598</td>
<td>15.708</td>
<td>38.279</td>
<td>G4, stage 2 vein</td>
</tr>
<tr>
<td>THR771</td>
<td>274.3</td>
<td>17.483</td>
<td>15.670</td>
<td>38.248</td>
<td>G4, stage 4 vein</td>
</tr>
<tr>
<td>THR773</td>
<td>184.1</td>
<td>17.483</td>
<td>15.685</td>
<td>38.233</td>
<td>G4, stage 3 vein</td>
</tr>
</tbody>
</table>

**Grevillea prospect**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>(^{206}\text{Pb}/^{207}\text{Pb}</th>
<th>(^{207}\text{Pb}/^{206}\text{Pb}</th>
<th>(^{208}\text{Pb}/^{206}\text{Pb}</th>
<th>\text{Pb} Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRD633</td>
<td>353.7</td>
<td>17.608</td>
<td>15.643</td>
<td>38.047</td>
<td>on ch-sm</td>
</tr>
<tr>
<td>TRD633</td>
<td>353.9</td>
<td>17.593</td>
<td>15.629</td>
<td>37.081</td>
<td>on bordering ch-sm</td>
</tr>
</tbody>
</table>

Table 9.2: Pb isotope data from the Rainbow, Holly, Goosewacker, and Grevillea prospects. Abbreviations as in Figure 9.2. Drill hole collar locations in AMG (Australian Mercator Grid). TRD6-762835mN, 337221mE; the location of the sample from Holly is unknown, TRD7-762936mN, 338830mE. Goosewacker prospect (Froid, 1997) drill hole collar location THR7665-7573350mN, 3850400mE; THR771-7573350mN, 3854600mE; THR773-7573550mN, 3859000mE. Grevillea martinsite pyrite prospect drill hole collar location TRD623-7631220mN, 341300mE.

Rainbow Pb isotope data has a high variability in both \(^{206}\text{Pb}/^{207}\text{Pb} and \(^{208}\text{Pb}/^{206}\text{Pb} (Fig. 9.1A-B). A single result from TRD 6, 216.7m (Smith, 1996) plots as the least radiogenic end-member of the Thorswell mineralisation trend. Other Rainbow results do not coincide with this trend but plot with higher \(^{208}\text{Pb}/^{206}\text{Pb} ratios. Discrepancy between Rainbow Pb data can be answered from a review of the Geological Survey of Western Australia and WMC Resources Ltd. records. These records indicate that the Geological Survey of Western Australia sample attributed by Smith (1996) and Reed (1996) to Rainbow came from another prospect known as Holly. Holly is located several kilometres away from the main Rainbow prospect and the relationship between the prospects is unclear because 1) there is no outcrop in the area, and 2) significant differences occur in drill core stratigraphy.

9.4.4 Goosewacker Pb-Cu-Au Vein Prospect

Froid (1997) collected galena from three of five paragenetic vein stages (Stages 2, 3, and 4) that were identified on the basis of cross-cutting relationships. Froid (1997) defined Stage 2 veins as having a sequence of quartz-siderite-pyrite followed by galena and then chalcopyrite; Stage 3 veins consist of quartz with early pyrite rimmed by galena then sphalerite-pyrite-rich and marcasite, and Stage 4 veins...
have early siderite and pyrite, followed by galena and later chalcopyrite. Samples were analysed at Curtin University in conjunction with samples from the Nifty Cu deposit. Pb isotope results from Goosenacker plot (Table 9.2 and Fig. 9.1-A-B) as a group with 206Pb/204Pb and 207Pb/204Pb ratios less than Maroochydore and greater than Nifty Cu deposit data. Sample 79W03765-262.9m is more radiogenic than the other two samples. On 206Pb/204Pb vs 207Pb/206Pb diagram (Fig. 9.1B) Goosenacker data plots with more radiogenic 206Pb/204Pb values than other Throssell Group mineralised occurrences.

9.4.5 Grevillea Massive Pyrite Prospect

Two analyses of hand-picked galena from dolomitic veins in drill hole THRD623 are presented in Figure 9.1A-B and Table 9.2. Both analyses plot within error of each other and have similar 206Pb/204Pb ratios to Nifty data but higher 206Pb/204Pb values. Grevillea and Maroochydore have similar 206Pb/204Pb ratios (Fig. 9.1B) with Grevillea more radiogenic than that of Maroochydore.

9.4.6 Summary of Throssell Group Data

Throssell Group Pb isotope data (Fig. 9.1A-B) from mineralised occurrences form a linear trend in 206Pb/204Pb vs 207Pb/206Pb space. At the least radiogenic end of the trend is Warrabury data and at the most radiogenic end is Maroochydore data. It could be argued that the linear trend is a feature of systematic error due to laboratory methods or 206Pb isotopic fractionation, however this is not supported because data from mineralised occurrences (Table 9.1-9.2 and Fig. 9.1) form distinct groupings along the trend. If machine error or fractionation were responsible for the trend then data would form a dispersed pattern with individual deposits being indistinguishable along the trend. Although the majority of samples have been analysed at Curtin University of Technology, samples from Warrabury and Maroochydore have been analysed at CSIRO, North Ryde and Curtin University.

Data from each mineralised occurrence plot as isolated groups not related to the analytical laboratory at which they were measured. The features outlined above suggest that the linear trend is a feature of the Pb isotope signatures of the deposits and prospects and not due to machine error or 206Pb fractionation.

9.5 Lamill Group Pb Isotope Signatures

A large amount of Pb isotope data exists for the Lamill Group and Teller Au-Cu deposit (Goellnicht, 1987; Goellnicht et al., 1989; McNaughton and Goellnicht, 1990; Goellnicht et al., 1991; Goellnicht, 1992; Rawins, 1994; Rawins et al., 1997; Rawins et al., 1998). Lamill Group Pb isotope data is presented in Figure 9.2A-D and consists of galena and pyrite results from the Teller Au-Cu deposit: Lamill Group whole rock data; whole rock and K-feldspar data from metamorphic suites; and pyrite analyses from mineralised prospect hosted by Lamill Group rocks.
9.5.1 Telfer Au-Cu Deposit

Telfer galena Pb isotope data (Fig. 9.2A-D) from the Main Dome plots with average 206Pb/204Pb ratio of ~18.07, 207Pb/204Pb ratio of ~15.72, and 208Pb/204Pb ratio of ~38.26 along a linear trend of least radiogenic Lamal Group. Pb isotope analyses of pyrite from the Main Dome, West Dome and Telfer syncline plot with similar values to the galena results (Fig. 9.2A-D). A field Pb isotope results from the Telfer Au-Cu deposit is defined in Figure 9.2C-D where this field plots above the Cumming and Richards (1975) growth curve. On a 208Pb/206Pb vs 206Pb/204Pb plot (Fig. 9.2D) the Telfer Au-Cu deposit field has a trend oblique to the growth curve.

9.5.2 Lamal Group Whole Rock

The least radiogenic Lamal Group whole rock data have 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb values of 18.79, 15.751, and 39.148, respectively (Fig. 9.2A-D). From this least radiogenic value whole rock data forms a linear trend in plots of 206Pb/204Pb vs 207Pb/204Pb (Fig. 9.2A) and in plots of 206Pb/204Pb vs 208Pb/204Pb whole rock data forms a dispersed pattern.

9.5.3 Granite Data

Galen Pb isotope data in from O’Callaghan’s Granite and Hanson Folly plot with more radiogenic Pb ratio than the Telfer galena data. O’Callaghan’s Hanson Folly data have average 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb ratios of approximately 18.75, 15.81 and 38.73 respectively. Whole rock and K-feldspar samples from the Minyari Granite plot with a wide range of 206Pb/204Pb ratios (Fig. 9.2). O’Callaghan’s Granite plots in a tight cluster in the region of the least radiogenic Throssell trend and a second group comprised of samples from the Desert Revenge Granite (a sub-group of O’Callaghan’s Granite) plots with 206Pb/204Pb ratios between 19.985-20.205 and 208Pb/204Pb ratios between 15.739-15.766. This sub-group plots below the sedimentary whole rock field but with greater spread and more radiogenic Pb isotope ratios than the other O’Callaghan’s Granite data. Data from the granite analysed, Mount Crofton Granite, has Pb isotope data that plots (Fig. 9.2) along the Cumming and Richards (1975) growth curve.

9.5.4 Lamal Group Mineralised Occurrences

Pb isotope from seven Lamal Group prospects were analysed by Goellnicht (1993). The least radiogenic Pb isotope values from these prospects plot to form a linear trend in 206Pb/204Pb vs 208Pb/204Pb space (Fig. 9.2C). At the least radiogenic end of this isotopic trend plot the Lamal and 17 Mile Hill prospects and data from these prospects has similar values to the least radiogenic values of the Mount Crofton Granite Suite. At the most radiogenic end of the trend are Minyari and Hauiti prospects and this data plots within the field defined by Telfer Au-Cu deposit data. Least radiogenic data from the Telfer deposit and Thompson’s prospect coincides. Big Tree prospect data plots within the field of Telfer deposit data and also coincides with that of the Minyari Granite.

149
Figure 9.2A-D: A. $^{206}_{140}$Pb vs $^{207}_{140}$Pb plot of Lampl Group galena, pyrite and whole rock analyses. B. $^{208}_{140}$Pb vs $^{206}_{140}$Pb plot (Goedlisch et al., 1989; Goedlisch et al., 1991; Goedlisch, 1992; Rowins, 1994; Rowins et al., 1997). The Cunningham and Richards (1975) growth curve is included for reference. Detail of the areas enclosed in boxes is contained in C-D.
9.5.3 Summary of Lampl Group Data
Lampl Group Pb isotope data forms a dispersed pattern above the Cumming and Richards (1975) growth curve. Least radiogenic data from mineralised occurrences form a linear trend on a plot of $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$. The Lampl and VI Mile Hill prospects plot at the least radiogenic end of the linear trend in close proximity to Mount Crofton and O’Callaghan’s Granite Suites. At the most radiogenic end of the linear trend the Hastics and Minyuri prospects plot within the field of Telfer Au-Cu deposit data.

9.6 Potential Pb Sources
Four potential sources for Pb at Nifty have been identified as 1) Rudall complex, 2) Pilbara Craton, 3) internally sourced Pb from the Broadhurst Formation or Coolban Sandstone, or 4) an unexposed intrusive body. This section will outline the stratigraphic relationships between the basement (Pilbara Craton or Rudall Complex) before defining a Pb isotope signature for those basement blocks. Whole rock Pb isotope data will provide the internally sourced signature and the intrusive will be defined using the Eva Well intrusive and Telfer district granites.

9.6.1 Potential Basements to Throssell Group Deposits
Basement to the Nifty Cu deposit is unknown, however there are two possible units, the Lower Proterozoic Rudall Complex and the Archaean Pilbara Craton. To the south of Nifty in the Maroochydore-Sunday Creek area, an unconformable contact between the Throssell Group and the Rudall Complex is exposed (Hickman and Clarke, 1994; Bagas and Smithies, 1996). The underlying Rudall Complex consists of an arenaceous and pelitic succession intruded by pre- to syn-cogenetic granitoids (now orthogneiss) and younger quartzite and schist (Hickman et al., 1994). The Rudall Complex has been subject to a long and complex structural history of multiple deformation and metamorphism, with a maximum metamorphism of amphibolite facies. Rudall Complex rocks are not exposed in the Nifty area.

The second option for basement rocks is the Pilbara Craton that is made up of 1) the Pilbara Supergroup which is a 3600 and 3000Ma granite-greenstone terrain, and 2) the overlying Mount Bruce Supergroup which is comprised of mainly 2800 to 2600Ma basaltic volcanic rocks of the Fortescue Group and 2600 to 2400 Ma banded iron formations of the Hamersley Group (Myers and Hickman, 1990). The major units of the Pilbara Supergroup are: the Warrawoona Group; Gorge Creek Group; and the Whin Creek Group. The Warrawoona Group is comprised of a 3600 to 3300Ma granite-greenstone terrain of mainly basaltic lavas with minor komatite, dacite, rhyolitic tuff, agglomerate and sedimentary rocks (Myers and Hickman, 1990). Unconformably overlying the Warrawoona Group are sedimentary and minor basaltic lavas of the Gorge Creek Group. The Gorge Creek Group in turn unconformably overlain by the Whin Creek Group of mafic and felsic volcanics and 3500 to 2400 Ma granitoids (Myers and Hickman, 1990).
Rocks of the Fortescue Group unconformably overlie the Whim Creek Group and consist of mafic volcanics and immature clastics (Harmsworth et al., 1990). The Fortescue Group consists of four formations: 1) Mount Roe Basalt, amygdaloidal, porphyritic metabasalt with tuft, agglomerate, and clastic sediments; 2) Harley Sandstone, coarse grained arkose, arenite and shale; 3) Kylensa Basalt, massive, amygdaloidal basalt and andesite; 4) Mount Jope Volcanics predominantly pillow basalts and basaltic pyroclastics; and 5) the Jeerinah Formation, thin basaltic lavas interbedded with clastics and chemical sediments (Harmsworth et al., 1990). On the eastern margin of the Pilbara Craton are rocks of the Gregory Granitic Complex and this unit forms part of the Fortescue Group. The Gregory Granitic Complex consists of the Koongaling Volcanic, Kylensa Basalt, Yullands Formation and PEARARA Basalt.  The 2500m thick Hamersley Group conformably overlies the Fortescue Group and consists of a sequence of banded iron formation (BIF), dolerite, pyroclastics/hemipelitic shale and acid volcanics (Harmsworth et al., 1990).

9.6.2 Rudall Complex Pb Isotope Signatures

Limited Pb isotope data is available for the Rudall Complex (Table 9.3). Goollnicht, (1992) analysed Pb isotopes (Fig. 9.3 and Table 9.3) on two age dated, Rudall Complex K-feldspar separates provided by the GSWA (Nelson, written comm.). This study adds results from an additional two Pb isotope analyses on K-feldspar separates (Fig. 9.3 and Table 9.3). Goollnicht (1992) analysed a garnet-plagioclase-ropicitic syenogranite gneiss from the Watarrka Inlier (GSWA 104932, AMG 751550mN, 403500mE) and a coarse grained to porphyritic albic-cristobalite metasedimentary gneiss (GSWA 104938, AMG 7509600mN, 451900mE). The samples analysed in this study were a sericite biotite biotite monzogranite (GSWA 112102, AMG 7499500mN, 419500mE), from the southern part of the Watarrka Inlier and a coarse grained porphyritic biotite monzogranite (argent) gneiss (GSWA 112397, AMG 7514500mN, 402600mE) also from within the Watarrka Inlier. Rudall Complex samples have been U-Pb zircon age dated by D. Nelson at Curtin University and the age dating results have been published in (Nelson, 1991), Goollnicht (1992), Nelson (1995), and Nelson (1996). Runtont #1&3 (Table 9.3 and Fig. 9.3) are from the Runtont Adamellite of the Rudall Complex (McNaughton, 1990).

No sampling locations or analytical details are available (McNaughton, 1990).

<table>
<thead>
<tr>
<th>Unit</th>
<th>Sample No</th>
<th>Age</th>
<th>$^{206}Pb/^{204}Pb$</th>
<th>$^{207}Pb/^{204}Pb$</th>
<th>$^{208}Pb/^{204}Pb$</th>
<th>$^{235}Pb/^{204}Pb$</th>
<th>Reference</th>
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<tr>
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<td>104938</td>
<td>1.29Ga</td>
<td>18.277</td>
<td>15.660</td>
<td>38.626</td>
<td>37.385</td>
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</tr>
<tr>
<td>Rudall Complex #3</td>
<td>112102</td>
<td>1.45Ga</td>
<td>16.984</td>
<td>15.525</td>
<td>37.585</td>
<td>37.585</td>
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</tr>
<tr>
<td>Rudall Complex #4</td>
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<td>1.78Ga</td>
<td>16.729</td>
<td>15.666</td>
<td>37.457</td>
<td>37.345</td>
<td>This study</td>
</tr>
<tr>
<td>Rudall Complex #10</td>
<td>104932</td>
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<td>16.758</td>
<td>15.591</td>
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<td></td>
<td>17.520</td>
<td>15.670</td>
<td>37.413</td>
<td>37.413</td>
<td>McNaughton, 1990</td>
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</tbody>
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Table 9.3: Pb isotope results from K-feldspar separates from the Rudall Complex. Samples are listed from youngest to oldest with locations and petrology discussed in the text.

Pb isotope data from the Rudall Complex plot in a dispersed pattern on a $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ diagram (Fig. 9.3). Rudall #1 and Rudall #4 plot close to each other with $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$...
Figure 9.3: Plot of Pb isotope data from the Rudall Complex. Analyses Rudall #1-#4 were conducted on K-feldspar separates with U-Pb zircon age dates. All separates provided by D. Nelson, Geological Survey of Western Australia. Rudall #1 and #2 are metasedimentary rocks (Gaillard, 1992), Rudall #3 and #4 are monazites from the Wairama Filler (this study). Runton #1-#3 are from the Runton Adamellite (McNaughton, 1990).
ratio of ~16.7 and ~15.58. Rudall #3 plots on the Cumming and Richards (1975) growth curve toward the base of the Traceyell and Lamal linear trends. Rudall #2 has a higher 206Pb/204Pb ratio and plots below the Lamal Group pyrite field. Data from the Ranton Activation plots parallel to the Cumming and Richards (1975) growth curve but with more radiogenic 206Pb/204Pb values. An implication of the existing limited amount of Pb data from the Rudall Complex is that this unit appears as a heterogeneous Pb source.

6.3 Pilbara Craton Pb Isotope Signature

Figure 9.4 shows Pb isotope data from the Pilbara and Mount Bruce Supergroups (Richards et al., 1981; Richards and Blockley, 1984; Thorpe et al., 1992). No Pb isotope data is available for the Hamersley Group. Pb isotope data is plotted in stratigraphic succession with the Talga Talga Sub-Group being the oldest unit of the Pilbara Supergroup and Kylena Basalt of the Fortescue Group the youngest. Duffer Formation samples from the volcanic-hosted massive sulphide deposits of Big Stubby and Lennor Find, plus with the least radiogenic Pilbara values although, the Talga Talga Sub-Group and Mount Ada Basalt are stratigraphically below the Duffer Formation. Data from the North Pole volcanic-hosted massive sulphide deposit, hosted by the Towers Formation, plot as a tight group above Duffer Formation data along the Cumming and Richards (1975) Pb growth curve. The Fortescue Formation data, and specifically the Kylena Basalt, plot along the Cumming and Richards (1975) growth curve as a tight cluster (see inset on Fig. 9.4). Other poorly defined Fortescue Group data are more radiogenic and some rocks have been interpreted to pre-date the Fortescue group.

Two K-feldspar separate samples from the Gregory Granite Complex were chosen for Pb-Pb isotope analysis on the availability of age dating and lack of spread in U-Pb concordia plots. Sample 118920 is an alkali granite with an age of 2762±4Ma (Nelson, 1996) from the Walla Rock area (121° 2’ 19”E, 21° 32’ 57”S). Nelson (1996) suggests some radiogenic Pb loss has occurred with this sample. The second sample, 119523, consists of a granophyre from the Nifty Access Road (121° 19’ 27”E, 21° 37’ 45”S) and this sample has been dated at 2763±4Ma (Nelson, 1996). Nelson (1996) suggested that 2 analyses of this sample indicate it may have been metamorphically disturbed and this data was not used in the calculation of an age.

<table>
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<tr>
<th>Unit</th>
<th>Formation</th>
<th>T (Ga)</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
<th>Reference</th>
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<td>Kylena Basalt</td>
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<td>13.524</td>
<td>14.64</td>
<td>33.29</td>
<td>Richards and Blockley, 1984</td>
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<td>2.763</td>
<td>20.342</td>
<td>15.841</td>
<td>42.473</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Gregory Granite Complex</td>
<td>2.772</td>
<td>17.536</td>
<td>15.416</td>
<td>40.562</td>
<td>This study</td>
</tr>
</tbody>
</table>

Table 9.4: Initial Pb ratios of potential Pb sources from the Pilbara Supergroup. Sampling locations and age dating details are given in the text.
Figure 9.4A-B: Pb-Pb data from the Pilbara Supergroup, Mt Bruce Supergroup, and the Rudall Complex with insets showing the Warrawoona and Fortescue Groups. The formations and units are listed in stratigraphic order in the key. Data from Richards et al. (1981), Richards and Blockley (1984), Groves (1987), McNaughton (1990), Coupland (1992), Thorpe et al. (1992), Blockley (1994), and this study. The Cumming and Richards (1975) growth curve is included for reference.
9.6.4 Whole Rock Sediments

Whole rock Pb isotope data from the Throssell and Lamil Groups is shown in Figure 9.5A-B. Reed (1996) presents six whole-rock results from unmineralized Broadhurst Formation samples from the Sunday Creek and Eva Well area. Smith (1996) analysed samples from Warrumbury, Rainbow, Grevillea, Nifty, Finich, and Moloch. Finich is a Cu prospect hosted at Broadhurst Formation shales at ten kilometers south-east of Nifty. Moloch is an exploration target located twenty kilometers west of Goomackwarra. Maroochydore pyrite analyses are included in Figure 9.5A-B for reference. Throssell and Lamil Group Pb isotope data from sediment whole rock and pyrite form a dispersed pattern above the Cumming and Richards (1975) growth curve. Throssell Group whole rock Pb isotope data is less radiogenic than Lamil Group data. Lamil Group whole rock data plots at two dispersed groups. The first group has average $^{206}Pb/^{204}Pb$ ratios of 19.5 and $^{207}Pb/^{206}Pb$ of 15.8. The second group has average $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ ratios of 22.0 and 16.0 respectively.

9.6.5 Intrusives

Data from intrusive bodies is restricted to granite suites that intrude Lamil Group rocks and the Eva Well Intrusive. Descriptions of the Pb isotope signature of the Mount Crofton, O'Caulfields, and Minyari Granite Suites are given above.

9.7 A Review of Existing Data

Previous modelling of the initial Pb ratio of Rudall Complex (Goellnicht et al., 1989; Goellnicht et al., 1991; Goellnicht, 1992; Rowins 1994; Goellnicht, 1992; Reed, 1996; Smith, 1996; Rowins et al., 1997) has relied on K-feldspar analyses of U-Pb zircon dated material (Goellnicht, 1992). Modelling based on the initial ratios of these K-feldspar separates is considered problematic because a concordia plot of sample Rudall #1 (Nelson, 1995) shows analyses fall into two broad groups. A younger group of six analyses (of a total of 18 analyses) returns an age of 2015±26Ma and a second older group with higher $^{207}Pb/^{206}Pb$ with ages of between 2577 and 2715Ma (Nelson, 1995). The petrographic description of sample Rudall #1 states that the specimen has been strongly metamorphosed to amphibibolite facies and has abundant garnet and muscovite. Nelson (1995) describes the presence of garnet and muscovite in an orthogneiss as unusual and suggests the possibility of a sedimentary component having been incorporated into this granite. Goellnicht (1992) quotes an unpublished company report for an initial age of 1981±21Ma for simple Rudall #1 while Nelson (1995) reports an age of 2015±26Ma for the same sample.

The second sample Rudall #2 (G5WA 104938) used by Goellnicht (1992) is a muscovite-quartz epidote-albite (microcline) metapotamogranite pegmatoid dyke believed to intrude orthogneiss (Nelson, 1995). Goellnicht (1992) interpreted this sample to have been deformed by Rudall D1 and therefore it contains crystallisation as pre-dating Rudall D1. A recent re-interpretation (Bagn, per comm.) of the outcrop from which the sample was collected suggests that the cleavage observed by Goellnicht was
Figure 4.5A-B: A. Whole rock (WR) Pb isotope data from the Throttell and Lamil Groups. A. $^{206}\text{Pb} / ^{207}\text{Pb}$ vs $^{206}\text{Pb} / ^{208}\text{Pb}$ data plots above the Cumming and Richard (1975) growth curve. The least radiogenic values are from the Maroonchydore prospect and this data coincides with galeana Pb data from that prospect. B. Whole rock (WR) $^{206}\text{Pb} / ^{207}\text{Pb}$ vs $^{204}\text{Pb} / ^{206}\text{Pb}$. Locations of the deposits and prospects are shown in Figure 1.1. The Cumming and Richard (1975) growth curve is included for reference.
Rudall D.). The implication of this is that the dyke may be significantly younger than the orthogneiss that it intrudes. A conflict also exists between the 1291±10Ma estimated crystallisation age quoted by Nelson (1995) and the 1247±5Ma of Goellnicht (1992).

The result from sample Rudall #1 (Goellnicht, 1992) is not considered reliable because the sample has an unusual petrology that suggests a possible sedimentary input and this is supported by the presence in a U-Pb concordia plot of multiple groups of data (Nelson, 1995). U-Pb concordia plot suggests the incorporation of detrital zircon from a sedimentary source and therefore Pb contamination (Nelson, 1995). The ages used by Goellnicht (1992) are in disagreement with that provided by Nelson (1995).

The second sample, Rudall #2, is also considered unreliable because of possible Pb-contamination from host rock (Nelson, 1995), and problems establishing the timing relationship between the dyke and orthogneiss host rock. The implication of this review of Rudall Complex Pb isotope data (Goellnicht et al., 1989; Goellnicht et al., 1991; Goellnicht, 1992; and Nelson, 1995) is that the Pb-Pb initial ratios of the Rudall Complex used in modelling (Goellnicht et al., 1989; Goellnicht et al., 1991; Goellnicht, 1992; Smith, 1996; and Reed, 1996) should be treated with caution. Rudall Complex samples analysed as part of this study were chosen to avoid the problems of Goellnicht (1992) in that samples selected had no evidence of zircon contamination, they have single zircon populations, and clear timing relationships.

The 816±6 Ma age for the Eva Well Variscian age is derived from six U-Pb SHRIMP analyses on two zircons and only five of the analyses were used to define a U-Pb isochron that provided a weighted average 206Pb/238U age of 816±6 Ma. Reed (1996) acknowledges that this number of analyses does not provide a sufficient number to rigorously define a U-Pb age but considers the age to be a reliable estimate of the age of the zircon population and, hence, crystallisation of the Eva Well intrusion (Reed, 1996).

9.8 Existing Pb Isotope Models

Existing Paterson Orogen Pb isotope models are reviewed and then a new Pb isotope model for Pb in Thromsell Group mineralisation is presented and discussed. Four Pb isotope models have been proposed for mineralised occurrences in the Yeneena Supergroup (Goellnicht et al., 1989; Goellnicht et al., 1991; Goellnicht, 1992; Rowins, 1994; Reed, 1996; Smith, 1996; Rowins et al., 1997; Rowins et al., 1998). Potential Pb sources of the Pilbara and Mount Bruce Supergroups have been modelled by Smith (1996) and Reed (1996). These studies used U-Pb ages and Pb-Pb data from 1) galena sphalerites within the Kyleena Basin of the Fortescue Group (Richards and Blockley, 1984) and 2) galena from the Big Stabby Deposit in the upper Duffer Formation of the Warrawoona Group, Pilbara Supergroup (Richards et al., 1981).
Goellnicht (1992) examined Teller mineralisation to test a genetic model that proposed that the ore fluid was a mixture of granitoid- and host-rock-derived fluids (Fig. 9.6). On the basis of differing initial Pb ratios Goellnicht (1992) sub-divided the granites into three suites and interpreted this to signify different granitic sources (Fig. 9.2). Goellnicht (1992) noted that a linear array (Fig. 9.6) was formed by the least radiogenic Pb isotope ratios of ore sulphides between the initial ratio of the Mount Crofton Suite (673±26Ma) and possibly the O’Callaghans Granite and the field for the host sedimentary sequence (Fig. 9.6). This linear trend was interpreted to indicate mixing between magmatic Pb (Mount Crofton Granite Suite) and Pb from sedimentary host rocks. The location of deposits plotted along the linear trend was taken to indicate the proportion of magmatic Pb and to relate to the proximity of the mineralisation to a granite (Goellnicht, 1992).

Figure 9.6: Summary 206Pb/204Pb vs 207Pb/204Pb plot of data presented in Goellnicht (1992). IR Mt Crofton Granite, JR O’Callaghans Granite, and IR Minyari Granite are the initial Pb isotope ratios of the respective granite suites. With the exception of the samples labelled Teller and IR, the data is from mineralised occurrences hosted in the Lamlit Group.

Goellnicht (1992) also investigated the origin of Teller granitoid suites based on interpretations of their initial Pb isotope ratios. Two models were proposed (Goellnicht, 1992). 1) That the Minyari Suite was derived from partial melting of an enriched, high-μ source, whilst the O’Callaghans and Mount Crofton were derived from a depleted, low-μ source. The source of the high-μ, Minyari Suite was interpreted as either the Rudall Complex or Pilbara Craton and that two sources were likely for low-μ, O’Callaghans and Mount Crofton Suites and that source was most likely lower crustal granite-facies rocks. The second model that was proposed by Goellnicht (1992) suggested mixing of mantle-derived magmas with older crustal-derived magmas. Goellnicht went on to conclude that at 642Ma that the lower crust of the Paterson Orogen was heterogeneous and consisted of the Pilbara Craton and/or Rudall Complex (high-μ) juxtaposed with a depleted (low-μ) granitoids.

155
9.8.2 Rowins (1994; Rowins et al., 1997; Rowins et al., 1998) Model

Rowins’ (1994) aim was to test the granitoid-related genetic-continuum model of Goellnicht et al. (1992) by examining a distribution of mineralised occurrence about the granite intrusives. Rowins (1994) noted that all Pb-Pb results (Fig. 9.2) from the mineralised occurrences of Telfer, West Dome, Middle Vale, and Westfield plotted with only minor variations on the margin of the Lamiul Group whole rock Pb field. Rowins et al. (1997) suggested that sulphide mineralisation from all stratigraphic levels, in both domes, and the intervening syncline, formed from hydrothermal fluids having similar mixtures of Pb from magmatic and sedimentary sources. As the Telfer mineralised data plotted closest to the sedimentary Pb field than the magmatic Pb field, Rowins (1994), Rowins et al. (1997), and Rowins et al. (1998) interpreted this to indicate that the major Pb source was Lamiul Group sediments. Rowins et al. (1997) went on to state that mineralisation at the Telfer Dome was related to an evolving hydrothermal system. Rowins (1994) concluded by agreeing with Goellnicht’s (1992) epigenetic-replacement model but suggested a higher sediment mixing component in the ore fluid and favoured the granite acting as a heat engine driving convection cells where fluids cycling through the sediment picked up gold and base metals.

The discussion between Goellnicht et al. (1991, 1992) and Rowins (1994; et al., 1997; et al., 1998) revolves around the relative contribution of magmatic Pb to the Telfer Au-Cu deposit. The Telfer granite suite were derived from different sources at similar times and that these sources were juxtaposed at 654-632 Ma (Goellnicht, 1992; Dunphy and McNaughton, 1998).

9.8.3 Secondary Isochrohom Model (Smith, 1996)

In an examination of Warrabary Pb-Zn prospect Smith (1996) characterised the Pb signature of mineralisation and modelled potential Pb sources of the Pilbara Craton, Yilgarn Complex and Yeneena Supergroup sediments. Smith (1996) noted that: 1) Pb isotope ratios of galenas from Rainbow, Warrabary, Nifty and Mnarochulyde defined a linear trend, 2) the continuation of that trend intersected data from the Big Nobby volcanic-hosted massive sulphide deposit hosted in Duffer Formation of the Pilbara Supergroup, and 3) a secondary isochrone calculated on the linear trend returned an age of 840 Ma (Fig. 9.7A). Smith (1996) interpreted this linear trend to indicate that a synchronously, basin-wide mineralising event at ~840 Ma formed all the deposit styles and that Pb was derived from leaching of Throssell Group sediments with a Pilbara provenance (Fig. 9.7A). He went on to state that the ~840 Ma age was consistent with a diagenetic timing for Warrabary mineralisation.

9.8.4 Mixing Isochron Model (Reed, 1996)

Reed (1996) modelled the origin of the metals at the Mnarochulyde Cu deposit using 1) pyrite, chalcopyrite, galena and whole rock Pb isotope analyses, 2) an Ar/Ar age of 717 ± 25 Ma on syn-mineralisation phlogopite, and 3) a U-Pb SHRIMP zircon age of 816 ± 28 Ma on the Eva Well intrusive. The modelling (Fig. 9.7B) undertaken by Reed (1996) was similar in approach to that of, and used the
Figure 9.7A-B: A. Secondary isochron model proposed by Smith (1996). Smith (1996) calculated an 840Ma age based on the slope of the Throssell linear trend. A projection of Smith's 840Ma isochron intersects Pb isotope data from the Warrawoona Formation of the Pilbara Supergroup. B. Reed (1996) constrained a 717Ma age of mineralisation using Ar-Ar dating of syn-mineralisation phlogopite from Marucchydro, Reed (1996) interpreted that the Throssell linear trend was the result of mixing at 717Ma between depleted Pilbara Pb and whole rock Pb.
same data as, Smith (1996). Reed (1996) defined a field of Maroochydore galema and Broadhurst Formation whole rock Pb isotope data and interpreted that the Pb in samples from this field was leached from Weddell Complex sediments. Reed (1996) also constructed palaeostratigraphy for the Warrawoona and Verrucae Groups at 717Ma and defined a second field of depleted lead from the Pilbara Craton at the intersection of those isochrons (Fig. 9.7b). Reed (1996) interpreted the Throssell linear trend to be a mixing trend isochron between sedimentary lead derived from the Weddell Complex and the field of older more depleted lead from the Pilbara Craton at 717Ma. Reed (1996) concluded that the metals at Maroochydore were derived from the Broadhurst Formation sediments.

9.8.5 Limitations with Existing Throssell Group Pb Isotope Models

The main difference between the two Throssell Group models (Reed, 1996 and Smith, 1996) is the timing of mineralisation. Smith (1996) favoured 840Ma and Reed (1996) 717Ma. Smith (1996) interpreted Warrawoona mineralisation as occurring after late diagenetic dolomitisation and bedded parallel pressure solution but before regional D₃ deformation. Smith (1996) suggested that mineralisation occurred simultaneously throughout the basin and that the mineralisation event forming three styles of deposit. Smith (1996) suggested that the Throssell linear trend is a function of the source provenance of basin sediments. Smith (1996) calculated an 840Ma age of mineralisation based on the slope of the Throssell linear trend and noted that an extension of the Throssell linear trend intersects Pb isotope data from the Pilbara Craton Big Stubby deposit. Smith (1996) interpreted the intersection of the linear trend with Big Stubby data to indicate that Pb was sourced from Pilbara Craton sediment. Smith (1996) considered the strong correlation between the Pilbara 840Ma isochron and the Throssell Group galema trend as good evidence that Pb from the Throssell Group prospects and deposits had a Pilbara Block source. Smith (1996) also suggested that the linear relationship of galema data on both 206Pb/204Pb and 207Pb/206Pb vs 208Pb/206Pb plots are more consistent with a single Pb source.

Reed (1996) directly dated mineralisation at 717±5Ma using Ar/Ar on syn-metamorphic phlogopite in chalcopyrite veins. Reed (1996) described the phlogopite as common on the margins of mineralised veins where it is intergrown with pyrite, pyrrhotite and chalcopyrite and that it forms inclusions in epidote-bearing. Reed (1996) also noted that the orientation of phlogopite is concordant to mineralised veins is parallel to D₃ continuous cleavage and that this is consistent with its formation during D₃ deformation (Reed, 1996 p190).

Interpretations of a pre-D₃ deformation timing of mineralisation at the Warrawoona Pb-Zn prospect and a syn-D₃ timing (717±5Ma) at the Maroochydore Cu deposit suggests strongly that mineralisation did not occur synchronously throughout the basin. It could be argued that the interpretation that all mineralisation occurring pre-deformation (Smith, 1996) is correct and that the 717±5Ma Ar/Ar age of syn-mineralised phlogopite (Reed, 1996) has been, 1) re-equilibrated or suffered Ar loss during subsequent metamorphism, or 2) chalcopyrite has been reorganized into phlogopite bearing veins. No evidence of re-equilibration or Ar loss was observed in the twelve step incremental heating plateau of the
It is possible to model a secondary isochron through the Throssell mineralisation trend at 217Ma. The resultant extension of this trend is a slightly higher formation in the Warnawonna Group, the Wyman Formation. Model secondary isochrons at 840 and 717Ma that pass through the Throssell linear trend suggest that reliance on this method to calculate the timing of mineralisation should be treated with care. If the calculation the secondary isochron method as used by Smith (1996, Equation 4) is applied to the Lamf linear trend the slope returns an age of 1.082 Ga. This age is contrary to existing evidence (Goethlicht et al., 1989; Goethlicht et al., 1991; Goethlicht, 1992; Rowins 1994; Rowins et al., 1997; Rowins et al., 1998) that suggests Teller Au-Cu mineralisation is associated with granitic intrusions data at approximately 632±5 and 645±4 for porphyritic biotite syenogranites from the Minyari suite and 654±8 and 640±8 for biotite monzogranites of the Mount Cooten suite (Demph and McNaughton, 1998).

9.9 New Throssell Group Model

The Throssell mineralisation Pb isotope trend is well defined by the Pb isotope ratios of mineralised occurrences. As discussed above, Warnabury formed before D3 and Marooyah and Nilly during D3. The differences in the timing of mineralisation suggest that a model of Pb isotope evolution for Throssell Group mineralisation should not use time as a component of the model. The position of a deposit on the linear trend is therefore interpreted to be a function of either, 1) mixing of Pb bearing fluids from different Pb sources, 2) a series of secondary isochrons for each deposit, reflective of initial source, or 3) leaching of Pb from detritus of different provenance. A model is proposed to explain the location of prospects or deposits along the Throssell mineralisation trend.

9.9.1 Source Mixing Model

The Throssell mineralisation trend represents a mixing line between a crustal Pb reservoir defined by least radiogenic sedimentary whole rock Pb data and a primitive reservoir defined by the Pb evolution trend of Pilbara data (Fig. 9.8). The position of prospects and deposits along the Throssell mineralisation trend is a function of the relative proportion of crustal and primitive Pb. It must be noted that this model makes no assumptions concerning the relative timing of mineralisation however the extraction of Pb from the source requires that extraction to occur at about the same time as the sources do not have fixed compositions.

Two Pb evolution curves (Fig. 9.8) were calculated using Equations 1 and 2, with a Tc of 3.7Ga and initial values of 206Pb/204Pb, 207Pb/204Pb of 11.152 and 12.998 respectively (Stacy and Kramers, 1975). The u-values in Equations 1 and 2 were varied until a more radiogenic curve (u=10.55) fitted the upper boundary of the Yenena Supergroup whole rock data and the less radiogenic curve (u=9.88) fitted
Figure 9.8: The source mixing model: The Throssell linear trend represents a mixing trend between a crustal Pb reservoir defined by least radiogenic sedimentary whole rock Pb data and a mantle reservoir defined by O'Callaghan's Granites data (or similar). The position of prospects and deposits along the Throssell linear trend is a function of the relative proportion of crustal and mantle Pb. Note that this model makes no assumptions concerning the relative timing of mineralization.
extension of Pilbara Craton trend and Pb isotope data from the Mount Crofton Granite Suite. The lower μ-value plots close to the Cumming and Richards (1975) growth curve. Calculating isotope evolution trends of Pb from two source reservoirs with differing μ-values (10.55 and 9.88) allows a source-mixing model to be assessed (Fig. 9.8). The Pb isotope signature of Throssell Group deposits and prospects reflects the relative contribution from each of the Pb reservoirs. Palaeo-current data on the Broadhurst map sheet establish a north-easterly and northerly directed flow and clastic petrology within lowermost conglomerate units of the Coolibah Sandstone suggest that the dominant detritus in this area, close to Maroochydore, was the Rudall Complex (Hickman & Clarke, 1994). The Warrabarry area is located on the western margin of the Paterson Orogen and is in closer proximity to the Pilbara Craton than the Rudall Complex. It is likely that sediment in the Warrabarry area was dominated by material derived from the Pilbara Craton and only minor concentrations of Rudall sediment. The Nifty Cu deposit is located approximately mid-way between Maroochydore and Warrabarry both geographically and its Pb isotope signature. Pb leached from sediment dominated by the Pilbara Craton or Rudall Complex detritus will have an isotopic signature consistent with the detritus source.

Two options exist for the timing of Pb mixing; these options are sequential or instantaneous mixing. Sequential mixing is the mixing of end member Pb sources as a series of events over time. This allows for the evolution of one or both Pb sources. The second option is for instantaneous mixing that would involve a single, basin-wide, mineralising event where fluid from the two sources provided Pb at varying proportions and this is effectively a secondary isochron mixing trend.

9.10 Discussion

A linear trend similar to the Throssell trend is defined by the least radiogenic Lamill Group data and the major difference is that the Lamill trend has a steeper slope (Fig. 9.9). The two linear trends have a coincident, least radiogenic endpoint where Warrabarry prospect data overlies the O‘Callaghan Granite Pb data (Fig. 9.9). The overlap between Warrabarry and O‘Callaghan Granite Pb isotope data may suggest that there is a common least radiogenic Pb source (Fig. 9.9). The linear trends formed by mineralised occurrences in the Throssell and Lamill Groups have several features in common, 1) both trends have a common least radiogenic endpoint, and 2) both trends are between a primitive Pb source defined by granites and the extension of the Pb evolution growth trend of the Pilbara Craton at the least radiogenic end and the field defined by whole rock Pb data at the most radiogenic end.

Previous Throssell Group models (Reed, 1996; Smith, 1996) have a common element of the mixing between a crustal and primitive sources of Pb. The main conflict concerns the relative timing of mineralization and therefore whether Throssell mineralization trend is a secondary isochron or a mixing trend. The secondary isochron model requires all deposits to have formed at the same time (Smith, 1996). This basin-wide mineralisation interpretation of Smith (1996) conflicts with a syn-D3 timing of Maroochydore (Reed, 1996) and Nifty mineralisation. If the evidence on the differences in mineralization timing for Maroochydore and Warrabarry (Smith, 1996; Reed, 1996) is accepted then
Figure 9.9: Common Pb-Pb plot of galena, pyrite and whole rock data from the Throssell and Lamill Groups (Goedlricht et al., 1989; Goedlricht, 1992; McKnight, 1992; Rawls, 1994; Reed, 1996; Smith, 1996; Froud, 1997; GSWA, written comm.; and this study). The Cumming and Richards (1975) growth curve, and the Throssell and Lamill trend are included for reference.
the linear trend cannot represent an isochron but must represent a sequential mixing trend. This difficulty in defining the relative timing of mineralisation suggests a model where the Throsville and Lamli linear trends representing a mixing between crustal and primitive sources of Pb and this is the favoured model. The difference in slopes of Throsville and Lamli linear trends may be function of the relative contribution of a radiogenic Pb source. Radull Complex rocks are high in uranium (Root and Robinson, 1994), and host several copper-uranium and uranium prospects, the largest of which is Kintyre. Therefore, sediment derived from the Radull Complex is likely to be more radiogenic. It would appear that the steeper Throsville trend is caused by a higher component of more radiogenic Radull Complex.

Linear Pb isotope trends in mineralised districts have been recorded previously by Andrew et al. (1984), LeHuray et al. (1987), Bilston (1989). Andrew et al. (1984) noted linear trends in Pb isotope data from south-eastern British Columbia and modelled these trends on the basis of mixing of Pb from two different sources. The sources were defined as a more radiogenic source approximated by the Shale Curve (Goodwin and Sinclair, 1982) and a uranium-depleted Pb source approximated using the Bluebell growth curve (Andrew et al., 1984). They also suggest that the simplest explanation for the mixing lines is the contamination of sedimentary Pb by Pb from intrusion and suggest three processes by which the contamination could occur: 1) assimilation of sedimentary rocks by magmas; 2) mixing between metoritic and magmatic hydrothermal fluids, and 3) contamination of ore fluids moving from the pluton into the sedimentary rocks (Andrew et al., 1984). They also suggest that the position of deposits on linear trends are related to the relative proportions of upper crustal Pb and lower mantle Pb and use the linear trend as an isochron from which model ages of mineralisation are obtained.

LeHuray et al. (1987) examined Pb isotope ratios of galenas from carbonate-hosted Zn-Pb deposits in central Finland and noted a linear trend in $^{208}$Pb/$^{206}$Pb vs $^{206}$Pb/$^{204}$Pb plots. LeHuray et al. (1987) interpreted the linear trend to represent either a two source mixing line or the preservation of the secondary isochron of a single source. They discounted the single source isochron because data in a $^{208}$Pb/$^{206}$Pb vs $^{206}$Pb/$^{204}$Pb diagram did not define a straight line and therefore concluded that the linear trend represented a two source mixing line.

Bilston (1989) modelled the Pb evolution of Early Pre-Cambrian Svecofennian sulphide ores in Sweden and Finland. Pb isotope data from these ore deposits formed linear trends sub-parallel to isochrons. Bilston (1989) proposed a three phase model to account for the linear trend and the model consisted of 1) a mantle residence, 2) two component mixing, and 3) a crustal residence phase. The mantle residence phase describes the Pb evolution along a mantle growth curve, followed by two component mixing between mantle and upper-crustal end members along a mixing line isochron. The third phase of Bilston’s (1989) model accounted for the sub-parallel nature of the present linear trend by modelling the variable in-situ decay of Pb at locations along growth curves.
9.13 Summary

New galena Pb isotope data from the Nifty Cu deposit and other regional prospects have been combined with existing galena data to further constrain the source of Pb. Previous Pb isotope studies have been conducted on the Nifty Cu deposit (Nelson, written comm., 1997), Maroonchydore Cu deposit (McKnight, 1992; Reed, 1996; Nelson, written comm., 1997) and Warrabury Pb-Zn prospect (Smith, 1996; Nelson, written comm., 1997). Pb isotope ratio data from these Throssell Group deposits and prospects plot as a linear trend with Warrabury at the least radiogenic end and Maroonchydore at the most radiogenic end. Data from the Nifty Cu deposit plots towards the least radiogenic end of the trend.

The Throssell Group mineralisation trend suggests mixing between two Pb sources. Potential sources of Pb are 1) Rudall Complex, 2) Pilbara Craton, or 3) internally sourced Pb leached from Throssell Group sediments. The Rudall Complex Pb signature is poorly defined as shown by initial Pb-Pb ratios of K-feldspars separates. Galena Pb isotope data from deposits in the Pilbara Craton lies on a Pb evolution trend similar to growth curve of Cumming and Richards (1975). The least radiogenic Warrabury data plots on the extension of this growth curve. Whole rock Pb isotope data from Throssell Group sediments form a field that encloses the Maroonchydore galena Pb data.

A source-mixing model is proposed where Pb from a primitive source (μ=9.45) is mixed with crustal Pb (μ=10.55). The position of deposits and prospects along the linear trend suggests that the Pb in the Warrabury Pb-Zn prospect is dominated by primitive Pb (Pilbara source) and that Pb at the Maroonchydore Cu deposit has a crustal source (Pb leached from sediments with a Rudall Complex provenance). Pb in the Nifty Cu deposit appears to have a mixed source.

Similar mixing models have been proposed previously, however these models have interpreted the Throssell Group linear trend to be a secondary isochron. The secondary isochron model requires all deposits to have formed at the same time, however textural evidence indicates that Warrabury mineralisation occurred Pre-D4 (Smith, 1996) and that Nifty (Anderson et al., 1996) and Maroonchydore (Reed, 1996) formed syn-D3. The differences in the timing of mineralisation suggests that the Throssell Group Pb isotope linear trend is not a secondary isochron but represent a mixing trend between crustal and magmatic sources of Pb.
Chapter Ten - Fluid Inclusion

10.0 Introduction

Fluid inclusion studies provide important information on fluid composition and specifically the temperature, pressure and chemical composition of fluids at the time of trapping (Roedder, 1984; Shepherd et al., 1983). The determination of those fluid characteristics rely on the basic assumptions (Roedder, 1984) that:

- The trapped fluid was a single homogenous phase.
- The cavity has not changed volume.
- That nothing is added to, or lost from the inclusion after sealing.
- The effects of pressure are insignificant or known.
- The origin of the inclusion is known (primary, secondary, pseudosecondary).
- That the determinations of homogenisation temperature are both precise and accurate.

This chapter presents the results of a fluid inclusion study conducted on Nifty vein material. Syn-mineralisation fluid inclusions provide information on constraints that influence the conditions of ore genesis and these constraints can then be applied to chemical and isotopic modelling. Results from Nifty will be compared to those of other mineralised occurrences in the Emerson Orogen and with selected other deposits. Polito (written comm., 1996, 1997) conducted a reconnaissance fluid inclusion study at Nifty as part of a soil gas study in 1998. As his samples are not constrained by paragenetic studies these fluid inclusion data are not included in the present study.

10.2 Methods

Samples of potentially suitable material from syn-mineralisation chalcopyrite-breccia veins (vein stage II A) and late, post-mineralisation, coarse quartz-dolomite veins (vein stage III A) were selected for fluid inclusion studies during diamond drill core logging (Table 10.1). Fifteen polished and doubly polished petrographic thin section plates were prepared and examined for suitable fluid inclusions. Of the fifteen thin sections, six plates contained workable inclusions (Appendix Six). Microthermometry was performed at the University of Tasmania using a modified USOS gas flow heating-freezing stage supplied by Fluid Inc. (Stormer and Boshart, 1984; Boshart and Stormer, 1985). The accuracy of the measurements was calibrated using synthetic fluid inclusions supplied by Syn Fluc Ltd, and the precision of the measured temperatures is ±1°C for heating and ±0.3°C for freezing. The precision of measurements in this chapter is influenced by fluid inclusion size and type, and host rock composition.
<table>
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<th>Depth</th>
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<td>575.3</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in SS-Black Silica</td>
</tr>
<tr>
<td></td>
<td>376.0</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in 22-Green Quartz</td>
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<tr>
<td></td>
<td>408.7</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in SS-Black Silica</td>
</tr>
<tr>
<td>TN123</td>
<td>321.1</td>
<td>IA</td>
<td>Coarse quartz + dol vein with remobilised cpy</td>
</tr>
<tr>
<td>TN123</td>
<td>368.7</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in 55-Mottled black and white quartz</td>
</tr>
<tr>
<td>THRD635</td>
<td>334.6</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein with wall rock inclusion</td>
</tr>
<tr>
<td>THRD636A</td>
<td>266.5</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in SS-Black Silica</td>
</tr>
<tr>
<td></td>
<td>298.4</td>
<td>IA</td>
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<tr>
<td></td>
<td>301.3</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in 52-Green Quartz</td>
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<tr>
<td>THRD647</td>
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<td>IA</td>
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<tr>
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<td>366.0B</td>
<td>IA</td>
<td>Cpy+qtz+sdol vein in 55-Mottled black and white quartz</td>
</tr>
<tr>
<td></td>
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<td>THRD753</td>
<td>400.1</td>
<td>IA</td>
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</table>

Table 10.1: Fluid inclusion data from the Nifty Cu deposit was collected from the samples listed in this table. Abbreviations: DDH—diamond drill hole, cpy—chalcopyrite, qtz—quartz, and dol—dolomite.

Petrographic associations and the location of sampled fluid inclusions in IA veins are shown in Figure 6.2. Stage IIA veins have a sequence of silicified foot rock with a fine-grained quartz on the quartz margin, then fibrous zone of chlorite followed by coarse-grained quartz in contact with chalcopyrite vein material. Fluid inclusion data was collected from isolated inclusions within single grains of coarse quartz in contact with chalcopyrite. Grain boundaries contained sulphides and numerous secondary inclusions; no data was collected from these zones. Primary fluid inclusions from IIA material (Fig. 10.1A-D) are scarce and are typically small (<5-10μm), equant and subrounded with slightly rounded rhombohedral shape (Fig. 10.1A-D). Inclusions are dominantly liquid and vapour with no daughter minerals and liquid is the most abundant phase. On simple warming to above approximately 30°C no homogenisation of liquid and vapour occurred suggesting the liquid is dominated by H₂O and not CO₂ (Roodder, 1984). The second group of samples were from IIA veins and these veins consist of cloudy, inclusion-poor quartz, with minor intergrown bright white dolomite (Fig. 6.3A-B). Data was collected from fluid inclusions contained within single grains in quartz-rich zones rather than from the dolomitic areas. Primary fluid inclusions in this late vein stage are larger (~20-50μm) than those observed in IIA veins, are elongate, irregularly shaped, and have sharp terminations (Fig. 10.1E-F). Post-mineralisation fluid inclusions have a similar petrology to that observed in mineralised veins consisting of liquid and vapour phases with no daughter minerals present. Also in common with the earlier phase, simple warming did not result in homogenisation suggesting H₂O-dominated inclusions.

Numerous groups of secondary inclusions occur as planar arrays on quartz grain boundaries in IIA and IB veins. Secondary inclusions range in size from <5-100μm and consist of vapour and liquid phases only. Fluid inclusion data was not collected from secondary inclusions.

163
Figure 10.1A-F: Photomicrographs of fluid inclusions from vein stages II-A-Chalcopyrite-dolomite (A-D) and IIIA-Curde quartz-dolomite (E-F). II-A veins have margins consisting of chlorite and quartz. Inclusions occur in the quartz as small (<5-10μm), equant and subhedral with slightly rounded terminations. Fluid inclusions consist of a single two phase, liquid and vapor with no daughter minerals observed. (A. THRD55, 334.1m. B. II-A-TND10, 408.7m. C. THRD56A, 266.6m. D. THRD753, 40.1m). IIIA veins consist of cloudy, inclusion-free quartz with minor dolomite. Inclusions are larger (20-50μm) than those observed in II-A veins and consist of liquid and vapor (E. TND12, 321.1m. F. TND12, 321.1m).
10.3 Results

This section presents the results of microthermometric analysis of primary fluid inclusions from quartz and dolomite material from vein stages at Nifty Cu deposit. Summary results are presented in Table 10.2 and data is listed in Appendix Three. The following abbreviations are used in this chapter: Th = temperature of homogenisation, Tm = temperature of first melting, TmH2O = temperature of final ice melting, eq. wt. % NaCl = equivalent weight percent NaCl.

<table>
<thead>
<tr>
<th></th>
<th>HA Syn-mineralisation</th>
<th></th>
<th>HA Post-mineralisation</th>
<th></th>
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<td></td>
<td>TmH2O</td>
<td>eq. wt. % Th</td>
<td>NaCl</td>
<td>TmH2O</td>
</tr>
<tr>
<td>n</td>
<td>24</td>
<td>24</td>
<td>46</td>
<td>17</td>
</tr>
<tr>
<td>Median</td>
<td>-10.6</td>
<td>14.6</td>
<td>288.7</td>
<td>-9.3</td>
</tr>
<tr>
<td>St Dev</td>
<td>5.5</td>
<td>5.9</td>
<td>50.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Maximum</td>
<td>-5</td>
<td>26.9</td>
<td>366.9</td>
<td>-7.4</td>
</tr>
<tr>
<td>Minimum</td>
<td>-26.4</td>
<td>7.9</td>
<td>200.4</td>
<td>-10.6</td>
</tr>
</tbody>
</table>

Table 10.2: Summary statistics from fluid inclusion data. HA is a chalcopyrite-quartz-dolomite vein stage and HIA is a post-mineralisation coarse quartz vein.

10.3.1 Melting Temperatures

Thirty-eight final melting temperatures were measured in syn- and post-mineralisation vein material from Nifty (Fig. 10.2). Final melting temperatures from syn-mineralisation HA veins data ranges between -26 and -5°C (median -10.6°C) and post mineralisation data has a narrow range between -10 and -7°C (median -9.3 °C). The majority of data from both vein stages overlap with the exception of four data from syn-mineralisation fluid inclusions that plot with melting temperatures approximately -25°C. These low values are below the eutectic point of -21°C and are best explained by the presence of CO2 in fluid inclusions (Collins, 1979) and therefore the salinity of fluids contained in these inclusions will be higher than calculated by the normal equations.

Salinity of fluid phases was calculated using temperature of the final ice melting applied to the equations of Bodnar (1993). The calculated salinity represents the total chloride concentration and therefore is expressed as equivalent weight percent NaCl (eq. wt. % NaCl). No analyses were undertaken to establish the chemical composition of fluid inclusions however estimates using first melting are made using the method of Bodrisko (1977). The small size of HA fluid inclusion limited the measurement of first melting temperature however those that were recorded occur between -44 to -31°C (n=8). This range of first melting temperatures is consistent with a Ca-K-Na-Mg brines (Bodrisko, 1977). The uncertainty in fluid inclusion chemistry makes it likely that estimates of the salinity calculated using the depression of freezing point method will have errors between -5% (Roedder, 1984; Shepherd et al., 1985). Calculated salinity of fluid inclusions at Nifty range between 8-21 (Stage IIB) and 11-15 (Stage III) eq. wt. % NaCl. The median salinity of syn-mineralisation fluids is approximately 15 eq. wt. % NaCl and post-mineralisation fluids are slightly less saline at approximately 13 eq. wt. % NaCl.
10.3.2 Homogenisation Temperatures

Sixty-four homogenisation temperatures were measured on syn- and post-mineralisation fluid inclusions and the data is presented in Figure 10.3. Homogenisation temperatures of IIA vein material range between 200-567°C (median 268°C) with identifiable modes at 220°C and 320°C. Vein stage IIA inclusions have homogenisation temperatures ranging between 111-189°C (median 120°C) but the majority of the data plots as a single group with a median of approximately 120°C.

Figure 10.3: Histogram of homogenisation temperatures of fluid inclusions from vein stage IIA and IIBA. Vein stage IIA has a broad distribution with two modes at 220°C and 320°C.

Figure 10.4 presents a plot of salinity vs homogenisation temperature of vein stages IIA and IIBA. Vein stage IIA data plots a dispersed field with a larger range of salinity values and higher temperatures.
values than lHA veins. The course quartz veins of lHA plot as a tightly constrained group with a single outlier. Data from lHA and lNA fluid inclusions do not overlap.

Figure 10.4: Salinity versus homogenisation temperatures of Nifty fluid inclusion data. Mineralising fluids have a broad distribution with a median of 270°C and salinity of 15 eq. wt.% NaCl. Post-mineralisation fluids form a tight cluster with lower homogenisation temperatures of approximately 120°C and similar salinity to the mineralising fluids. Note data without Tm, has not been included.

10.4 Physicochemical Characteristics of the Fluids

Homogenisation temperatures underestimate the trapping temperature of the fluid because no correction has been applied for lithostatic pressure (Shepherd et al., 1985). Smith (1996) estimated three to six kilometres of sediment cover at Warraburra during white stage mineralisation and calculated a temperature correction of 85°C. McKnight (1995) estimated approximately eight kilometres of sedimentary rocks overlying the Maroochydore deposit during chalcopyrite mineralisation and applied a correction of 183°C to fluid inclusion data. Reed (1996) suggested that the eight-kilometre overburden suggested by McKnight (1992) was too high and that the lithological temperature overburden was probably closer to 2500-3500m (0.7-0.9kb) and up to a maximum of approximately 1.3Kb when organic thickening of the sedimentary pile was taken into account. Reed (1996) went on to support a 0.7-0.9Kb pressure by calculating trapping pressures using decrepitation of inclusions. Reed (1996) concluded that a 100°C pressure correction was required for fluid inclusion homogenisation temperatures at Maroochydore.

Roedder (1984) suggested that temperature corrections are precisely appropriate only if 1) the inclusion contains a pure NaCl solution, 2) the salinity of the fluid has been correctly determined, 3) the estimates of the pressure of formation is correct, and 4) the inclusion homogeneities in the fluid phase. The second through to the fourth parts of the previous sentence can be complied with however the
composition of the inclusion is questionable. Roedder (1984) suggested that experimental studies of brine salinity in the system Na-K-Ca-Mg-Cl-Br-SO₂-H₂O are predicted to within 1% by the properties of an NaCl solution. Pressure corrections for inclusions containing CO₂ or other exotic or highly concentrated solutions are best calculated by assuming corrections for fluids with 25 wt.% NaCl. The constraints on the pressure correction are the thickness of the sediment pile overlying Nifty at the time of inclusion trapping and the conditions that overburden creates. An indication of the thickness of cover can be obtained from indicator minerals in syn-mineralisation vein stages. Equilibrium mineral assemblages define the peak metamorphic grade at Nifty as being quartz and dolomite stable and therefore sub-greenschist facies. Using mineral-fluid equilibrium in the system CaO-MgO-SiO₂-CO₂-H₂O-NaCl (Bowers and Helgeson, 1983a,b) and using three modified Redlich-Kwong equation of state (Bowers and Helgeson, 1983a) at 350°C, for quartz-dolomite stable assemblage and with no phase separation indicates that the pressure must be greater than 750bars. This suggests that the thickness of overburden at Nifty was be similar to the 3.6 km cover interpreted at Warrabarty (Smith, 1996) and 2.5-3.5 km of cover at Marnochydon (Reed, 1996).

A temperature correction of between 70-90°C is made using Th and pressure correction graphs of Potter (1977, in Roedder, 1984) assuming 0.75-1.0kb pressure, a geothermal gradient of 90°C/km, that P_th = P_flu = 0.75-1.0kb, and that the average salinity was ~15 eq. wt.% NaCl therefore the trapping temperatures of mineralising fluids at Nifty range between 270-457°C (median 358°C) and salinities of 8-27 eq. wt.% NaCl (median 15 eq. wt.% NaCl). Trapping pressures are difficult to determine for the post-mineralisation vein data because of the lack of defining indicators and uncertainties concerning the relationships between post-mineralisation features. The style of D₄e deformation and the presence of bladed carbonate veins may indicate a rapid denudation of sediment cover at Nifty and therefore a low pressure. However, because of the uncertainties discussed above the overburden is unlikely to exceed that of the syn-mineralisation data and may be lower. Therefore a pressure correction of 70°C is applied to post mineralisation vein homogenisation data to give trapping temperatures of 181-269°C (median 190°C) and salinities of 11-15 eq. wt.% NaCl (median 13 eq. wt.% NaCl).

Ck crack seal veining described in earlier chapters suggests periodic fluctuations in both lithostatic and hydrostatic pressures during this later veining stage. The extent of these fluctuations cannot be determined however pressure correction estimates based on lithostatic pressure are likely to suFfice.

10.5 Comparison with other mineralised systems

This section outlines previous fluid inclusion studies conducted in the Paterson Orogen. A summary of findings is presented in Table 10.3 and Figure 10.5 and these results are expanded in the following sections.
<table>
<thead>
<tr>
<th>Deposit</th>
<th>Salinity (eq.- wt.% NaCl)</th>
<th>Homogenisation temperature (°C)</th>
<th>Reference</th>
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<td></td>
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<tr>
<td></td>
<td>11.43</td>
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<td></td>
<td>9-25</td>
<td>178-454</td>
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<td>Warrabarty</td>
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</table>

Table 10.3: Summary of fluid inclusion data from deposits and prospects in the Paterson Orogen of Western Australia. An outline of each of the mineralised occurrences can be seen in Chapter Two.

![Fluid inclusion data from mineralised occurrences in the Paterson Orogen. Data sources - Nifty (this study), Maroochydore (Reed, 1996), Warrabarty (Smith, 1996), Goonwarrow (Froud, 1997), Rainbow and Citadel (Smith, 1997), and Telfer (Geislbracht, 1987; Geislbracht et al., 1989).](image)

Figure 10.5: Fluid inclusion data from mineralised occurrences in the Paterson Orogen. Data sources - Nifty (this study), Maroochydore (Reed, 1996), Warrabarty (Smith, 1996), Goonwarrow (Froud, 1997), Rainbow and Citadel (Smith, 1997), and Telfer (Geislbracht, 1987; Geislbracht et al., 1989).

10.5.1 Maroochydore Cu Deposit

Two fluid inclusion studies (McKnight, 1992; Reed, 1996) have been conducted on mineralisation at Maroochydore (Figs. 10.5 and 10.6). McKnight (1992) conducted a reconnaissance fluid inclusion study of chalcopyrite-mineralised quartz-dolomite veins and interpreted that the trapping of the inclusions occurred during the early stages of chalcopyrite crystallisation. Two distinct groups of fluid inclusions were identified, 1) pseudo-secondary inclusions in clusters and planar arrays, and 2) irregularly shaped, pseudo-secondary, inclusions within fracture planes that cross-cut host crystals. McKnight (1992) reported a narrow range of eutectic temperatures between -24.4 and -31.1°C, yielding

168
temperature from −21.1 to −7.5°C (11.43 eq. wt.% NaCl), and homogenisation temperatures from 200-380°C with the bulk of data between 210-240°C (Figs. 10.5 and 10.6).

Reed (1996) and Reed et al. (1995) sampled quartz and dolomite cements from sulphide-bearing veins that included: 1) small (<3mm wide) discordant intraclast veins, 2) bedding parallel pyrite- and pyrrhotite-rich veins, and 3) discordant quartz- and dolomite-rich veins oriented axial plane to D2 fold structures. Four types of fluid inclusion were observed and classified in Maarocchidore samples: 1) isolated inclusions, 2) random three-dimensional arrays, 3) linear arrays matching crystal zonation and terminating within the host crystal, and 4) linear arrays which are discordant to any observed zonation and that commonly terminated at the grain margin or cross-grain boundaries. The range of eutectic temperatures measured by Reed (1996) were between −32.1 and −11.9°C and the melting temperatures −26.2 and −5.6°C (9.25 eq. wt.% NaCl). Homogenisation temperature of sulphide mineralisation (Fig. 10.5 and 10.6) ranged between 178-454°C (average 257±27°C [1σ]). Reed (1996) applied a 100°C correction to homogenisation temperature and concluded that trapping temperatures during mineralisation were between 278-545°C (median 343°C) and that the salinity ranged between 9-25 eq. wt.% NaCl.

10.5.2 Warrabarry Pb-Zn Prospect
Smith (1996) measured primary fluid inclusions in sphalerite and dolomite of syn-mineralisation grey vein stage and sphalerite in post-mineralisation white vein stage from the Warrabarry Zn-Pb prospect (Fig. 10.5 and 10.6). Grey stage sphalerite (Smith, 1996) show a bimodal distribution of homogenisation temperatures with a low population between 80-120°C and a higher population between 130-160°C. Grey stage sphalerite final melting temperatures ranged between −28 to −21°C (23.4-27.9 eq. wt.% NaCl). Homogenisation temperatures for grey stage dolomite were measured in a narrow range of 142-191°C and Smith (1996) suggested that this was similar to the high temperature, grey stage sphalerite population. Final melting temperatures of the grey stage dolomite are reported as −29 to −10°C (14.1-28.6 eq. wt.% NaCl). Limited data was able to be determined on white stage sphalerite homogenisation temperatures due to inclusions leaking during heating however, four measurements of 175°C, 176.5°C, and two at 270°C were recorded. Final melting temperatures of white stage sphalerite were measured at −26.8 to −23.0°C (15-22 eq. wt.% NaCl). Smith (1996) applied a pressure correction of 85°C to obtain trapping temperatures for grey stage sphalerite of 165-245°C, grey stage dolomite 227-275°C, and white stage sphalerite 258-263°C.

10.5.3 Rainbow and Citadel Cu Prospects
In addition to measuring fluid inclusion data from the Warrabarry prospect Smith (1996) also examine vein material from the Rainbow and Citadel prospects. Combined data from Rainbow and Citadel (Fig. 10.5) show homogenisation temperatures ranging from 125 to 188°C and final melting temperature ranges between −22 and −2°C. Rainbow data shows bimodal populations with peaks at −20 and −10°C.
10.5.4 Geoswacker Pb-Cu-Au Vein Prospect

A limited quantity of fluid inclusion data (Fig. 10.5 and 10.6) exists for the Geoswacker prospect (Foord, 1997). Thirteen primary fluid inclusions from stage two quartz-siderite sulphide veins were analysed and revealed melting temperatures between -6.0 to -2.8°C (4.6 to 9.2 eq. wt.% NaCl) and homogenisation temperatures between 171 - 236°C. Five primary inclusions from syn-mineralisation sulphate-quartz-carbonate veins were analysed and provide final melting temperatures of -6.4 to 1.9°C (salinity indeterminate) and two homogenisation temperatures of 209°C and 223°C. The majority of fluid inclusions from the Geoswacker prospect is from late-stage four sulphide-carbonate-quartz veins and final melting temperatures were measured ranging between -2.5 to -4.4°C and homogenisation temperatures between 273-382°C. Salinities were unable to be calculated conventionally therefore laser raman spectroscopy was used to measure the salinity’s of stage four inclusions at 17.3, 17.4, and 24.1 eq. wt.% NaCl and determined the gas content of the vapour bubbles to be CO₂, CH₄ and lesser N₂.

10.5.5 Telfer Au-Cu Deposit and other Lamill Group Studies

Goellnicht (1987) and Goellnicht et al. (1989) examined vein and Middle Vale reef quartz from the Telfer Au-Cu deposit and suggested that the fluid inclusion data (Figs. 10.5 and 10.6) showed a compositional variable, complex saline fluids with homogenisation temperatures between 225-440°C, and salinities between 21-54 eq. wt.% NaCl. Goellnicht et al. (1989) noted that very high salinity inclusions (35-54 eq. wt.% NaCl) tended to homogenise at higher temperatures (350-650°C) than the less saline inclusions (20-35 eq. wt.% NaCl and 225-250°C). This temperature/salinity relationship was ascribed to the mixing of hot, high-salinity fluids of magmatic origin with cooler lower salinity fluids of basinal brine or meteoric water (Goellnicht et al., 1989). Rowins (1994) and Rowins et al. (1997) disagreed with Goellnicht’s model and interpreted the intrusion of the gabbro intrusive as a heat source that drove the thermal convection cells in which heated saline formational-contact metamorphic fluids scavenged metals and sulphur from surrounding sedimentary rocks.

10.5.6 Mount Isa Cu Deposit

Fluid inclusion data from Mount Isa Cu ore body is presented by Heinrich et al. (1989) and summarised in Figure 10.6. Heinrich et al. (1989) defined four fluid inclusion types: Group 1 inclusion consists of high temperature, CaCO₃-bearing inclusions with total salinity of approximately 25 eq. wt.% or less and Na₂CO₃/K₂CO₃ ratios of ~100:100:30:10. Homogenisation temperature for this group ranged between 170-270°C. Group 2 inclusions consist of CO₂-rich inclusions with 17-24 mole % CO₂ and low salinity of <5 eq. wt.% NaCl. Final homogenisation temperature of this group occurred between 268-
285°C. Group 3 consists of NaCl-rich inclusions (quartz-chalcopyrite mineralisation). Total salinity of this group is widely variable from 3 to 21 eq wt.%. This group of fluid inclusions spans the bulk of chalcopyrite formation. Early inclusions are higher in salinity. Na/Ca/K/Mg = 300:10:30:1.

Homogenisation temperatures occurred between 130 to 250°C but mostly in the range 140 to 180°C. The final, post mineralisation group of consists of CaCl2-rich inclusions reported low temperatures and with salinity of 25-35 eq wt. % NaCl. Heinrich et al. (1989) suggested that high salinity inclusion (25 eq wt. % NaCl) at Mount Isa are similar to recent brines in the Salton Sea geothermal field (McKibben et al., 1988) and that these brines acquired their high salinity by leaching the of evaporite minerals.

10.5.7 Ruby Creek Cu Deposit

Ten samples of C vein dolomite from Ruby Creek (Hitzmann, 1986) provided homogenisation temperatures of 120-215°C and salinities of 7-13 eq wt. % NaCl (Fig. 10.6). Hitzmann (1986) noted a zoned distribution of temperature, with the lower portion of the ore system having hotter homogenisation temperature of 170-205°C (average 200°C) and the upper portion having significantly lower homogenisation temperatures between 125-180°C. Calcite-bearing veins and dolomite-calcite intergrown with massive copper sulphide gave the lowest homogenisation temperatures of 100-125°C and salinities of 4-9 eq wt. % NaCl (Hitman, 1986). Pressure corrections of approximately 10°C to a maximum of 20°C were applied to give maximum trapping temperatures of 225°C for the lower portion of the ore system and 120-130°C as the temperature of massive sulphide deposition (Hitman, 1986).

Figure 10.6: Summary of salinity and homogenisation temperatures for Nifty (this study), Maroochydore (McKnight, 1992: Reed, 1996), Warrabarty (Smith, 1986), Telfer (Goecnecht et al., 1989), Goosewacker (Froud, 1997), and Mount Isa (Heinrich et al., 1989; Heinrich et al., 1995)
10.6 Discussion

At Nifty only two vein stages have suitable material for fluid inclusion studies and of these vein stages syn-mineralisation inclusions were characterised by a high proportion of small to very small fluid inclusions, whereas the later course quartz-dolomite veins of stage IIIA has numerous large inclusions. The trapping temperature during mineralisation (IIA) was approximately 360°C (270-457°C) and this temperature decreased to approximately 190°C (181-267°C) after mineralisation. Nifty mineralising fluids had a wide range of compositions with a median salinity of ~15 eq. wt.% NaCl. The later and cooler fluids have similar salinities. Fluid temperature and salinity data recorded at Nifty is similar to the 360°C trapping temperature and 9 to 25 eq. wt.% NaCl reported at Mountchydmore (McKnight, 1992; Reed, 1996). Warrambury Pb-Zn mineralisation and grey stage dolomite alteration occurred at trapping temperatures of 227-276°C and with fluid salinity between 14-5-26 eq. wt.% NaCl. Grey stage sphalerite trapping temperatures are generally cooler than the temperature of dolomite alteration and form two groups of between 165-205°C and 215-245°C. Smith (1996) suggested that his white stage formed at a similar time to Nifty mineralisation and at temperatures of 300-400°C and from fluids with salinities of 15-22 wt.% NaCl and 2.5-5.5 wt.% CaCl₂. Fluid inclusion data from the Telfer Au-Cu deposits suggests that mineralising fluids were considerably more saline and generally hotter than those recorded in Throssett Group mineralisation. The higher Telfer salinity and temperature data suggest that the source of fluid was different to those responsible for mineralisation in the Throssett Group. The temperature and salinity of Mount Isa mineralising solutions appears to be similar to those recorded at Nifty. Ruby Creek massive copper sulphide mineralisation appears to have precipitated at cooler temperatures and from lower saline solutions.

Figure 10.7 plots trapping temperature against salinity and overlays fields for potential fluid sources. IIA fluid inclusion plots in the cotunnate brine and magmatic water fields while IIB fluid plots within the conjugate brine field. The salinity of IIA and IIB fluids exceed that defined for metamorphic, seawater, and meteoric waters.

The salinity of the majority of Throssett Group deposits and prospects are between 10-25 eq. wt.% NaCl and Telfer Au-Cu deposit hosted in the Lamill Group has higher salinities between 21-54 eq. wt.% NaCl. Smith (1996) suggested that the occurrence of syn-D₂ pyrite replacing diagenetic gypsum at Mountchydmore indicated that evaporites existed until D₃ and that the replacement of these evaporites created the high salinity. Reed (1996) noted a positive correlation between the salinity of fluid inclusion data and the presence of evaporitic textures in the surrounding host rocks. Goldinich (1987) concluded that the high salinity fluids could only be obtained by mixing of evaporitic brines with connate brines or by introducing magmatic hydrothermal solutions. Goldinich (1987) favoured a magmatic source, as evaporitic sequences have not been recognised in either underlying or overlying formations. Rowins (1994) and Rowins et al. (1997, 1998) used the data of Goldinich (1987) and interpreted that the high salinity was due to both heated formational brines and evolved granitic fluids. Rowins (1994) and Rowins et al. (1997, 1998) went on to suggest, based on geochemical studies, that the ore fluid and its contained solutions were sourced predominantly from sedimentary sources and that
granitoids acted primarily as a heat source to initiate and drive hydrothermal convection cells. Using tourmaline B isotopes, Rowins et al., (1998) excluded a marine evaporitic origin for the ore fluids. The conclusion of a sedimentary fluid source and not marine evaporitic or magmatic in origin (Rowins, 1994; Rowins et al., 1997, 1998) does not account for the high salinity at Telfer.

![Figure 10.7: Trapping temperature vs salinity plot of Nifty fluid inclusion data with fields for different fluid sources. Nifty syn-mineralisation fluid inclusion data plots within the fields for connate brines and magmatic waters. Post-metamorphic data plots in the connate brine field but has the similar salinities to the earlier fluid and therefore may represent the earlier fluid coated. Fluid fields after Roedder (1984).](image)

Several factors will influence the composition of fluids derived from the leaching of evaporite, 1) volume and composition of the leached evaporites, and 2) the timing when the leaching occurred. Large volumes of fluid would be required to precipitate the high concentrations of quartz and chalcopyrite at Nifty and this suggests that such concentrations of evaporites would need to be leached to achieve the high salinity. At Nifty, evaporitic minerals are present as disseminated gypsum blades in carbonaceous and pyritic shales of the uppermost, upper shale and the pyrite marker bed. Evaporitic minerals are pseudomorphed by quartz, dolomite and rarely by chalcopyrite. TNDJ, located 15 km north of the open pit, contains high concentrations of gypsum pseudomorphed by quartz and dolomite. The second issue is the timing of evaporite leaching. Smith (1996) suggests a late diagenetic timing for Pb-Zn mineralisation associated with carbonate replacement at Warramba and high salinity fluid inclusion data suggests that leaching occurred early in the basin’s history. Nifty Cu deposit and Macvachydoore Cu prospect formed during D2 and have similar syn-mineralisation salinity ranges. These salinities are lower than those of the Warramba prospect. If the high salinity is the result of leaching evaporitic minerals then the ore fluid should record high concentrations of sulphate and this would be reflected by a trend of syn-mineralisation sulphides to heavy sulphur isotope values.

173
10.7 Conclusion

The trapping temperature of Nilly mineralising fluids was approximately 360°C (270-458°C) and the fluid was H₂O-dominated with a median salinity of approximately 15 eq. wt. % NaCl. Salinity data suggests that the fluid source has characteristics consistent with magmatic or connate brines. Post-mineralisation fluids have similar salinity but are cooler (median 190°C, range 181-267°C) than the mineralising fluids. The late, post-mineralisation fluids are interpreted to be sourced from connate water source or from a cooled magmatic fluid.
Chapter Eleven - Stable Isotope Geochemistry

11.0 Introduction

This chapter presents stable isotope results and is set out in two sections. The first section contains results of sulphur isotope analyses from Nifty followed by a summary of results from Yenena Super group deposits and prospects, and the Cu deposits of Mount Isa and Ruby Creek. The second section presents carbon and oxygen isotope results and follows a similar format to the sulphur section, in that Nifty results will be presented and then compared to results from other deposits and prospects followed by a discussion on the implications of these results. After the presentation of carbon and oxygen isotope results, the data from Nifty will be modelled to examine carbonate precipitation mechanisms. This chapter finishes with a discussion and summary of the stable isotope results and the implication of those results on the composition and nature of ore fluids.

Sulphur Isotopes

11.1 Introduction

A major internal WMC Resources Ltd. SHRIMP sulphur isotope study on Nifty primary mineralisation was conducted by Eldridge (1994a,b). The aim of Eldridge's (1994a,b) study was to characterise the sulphur isotope signature of primary sulphides at Nifty. The aim of the sulphur isotope study, undertaken as part of this thesis, is to analyse sulphur isotopes from a range of sulphide generations and compare that data to Eldridge (1994a,b). Then using both datasets to 1) characterise the sulphur isotope signature of Nifty mineralisation, 2) establish possible sources of sulphur and 3) highlight implication that this has for the mineralisation at Nifty. A secondary aim of this sulphur isotope study is to compare the Nifty sulphur isotope signature with that of other deposits and prospects within the Paterson Orogen, and with select copper deposits from other regions.

11.2 Methods

Twenty samples of pyrite and chalcopyrite from host-rock, vein and gangue were drilled using standard diamond drilling techniques. Sulphur isotope analyses were carried out at the Central Science Laboratory of the University of Tasmania using the methods described by Robinson and Kusakabe (1975). Samples were equilibrated in vacuum with excess O2 to produce SO2 (Robinson and Kusakabe, 1975) and the excess sulphur gases seperated to determine 34S/32S ratios. Isotopic ratios (34S/32S) are reported using the conventional δ and ‰ notations and the isotopic compositions are reported with respect to the CDT standard (Canyon Diablo Troilite). The analytical uncertainty is estimated to be ±0.2‰. Internal standards used by the Central Science Laboratory are homogeneous galenas from Broken Hill, Rosebery, and Tullah, together with a SO2 reference gas. All internal standards were calibrated against international sphalerite standards IAEA NZ1 and NBS 123. Conventional sulphur isotope measurements were performed using a VG Micromass 602D mass spectrometer.
Elridge (1994a,b) conducted in excess of 100 analyses (Appendix Four) of δ34S of pyrite and chloropyrite using SHRIMP methods at the Research School of Earth Sciences, Australian National University. Details of the analytical methods used are described in Elridge et al. (1993). Samples analysed were from THRD645 (320.2m, 324.1m, 340.2m, 355.5m, and 383.6m) and THRD780 (390.3m, 400.0m, 413.7m, 450.3m, and 488.5m).

11.3 Results

Sulphur isotope results measured as part of this study are presented in Table 11.1 and Appendix Four and these results are combined with those of Elridge (1994a,b) in Figures 11.1A-B and 11.2. Conventionally analysed chloropyrite from this study range between −3.3 to +5.6‰ (average +1.3±2.6‰, 1σ) and overlap the earlier chloropyrite results with a range of −6 and +6‰ (Elridge, 1994a,b). The total range of conventional δ34S data for euhedral and frambooidal pyrite ranges from −5.2 to +3.8‰ and this is a similar range to that of chloropyrite.

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Table 11.1: Sulphur isotope result from the Nifty Cu deposit. Results generated as part of this study used conventional analytical methods and Elridge (1994a,b) used SHRIMP methods. Data is presented as histograms in Figures 11.1A—B and 11.2.

Figure 11.1A—B: Histograms of pyrite (A) and chloropyrite (B) sulphur isotope data from the Nifty Cu deposit. Data is from Elridge (1994a,b) in light grey and this study in dark grey.

176
The data of Eldridge (1994a,b) indicates that frambooidal pyrite has a large range from -27 to +16% (average -2.7±3.2%, 1σ) and chalcopyrite has a narrow range between -6 to +6% (average -1.4±3.0%, 1σ). Eldridge (1994a,b) did not differentiate between the various euhedral pyrite forms and therefore interpretations made using this grouping of data should be treated with caution, however Eldridge (1994a,b) noted a variation in coarse-grained pyrite results between -12 to +3% (average -3.2±3.6%, 1σ).

Figure 11.2: Combined δ34S data from frambooidal pyrite, euhedral pyrite and chalcopyrite samples (Eldridge, 1994a,b; this study). Frambooidal pyrite has δ34S values ranging -27 to +16%, euhedral pyrite ranges between -12 to +4%, and chalcopyrite between -6 to +6%.

Figure 11.2 combines all δ34S data from the Nifty Cu deposit. Frambooidal pyrite δ34S values range between -27 to +16%, however the majority of the data plots between δ34S values of -18 to +10%. Paragenetic studies (Chapter Seven) identified three coarse-grained pyrite textures, 1) euhedral pyrite with dissolution spots that occurs in S2-Silicified Pyritic Shale, S3-Hydrothermal Quartz-Dolomite and S4-Silicified Dolostone, 2) euhedral pyrite in IDA-Chalcopyrite-dolomite and IIB Alteration margin dolomite-quartz veins, and 3) euhedral to anhedral pyrite in IDA-Coarse quartz veins. All euhedral pyrite phases precipitated after the formation of frambooidal pyrite. Combined data shows (Fig. 11.2) a broad range of euhedral pyrite δ34S values between -12 to +4%, however the majority of the data is between -8 to +4%. Combined chalcopyrite δ34S data has a mean of -0.8% and a narrow standard deviation of 3.1% (1σ).

Eldridge (1994a,b) reports isotopically light (-18%) pyrite frambooids in close proximity to chalcopyrite with δ34S of -5%. This is a common comment in Eldridge’s reports (1994a,b) where finer-grained pyrite has values of approximately -20% and coarse-grained pyrite and chalcopyrite is slightly less than 0% (average -1.4±3.0%, 1σ). Eldridge (1994a,b) concluded that while the two
11.4 Results from Other Deposits

This section presents sulphur isotope results from Maroochydore Cu deposit (Reed et al., 1995; and Reed, 1996), Warrabarry, Pb-Zn prospect (Smith, 1996), Rainbow Cu prospect (Smith, 1996), Goonewacket Pb-Zn prospect (Foord, 1997), Telfer and the Lamal Group (Goellnicht and McNagnut, 1989; Rewiin, 1994; and Rewiin et al., 1997), Mount Isa (Andrew et al., 1989; Heinrich et al., 1989; Waring, 1999; and Waring et al., 1998), and Ruby Creek (Runnels, 1969; and data in Huggett, 1983).

11.4.1 Maroochydore Cu Deposit

Reed et al. (1995) and Reed (1996) established a complex sulphide genesis for the Maroochydore Cu deposit. Framboidal pyrite was reported as having low δ34S values between ~31% and ~22% (Fig. 11.3). Coarse-grained pyrite and pyrrhotite has values between ~10 to ~4%, while fine-grained chlorapatite which has pseudomorphed pyrite framboids returned the same results as the pyrite (~31 to ~23%). Coarse-grained chlorapatite has slightly higher δ34S values between ~23 to ~13%. Reed et al. (1995) and Reed (1996) interpreted these results to indicate that the early framboidal pyrite was characteristic of sulphur of biogenic origin derived from a system open to SO₂ emission. The coarse-grained pyrite and pyrrhotite represented the preferential concentration of δ34S during replacement of diagenetic sulphate. Fine-grained chlorapatite adopted a signature similar to that of framboidal pyrite while the coarse grained chlorapatite was the result of the mixing of sulphur derived from biogenic sulphide and that derived from the dissolution of early forming pyrite and pyrrhotite.

11.4.2 Warrabarry Pb-Zn Prospect

Smith (1996) measured sulphur isotope values on diagenetic pyrite nodules, grey and white stage sulphides using conventional and laser ablation methods (Fig. 11.3). The results of six analyses of pyrite nodule have a wide δ34S range between ~15.5 to ~1.5%. The total range of δ34S grey stage sulphides is between +1.5 +20.4% and this range can subdivided into sphalerite (i) with a range of ~4.4 to +14.3% (n=22), eleven analyses of pyrite between +1.5 to +13.9% (n=11), and galena between +1.9 to +20.4% (n=8). White stage sulphides results range between ~6.9 to ~16.0% and this can be subdivided into sixteen analyses from sphalerite (iii) between ~6.9 to ~16.0% and eight analyses from pyrite with a narrow range between ~9.8 to ~6.3%.

Smith (1996) interpreted the grey stage sulphur isotope data to indicate that Proterozoic seawater was the dominant sulphur source and that minor sulphur was leached from diagenetic pyrite in the Broadhurst Formations sediments. Smith (1996) suggested that white stage sulphur was from a different reservoir to that of grey stage sulphur but that remobilization of grey stage sulphur had occurred. Smith
Figure 11.3: Summary histograms of sulphur isotope data from Nifty (this study; Eldridge, 1994a,b), Maroonchydore (Reed, 1996), Warrabarty (Smith, 1996), Goosewacker (Froud, 1997), Telfer (Rowins et al., 1997), Ruby Creek (Runnels, 1969), and Mount Isa (Andrew et al., 1989). The y-axis represents the frequency.
(1996) postulated that the source of white stage sulphur could be diagenetic sulphides, organic bound sulphur or H₂S released by metamorphic pyrite to pyrrhotite reactions.

11.4.3 Rainbow Cu Prospect

Limited sulphur isotope data is available from the Rainbow prospect (Smith, 1996). Rainbow sulphides were collected and analysed as part of the study on the Warrabury Pb-Zn prospect (Smith, 1996) and samples were collected from coarse-grained masses in quartz-chalcopyrite-pyrite-galena and chlorite veins sub-parallel to bedding. Smith (1996) suggests that these veins are texturally similar to the syn-D₂ bedding parallel coarse-grained chalcopyrite veins observed at Macrauchyrene. Chalcopyrite δ⁸S results have a narrow range between -2.2 to +3.3% (n=6), pyrrhotite δ⁸S ranges between -14.0 to +6.3% (n=8), and pyrite δ⁸S range between -11.1 to +14.2% (n=4). A single analysis of galena returned a result of -0.7%.

11.4.4 Goosewacker Pb-Zn Prospect

Froud (1997) conducted twenty-seven conventional sulphur analyses on host rock and vein stage sulphides at the Goosewacker prospect (Fig. 11.3). The majority of analyses conducted (n=23) were of pyrite and the results have a wide range of values between -10.6 to +17.3%. In addition to the pyritic results, Froud (1997) reported two galena results of -0.9 and 3.0% and two pyrrhotite results of -2.8 to -0.7%. Sulphur isotope results were classified based on paragenetic relationships (Froud, 1997).

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<td>Stage 4 veins</td>
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<td>-4.5%</td>
<td>+8.8%</td>
</tr>
<tr>
<td>Host rock</td>
<td>5</td>
<td>-3.0%</td>
<td>+3.2%</td>
</tr>
</tbody>
</table>

Table 11.3: Sulphur isotope results from the Goosewacker prospect (Froud, 1997). Vein mineralogy and paragenetic relationships are as described by Froud (1997).

11.4.5 Telfer Au-Cu Deposit

Rowins (1994) noted a wide range of δ⁸S values (Fig. 11.3) from hypogene pyrite in veins and reefs from Main Dome (-2 to +9.3%) and West Dome (-7 to +10%). It was noted that syn-metamorphisation data overlapped data from eleven analyses of diagenetic/epigenetic sulphides in carbonaceous rocks (-23.8 to +11.2%, mean between -3 and +11%). The -23.8% result is an isolated outlier and the only sample of marcasite analysed. Results from two analyses of sulphuric pyrite grains (+1.8 and +2.0%) in mafic rocks in copper Cretaceous granite overprint diagenetic and syn-metamorphisation data. On the basis of the overlapping sedimentary and syn-mineralisation data, Rowins (1994) concluded that the sulphates in the ore fluid were derived chiefly from sedimentary host rocks rather than Neoproterozoic granitoids. Rowins et al. (1997) attributed the source of sulphur at Telfer to be host rock sediments.
11.4.6 Mount Isa Cu Deposit

Numerous studies have examined the sulphur isotope signature of the Mount Isa ore deposit (Solomon and Jenien, 1965; Smith et al., 1978; Eldridge et al., 1985; Scott et al., 1985; Andrew et al., 1989; Waring, 1990). Andrew et al. (1989) described fine-grained and banded pyrite I as having δ34S values of ±9%, fine-grained recrystallised pyrite II between +9 to +15% and coarse-grained disseminated

\[ δ_{34}S \text{ of pyrite II} \] = -20 to +27% (Fig. 11.3). Results from Cu ore (chalcopyrite, pyrite, and pyrrhotite) range between +8 to +21% and the results of the 1100 copper ore body have a narrow range between +9.5 to +13.5% (Andrew et al., 1989). Heinrich et al. (1995) suggest that the majority of δ34S data measured on chalcopyrite, pyrite and pyrrhotite from the main copper orebodies at Mount Isa is between +10 to +16% and that the stratiform and stratiform pyrite results are between +1 to +24%. Andrew et al. (1989) concluded that the highly pyritic Unquilt Shale provided a major sulphur component to the copper ores and that there was a variable contribution from an δ34S-enriched source that was added along with the copper from hydrothermal fluids.

11.4.7 Ruby Creek Cu Deposit

Sulphur isotope of altered host-rocks from Ruby Creek deposit were analysed by Rummell (1969). Four-six samples of chalcopyrite, bornite and pyrite from host-rocks of dolomite, limestone, ankerite, or sideritic composition where analysed (Fig. 11.3). Cu sulphides and pyrites have averages δ34S of -3.7 (range -7.3 to +1.6%, n=24) and -0.8% (range -6.5 to +14.9%, n=20) respectively. Sulphides hosted by phyllitic metasediments have an average δ34S of -9.3 (-23.2 to +3.7%, n=17) and a small sample set of four analyses of copper-bearing sulphides have an average δ34S of -9.4% and a range of +23.1 to +11.2%.

Rummell (1969) suggested that metals at Ruby Creek were derived from either 1) phyllitic metasediments or metamorphosed mafic igneous rocks, or 2) hydrothermal solutions related to intrusive igneous rocks. Although no igneous rocks were encountered in diamond drilling Rummell (1969) concluded, based on a copper sulphide average close to 0%, that the origin of sulphur at the Ruby Creek Cu deposit was of a magmatic hydrothermal origin. Hitzman (1983) suggested that the magmatic hydrothermal source was unlikely since late B and C sulphides replaced sulphur deficient hydrothermal dolostone. Hitzman (1986) proposed that early pyrites from the deep B dolostone formed from an isotopically heavy solution that interacted with lighter diagenetic sulphides. Hitzman (1986) went on to suggest that the late C sulphides formed from a progressive mixing of an isotopically heavy mineralising brine with an isotopically light sulphur source from early B sulphides. The isotopically heavy basin brine was interpreted to be sourced from an adjacent basin composed of a thick sequence of Devonian clastic sediments (Hitzman, 1986).

11.4.8 Deposit Comparison

Mount Isa Cu ores have δ34S values that range between +5 and +12%, which is heavier than Nifty whereas data from Ruby Creek is similar to that of Nifty. Maroonclayore has light framoidal pyrite
values and both fine and coarse-grained chalcopyrite below -23% suggesting that mineralisation at Macrauchyphone occurred in a sulphur deficient system that resulted in the utilisation of existing sulphur (Reed, 1996). Warrabytary grey and white stage sulphur isotope data is heavier than the majority of Nifty data (Fig. 11.3) and Smith (1996) concluded that the source of Warrabytary sulphur was Proterozoic seawater (as connate brines or from leaching evaporites). The δ34S of sedimentary and syn-mineralisation sulphides from Teller are higher than those similar to those measured as Nifty. Rowins et al. (1995) suggested that sulphide precipitation occurred below the SO4²-/H2S boundary. Sulphur isotope data from the Rainbow Ca prospect is similar to Nifty. Chalcopyrite overlaps Nifty chalcopyrite data. Rainbow pyrite δ34S is also similar to Nifty pyritic data, however the pyrite generations have not been defined for Rainbow data. The narrow range of Rainbow δ34Spy may indicate that the source of chalcopyrite sulphur was the same as at Nifty. The limited amount of Goosewacker δ34S data limits the interpretations based on this data. The majority of Goosewacker δ34S data plots between -10‰ and +10‰ and a mode occurs at approximately -4‰.

11.5 Sulphur Isotope Discussion

Under equilibrium conditions δ34S of hydrothermal minerals is determined by the physical chemical conditions of the hydrothermal fluid (T, pH, fO2), as well as the isotopic composition of sulphur in the ore fluid δ34Sore (Ohimoto, 1972; Rye and Ohimoto, 1974). The conditions of pH and fO2 have been constrained by mineral assemblages present in the ore body and surrounding alteration halo as reduced and acidic while trapping temperature has been constrained at approximately 360°C by fluid inclusions data. The isotopic signature of syn-mineralisation sulphides provides important clues to the source of sulphur in the hydrothermal fluid. Potential sources of sulphur are seawater, sulphates, magmatic sulphur, sulphur leached from sedimentary host rock.

The isotopic signature of seawater sulphate has varied through time and estimates of the composition are provided by δ34S of evaporates. The precipitation of evaporite minerals from seawater results in a small positive fractionation of approximately 1.6‰ and therefore δ34S from evaporites will closely resemble the composition of seawater. No data was collected from Throssell Group evaporites during this, or any previous study in the Yeneena Basin. Strauss (1993) constructed a seawater sulphate curve for the period of 140Ma-700Ma for the Cambrian. For the majority of the curve (1400-700Ma), seawater sulphate was interpreted to be between 12-20‰ and during the deposition age range of the Throssell Group (1172-816Ma) values of 15-20‰ were proposed. Sulphate from evaporites (now pseudomorphed) in the upper shale, immediately below the pyrite marker bed, may have caused the heavy δ34S values up to +16‰ and therefore these positive values are interpreted to represent seawater sulphate fixed in evaporitic minerals. The low δ34S values of framoidal pyrite are interpreted to be the result of bacterial reduction of seawater sulphate. Bacterial reduction of seawater sulphates results a fractionation of -40±10‰ (Ohimoto, 1972). Using the seawater sulphate curve of Strauss (1993) a 40‰ decrease is approximately the light values of Nifty framoidal pyrite.
Syn-mineralisation results suggest that evaporites are unlikely to have had a major impact on $\delta^{34}$S as they are likely to have been replaced early in the evolution of the area (eg Andrews et al., 1985). The narrow range of syn-mineralisation sulphide data suggest that source of sulphur during the Nifty mineralising event was relatively homogenous, that there was minimal interaction with other sulphide sources at the site of deposition, and it also follows that syn-mineralisation chalcopyrite did not utilise existing sulphur from sedimentary pyrite. Although the $\delta^{34}$S values between chalcopyrite and the host sulphides overlap, the narrow range of chalcopyrite suggests that the formation of chalcopyrite involving $H_2S$ in the hydrothermal fluid rather than the host-rock sulphides or sulphates (Ohmoto and Goldhaber, 1997).

The $\delta^{34}$S value of hydrothermal fluids responsible for the formation of sulphide-bearing ore deposits can be estimated from the $\delta^{34}$S of the sulphide minerals by using the equilibrium fractionation factors between aqueous and solid species of the same valence (Ohmoto and Goldhaber, 1997).

$$
\delta^{34}S_{SS} = \delta^{34}S_{H2S} + \Delta_{SS-H2S} \left( \frac{R}{1+R} \right)
$$

where $\Delta_{SS-H2S}$ is the equilibrium fractionation factor between $SO_2$ and $H_2S$, which is a function of temperature; $R$ is the mole ratio of sulphate and sulphide in solution (Ohmoto and Goldhaber, 1997). At temperatures $>200^\circ$C all sulphur species may be expected to be in equilibrium before arriving at the depositional site and at temperatures above $300^\circ$C, $SO_2$ is the dominant oxidised species rather than $H_2S$ (Ohmoto and Goldhaber, 1997). $R$ in Equation 1 can be estimated using fluid inclusion data and mineral assemblages. Because the Nifty hydrothermal fluids are pyrite stable and little or no isotopic exchange occurred at the site of deposition between the ore sulphides and pre-existing pyrite, it is interpreted that hydrothermal $H_2S$ is the dominant species in the fluid and therefore $R$ is likely to be $<0.01$ (Ohmoto and Goldhaber, 1997). If $R$ is small then $R \times \Delta_{SS-H2S}$ will also be small and therefore $\delta^{34}S_{SS} \approx \delta^{34}S_{H2S}$. This reasoning suggests that $\delta^{34}S_{SS}$ of Nifty hydrothermal fluids was approximately 0‰.

A potential mechanism to achieve a $\delta^{34}S_{SS}$ of 0‰ is the reduction seawater sulphate by Eu$_{j1-}$-bearing minerals that results in the generation of $H_2S$ (Shanks et al., 1981; Ohmoto and Goldhaber, 1997). Studies of sulphur isotope associated with mid-ocean ridge hydrothermal vents (Kerridge et al., 1983; Gemmell and Sharpe, 1998) and the Kuroko deposit (Ohmoto et al., 1970; Ohmoto and Rye, 1974) noted that $\delta^{34}$S values of sulphide minerals are intermediate between primary basaltic sulphide (close to zero) and contemporaneous seawater sulphate. The isotopic signature of sulphide minerals precipitated from this inorganic reduction mechanism is dependent on the temperature of reduction and the starting composition of seawater. Sulphide minerals precipitated from inorganic reduction of seawater sulphate are typically between +5 and +15‰ (Ohmoto et al., 1970; Ohmoto and Rye, 1974; Kerridge et al., 1983; Gemmell and Sharpe, 1998). The range of values produced from inorganic reduction of seawater sulphate are more positive than the results from Nifty, therefore inorganic reduction of seawater sulphate is unlikely to be the source of sulphur at Nifty. The $\delta^{34}$S of 0.88±0.1‰ (1σ) for chalcopyrite is

182
consistent with a magmatic hydrothermal source of sulphur (Ohimoto and Rye, 1979). The source of the sulphur may be from a magmatic body or from the leaching of an igneous sulphur from intrusive or extensive rocks by hot hydrothermal fluids. No intrusive of similar age to the Nifty mineralisation has been recorded introdicing the Throssell Group. The absence of appropriately aged intrusive may be related to the lack of exposure in the Paterson Province, however, deformed, circular geophysical anomalies are observed in the area of the Grevillea prospect may indicate an intrusive body at depth but the exact nature of this anomaly is uncertain. In the absence of evidence supporting intrusive it is difficult to invoke a magmatic fluid source. A more likely explanation for the magmatic signature is that hot hydrothermal fluids have leached igneous basement rocks and/or igneous detritis in basin sediments.

Galena and sphalerite in the pyrite marker bed and footwall beds have replaced frambooidal pyrite suggesting that the mineralising fluid was sulphur depleted when it reached these pyrite-rich intervals. Therefore, these hydrothermal fluids utilised the pre-existing sulphur in frambooidal pyrite during the precipitation of galena and sphalerite.

11.6 Conclusion

Frambooidal pyrite δHs values range between ~27 to +16‰, however the majority of the data plots between δHs values of ~18 to +10‰. Cathedral pyrite δHs values between ~12 to +4‰, with the majority of the data between ~8 to +4‰. Chalcopyrite has a mean δHs value of ~0.8‰ and a narrow standard deviation of 3.1‰ (1σ). The sulphur isotope signature of frambooidal pyrite is consistent with biogenic reduction of seawater sulphate. Several results from frambooidal pyrite have positive sulphur isotope values and these sulphides are likely to have utilised sulphate from minor evaporites. Nifty chalcopyrite and pyrite mineralisation pyrite have a narrow range with a mean close to 0‰, and this range suggests a magmatic source of sulphur. No intrusive bodies of an appropriate age are known and therefore it is interpreted that the sulphur was leached from basement rock or igneous-derived sediments deeper in the basin.

Carbon and Oxygen Isotopes

11.7 Aims of using Carbon and Oxygen Isotopes

The aim of using the stable isotopes of carbon, oxygen and sulphur is to characterise the isotopic signature of 1) host rock, 2) vein stages and 3) gangue carbonates in order to determine the source of carbon and oxygen in the mineralisation fluids. Using this information the processes of fluid evolution can be examined by modelling fluid mixing, fluid-rock interactions and isotopic exchange during alteration. Carbon and oxygen isotopes can also assist in determining fluid evolution pathways, help identify the proximity and distribution of hydrothermal systems, and be used to compare other mineralised occurrences.
11.8 Methods

Samples of host-rock, vein and gneiss carbonates were hand-drilled using diamond tipped dental drills. Carbon and oxygen isotope analyses were carried out at the Central Science Laboratory of the University of Tasmania using the methods described by McCrea (1950). Samples were equilibrated to 50°C in a water bath before CO₂ was liberated by reacting samples with H₃PO₄. International standards used by the Central Science Laboratory is the Biggenden calcite. Isotopic ratios (¹³C/¹²C and ¹⁸O/¹⁶O) are represented using the conventional δ and reported in ‰ notations and the isotopic compositions are reported with respect to the standards VSMOW (Vienna Standard Mean Ocean Water) and VPDB (Vienna Pee Dee Belemnite) for oxygen and carbon isotope respectively (Commission on Atomic Weights and Isotopic Abundance, 1997). Conventional carbon and oxygen isotope measurements were performed using a VG Sira 10 mass spectrometer and the analytical uncertainty is estimated to be ±0.06‰ for δ¹³C and ±0.1‰ for δ¹⁸O.

11.9 Sampling Strategy

A total of 135 carbonate samples from drill hole samples were collected for carbon and oxygen isotope analysis (Appendix Five). Carbonate material was collected from host rock, vein stages and alteration listed below (Table 11.3) and detailed descriptions of host rock textures are given in Chapter Three. Vein stages and their paragenetic relationships are given in Chapters Five and alteration stages in Chapter Six. Sampling concentrated on cross-sections 102080mE and 102240mE with other distal drill holes sampled to examine the extent of possible isotopic halos.

<table>
<thead>
<tr>
<th>Sample Classification</th>
<th>n</th>
</tr>
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<tbody>
<tr>
<td>Host rock</td>
<td>12</td>
</tr>
<tr>
<td>Carbonaceous dolomite shales</td>
<td>30</td>
</tr>
<tr>
<td>Pre-mineralisation</td>
<td>8</td>
</tr>
<tr>
<td>IA - Bedding parallel dolomite veins</td>
<td>7</td>
</tr>
<tr>
<td>IB - Folded bedding parallel pyrite-quartz-dolomite veins</td>
<td>6</td>
</tr>
<tr>
<td>IC - Fracture dolomite veins</td>
<td>6</td>
</tr>
<tr>
<td>300-mineralisation</td>
<td>7</td>
</tr>
<tr>
<td>IIIA - Chlorite-dolomite veins</td>
<td>15</td>
</tr>
<tr>
<td>IIIB - Alteration margin quartz-dolomite veins</td>
<td>10</td>
</tr>
<tr>
<td>IIIC - Chalcopyrite-quartz-dolomite veins</td>
<td>2</td>
</tr>
<tr>
<td>III - Hydrothermal Quartz-Dolomite</td>
<td>10</td>
</tr>
<tr>
<td>Post-mineralisation</td>
<td>7</td>
</tr>
<tr>
<td>IIIB - Bladed carbonate veins</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 11.2: Carbonate material from host rock, pre-, syn-, and post mineralisation vein stages, and hydrothermal quartz dolomite alteration were analysed for carbon and oxygen isotope. Host dolomitic mudstones are described in Chapter Three, quartz-dolomite alteration is described in Chapter Five and vein mineralogy and paragenetic relationships are as described in Chapter Six.
11.10 Results

Data from carbon and oxygen isotopic analyses are listed in Appendix Four and the results are described for each of the host rock, pre-, syn-, and post-mineralisation phases.

11.10.1 Unaltered Host Rock

Twelve samples of unaltered dolostone and calcareous marlstone (Fig. 11.4) from the Nifty upper carbonate bed were analysed for the isotopes of carbon and oxygen. Data consists of $^{13}$C values between ±0.4 to +4.9% (average 2.4%) and $^{18}$O between +18.8 to +23.3% (average 20.8%). Nifty host rock carbonates are lighter than the majority of Ypresian Supergroup unaltered dolostones reported by other workers (Roweis, 1994; Reed, 1996; Smith, 1996) however some overlap does occur with Maroochy Shale host rock data.

11.10.2 Pre-mineralised

Pre-mineralised samples (Fig. 11.5) from the vein classifications IA, IB and IC consist of 1) bedding parallel dolomite veins from hangingwall beds, 2) thin sets of parallel dolomite-quartz veins that cross-cutting bedding at high angles also from hangingwall beds, and 3) folded bedding parallel pyrite-dolomite-quartz veins from the footwall beds. Samples showed no evidence of mineralisation or alteration and have been deformed by D3 and are overprinted by later vein stages.

Forty-four analyses from pre-mineralised vein carbonates form a positive carbon and oxygen trend away from the Nifty host rock field to values of -8% for $^{13}$C and -13% for $^{18}$O. Vein stages are distributed along the linear trend with a sequence away from the unaltered host rock field of IC, IA, and IB. IA data do not overlap the host rock field but isotopically heaviest results plot with similar carbon and slightly lighter $^{18}$O values (Fig. 11.5). As $^{13}$C ratios become lighter, the range of $^{18}$O also increases so that at $^{13}$C of approximately -4% the $^{18}$O range is approximately +5%. IB data form a dispersed field with a $^{13}$C range of about 7% and this field overlaps that of IA but with generally lighter carbon and oxygen isotopes. Figure 11.5 shows vein style IC plotting with a bimodal distribution with several results within the unaltered host rock field and a second group of two data plotting with lighter carbon and oxygen isotope ratios within the IA field. This bimodal spread of data may reflect contamination of samples during drilling as this vein stage can be very thin and therefore prone to contamination by host rock material.

11.10.3 Syn-mineralised

Data from thirty-seven samples of vein carbonates and hydrothermal alteration dolomite (Fig. 11.6) from the classifications IA, IB, IC and SJ plot within a triangle field with co-ordinates in $^{18}$O - $^{13}$C space of (+14%, -10 %), (+18%, +15%) and (+21%, -10%) respectively. IA veins consist of chalcopyrite-quartz-dolomite veins and the data from this vein stage overlaps pre-mineralisation data

185
Figure 11.4: Carbon and oxygen isotope data from host rock limestones, dolomites, and calcarenous mudstones from the Broadhurst Formation, Throssell Group. Additional data sources are Maroochydore (Reed, 1996), Warrabarty, Warrabarty limestone, Moses, Nitty (Smith, 1996), Goosewacker (Froud, 1997).

Figure 11.5: Carbon and oxygen isotope compositions from pre-mineralisation vein stages of IA-Bedding parallel dolomite veins, IB-Folded bedding parallel pyrite-quartz-dolomite veins, IC-Fracture dolomite veins. IA veins are typically observed in the hangingwall beds while IC veins are observed in the footwall beds.
and forms a diapiric group dominated by several outliers. HII-alteration margin quartz-dolomite veins form a small group with a narrow δ18O range between +17.8 to +20.0‰ and this data plots within the fields of HIA data. Two results from HIC-cleavage parallel dolomite veins plot below the host rock field with δ18O of −2.3‰ and −1.0‰. S3-Hydrothermal Quartz dolomite alteration show a wide distribution. Considerable overlap exists between pre- and syn-mineralized isotopic data however a shift has occurred toward heavier δ18O and lighter δ13C ratios in each dataset (Fig. 11.6). Although not as well defined as other phases, syn-mineralisation carbonates form a negative covariance trend but with a large spread.

11.10.4 Post-mineralised
Forty-two post-mineralisation samples consisting dolomite from HIA-Quartz veins and HIB-Bladed carbonate veins were assayed. Both veins types are observed throughout the footwall beds, Nifty member and hangingwall beds. Timing relationships between these two vein styles could not be determined. Data from post-mineralised veins (Fig. 11.7) form a negative trend in δ18O - δ13C space with only a minor δ18O variation of approximately 5‰ and a larger δ13C variation of approximately 16‰. HIA (coarse quartz-dolomite veins) dominate the negative linear trend with a narrow δ18O range and δ13C between 7‰ and −11‰. Data from HIB (bladed carbonate veins) form a tight group with an average δ18O of 16.2‰ and δ13C of −3.3‰. A single result of a sample collected from THRD635, 419.4m has a δ13C value heavier than unaltered Theostell Group host rock data.

11.11 Spatial Distribution at Nifty
Figure 11.8A-F shows contoured pre-, syn-, or post-mineralisation carbon and oxygen isotope data from cross-section 1020990mE. The variation of δ13C in pre-mineralised carbonates (Fig. 11.8A) shows light values around −1‰ in the centre of the syncline and rising to >3‰ in the syncline limbs. The stratigraphic levels from which samples were collected may have created this apparent distribution to heavier values in the centre of the syncline but this is unlikely because with the exception of host rock data results are from vein stages. Syn-mineralisation carbon isotope data (Fig. 11.8B) show a trend toward light carbon values of around −6‰ toward the northern limb and this is in contrast to the distribution of δ13C in post-mineralised veins (Fig. 11.8C). Distribution of δ18O in the three phases of pre-, syn-, and post mineralisation (Fig. 11.8D-F) shows a similar trend with low values toward the north of the syncline (5000mN). Within the copper-rich core of the deposit δ18O values range between approximately +16 to +20‰, although there is limited data in this area from the pre-mineralisation phase. Data from the northern limb, in the area of the 5000mN northing also has values close to those areas of high-grade mineralisation.

Figure 11.9A-B shows a plan of the distribution of syn-mineralisation carbon and oxygen isotope projected to ground surface. Diamond drill holes from which samples were analysed are shown as filled and labelled black circles while of drill holes are shown as open circles. Included in the figure are
Figure 15.6: Carbon and oxygen isotope compositions from H4A-Chalcopyrite-dolomite veins, H5A-Alteration margin quartz-dolomite-chlorite veins, H5C-Quartz parallel dolomite-quartz veins, and S3-Hydrothermal Quartz-Dolomite alteration.

Figure 11.7: Carbon and oxygen isotope compositions from post-mineralisation vein stages of H4A-Coarse quartz veins and H5B-Bladed carbonate veins.
Figure 11.8A-F: Downward variations of carbon and oxygen isotopes on cross-section 102080mE for each of the pre-, syn- and post-analysation phases. The cross-sections have structural and stratigraphic overlays. Note that in all phases the lowest δ18O values are located on the northern limb. Abbreviations: UC-upper carbonate bed, HW-Sh-Hangingwall shale, PMB-pyrite marker bed, NM-Nifty member, FWB-footwall beds. Diamond drill holes and faults are labeled in A and D.
Figure 11.9A-B: Plan views of the distribution of syn-mineralisation carbon and oxygen isotopes from the primary ore body. The diagrams also contain interpreted geology, surface traces of faults and the surface projection of the primary Cu ore body at 0.5% and 1.5% Cu cutoffs.
the outlines of the 0.5% and 1.5% Cu-grade cut-offs for the primary chalcopyrite ore body and the surface traces of faults. The distribution pattern of δ¹⁸O in Figure 11.9A show broadly spaced contours with values between −1 to −4‰ in most areas except for the northern four drill holes on cross-section 102240E. In these four drill holes contours have been influenced by two samples with low δ¹⁸O (approximately −10‰). Figure 11.9F shows the distribution of δ⁰¹⁸O as a broad zone of similar values between faults labelled X and Y, a trend toward lower values to the north, and higher values to the east.

11.12 Comparison of Carbon and Oxygen Isotope Signatures

This section presents a compilation of carbon and oxygen isotope results from mineralised occurrences in the Yeneena Super group of the Warriabary Pb-Zn prospect (Smith, 1996), Maroochydere Cu deposit (Reed, 1996) and the Teller Au-Cu deposit (Rowins, 1994; Rowins et al., 1997; Rowins et al., 1998). Each of the Yeneena Super group mineralised occurrences has a distinct isotopic signature and this suggests the potential for carbon and oxygen isotopes to be used as an exploration vector. In addition to data from the Paterson Orogen, the Cu deposits of Mount Isa (Andrew et al., 1989; Heinrich et al., 1989; Waring, 1990; Waring et al., 1998) and Ruby Creek (Hitzman, 1983) are also included in this comparison.

Figure 11.4 shows regional host rock carbon and oxygen isotope data from deposits and prospects in the Yeneena Super group and Figure 11.10 show the data from Warriabary (Smith, 1996), Maroochydere (Reed, 1996) and 17 Mile Hill in the Teller district (Rowins, 1994). Also in Figure 11.10 is data from Ruby Creek and Mount Isa Cu deposits.

11.12.1 Maroochydere Cu Deposit

Unmineralised dolostone data from Maroochydere (Reed, 1996) forms a tight group with δ¹³C between +0.2 to +4.1‰ and δ⁰¹⁸O between +19 to +23.3‰ (mean ±20.6‰). Syn-D3 mineralisation vein data (Fig. 11.10) forms a group separated the host-rock field and the data is more dispersive with δ¹³C between −1.6 to +3.1‰ and δ⁰¹⁸O between +18.3 to +27.3‰. Reed’s (1996) conclusions for seawater origin for the carbon and oxygen contained in host rock dolomites at Maroochydere was consistent with textural studies and indicated the formation of dolostone during diagenesis, and 2) vein dolomites precipitated from metamorphic fluids of marine origin and that these fluids were in equilibrium with saline and carbonate sedimentary rocks sequences at Maroochydere.

11.12.2 Warriabary Pb-Zn Prospect

Carbon and oxygen isotope data (Smith, 1996) from Warriabary syn-mineralisation carbonates and unmineralized dolostones from the Thorsett Group (Table 11.3, Figs. 11.4 and 11.10) plot in overlapping fields.
Figure 19.10: Summary plot of carbon and oxygen isotope data from deposits and prospects in the Yunaena Supergroup and the Mount Isa and Ruby Creek Cu deposits.
Table 11.3: Carbon and oxygen isotope data from the Warrubarty Pb-Zn Prospect (Smith, 1996). Dolostone B is an early diagenetic dolomite, whereas grey stage dolomite formed during Pb-Zn mineralisation prior to regional D2 deformation (Smith, 1996). White stage dolomite sourced during regional D2 deformation and Smith interpreted this stage to be synchronous with Nifty and Maroochy ore mineralisation.

Smith (1996) concluded that the source of carbon and oxygen in grey stage gangue carbonates was Broadhurst Formation carbonates and that the later white stage carbonates were sourced from fluids containing a component from metamorphic volatilisation.

11.12.3 Telfer Au-Cu Deposit.

Lampl Park host rock field is defined by nineteen analyses of sedimentary rocks from the Puntapunui. Telfer and Indeill Formations (Goellnicht and McNaughton, 1989; Rowins, 1994; Rowins et al., 1997) and this data is shown in Figure 11.10. Data from each of the formations forms a well-defined field. Twenty-one samples from diamond drill hole MRC230-33 were analysed by Rowins (1994) and these samples provide data through the mine sequence of the Telfer Formation. Another group of results consists of thirty-two analyses of dolomite and calcite from altered host rocks and concordant to discordant quartz-carbonate-sulphide veins at Main Dome (Rowins, 1994; Rowins et al., 1997). Main Dome data was separated into early, main, and late stages and summary data from these groups is shown in Table 11.5 (Goellnicht and McNaughton, 1989).

<table>
<thead>
<tr>
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<th>Minimum δ13C (%)</th>
<th>Maximum δ13C (%)</th>
<th>Average δ18O (%)</th>
<th>Minimum δ18O (%)</th>
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<td>-2.4</td>
<td>2.9</td>
<td>26.3</td>
<td>26.0</td>
<td>26.7</td>
</tr>
<tr>
<td>Telfer</td>
<td>4</td>
<td>2.9</td>
<td>1.9</td>
<td>3.4</td>
<td>26.0</td>
<td>25.7</td>
<td>26.3</td>
</tr>
<tr>
<td>Indeill</td>
<td>7</td>
<td>0.1</td>
<td>-1.3</td>
<td>1.0</td>
<td>25.4</td>
<td>24.6</td>
<td>26.9</td>
</tr>
<tr>
<td>Early stage</td>
<td>3</td>
<td>-1.6</td>
<td>-4.7</td>
<td>-0.4</td>
<td>16.2</td>
<td>13.3</td>
<td>18.1</td>
</tr>
<tr>
<td>Main stage</td>
<td>16</td>
<td>-0.1</td>
<td>-5.4</td>
<td>4.6</td>
<td>18.6</td>
<td>13.0</td>
<td>26.4</td>
</tr>
<tr>
<td>Late stage</td>
<td>16</td>
<td>-2.4</td>
<td>-5.4</td>
<td>-0.1</td>
<td>15.0</td>
<td>12.9</td>
<td>26.2</td>
</tr>
</tbody>
</table>

Table 11.4: Summary of Lampl Park host rock carbon and oxygen isotope data (Goellnicht and McNaughton, 1989; Rowins, 1994; Rowins et al., 1997)

The carbon and oxygen isotope data from vein material has a wide range of values that are clearly distinct from the host rock values. Four features of Telfer carbon and oxygen isotope data are noted by Rowins et al. (1997): 1) δ13C in vein and host rock typically plus within the range defined by Lampl Park host rocks, 2) that a strong stratigraphic control of δ13C was evident in vein and host rocks and no stratigraphic control of δ18O was evident, and 3) hydrothermal carbonates have a narrow range of δ18O values (-6‰) and the majority of data is approximately 10‰ lighter than the field defined by host rock.
A considerable amount of data from altered rocks plots with values outside the range of the Lamill Group host rocks and this is contrary to the assertion of Rowins et al. (1997). The suggestion that no stratigraphic control of δ¹⁸O is also not supported because δ¹⁸O from diamond drill hole MRC 250-33 show a depletion in δ¹⁸O and enrichment in δ¹³C toward the Middle Valsey Reef.

Rowins et al. (1997) suggested several fluid-rock interaction models to account for the large negative shift in oxygen isotope data but excluded metamorphic decarbonation reactions at elevated temperature because of the absence of shales, marbles and calc-silicate rocks. Rowins et al. (1997) went on to suggested two possible precipitation mechanisms of static recrystallisation and/or dissolution and reprecipitation of marial carbonates during low-grade metamorphism or precipitation from externally sourced fluids. Rowins et al. (1997) suggested that the first option was a rock buffered system with low waterrock interaction but they did not favour this option because the carbon and oxygen isotope data should have reflected the composition of the Lamill Group marine carbonate. The second option was precipitation from externally sourced fluids (Rowins et al., 1997) and this was favoured because rocks with high concentrations of carbonate produced fluids and equilibrium carbonates with isotopic concentrations close to that of marine carbonates. Rocks with minor carbonate composition produced carbonates with lower δ¹⁸O values since detrital silicates (quartz and feldspar) have significantly less δ¹⁸O than marine carbonates (McNaughton and Wintner, 1990).

11.12.4 Mount Isa Cu Deposit

A large amount of published carbon and oxygen isotope data (Andrew et al., 1989; Heinrich et al., 1989; Waring, 1990; Waring et al., 1998) exists for the Mount Isa Cu ore body (Fig. 11.10). Isotope data from silica-dolomite alteration have a narrow range with δ¹⁸O between +10 to +12% and δ¹³C between -5 to -3%. (Waring et al., 1998). Waring et al. (1998) also noted that the results from the silica-dolomite altered areas contrasted to unaltered dolomitic shale host rocks with δ¹⁸O of +20 to +22% and δ¹³C of -2 to 0%.

Heinrich et al. (1989) and Waring (1990) noted a δ¹⁸O depletion in the quartz-chlorite-pyrite mineralised core of the silica-dolomite altered rocks and concluded that the copper ore bodies resulted from the interaction of oxygen-rich forming hydrothermal fluids with dolomite-host-rock. Heinrich et al. (1989) interpreted their results to suggested that a slight variation in the temperature of dolomite crystallisation occurred and that the fluid was from an external origin, with a reduced carbon (C, CH₄), at high fluid/rock ratio, and that the carbon and oxygen of the external fluid was dominant.

11.12.5 Ruby Creek Cu Deposit

Limit carbon and oxygen isotope data is available from the Ruby Creek deposit. Hitzman (1963) presents a graph of unpublished data from J. Whelan and suggests that complete results and methods
will be described in a forthcoming publication of Whelan and others. Apart from Hitzman (1983) no carbon and oxygen isotope data from Ruby Creek has been published. Estimates of the isotopic results have been taken from Figure 49 in Hitzman's (1983) thesis and a field of Ruby Creek is included in Figure 10.10. Hitzman (1983) describes grey ceramic dolomite as having a scattered array of values with δ18O between +19.4 to +25.1‰ and δ13C between -0.38 to +1.24‰. Dolomites plot a linear trend from δ13C of -0.70 to +0.88‰ and oxygen from +21.5 to +26.3‰. Hitzman (1983) noted that the C carbonates have values distinct from the earlier hydrothermal dolomites and defined a field extending from δ13C of -1.65 to -0.45‰ and δ18O of +18.8 to +23.0‰. Hitzman (1983) concluded that the two fluids of different isotopic composition were responsible for the hydrothermal carbonates at Ruby Creek and that a change in temperature was the main precipitation mechanism.

11.1.2.6 Deposit Comparison

Table 11.6 compares stable isotope data from Mount Isa and Ruby Creek Cu deposits, and Yeneena Supergroup-hosted deposits and prospects. Nifty has distinct δ13C and δ18O signatures when compared to these deposits. Reed (1996) interpreted Maroochydore vein dolomites to have precipitated from metamorphic fluids of marine origin and that these fluids were in equilibrium with shale and carbonate sedimentary rocks sequences. Smith (1996) concluded that the source of Warrabury carbon and oxygen isotopes in grey stage gangue carbonates was Broadhurst Formation carbonates and that the later white stage carbonates were sourced from fluids containing a component from metamorphic volatilisation. Compared to Lamil Group host rock data Telfer has a strong shift toward lighter oxygen isotope values and a small increase in the spread of δ13C (Table 11.6). Rowsins (1994) and Rowsins et al. (1997, 1998) suggested that the Telfer δ13C and δ18O signature is the result of the dissolution of marine carbonates and the oxidation and 18O hydrolysis of reduced carbonaceous matter in sedimentary host rocks. Precipitation occurred from externally sourced fluids (Rowsins, 1994; Rowsins et al., 1997, 1998). Mount Isa fluids are interpreted as being externally derived, weakly CH4, CO2 bearing, NaCl-rich, reduced fluid at high fluid/rock ratios over small temperature range (Heinrich et al., 1989). Heinrich et al. (1989) suggested that Mount Isa fluids originated as a highly evolved basin brine or an evaporate-derived metamorphic fluid. Hitzman (1983) suggested that two fluids of different isotopic composition were responsible for the hydrothermal carbonates at Ruby Creek and that a change in temperature was the main precipitation mechanism.

11.13 Summary of Carbon and Oxygen Isotope Results

Broadhurst Formation host rocks at Nifty consist of carbonaceous and dolomitic shales and have carbonate oxygen isotope compositions that are consistently low with respect to other Yeneena Supergroup host rocks. Pre-mineralization alteration has occurred as E1-Fe Mg Carbonates and E2- Green-Quartz alteration. The distribution of E1 is restricted to thin bands in the hangingwall shales, several metres above the pyrite marker bed and E2 occurs in rocks of the Nifty member. The pre-mineralization vein stages have a stratigraphic distribution with E4 and E5 in the hangingwall beds and
Figure 11.11: Summary plot of carbon and oxygen isotope data from deposits and prospects discussed in the text and showing the trend between fields of syn-mineralised data and the respective host rock carbonates fields. No significant shift is observed between host rock and syn-mineralisation carbonate fields for Warrabary or Ruby Creek.
<table>
<thead>
<tr>
<th>Deposit/Prospect</th>
<th>δ^13C</th>
<th>δ^18O</th>
<th>Interpreted fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nifty</td>
<td>Host rock: +0.4 to +3.5%</td>
<td>Host rock: +18.8 to +21.4%</td>
<td>See discussion below</td>
</tr>
<tr>
<td></td>
<td>Pre-min: -7.5 to 3.5%</td>
<td>Pre-min: +13.5 to +21.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Syn-min: -10.3 to 2.4%</td>
<td>Syn-min: +14.3 to +21.5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Post-min: -9.9 to 7.9%</td>
<td>Post-min: +13.6 to +21.6%</td>
<td></td>
</tr>
<tr>
<td>Maroochydore</td>
<td>Host rock: +5.2 to 4.1%</td>
<td>Host rock: +19 to 23.3%</td>
<td>Vein dolomites precipitated from metamorphic fluids of marine origin and that these fluids were in equilibrium with shale and carbonate sedimentary rock reservoirs at Maroochydore.</td>
</tr>
<tr>
<td></td>
<td>Syn-min: -1.6 to 3.1%</td>
<td>Syn-min: +18.3 to +27.3%</td>
<td></td>
</tr>
<tr>
<td>Warrabary</td>
<td>Host rock: -0.8 to +6.1%</td>
<td>Host rock: +19.3 to +27.1%</td>
<td>Smith (1996) concluded that the source of carbon and oxygen in grey stage janicite carbonates was Broadwater Formation carbonates and that the later white stage carbonates were sourced from fluids containing a component from metasomorphically altered carbon.</td>
</tr>
<tr>
<td></td>
<td>Dolomite: B δ +2.8 to +0.6%</td>
<td>Dolomite B δ +23.4 to +28.4%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grey stage dol: +0.5 to +6.3%</td>
<td>Grey stage dol: +23.7 to +27.8%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>White stage dol: +6.7 to +27.3%</td>
<td>White stage dol: +16.7 to +27.3%</td>
<td></td>
</tr>
<tr>
<td>Teffer</td>
<td>Host rock: -1.4 to +3.1%</td>
<td>Host rock: +22.8 to +25.9%</td>
<td>Dissolution of marine carbonates and the oxidation and for hydrolysis of reduced carbonaceous matter in sedimentary host rocks. Precipitation occurred from externally sourced fluids.</td>
</tr>
<tr>
<td></td>
<td>Early stage: -2.7 to +0.0%</td>
<td>Early stage: +13.3 to +18.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Main stage: -3.4 to +3.4%</td>
<td>Main stage: +13.0 to +26.1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Late stage: -5.4 to -0.1%</td>
<td>Late stage: +12.9 to +26.2%</td>
<td></td>
</tr>
<tr>
<td>Mount Isa</td>
<td>Host rock: -2.0 to 0.0%</td>
<td>Host rocks: +20 to +225%</td>
<td>Externally derived, weakly CH₄, CO₂ bearing, NoCl-rich, reduced fluid at high fluidrock ratios over small temperature range. Fluid originated as a highly evolved brine that on an evapentic-derived metamorphic fluid.</td>
</tr>
<tr>
<td></td>
<td>Silica-dolomite: -8 to -3%</td>
<td>Silica-dolomite: +10 to +12%</td>
<td></td>
</tr>
<tr>
<td>Ruby Creek</td>
<td>Grey ceramic dol: +19.4 to +25.1%</td>
<td>Grey ceramic dol: +1.4% to +3.4%</td>
<td>Two fluids of different isotopic composition were responsible for the hydrothermal carbonates at Ruby Creek and that a change in temperature was the main precipitating mechanism.</td>
</tr>
<tr>
<td></td>
<td>B dol: -0.7 to +0.9%</td>
<td>B dol: +21.5 to +26.3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C carbonates: -1 to -0.5%</td>
<td>C carbonates: +1.8 to +3.0%</td>
<td></td>
</tr>
</tbody>
</table>

Table 12.7: Summary of stable isotope data from Nitty Cu deposit, Maroochydore Cu prospect (Reed, 1986), Warrabary (Smith, 1996), Teffer (Rowins, 1994; Rowins et al., 1997; Rowins et al., 1998), Mount Isa (Heinrich et al., 1989), and Ruby Creek Cu deposit (Hitzman, 1983, 1986). Abbreviations; dol-dolomite, min-mineralisation.
In the footwall beds. The temperature of pre-mineralisation vein precipitation is likely to be between diagenetic (~25°C) to sub-greenish facies metamorphic (~200°C) temperatures. Isotopic data forms a positive C-O trend that overlaps the host-rock field and at the other end of the trend has δ18O ratios of -8% and δ13C ranging between +13 to +17% and therefore, the incoming fluid has light carbon and oxygen isotopes values with respect to the host-rock values.

Syn-mineralisation isotopic data forms a triangle with the apex at δ18O of +17.1%, δ13C of +2.4‰ and the base at δ18O of approximately +10.2‰ and δ13C ranging between +14.3 to +21.5‰. During the mineralisation event formation of the pervasive quartz-dolomite alteration and 1B-Minesorit Margin vein textures suggest very high fluid-rock interaction. Post-mineralisation data forms a varying linear trend with a large carbon range of 15.5‰ and an oxygen isotope range of approximately 6‰. δ13C plots with much of the data, as heavy as the host rock fields and with one data point heavier (approximately 7‰).

Generalised trends can be deduced from examining the shift of carbon and oxygen isotope ratios between host rock sequences and mineralised samples throughout the Yandora Basin (Fig. 11.11). Nifty trends have a large shift, mainly in carbon, with a positive slope, Maroochydore has a small negative trend in both carbon and oxygen, no shift in δ18O or δ13C is observed in Warraby or Ruby Creek data. Telfer shows a large spread of data and a shift toward lighter oxygen isotope ratios. Mount Isa shows a curved trend toward lighter carbon and oxygen ratios. The difference in isotopic values and trends from host-carbonates to deposits suggests that carbon and oxygen isotopes have potential as a exploration tool within the Paterson Orogen.

11.14 Carbon and Oxygen Isotope Discussion

The ranges of isotopic values recorded at Nifty are different from those of the host rocks and are not reported elsewhere in Throssell Group mineralised occurrences. Data from the three stages of pre-, syn- and post-mineralisation overlap however in isolation each phase has identifiable trends. As shown in Figure 11.10 the trend formed during mineralisation produces unique patterns and Nifty data patterns suggest that 1) that the processes that acted on Nifty did not occur at other prospects, and/or 2) the isotopic composition of the fluids involved was different from other deposits in the region. Identification of the isotopic composition of the mineralising hydrothermal fluid can provide information on the source and mechanism responsible for the precipitation of the carbonates. Pre-mineralisation veins have a distribution restricted to the hangingwall and footwall beds and the timing relationships of post-mineralisation veins to earlier phases are unclear. This discussion focuses on the syn-mineralisation results and the processes that could generate the patterns in that data. Syn-mineralisation data is used because it is best constrained by fluid inclusion temperatures, geochemistry, mineralogy and isotopic data. As thermal or fluid flow events may equilibrate early isotopic signatures it would be expected that the later events thermal or isotopic exchange systems would increase the spread of data in the early results. This does not appear to be the situation at Nifty and therefore it is
interpreted that post-mineralisation thermal or isotope exchange event have had a minor impact on earlier $^{13}C$ and $^{18}O$ signatures.

The isotopic composition of hydrothermal carbonates is controlled by 1) the composition of the initial fluid and the wall rock, 2) temperature, and 3) the dissolved carbon species involved (Zheng & Hoefs, 1993). Using estimates of these controlling factors three mixing processes can be modelled using mass balance methods; these processes are: 1) the mixing between two different fluids, 2) mixing between a fluid and rock by a fluid-rock interaction, and b) alteration of primary carbonates.

This discussion examines carbon speciation and temperature because they strongly influence equilibrium fractionation of carbon and oxygen isotopes during the precipitation of carbonates. Fractionation factors used in this discussion are presented in Section 11.14.1. The carbon speciation section is followed by an examination host rock data and how it provides insights into regional processes and how this knowledge can be used to constrain features associated with mineralisation. Potential carbonate precipitation mechanisms of temperature change, decarbonation, sulphate reduction, melt/melt oxidation, fluid-rock interaction, and fluid mixing are examined to identify if they occurred during mineralisation at Nifty.

### 11.14.1 Speciation of Carbon

The $^{13}C$ value of a mineral species is heavily dependent on the carbon species involved. The common species of carbon are $\text{CO}_2\text{gasp}$, $\text{HCO}_3\text{aq}$, $\text{H}_2\text{CO}_3\text{aq}$ and $\text{CH}_4\text{gasp}$. The dominant carbon species in seawater is $\text{HCO}_3$. At temperatures greater than 100°C $\text{HCO}_3\text{aq}$ is negligible when compared to $\text{H}_2\text{CO}_3\text{aq}$ (Ohmoto, 1986) and $\text{H}_2\text{CO}_3\text{aq}$ behaves isotopically like $\text{CO}_2\text{gasp}$, $\text{H}_2\text{CO}_3\text{aq}$ is used here calculate fractionation for both $\text{H}_2\text{CO}_3\text{aq}$ and $\text{CO}_2\text{gasp}$. The isotopic fractionation between mineral $x$ and carbon species $y$ are determined using Equation 2 and the values listed in Table 11.7.

\[
1000 \ln \alpha_{x,y} = A \cdot \frac{R(y)}{T} + \frac{C(10^5)}{T^2} + \frac{D(10^7)}{T^3}
\]

(2)

where $\alpha_{x,y}$ is the isotopic fractionation between mineral $x$ and carbon (or $\text{H}_2\text{O}$) species $y$, $T$ is the temperature in degrees Kelvin and $A$, $B$, $C$, and $D$ (Table 11.7). Fractionation factors are from O'Neil et al. (1983), and Truesdell (1974), Ohmoto and Rye (1979), and Lund (1983).

<table>
<thead>
<tr>
<th>Species</th>
<th>A ($10^5$)</th>
<th>B ($10^7$)</th>
<th>C ($10^6$)</th>
<th>D ($10^9$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{CO}_3\text{aq}$</td>
<td>8.44</td>
<td>-18.11</td>
<td>8.7307</td>
<td>-8.914</td>
</tr>
<tr>
<td>$\text{CO}_2\text{gasp}$</td>
<td>7.53</td>
<td>-18.11</td>
<td>8.7307</td>
<td>-8.914</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3\text{aq}$</td>
<td>12.9%</td>
<td>-18.11</td>
<td>7.638</td>
<td>-8.914</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3\text{aq}$</td>
<td>-35.70</td>
<td>-20.16</td>
<td>-2.16</td>
<td>-13.108</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3\text{aq}$</td>
<td>-4.40</td>
<td>-9.18</td>
<td>13.947</td>
<td>-13.108</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3\text{aq}$</td>
<td>-2.00</td>
<td>-3.14</td>
<td>-2.78</td>
<td>-3.14</td>
</tr>
</tbody>
</table>

11.14.2 Host Rock Data as a Control

Host rock data provides a control against which the mineralising system can be compared. The source of carbon and processes of sedimentary and diagenetic carbonate formation are likely to be the same, and have acted in a similar manner to all Throssell Group deposits and prospects. Also, regional events such as diagenesis and metamorphism are likely to have been of similar magnitude and timing throughout the basin.

An estimate of the composition of Yeccenas Basin seawater can be made if several assumptions are accepted. These assumptions are 1) Throssell Group unaltered host rock carbonates precipitated from a single seawater source, 2) that the temperature of precipitation was approximately 50°C, 3) the fluid was HCO_{3} dominantly, and 4) that no re-equilibration has occurred during subsequent isotopic, thermal or diagenetic events. A value for isotopic composition of Yeccenas seawater is calculated 1) using the oxygen isotope fractionation factors for protodolomite-water (Land, 1983), 2) carbon isotope fractionation factor for dolomite-HCO_{3} (Friedman and O'Neil, 1977, see Table 11.7), and an average Throssell Group host rock value of δ^{18}O +23.1 and δ^{13}C +3.2‰. At 50°C, Δ{eq}_{\text{dolomite-HCO}_{3}} is 26.8‰ and Δ{eq}_{\text{carbonate-HCO}_{3}} is 3.7‰ and subtracting these fractionation results in calculated Yeccenas Basin waters of δ^{18}O of -3.7‰ and δ^{13}C of -0.5‰. If the temperature of formation were raised to 75°C then Yeccenas Basin seawater δ^{18}O and δ^{13}C would increase to -0.7‰ and +0.4‰ respectively and if the temperature was lowered to 25°C then δ^{18}O and δ^{13}C would increase to -8.3‰ and -1.3‰ respectively. Compiled data and compilation values for the Mesozoic Neoproterozoic (Knoll et al., 1992; Buick et al., 1995; Kaufman and Knoll, 1995) record that the composition of Neoproterozoic seawater was consistently close to δ<sub>18</sub>O +0.2‰. In the Neoproterozoic rapid changes occurred in carbon isotopic composition and during the age range 850-570 δ^{13}C was enriched by 4 to 8‰ with brief excursions at approximately 760 and 810 Ma to -2‰. (Kaufman and Knoll, 1995; Knoll et al., 1995). The high δ^{13}C values of Throssell Group carbonates are consistent with Neoproterozoic values however, carbonate sequences precipitated in hypersaline environments typically record heavier δ^{13}C values than equivalent seawater carbonates (Beaumais and Knauth, 1985; Southgate et al., 1989). While acknowledging that there is a large range of Throssell Group host rock data and that δ18O plots with light oxygen isotope values relative to other host rock samples, it is likely that the calculated Yeccenas Basin seawater values of δ^{18}O of -3.7‰ and δ^{13}C of -0.4‰ are an adequate approximation.

11.14.3 Carbon Species in the Nifty Hydrothermal Fluid

At temperatures above 100°C HCO_{3} is negligible compared to H_{2}CO_{3} (Qimoto, 1986) therefore, HCO_{3} is unlikely to the carbon species in the Nifty hydrothermal fluid. At equilibrium, the carbonate speciation will be controlled by fluid pH. Mineral assemblages associated with Nifty mineralisation indicate that the Nifty hydrothermal fluids were reduced (pyrite stable) and moderately acidic (muscovite stable). HCO_{3} dominated fluids would be too alkaline and oxidised to be associated with Nifty hydrothermal fluids. The reduced and moderately acidic composition of the Nifty
hydrothermal fluid suggests CH₄(g)+H₂CO₃(aq)/CO₂(g) as the dominant carbon species. SS-Black. Silica contains high concentrations of carbonaceous material, however, no evidence of CH₄(g) was observed in syn-mineralisation fluid inclusions and the absence of pyrrhotite as the dominant sulphide makes it unlikely that high concentrations of CH₄(g) were present in the Nifty hydrothermal fluid. During fractionation, H₂CO₃(aq) and CO₂(g) behaviour is similar making it difficult to differentiate between the species. It is interpreted that the dominant carbon species in Nifty hydrothermal fluid was H₂CO₃(aq).

11.14.4 Temperature Change
The largest equilibrium fractionation in oxygen isotopes is in response to changes in temperature. Syn-mineralisation fluid inclusion trapping temperatures constrain mineralisation to between 290-470°C (median 360°C). The fractionation of δ¹⁸O during a temperature change from 470-290°C is approximately ~4.2%. Over the same temperature range the δ¹³C fractionation effects for Dol-H₂CO₃ and Dol-H₂O are ~0.6% and ~1.1% respectively. A temperature change may account for the shift in δ¹³C but the fractionation of H₂CO₃(aq) and H₂O during a temperature change is negligible and cannot account for the large shift in δ¹³C. This may suggest that CH₄ was the dominant carbon species and this will be examined in a following section. Another complication for temperature change acting as the precipitation mechanism is that the solubility of carbonate decreases with increased temperature therefore a cooling fluid will dissolve rather than precipitate carbonates (Fournier, 1985; Ohmoto, 1986). It is concluded that a change in temperature was not the mechanism responsible for range of δ¹³C values of syn-mineralisation dolomite at Nifty.

11.14.5 Decarbonation
The coupled carbon and oxygen isotope trends formed by decarbonation (volatilisation) during metamorphism show large depletions in heavy δ¹³C (Valley, 1986). Valley (1986) describes Rayleigh volatilisation as the continuous exchange and removal of small aliquots of fluid before the volatilisation of the rest. The isotopic trend from host rock to syn-mineralisation carbonates is very different at Nifty compared to other mineralised occurrences and therefore decarbonation is unlikely to have caused the shift to lower δ¹³C observed at Nifty. There is no evidence of regional decarbonation but the change from SS to S in S/S includes decarbonation i.e. all carbonate is lost. The process of decarbonation during mineralisation at Nifty is likely to have been minor as compared to the volume of introduced fluid and any associate CO₂ and CH₄.

11.14.6 Sulphate Reduction-Methane Oxidation
Another mechanism capable of generating large shifts in carbon isotope ratios is coupled sulphate reduction and methane oxidation. This process initially involves sulphate reduction occurring until sufficient sulphate is removed from the pore water to allow methanogenesis to occur (Reeburgh, 1980). This may allow high concentrations of methane to occur at shallow sediment depths (Burns, 1998). The methane produced may 1) diffuse upward into the overlying sediment, 2) be buried as a dissolved gas, or 3) lost by bubble ebullition (Martens and Klump, 1980). Where the methane diffuses upward into
overlying sediment much of, or all of it is oxidised to CO$_2$, resulting in a narrow zone of coupled sulphate reduction-methane oxidation near the base of the sulphate reduction zone (Martens and Berner, 1977; Reeburgh, 1980; Burns, 1998). Niewöhner et al. (1998) describes the coupled sulphate-methane reaction as:

\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \]  

(1)

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \]  

(2)

Within the zone of sulphate reduction, oxidation of sedimentary organic carbon produces CO$_2$ with values of approximately -20‰. The fractionation of carbon isotopes by CO$_2$ reduction during methanogenesis is approximately -60‰. During methane oxidation $\delta^{13}$C$_{\text{CO}_2}$ values steadily increase and typically reach values of 0 to +5% (Burns, 1998). As discussed above, mineral assemblages constrain the fluid composition as being acid and reduced. The absence of pyrite suggests that CH$_4$ is unlikely to be the dominant carbon species. It further suggests that if sulphate reduction-methane oxidation was the reason for the range of carbon isotope values then the CH$_4$ must have been oxidised to CO$_2$ before reaching the site of Nifly mineralisation.

11.14.7 Fluid Mixing

Fluid mixing is an efficient means of precipitating carbonate and generating large ranges of $\delta^{13}$C. Further evidence of fluid mixing is provided by the salinity range of syn-metamorphosed fluid and these results overlap the fields of carbonate and magmatic fluids perhaps suggesting the mixing of those fluids. Modelling of the isotopic composition of carbonates precipitated from mixing between fluids from two sources with different carbon and oxygen isotope signatures is calculated by mass balance equations (Zheng and Heefs, 1993):

\[ \delta^{13}C_{\text{dolomite}} = \frac{X_A (\delta^{13}C_A + 10^4 \ln \alpha_{\text{dolomite}}^{\delta^{13}C}) + P (1-X_A) (\delta^{13}C_A + 10^4 \ln \alpha_{\text{dolomite}}^{\delta^{13}C})}{P + X_A} \]  

(4)

\[ \delta^{18}O_{\text{dolomite}} = \delta^{18}O_A + 10^4 \ln \alpha_{\text{dolomite}}^{\delta^{18}O} + X_A (\delta^{18}O_A - \delta^{18}O_B) \]  

(5)

where: $X_A$ represents the mole fraction of fluid A in the mixing fluid; $\delta^{18}O_A$, $\delta^{18}O_B$, $\delta^{13}C_A$, $\delta^{13}C_B$ represent the isotopic composition of fluid A and B; $10^4 \ln \alpha_{\text{dolomite}}^{\delta^{13}C}$ is the equilibrium fractionation factor between dolomite and fluid a, b or H$_2$O; fluids a and b can be modelled using the appropriate fluids species and the fractionation factors (Table 11.7), and P is the proportion of carbon content in fluids A and B so that P=X_A C_A.

Equation 4 has three main components, the first $X_A (\delta^{13}C_A + 10^4 \ln \alpha_{\text{dolomite}}^{\delta^{13}C})$ describes the proportion of component A, its isotopic composition and the fractionation of the involved carbon species and mineral. The second term is similar to the first except that it applies to the second fluid and introduces the term P. P accounts for differences in the carbon content between fluids A and B. The third term, the denominator, relates the ratio of carbon isotopes in fluids A and B to the proportion of fluid A. Equation 5 calculates the resultant composition $\delta^{18}O$ of a dolomite precipitated from the fluid mixing.

The equation uses the composition of fluid B added to a value for isotopic equilibrium fractionation
Figure 11.12: Modelled covariance trends of the carbon and oxygen isotope compositions of dolomite precipitated during the mixing of two fluids (A and B). Fluid A is a H$_2$CO$_3$/CO$_2$-bearing fluid modelled at 470°C with initial isotope values of $\delta^{13}$C$\approx$−10.0‰ and $\delta^{18}$O$\approx$−11.0‰. Fluid B is cooler (200°C), HCO$_3$ dominated fluid with an initial composition of $\delta^{13}$C$\approx$+3.4‰ and $\delta^{18}$O$\approx$+8‰. Each calculated mixing trend uses a different P-values where P represents the proportion of carbon content in fluids A & B so that P=Ch/Ca. Xa is the proportion of Fluid A in the fluid mixing and varies between 0-1. When Xa=0 the fluid consists only of fluid B.
during the precipitation of dolomite. This is then added to the proportion of fluid A multiplied by the difference in isotopic composition between fluids A and B.

The isotopic compositions of carbonates precipitated during the mixing of the two fluids are presented as Figure 11.12 and this model has been generated using Equations 4 and 5 (after Zheng and Hoefs, 1993). The fluids used in the mixing model are a low temperature (200°C), HCO₃⁻-bearing fluid with an isotopic composition of δ¹⁸O = +3.4% and δ¹³C = +8% and a hot (470°C), H₂CO₃-bearing fluid with an initial composition of δ¹⁸O = +10% and δ¹³C = −10%. The low temperature HCO₃⁻-bearing fluid, Fluid A, is modelled on the likely composition of Thrombolite Group (proto-seawater δ¹⁸O = −3.7% and δ¹³C = −0.5‰) that has trended toward higher δ¹⁸O due to equilibration with host rock. The second fluid, Fluid B, is hot, H₂CO₃-rich and has an isotopic signature consistent with a hydrothermal magmatic origin (Ohimoto and Rye, 1979). Figure 11.12 shows individual trends that are calculated for P values where P=Ca/Ca of 10, 5, 2, 1, and 0.1.

Although fluid mixing is a viable mechanism for the precipitation of carbonates, and there is evidence for fluid mixing, the modelled trends do not account for the variability in syn-mineralization carbon and oxygen isotope data. A limitation with this model is that the measured carbonate isotopic values plot over a range of calculated fluid mixing trends with different P-values. This implies that the ratio of carbon in fluid A and B varied during the precipitation of the carbonates. The P ratio has a significant effect on the slope of the covariation trend. High P-values tend toward unity at low δ¹⁸O, with large shifts in δ¹³C at higher temperatures (Fig. 11.12) than low P-value trends.

11.14.8 Fluid-Rock Interaction

The pervasive quartz-dolomite alteration of host rocks suggests that significant water/rock interaction has occurred and the amount of quartz precipitated indicates large fluid fluxes. Mass balance equations that model fluid-rock interaction use the general equation (6) of Taylor (1977),

\[
W \delta^{18}O_{\text{fluid}} + R \delta^{18}O_{\text{rock}} = W \delta^{18}O_{\text{fluid}} + R \delta^{18}O_{\text{rock}}
\]

where W and R represent the atom percentage of the isotopic in the fluid and rock respectively and the superscripts i and f are the initial and final isotopic compositions (Taylor, 1977). Modelling of alteration processes relates changes in isotopic signatures during hydrothermal alteration of host carbonates. Zheng and Hoefs (1993) adapted the equation of Taylor (1977) to allow modelling of alteration in open and closed isotopic systems (Equation 7-10). An open system is one where a single fluid plus exchange process occurs (Taylor, 1974) whereas a closed system is one where a complete and continual equilibrium is maintained between fluid and rock (Taylor, 1977; Zheng & Hoefs, 1993). Equations 7-10 apply a mass balance approach to calculate changes in isotopic composition (Zheng and Hoefs, 1993). These equations are based on the initial composition of the carbon species in a fluid and the change resulting during fractionation. This value is subtracted from the difference between the calculated carbonate and the initial rock value. Both the calculated precipitate and difference between the precipitate and initial rock are multiplied by a factor that models the water-rock interaction. Taylor (1977) suggested that because of the equation lack of attainment of isotopic equilibrium among various
Figure 11.13: Modelled covariance trends of the carbon and oxygen isotope compositions of dolomite precipitated during the alteration of a host dolostone with initial values of $\delta^{13}C=+3.2\%$ and $\delta^{18}O=+23.1\%$, and a fluid with $\delta^{13}C=+10\%$ and $\delta^{18}O=+7\%$. The trends are modelled with temperatures of 290 and 470°C with $X\text{H}_2\text{CO}_3=0.1$. Open and closed isotope systems are modelled and the trends calculated are virtually indistinguishable. The majority of the data plots in the area of low W/R ratios. The field for magmatic fluids is taken after Taylor (1997). Inset are trends modelled using the same conditions as above with the exception that the fluid has $\delta^{13}C=-5.0\%$ representing a possible connate brine composition or the mixing of a connate brine with magmatic fluid. See text for discussion of both models.
minerals that separate water/rock ratios should be calculated for each isotopic system, hence W/R and W/R'. Zheng and Hoefs (1993) suggested a simplified approach for theoretical modelling of assuming that W/R=W/R' and that approach is followed here. The isotopic composition may be calculated for an open system using Equations 7 and 8 or a closed system using Equations 9 and 10 (Zheng and Hoefs, 1993):

\[
\delta^{13}C_{\text{dolomite}} = (\delta^{13}C_{\text{fluid}} + \Delta^{13}C_{\text{dolomite}}) - (\delta^{13}C_{\text{fluid}} + \Delta^{13}C_{\text{dolomite}} - \delta^{13}C_{\text{dolomite}}) \cdot e^{-\frac{W}{R} \cdot X_{\text{fluid}}} \quad (7)
\]

\[
\delta^{18}O_{\text{dolomite}} = (\delta^{18}O_{\text{H}_{2}O} + \Delta^{18}O_{\text{dolomite}}) - (\delta^{18}O_{\text{H}_{2}O} + \Delta^{18}O_{\text{dolomite}} - \delta^{18}O_{\text{dolomite}}) \cdot e^{-\frac{W}{R}} \quad (8)
\]

where \(\delta^{13}C_{\text{dolomite}}\) and \(\delta^{18}O_{\text{dolomite}}\) are the initial isotopic composition of fluid or precipitate species; \(\Delta^{13}C_{\text{dolomite}}\) is the equilibrium oxygen isotope fractionation between dolomite and water; \(\Delta^{18}O_{\text{H}_{2}O}\) is the equilibrium carbon isotope fractionation between dolomite and carbon species (Table 11.7); \(W/R\) is the ratio of water to rock interaction (Taylor, 1974; 1977); and \(X_{\text{fluid}}\) is the mole fraction of the carbon species in the fluid.

In a closed system where a complete and continual equilibrium is maintained between fluid and rock (Zheng and Hoefs, 1993) the \(\delta^{13}C\) and \(\delta^{18}O\) of precipitated carbonates is calculated by Equations 9 and 10:

\[
\delta^{13}C_{\text{dolomite}} = \frac{\delta^{13}C_{\text{fluid}} + \frac{W}{R} \cdot X_{\text{fluid}} \cdot (\delta^{13}C_{\text{fluid}} + \Delta^{13}C_{\text{dolomite}})}{1 + \frac{W}{R} \cdot X_{\text{fluid}}} \quad (9)
\]

\[
\delta^{18}O_{\text{dolomite}} = \frac{\delta^{18}O_{\text{H}_{2}O} + \frac{W}{R} \cdot (\delta^{18}O_{\text{H}_{2}O} + \Delta^{18}O_{\text{dolomite}})}{1 + \frac{W}{R}} \quad (10)
\]

Figure 11.13 shows paired \(\delta^{13}C-\delta^{18}O\) trends calculated for the alteration of the Thrussell Group host carbonates by a \(\text{H}_{2}\text{CO}_{3}/\text{CO}_{2}\) dominated fluid with an isotopic composition of \(\delta^{18}O = +10\%\) and \(\delta^{13}C = -10\%\). A mole fraction of 0.1 \(\text{H}_{2}\text{CO}_{3}\) is used in the calculations and the trends are modelled for open and closed isotope systems at 290 and 470°C. The initial composition of host carbonates used in the modelling is the average of Thrussell Group data. The calculated open and closed system trends for each temperature are virtually indistinguishable. The majority of measured syn-mineralisation data plots between the two calculated trends with the majority of data close to the 290°C trend. Data with low carbon isotopic values plot close to high values of water rock interaction. Nity host carbonate data plots in an area that suggests that isotopic exchange has occurred at low water rock ratios.

A comparison of the 290 and 470°C modelled trends (Fig. 11.13) indicates that changes in temperature cause shifts predominantly in the oxygen isotope value. A line joining the same water-rock ratios is therefore a temperature fractionation trend. Changing X, the mole fraction of the carbon species in the fluid, influences the slope of the modelled trend and with higher mole fractions the slope is less. The
isotopic composition of the modelled hydrothermal fluid is within the range defined for primary magmatic H_2O and carbonate brines (Taylor, 1997). At the temperatures experienced by the Throssel Group (sub-greenschist metamorphism) HCO_3^- is unlikely to be the dominant carbon species. Reacting seawater (HCO_3^- bearing) with an acid, in a hydrothermal fluid, will create a CO_2(aq) bearing fluid (eq. HCO_3^- + H^+ ⇌ CO_2(aq) + H_2O). During that reaction the δ^13C isotope value will change due to fractionation. The equilibrium fractionation factor for this reaction at temperatures <290°C (Ohmoto and Rye, 1979) is listed in Table 11.7 and ΔC_COO-CO_2 is shown in Table 11.8. If the reaction occurred at the higher end of the fractionation factors temperature range (Ohmoto and Rye, 1979) then ΔC_COO-CO_2 of ~5.05 to ~6.71‰ could occur. The inset of Figure 11.13 shows trends modelled for the same conditions as above, with the exception that the fluid has a δ^13C of ~5‰.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>ΔC_COO-CO_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.63</td>
</tr>
<tr>
<td>50</td>
<td>6.01</td>
</tr>
<tr>
<td>100</td>
<td>2.82</td>
</tr>
<tr>
<td>150</td>
<td>-0.11</td>
</tr>
<tr>
<td>200</td>
<td>-2.73</td>
</tr>
<tr>
<td>250</td>
<td>-5.05</td>
</tr>
<tr>
<td>290</td>
<td>-6.71</td>
</tr>
</tbody>
</table>

Table 11.6: ΔC_COO-CO_2 for the reaction HCO_3^- + H^+ ⇌ CO_2(aq) + H_2O between 25-290°C. Equilibrium fractionation factor (Ohmoto and Rye, 1979) used to calculate Δ is listed in Table 11.7.

The main difference between the models with different initial δ^13C values is that the trends modelled using a δ^13C of ~5‰ fluid do not extend to the low δ^13C of ~10‰ observed in the area and therefore do not account for the results with light δ^13C values. Mass balance modelling of fluid-rock interaction suggests that this process is capable of generating the trends observed in Nifty syn-mineralisation data when the hydrothermal fluid has low δ^13C values. A magmatic fluid or carbonate brine (or mixture) with low δ^13C can produce the range of δ^13C observed in the deposit by fluid rock interaction. Fluid mixing at the site of carbonate precipitation seems improbable and no other mechanism explains the range of δ^13C values.

11.14.9 Comparison with Other Nifty Carbonate Data

The Nifty pre-mineralisation isotopic data forms a positive trend with one end of the trend overlapping the unaltered host rock field and the other end plots with light carbon and oxygen ratios. The overlap of pre-mineralisation data with the host rock field and the trend of data away from that field suggests that fluid-rock interaction has been involved. Post-mineralisation carbonates were collected from coarse quartz-dolomite and bladed carbonate veins and the timing relationships between these two vein styles are uncertain. The majority of the data is from the coarse quartz-dolomite vein and this data shows a narrow range of oxygen and a large variation in carbon isotope data, with many carbon isotope values
as heavy as the host dolostones and one data-point heavier than the host field. Bladed carbonate result plot in a tight group within the coarse quartz-dolomite vein field. The dominant process or processes involved in the formation of post-mineralisation carbonates can be excluded because, 1) no alteration of vein margins has been observed with late veining and therefore fluid-rock interaction shifts are unlikely, 2) the narrow range of oxygen ratios suggests that changes in temperature were not the dominant precipitation mechanism, however 3) the wide range of carbon ratios with several values heavier than the unaltered host rock field suggest mixing of carbon reservoirs. Therefore two fluid mixing is a potential mechanism for the formation of post-mineralisation carbonates.

1.15 Summary of Carbon and Oxygen Isotope Result
Carbon and oxygen isotope data from host rock and vein carbonates Pre-mineralisation isotopic data forms a positive C-O trend that overlaps the host rock field and at the other end of the trend has δ13C ratios of ~8% and δ18O ranging between +3 to +17%. Syn-mineralisation isotopic data forms a triangle with the apex at δ18O of +17.1%, δ13C of +2.4% and the base at δ13C of approximately +10.3% and δ18O ranging between +14.3 to +21.5%. Post-mineralisation data forms a strong linear trend with a large carbon range of 15.5% and an oxygen isotope range of approximately 6%. δ13C plots with much of the data, as heavy as, the host rock fields and with one data point heavier (approximately 7%).

An estimate of the isotopic signature of Yemeena Basin waters is δ18O of ~3.7% and δ13C of ~0.5%. At the 360°C with reduced and moderately acidic fluids it is interpreted that HCO3-, CO32- and CO2 are the dominant carbon species in the hydrothermal fluid. The processes of temperature change, decarboxylation (volatilisation) during metamorphism, and coupled sulphate reduction and methane oxidation are not favoured as the mechanisms responsible for Nifty syn-mineralisation carbonate precipitation. A mass balance model of carbonate precipitated in response to fluid mixing was examined. Although fluid mixing is a viable mechanism for the precipitation of carbonates the modelled trends do not account for the variability in syn-mineralisation carbon and oxygen isotope data. Therefore this mechanism is not favoured. A second mass balance model of fluid-rock interaction was examined and this model suggests that fluid rock interaction is a viable mechanism for the precipitation of carbonates with δ13C values consistent with Nifty data. It is interpreted that Nifty hydrothermal fluids were HCO3-, CO32- dominant and that fluid rock interaction was the main mechanism responsible for the precipitation of syn-mineralisation carbonates.
Chapter Twelve - Genetic Model and Conclusions

12.0 Introduction

This chapter presents chemical and physical models for the formation of Nifty Cu-mineralization. A genetic model for Nifty-style mineralization is hindered by the lack of comparative deposits and therefore an examination is made using Maroonchylee, Mount Isa and Ruby Creek Cu deposits. The genetic models are followed by the conclusions of this thesis and a summary.

12.1 Chemical Model

12.1.1 Fluid Chemistry and Source

The transport of base metals in hydrothermal fluids is dependent on the thermal and physiochemical characteristics of the hydrothermal fluid and precipitation of base metals needs changes in those conditions to occur. Figure 12.1 presents a logF O₂ - pH diagram at 350°C showing the solubility contours for Cu, and Au, the stability fields for the minerals in the Cu-Fe-O system and the stability fields for K-feldspar, muscovite and pyrophyllite (after Huston et al., 1993). Huston et al. (1993) used a salinity of m NaCl = 3.5 and this value is based on the average of measured fluid inclusion salinity (20 eq. wt.% NaCl). A salinity of 20 eq. wt.% NaCl (and m NaCl) is similar to the salinity measured on Nifty fluid inclusions (average 15 eq. wt.% NaCl). The values of m NaCl=3.0, m NaCl=0.30, and m NaCl=0.05 were estimated from first melting temperatures of fluid inclusions. A value of m NaCl=10⁻¹⁰ was used by Huston et al. (1993) for the solubility of sulphur in the calculation of the logF O₂ - pH diagram. In a later section the validity of using this value for the m NaCl of Nifty hydrothermal fluids is examined.

Nifty geochemical data suggests that Ba has been mobilised from within the ore zone and deposited in carbonate reservoirs of the upper shale. A barite soluble/insoluble boundary is shown in Figure 12.2 and this boundary was calculated by Ohmoto (1972) using m NaCl=x NaCl=10⁻³, m NaCl=10⁻², an ionic strength of 1.0 and at 350°C. Ohmoto et al. (1972) uses a higher mobility of sulphur and lower ionic strength to calculate the barite boundary than those used by Huston et al. (1993). Higher values of x NaCl will shift the barite soluble/insoluble boundary toward lower pH and lower F O₂ values (Brinell and Coffer, 1987). The stability boundaries for calcite and graphite have also been added to Figure 12.2. These boundaries were calculated by Ohmoto (1972) at 350°C using m NaCl=3.0, and an ionic strength of 1.0. Ohmoto (1972) suggests that the uncertainty associated with the calcite soluble/insoluble boundary is probably as much as ±1.0 pH at the 350°C.

Further constraints on the physio- and thermo-chemical conditions of ore precipitation can be gained from the absence of several important indicator minerals. At Nifty magnetite (Fe₄₋₅Fe₂₅O₄) does not occur and pyrrhotite (Fe₇₅Fe₂₅S₅) occurs in trace concentrations. Hexinite is not associated with the syn-mineralisation alteration phase. The main Fe-bearing phases present during mineralisation are
Figure 12.1: Log fO₂-pH diagram at 350°C showing the solubility contours for Cu and Au, the stability fields for the minerals in the Cu-Fe-O system, the stability fields for K-feldspar, muscovite and pyrophyllite (after Haszeldine et al., 1993) and the stability fields for graphite, barite and calcite (after Ohmoto, 1972). Purple and green arrows indicate potential fluid evolution pathways involved in the formation of the Nifty Cu deposit.
chalcopyrite, pyrite and chlorite. During mineralisation pyrite formed as cubical grains in the centre of chalcopyrite veins and for the conditions under which the mineral stability boundaries in Figure 12.1 were calculated, this constrains the mineralising fluid to within the pyrite stable field on Figure 12.1. The absence of bornite and chalcocite further constrains the hydrothermal fluid to logfO₂ of approximately -26 to -29 (Fig. 12.1).

The concentration of carbonaceous material in SS-Black Silica is approximately 5.10% and this is more than could be generated from the dissolution of host carbonate and organic material contained in the Nifty member shale. This carbon surplus suggests an additional source of carbon. Modelling of methane concentration for the conditions specified in Figure 12.1 shows that a carbon minima occurs at approximately logfO₂ of -32 and that the concentration of methane at this fugacity has a mole fraction of 1.6. The mole fraction decreases rapidly with increasing fugacity and in the pyrite stable field the mole fraction of methane is 1.3x10⁻² to 5.3x10⁻¹⁰. Increasing the value of mCH₄ will increase the size of the pyrite field at the expense of the magnetic field and lowering this boundary will allow for minor concentration of CH₄ to be present in the fluid. At the high water/fugacity ratios interpreted to have occurred at Nifty, the CH₄ in the fluid may have acted as a source of additional carbon. This further constrains the composition of Nifty hydrothermal fluids to low fugacity values within the pyrite stable field and that mCH₄ at Nifty was greater than the 10⁻²⁵ used by Hutton et al. (1993).

Figure 12.1 shows the stability fields for pyrophyllite, muscovite, and K-feldspar. No pyrophyllite was observed in thin sections at Nifty. Mica at Nifty consists of muscovite, K-feldspar/muscovite destruction has occurred within the ore zone and K-metasomatism has occurred as a subtle outer halo in hangingwall shales above the ore zone. These features constrain the pH of the hydrothermal fluid to the muscovite stable field in the footwall evolving to K-feldspar stable as it interacts with the dolomitic host rocks. The barite soluble/insoluble boundary (O'Brien, 1972) divides the field of pyrite and muscovite stability into two zones. Ba has been mobilised from the ore zone and footwall and precipitated in the upper shale and pyrite marker bed and this constrained the ore fluid to the barite soluble area of the pyrite and muscovite stable fields. The mobilisation of Ba also suggests that the fluid evolved to increased pH and/or fO₂ resulting in the precipitation of barite. Dolomite occurs in the outer alteration halo and as a late phase in chalcopyrite veins.

Two fluid evolution pathways are shown in Figure 12.1 as purple and green arrows. The purple pathway involves the hydrothermal fluid undergoing an increase in pH and during this change in composition the fluid crosses Cu and Au solubility contours at a high angle. The other fluid evolution pathway, shown in green, suggests that the fluid increased pH and decreased logfO₂. This second pathway is sub-parallel to the Au contours and therefore the fluid will not precipitate Au while precipitating Cu. The green pathway matches the observations from Nifty more closely, specifically the additional carbon from CH₄ and the absence of Au.
12.1.2 Formation Reactions

In the pyrite field (Fig 12.1) a reaction that controls the precipitation of chalcopyrite is:

\[ 4CuCl_{(aq)} + 4FeS_{2} + 2H_{2}O \rightarrow 4CuFeS_{2} + 4Cl^{-} + 4H^{+} + O_{2(g)} \]  

(1)

This reaction suggests the utilization of pre-existing pyrite as a sulphur source. Sulphur isotope data suggests that chalcopyrite did not utilise sulphur from the sedimentary framboidal pyrite, therefore the formation of the chalcopyrite at Nifty involved H_{2}S in hydrothermal fluids rather than only from the host sulphides (Ohimoto and Goldhaber 1997). Therefore, the formation of chalcopyrite is more likely to be based on the reactions:

\[ Cu^{2+} + Fe^{3+} + 2H_{2}S \rightarrow CuFeS_{2} + 3H^{+} + H_{2} \]  

(2)

\[ Cu^{2+} + Fe^{3+} + 4H^{+} \rightarrow CuFeS_{2} + H_{2} + H_{2}O \]  

(3)

Note that the right side of the equation liberates acid and this excess H^{+} will be consumed during the reaction of the hydrothermal fluid with the detritic mudstone by the following reaction:

\[ CuMg(CO_{3})_{2} + 2H_{2}S \rightarrow Cu^{2+} + Mg^{2+} + H_{2}O + 2CO_{2} + O_{2} \]  

(4)

Combining Reactions 2 and 4 results in a possible total reaction of:

\[ Cu^{2+} + Fe^{3+} + CuMg(CO_{3})_{2} + 2H_{2}S \rightarrow CuFeS_{2} + Cu^{2+} + Mg^{2+} + 2H_{2}O + 2CO_{2} \]  

(5)

This reaction governs the dissolution of host rock carbonate and the precipitation of chalcopyrite in the primary sulphide ore body at Nifty.

12.1.3 Missing Au

In a muscovite stable field (Fig. 12.1) between log f_{O_2} of -26 to -29 the solubility contours for Au and Cu are parallel and conditions that are conducive for the precipitation of chalcopyrite should also precipitate Au. Nifty has low and sporadic Au grades. Potential reasons for the absence of high concentrations of Au are 1) the source of hydrothermal fluids may be low in Au or 2) Au may have precipitated earlier (with or without Co).

If the initial composition of the Nifty hydrothermal fluid was constrained within the area of carbon and muscovite stability with log f_{O_2} of approximately -32, and the final composition was within the field of pyrite stable, barite and calcite insoluble, then the resulting fluid evolution pathway would see an increase in log f_{O_2} and an increase in pH. This fluid pathway is sub-parallel to Au solubility contours and therefore Au would not precipitate. However, this fluid evolution pathway would cross Cu solubility contours and Cu would precipitate (green trend on Fig. 12.2). This approach assumes a more reduced initial fluid species and this is valid if a m_{2}S\textsuperscript{2-} higher than the 10\textsuperscript{-24} used to calculate the stability boundaries in Figure 12.2. As discussed above, a higher m_{2}S\textsuperscript{2-} is likely because insufficient carbon is available from host rocks to form the high concentration of carbonaceous material in the 55-Black Silica. Therefore, a hydrothermal fluid with log f_{O_2} of approximately -32 is favoured.
12.2 Physical Model

12.2.1 Model

Figure 12.2A-B presents a model for the formation of the Nifty Cu deposit. Compression associated with the Miles Orogeny caused the expulsion hydrothermal fluids from deep in the Yenena Basin. Fluid expulsion was driven by lithostatic loading due to overlying thrust sheets. Hydrothermal fluids travelled along a basement decollement and then ascended D5 thrust faults toward zones of low pressure. During tightening of the Nifty syncline thrust faulting penetrated carbonaceous and dolomite shales allowing hydrothermal fluids to enter the Nifty member. Early fluid pulses were weakly oxidised and contained low concentrations of base metals. These fluids altered the host rock and precipitated E2-Green Quartz. The composition of later hydrothermal fluid changed, increasing the concentration of base metals and becoming more hot, saline, reduced and moderately acidic. The dominant sulphur species in the hydrothermal fluid was H2S. The change in fluid composition is interpreted to be the result of the fluids being sourced from deeper in the basin or from interacting with an intrusive body. On encountering the Nifty member, hydrothermal fluids reacted with dolomite-dominated beds forming eldolomite alteration textures that in turn are overprinted by siliceous replacement. Alteration occurred parallel to bedding and cross-stratal fluid flow occurs through veining, S3 cleavage and faulting. Chalcopyrite precipitation was controlled mainly by a change in pH caused by the reaction of acidic, hydrothermal fluids with the dolomite-bearing host rock. Minor changes in temperature (370°C to 320°C) and logfO2 (35 to 27) may have contributed to the formation of the deposit.

Ba was remobilised from within the ore zone and precipitated as barite on outer margin of the deposit in the upper shaly and pyritic marker bed. Pb and Zn mineralisation occurs in the uppermost footwall beds, pyritic marker bed, and lowermost hangingwall beds. It is interpreted that sphalerite and galena precipitated in these restricted zones because the hydrothermal fluid was cooler and sulphur deficient by this stage. The pyritic shaly beds acted as the sulphur source allowing precipitation of sphalerite and galena. The acidic hydrothermal fluids also destroyed feldspars in the ore zone and reprecipitated these as sulphide zone of high K in hangingwall shales above the pyrite marker bed. Further from the fluid conduit the hydrothermal solutions no longer had the ability to alter the host rock package.

High temperature and salinity data, δ34S of chalcopyrite with an average of 0% and narrow range of values, pronounced δ13C range of syn-mineralisation vein carbonates, and syn-mineralisation Fe-enriched apatite, suggests the involvement of a magmatic fluid. The leaching of evaporite-bearing units can generate the high salinity, however this would result in positive δ34S values and more oxidised mineral assemblages (sulphide/sulphate boundaries on Fig. 12.2). As no intrusions of an appropriate age has been observed in the Paterson Orogen, a more likely origin for the magmatic signature is that the hydrothermal fluids leached sulphur and other components from igneous units deep in the basin.

Figure 12.3 shows quartz-dolomite alteration in the Nifty footwall beds. Footwall beds are dominated by chlorite, pyritic, and carbonaceous shaly with minor micaceous sandstone and dolomite. Carbonate
Figure 12.2: Model for the formation of Cu mineralisation at the Nifty Cu Deposit. Hot, saline, reduced and acidic fluids ascend D2 thrust faults and enter the carbonaceous shales and dolomitic mudstones of the Nifty member. The hydrothermal fluid reacts with the dolomitic component of the Nifty member precipitating Cu. Further from the fluid conduit, in cooler and sulphur-rich pyritic shales, Pb and Zn is precipitated.
beds in the deposit footwall are likely to be mineralized and in THRD780, below the main ore body, zones of weak alteration and Pb-Zn mineralisation are observed. The thrust conduit model proposed above suggests that there is the potential for Cu concentration in the carbonate-rich units deeper in the footwall beds below the Nitty Cu deposit.

12.5.2 Examples of Thrust Induced Fluid Flow

Oliver (1986) presented a hypothesis where continental margins in zones of convergence are buried beneath thrust sheets. Burial expels fluids from the margin into the foreland basin and continental interior. Oliver (1986) described the thrust sheets as acting like a great squeegee that drive fluids ahead of it. Silson et al. (1975) and Silson (1981, 1987) proposed a method of fluid flow by seismic pumping where pore pressure increases until it exceeds lithostatic pressure causing hydro-fractures to open and allowing pore pressure to drop. Repeated cycles of seismic pumping are interpreted to move large volumes of fluid during deformation (Silson et al., 1975; Silson, 1981, 1987; Cathles and Smith, 1983). Other fluid flow mechanisms which have been suggested are gravity-driven flows from topographical highs (Garven, 1985; Bettske, 1986) or buoyancy-driven fracture flows (Steem et al., 1987; DeLoulde and Turcotte, 1989). Hydro-mechanical modelling of tectonically driven groundwater flow has demonstrated the feasibility of compression causing regional-scale fluid flow (Cathles and Smith, 1983; Ge and Garven, 1992, 1994).

In terms of Oliver's (1986) model, the eastern part of the Paterson Orogen (including the Throssell and Lamill Groups) are overridden by thrust sheets from the north-east and connate brines are expelled from buried sediments. These brines interact with igneous-derived sediments in the basement. In the zone between the basement and foot and thrust belt sheets a shallow foreland basin, represented by the Tarrawah Group, is formed.

Examples of thrust induced fluid flow are the Mississippi Valley-type Pb-Zn deposits, the Kupferschiefer Cu deposit and late Cu mineralisation at the White Pine deposit. Although the fluid composition of Mississippi Valley-type and sediment-hosted stratiform copper are different from Nifty, the mechanisms responsible for fluid movement are similar to those proposed for Nifty. The formation of Mississippi Valley-type Pb-Zn deposits has been associated with expulsion of basinal brines during sediment compaction (Jackson and Bose, 1967) or tectonic activity (Cathles and Smith, 1983; Sangster, 1989). Deposits are commonly associated with pinchouts surrounding domal structure, basin growth faults, and near shore reefs. Mineralising fluids are typically 100-150°C with high salinity fluids (10-30 eq. wt% NaCl), and with stable isotope characteristics similar to modern oil field brines (Anderson and MacQueen, 1987). The Kupferschiefer Cu deposits occur in pyritic black shales of the lowermost unit of the Late Permian Zechezeit marine evaporite sequence (Cathles et al., 1993). Unconformably below the Zechezeit Formation were brine-saturated oxidised volcanics and sediments of the early Permian Rotliegende sequence (Wagner et al., 1980; Jowett and Jarvis, 1984; Jowett, 1986). Ostenpolski (1989) described Kupferschiefer mineralisation as forming when oxidised
metalliferous chloride Rotliegendes formational waters were introduced to organo-rich sediments that contained biogenic sulphides and pyrite. Direct contact of red beds with reduced depositional site allowed the mixing of metal bearing basinal brines with H$_2$S-bearing interstitial waters of the unconsolidated Kuferschiefer (Oszczepalski, 1989). Compactive expulsion of ore-forming fluids occurred up boundary faults during and shortly after deposition of the host sediments. Fluid expulsion was caused by the loading of oxidised basin sediments with Kupferschiefer shales and Zechestein marine evaporitic sequences (Jewett, 1986; Oszczepalski, 1989; Cahles et al., 1993). Musk et al. (1992) proposed a two stage, Cu mineralisation model for the White Pine deposit in northern Michigan. During the first, main stage of mineralisation a sediment-hosted strataform Cu deposit formed during early diagenesis. Musk et al. (1992) suggested that syn-sedimentary faults may have provided the fluid conduit for Cu-bearing brines from red-bed of the Copper Harbour Conglomerate into enter reduced shales of the Nonesuch Formation. The second stage of Cu mineralisation was synchronous with thrust faulting and introduced additional Cu into the White Pine ore body (Musk et al., 1992).

12.3 Deposit Comparison

Table 12.1 lists summary data from deposits and prospects in the Paterson Orogen. Smith (1996) interpreted Warrabarty formation to have occurred before regional D$_2$. The interpreted timing of mineralisation at Nifty, Marouchehyde and Telfer is syn-D$_2$ and another common feature is that these three deposits are all Cu-rich systems hosted in low-metamorphic grade rocks (Table 12.1). Telfer has high concentrations of Au whereas Nifty and Marouchehyde do not. The interpreted composition of hydrothermal fluids associated with Nifty, Marouchehyde and Telfer mineralisation are similar, reduced, low log$_{10}$, high temperature and salinity (Table 12.5). The interpreted pH of hydrothermal solutions ranges (Table 12.1) from near neutral to mildly acidic (Reed, 1996), acidic to mildly alkaline (Rowins 1994; Rowins et al., 1997, 1998), to acidic (this study).

Mineralisation at Marouchehyde is interpreted to result from an increase in the activity of H$_2$S and decrease in log$_{10}$O$_2$ (Reed, 1996). The dispersed nature of mineralisation at Marouchehyde suggests that this deposit may have lacked an efficient fluid focusing mechanism. Reed (1996) proposed a model whereby Cu-bearing fluids utilised structurally generated pathways to move into zones of high strain and low mean stress. Reed (1996) suggested that the Marouchehyde lacked a focusing mechanism and that the fluid was sulphur deficient. Descriptions of the alteration at Telfer (Rowins, 1994; Rowins et al., 1997, 1998) lack detail on which to make accurate comparisons, however available descriptions of the silicate alteration and sericite-carbonate alteration suggest possible similarities to Nifty. Telfer fluid inclusion data indicates similar homogenisation temperature to Nifty but a higher salinity (Table 12.1) was measured (Table 12.3). Telfer sulphur isosues have a narrow peak at +6% which is heavier than the B$_{188}$ at Nifty (Table 12.3). Smith (1996) states that Pb-Zn mineralisation at Warrabarty occurred before the onset of D$_{32}$ deformation and that the main alteration features are deformation, brecciation and the development of veining. The early timing of Warrabarty mineralisation makes it unlikely that there would be similarities in the mechanism and fluids responsible for the alteration of
<table>
<thead>
<tr>
<th></th>
<th>Nifty<strong>D</strong></th>
<th>Marocchondere<strong>M</strong></th>
<th>Warrarity<strong>D</strong></th>
<th>Telfer<strong>MA</strong>/LUM<strong>D</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Age of Host Rocks</strong></td>
<td>Upper Broadhurst Fms</td>
<td>Upper Broadhurst Fms</td>
<td>Upper Broadhurst Fms</td>
<td>Telfer Fms, Lamal Group</td>
</tr>
<tr>
<td>Deposit size</td>
<td>Oxide 12.2Mt@2.52% Cu</td>
<td>Oxide 14Mt@ 1.6% Cu</td>
<td>Oxide 14Mt@ 0.5% Cu</td>
<td>4Moz. Au produced since 1977, current resource <a href="mailto:175Mt@1.4g">175Mt@1.4g</a>/t Au</td>
</tr>
<tr>
<td>Styles of Mineralisation</td>
<td>Stratiform replacement and Cu vein</td>
<td>Stratiform disseminated Cu</td>
<td>Carbonate replacement breccia, vein, and zones of disseminated to massive Zn and Pb sulphides</td>
<td>Series of vertically stacked, stratiform to stratiform gold-copper reefs linked by zones of stockwork and sheared veinteins</td>
</tr>
<tr>
<td>Host Rock Lithology</td>
<td>Carbonaceous shale and dolomitic mudstone</td>
<td>Carbonaceous and dolomitic shale</td>
<td>Dolomite</td>
<td>Calcareous, argillaceous, and locally carbonaceous silstone, sandstone and dolomitic rocks</td>
</tr>
<tr>
<td>Metamorphic Grade</td>
<td>Greenschist</td>
<td>Greenschist</td>
<td>Greenschist</td>
<td>Lower to sub-greenschist facies</td>
</tr>
<tr>
<td>Host structure</td>
<td>Syncline</td>
<td>Syncline</td>
<td>Syncline</td>
<td>In enchelon asymmetric doubly plunging anticline</td>
</tr>
<tr>
<td>Element zonation</td>
<td>Cu - Fe - Zn - X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Isotope</td>
<td>Host rock +0.4% to +4.9%</td>
<td>Host rock +0.3% to +4.1%</td>
<td>Host rock -0.8% to +6.1%</td>
<td>Host rock -1.4% to +3.1%</td>
</tr>
<tr>
<td></td>
<td>Pre-min -7.5 to 3.6%</td>
<td>Syn-min -10.3 to 2.4%</td>
<td>Dolomite B -0.8% to +6.8%</td>
<td>Early stage -4.7 to +0.9%</td>
</tr>
<tr>
<td></td>
<td>Syn-min -9.9 to 6.7%</td>
<td></td>
<td>Grey stage dol +0.4% to +6.3%</td>
<td>Main stage -5.4 to +3.4%</td>
</tr>
<tr>
<td></td>
<td>Post-min +9.9 to 6.7%</td>
<td></td>
<td>White stage dol +0.9% to +4.5%</td>
<td>Late stage -5.4 to -0.1%</td>
</tr>
<tr>
<td>Oxygen Isotope</td>
<td>Host rock +18.8% to +21.4%</td>
<td>Host rock +19.3% to +27.1%</td>
<td>Dolomite B -23.4% to -28.4%</td>
<td>Host rock +22.8% to +36.9%</td>
</tr>
<tr>
<td></td>
<td>Pre-min +13.5% to +20.1%</td>
<td>Syn-min +18.3% to +27.3%</td>
<td>Grey stage dol +21.7% to +27.8%</td>
<td>Early stage +13.3% to +18.1%</td>
</tr>
<tr>
<td></td>
<td>Syn-min +14.3% to +21.5%</td>
<td></td>
<td>Whole stage dol +16.7% to +27.5%</td>
<td>Main stage +13.0% to +26.4%</td>
</tr>
<tr>
<td></td>
<td>Post-min +13.5% to +21.5%</td>
<td></td>
<td></td>
<td>Late stage +12.9% to +26.2%</td>
</tr>
<tr>
<td>Sulphur Isotopes</td>
<td>Fe/Ni py +4 to +6%</td>
<td>Ni/Fe py +1.5 to +20.4%</td>
<td>Whole stage dol -6.9% to +16.0%</td>
<td>Enriched to -23.8% to +10.1%</td>
</tr>
<tr>
<td></td>
<td>Fe/Ni py +16 to +27%</td>
<td>Grey stage dol +1.5 to +20.4%</td>
<td></td>
<td>Main domain +1.3% to +9.3%</td>
</tr>
<tr>
<td></td>
<td>Sulfur py -20 to -6%</td>
<td></td>
<td></td>
<td>West dome -4.0 to +6.8%</td>
</tr>
<tr>
<td>Geochemical associations</td>
<td>Enriched in Cu, SiO2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluid Inclusion</td>
<td>T&lt;sub&gt;i&lt;/sub&gt; 200-367°C, median 268°C, T&lt;sub&gt;g&lt;/sub&gt; 270-457°C, median 338°C, 8-27 eq. wt% NaCl, median 15 eq. wt% NaCl, T&lt;sub&gt;g&lt;/sub&gt; 178-454°C median 257°C, T&lt;sub&gt;l&lt;/sub&gt; low temp 165-205°C, T&lt;sub&gt;l&lt;/sub&gt; high temp 215-245°C, grey stage-dol, T&lt;sub&gt;g&lt;/sub&gt; 227-277°C, 15-26 eq. wt% NaCl, White stage, T&lt;sub&gt;g&lt;/sub&gt; 265-395°C, 15-32 wt% NaCl and 2-6 eq. wt% CaCl&lt;sub&gt;2&lt;/sub&gt;, T&lt;sub&gt;l&lt;/sub&gt; Type A 225-250°C, 20-35 eq. wt% NaCl, Type B&amp;C 350 to 450°C, 35-54 eq. wt% NaCl, Type D&amp;E 265-417°C.</td>
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<td>-------------------------------------------------</td>
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<tr>
<td>Fluid Composition</td>
<td>Reduced (pyrite stable) likely to be logarithmic, T&lt;sub&gt;g&lt;/sub&gt; 178-454°C, near neutral to mildly acidic, reduced (log F&lt;sub&gt;p&lt;/sub&gt; = -30), Reduced, pyrite stable, Low F&lt;sub&gt;P&lt;/sub&gt;, reduced, Fe stable, Hm, mag, and sulphate absent, F&lt;sub&gt;p&lt;/sub&gt; above CO&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;4&lt;/sub&gt; boundary, pH acid to mildly alkaline.</td>
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</tr>
<tr>
<td>Depositional Mechanism</td>
<td>pH and F&lt;sub&gt;p&lt;/sub&gt; increase during fluid rock interaction, cooling may have had a minor role, Increase in pH&lt;sub&gt;H&lt;/sub&gt;S and decrease in log F&lt;sub&gt;p&lt;/sub&gt;, Increase in pH.</td>
<td>Coolings, dissolution, and changes in pH and F&lt;sub&gt;p&lt;/sub&gt; due to fluid mixing and interaction with host rock.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alteration features</td>
<td>Anderson, this study, Anderson et al., 1997; Reed (1996); Reed et al. (1995); Smith (1995); Goelz, 1987; Goelz and McNaughton, 1989, 1990; Goelz et al., 1989, 1991; Rowins (1994); Rowins et al. (1997, 1998).</td>
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</table>
host rocks. Smith (1996) concluded that mineralisation occurred because of externally \textit{supplied} fluids dissolving marine carbonates which resulted in an increase of pH. Oxidation and/or hydrolysis of reduced carbonaceous matter in sedimentary host rocks was also interpreted to be important in the mineralising process. Mineralisation during D$_{50}$ at Nifty, Moonta hydrotype, and Telfer provide strong evidence of regional-scale base metal (and in Telfer's situation, Au) fluid movement during that deformation event.

Table 12.2 presents a second series comparative summary data from the Paterson Orogen, Zambian Copperbelt, Western Succession of the Mount Isa Inlier, and Ruby Creek. The Nifty Cu deposit was discovered using a red-bed Zambian model (Haynes et al., 1996). Many features reported for Zambian Copperbelt deposits are similar to those observed at Nifty (Table 12.2) however there are significant differences. Sediment-hosted stratiform Cu deposits are thought to form in anoxic, paralic marine (or large-scale saline lacustrine) sedimentary rocks that overlying typically red, continental classic sedimentary rocks (Kirkham, 1989). Timing of mineralisation has been a topic of discussion for a considerable time with a syn-diagenetic timing presently favoured (Kirkham, 1989). Sediment-hosted stratiform Cu deposits are interpreted to occur at low temperatures where oxidised Cu-bearing brines precipitate Cu – Pb – Zn at a redox boundary between oxidised rocks and overlying reduced rocks. A sediment-hosted stratiform Cu deposit model is inappropriate for Nifty because the model suggests a diagenetic timing of mineralisation, low temperature of formation, oxidised Cu-bearing hydrothermal fluids, and a spatial association with a redox boundary. These features do not occur at Nifty.

Ruby Creek and Mount Isa have been suggested as analogues for Nifty-style mineralisation (Waring et al. 1998). Summary data from Ruby Creek and Mount Isa is presented in Table 12.2. Hitzman (1983, 1986) suggested that two fluids of different isotopic composition were responsible for the hydrothermal carbonates at Ruby Creek and that a change in temperature was the main Cu precipitation mechanism. The hydrothermal dolostone-hosted ore body and two stage alteration scheme described for Ruby Creek (Hitzman, 1983, 1986; Bernstein and Cox, 1986) is not consistent with observations of alteration and mineralisation textures at Nifty. Heinrich et al. (1989) and Andrews et al. (1989) suggested that Mount Isa fluids were externally derived, weakly CH$_4$-CO$_2$ bearing, NaCl-rich, reduced fluid at high fluid/rock ratios over small temperature range (Table 12.2). Fluid originated as a highly evolved basinal brine or an evaporite-derived metamorphic fluid (Heinrich et al., 1989). The Mount Isa alteration scheme appears to have the most similarities to that of Nifty alteration. Both deposits have a zonal sequence of alteration arranged about high grade Cu and early syn-mineralisation alteration textures being overprinted by later, more intense textures. A significant difference between the deposits is the extent and timing of Pb-Zn mineralisation. At Mount Isa it is suggested that large-scale Pb-Zn mineralisation formed during an earlier, separate magmatic event than Cu mineralisation (e.g. Waring, 1999) while at Nifty Pb and Zn occurs in minor, scattered concentrations in pyrite-rich beds of the outer alteration halo. At Nifty ore textures indicate that Pb-Zn occurred after framboidal pyrite and during later quartz alteration and the precipitation of quartz, pyrite and chalcopyrite.
<table>
<thead>
<tr>
<th></th>
<th>PATERNOSTER OROGENY, WA</th>
<th>ZAMBIA COPPERBELT</th>
<th>MOUNT ISA</th>
<th>RUBY CREEK, ALASKA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age of Host Rocks</td>
<td>Pale Proterozoic (poorly constrained)</td>
<td>Late Proterozoic</td>
<td>1.6 Ga-1.7 Ga</td>
<td>Middle Devonian</td>
</tr>
<tr>
<td>Deposit Size</td>
<td>Nifty - oxide 12.2 Mt @ 2.5% Cu and sulfide 26.3 Mt @ 4.6% Cu</td>
<td>Konkola - 53.5 Mt @ 4.06% Cu (P), 51.8 Mt @ 3.82% Cu (R), 421.0 Mt @ 3.06% Cu (R)</td>
<td>Mount Isa 255 Mt @ 3% Cu</td>
<td>100 Mt @ 1.2% Cu</td>
</tr>
<tr>
<td></td>
<td>Telor</td>
<td>Nchanga - 203 Mt @ 5.03% Cu (P), 112.2 Mt @ 3.96% Cu (R), 197.0 Mt @ 2.22% Cu (R)</td>
<td>Mount Oxide 28 Mt @ 0.5% Cu</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Manyuchindu - oxide 14 Mt @ 1.6% Cu and sulfide 140 Mt @ 0.5% Cu</td>
<td>Chambishi - 33.9 Mt @ 2.88% Cu (P), 25.5 Mt @ 2.79% Cu (R), 43.4 Mt @ 2.38% Cu (R)</td>
<td>Lady Anne, Plying Pig 6.4 Mt @ 1.4% Cu</td>
<td>Numerous smaller deposits, Mount Kelly, Esperanza, Redbank, Cooley Hill,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chilula - 11.1 Mt @ 4.33% Cu (R)</td>
<td></td>
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<td></td>
<td></td>
<td>Mulungu - 208.1 Mt @ 3.5% Cu (P), 86.8 Mt @ 3.01% Cu (R), 157.0 Mt @ 2.95% Cu (R)</td>
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<tr>
<td></td>
<td></td>
<td>Ndola - 178.2 Mt @ 3% Cu (P)</td>
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<td></td>
<td></td>
<td>Luanshya - 213.6 Mt @ 2.91% Cu (P), 41.9 Mt @ 2.41% Cu (R), 19.9 Mt @ 2.61% Cu (R)</td>
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<tr>
<td></td>
<td></td>
<td>P = production, R = reserves, 2nd</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>reserves sources 1 April 1985</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tectonic Setting</td>
<td>Overall plate convergence but with possible local rift-basin development.</td>
<td>Continental rift</td>
<td>Either, evolving continental margins, or intraplate continental rift</td>
<td>Transitional between carbonate platform and shale basin</td>
</tr>
<tr>
<td>during host rock</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Host Rock</td>
<td>Lamfil and Thornewell Gp of the Yenner Supergroup, Cu mineralisation only in carbonaceous beds of the underlying sequence.</td>
<td>Kasanga System of pyritic, marine of continental Ore Shale and the upper beds of the underlying sequence</td>
<td>Carbonaceous dolomitic shale of the Urquhart Shale, Mount Isa Group</td>
<td>Carbonaceous dolomitic dolostone breccia of the Breite carbonate sequence</td>
</tr>
<tr>
<td>Metamorphic Grade</td>
<td>Lower greenschist</td>
<td>Low-grade greenschist</td>
<td></td>
<td></td>
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<tr>
<td>-------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Lamal and Throssell Group green-schists and Radull Complex amphibolite</td>
<td>Lower greenschist</td>
<td>Low-grade greenschist</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basement</td>
<td>Lithostratigraphic units formed by the Radull Complex and granite-greenstone and volcanic rocks of Pilbara Supergroup</td>
<td>Eastern Creek Volcanics</td>
<td>Kogolukitok shist</td>
<td></td>
</tr>
<tr>
<td>Volcanics</td>
<td>No volcanic rocks in Zaahia Derrymore beds</td>
<td>Eastern Creek Volcanics, numerous tuff marker beds</td>
<td>Extensive, footwall and hangingwall, numerous tuff marker beds</td>
<td></td>
</tr>
<tr>
<td>Styles of Mineralisation</td>
<td>Metamorphic Cu-Nifty [\text{Epigenetic Cu-Macroclay} ] [\text{Stratiform Cu-Rainbow} ] [\text{U unconformity-Kimtyni} ] [\text{Cu-Au-Yeller} ] Pb-Zn-Warrabary, Moses Chew Cu-Pb-Au-Goosewacket.</td>
<td>Mt Isa - Metamorphic sediment-hosted [\text{Minnominath - Structurally controlled} ]</td>
<td>Fracture controlled</td>
<td></td>
</tr>
<tr>
<td>Mineralogy</td>
<td>Oxide [\text{Cu, Pb, Zn} ]</td>
<td>Rossing and Kontola affected by supergene processes</td>
<td>A. dol-organite B. Fe-Fe-dol-py-pyr-cyano-org C. dol-cal-py-Cu-sp-Ba-mica</td>
<td></td>
</tr>
<tr>
<td>Alteration features</td>
<td>Nifty[\text{Zoned quartz-dolomite with high illicite and central core} ] Macroclay - none reported</td>
<td>Zoned silica dolomite</td>
<td>Early dol + py (A and B dolostones) and later fracture controlled Cu mineralisation (C assemblages)</td>
<td></td>
</tr>
<tr>
<td>Carbon Isotopes</td>
<td>See Table 12.1</td>
<td>Kontola [\text{Host rocks -2 to 0%}}] [\text{silica-dolomite -8 to -3%}}] [\text{Postwall -4.2 to -9.7%}}]</td>
<td>Grey dolomite -13.6 to +21.5% B dol: +1.8 to +30.3% C carbonate +18.8 to +33.6%</td>
<td></td>
</tr>
<tr>
<td>Oxygen Isotopes</td>
<td>See Table 12.1</td>
<td>Kontola [\text{Host rocks +20 to +22%}}] [\text{silica-dolomite +10 to +12%}}] [\text{Postwall 20.82 to 26.35%}}]</td>
<td>Grey dolomite -13.6 to +21.5% B dol: +1.8 to +30.3% C carbonate +18.8 to +33.6%</td>
<td></td>
</tr>
<tr>
<td>Sulphur Isotopes</td>
<td>See Table 12.1</td>
<td>Kontola [\text{Fg, bedded Py +4.9%}}] [\text{Fg, pyrd Py -9 to +15%}}</td>
<td>Host rock -23.2 to +7.7% Cu sulphides -7.3 to +1.6%</td>
<td></td>
</tr>
</tbody>
</table>
Waring et al. (1998) pondered on a "most puzzling" feature:

"...common to both Mount Isa and Nifty, is the spatially and texturally distinct Cu ore occurs with stratiform-diagenetic pyrite and Pb-Zn-Ag mineralisation. This clear association has been difficult to explain by just coincidence by those advocating, at Mount Isa, two giant ore systems next to each other, but separated by about 150Myr and a major orogenic event (Page and Bell, 1986; Perkins et al., in press). This association, and the comparative rarity of Mount Isa type Cu deposits, are best rationalised by processes in which the specific geochemical, mineralogical and/or mechanical properties of the rock created by the early diagenetic Pb-Zn-Ag system were required in some way to be essential triggers or controlling factors for later copper mineralisation."

Nifty does not have associated Pb-Zn-Ag mineralisation, however Pb and Zn are present in minor concentrations. In the Throssell Group the equivalent to Mount Isa Pb and Zn is Warnarbarry and this deposit is not spatially related to Nifty except that they are in the same basin. Waring et al. (1998) also suggested that widespread K-feldspar and siderite-sulphide alteration surrounding stratiform Pb-Zn-Ag mineralisation created a site for the preferential development of a metamorphic vein network. They went on to suggest that the vein network formed due to lower temperatures of FeCO₃ decarbonation reactions compared to dolomitic reactions and that the vein networks provided an intricate hydro-fractured path (CO₂ release) for the focusing of retrograde-metamorphic fluids causing copper mineralisation. Waring (1998) suggests that FeCO₃ and K-feldspar anomalous host meta-sediments (metamorphic vein initiation) ± graphite ± pre-existing sulphide associated with early-diagenetic Pb-Zn-Ag mineralisation formed as ground preparation for syn-deformational, late metamorphic Cu mineralization.

From a cursory examination of the Nifty deposit, Waring et al. (1998) suggested that Nifty formed from the mechanism described for Mount Isa. Waring et al. (1998) suggest that an FeCO₃-rich stratigraphic interval close to stratiform pyritic-Pb-Zn mineralisation broadly correlates with the stratigraphic position of strata-bound Cu mineralisation. It was further suggested that narrow planar veins overprinted by course-grained irregular dolomite-chalcopyrite veins are consistent with a similar sequence of metamorphic vein development at Mount Isa (Waring et al., 1998). The interpretation of Waring et al. (1998) for Nifty is not supported in this thesis because 1) there is no significant Pb, Zn or Ag mineralisation at Nifty, 2) textural evidence indicates that the minor Pb+Zn precipitation occurred during chalcopyrite mineralisation, and 3) no FeCO₃-rich stratigraphic interval occurring close to pyrite-galena-sphalerite mineralisation has been observed by WMC Resources Ltd. geologists or during this study. Unlike Mount Isa where syn-tectonic Cu replaces syn-genetic Pb and Zn mineralisation, minor Pb and Zn at Nifty occurred coincident with Cu precipitation. The early planar veins suggested by Waring et al. (1998) are restricted in their distribution to the hangingwall beds and there is no evidence that this vein stage occurred in the Nifty member. Furthermore, the Waring et al. (1998) premise suggests that the concentration of planar veins should increase toward copper mineralisation. Early planar veins do not increase in concentration toward the high-grade core.
Mount Isa has several features in common with Nifty and these features can be summarised as: 1) alteration textures and zonation patterns, 2) interpreted fluid composition, and 3) the association between Cu-mineralisation and deformation. The main differences between Mount Isa and Nifty are: 1) size of the alteration and mineralisation system, 2) that alteration at Nifty is dominated by high concentrations of siliceous alteration, 3) relationship between Pb-Zn and Cu, 4) fluid inclusion data indicates that Nifty fluids are hotter, and 5) Nifty sulphur isotope data has an average of 0%, while 834S at Mount Isa has an average of +9%.

12.4 Conclusions

12.4.1 Nifty-style Mineralisation

The primary sulphide and secondary oxide mineralisation at the Nifty Cu deposit consists of 94Mt @ 1.63% Cu with a cutoff of 0.5%. The deposit is hosted in Proterozoic carbonaceous shale and dolomitic mudstone of the Broadhurst Formation, Paterson Orogen, Western Australia. Mineralisation is hosted in shallowly plunging syncline of carbonaceous and dolomitic shales of the upper Broadhurst Formation. The depositional age of the Broadhurst Formation is constrained to between 1332±21 (Miles and Bagn, 1997) and 816±6Ma (Reed, 1996). Regional metamorphic grade is sub-greenschist facies.

The Broadhurst Formation forms part of the Thrussell Group that unconformably overlies basement rock of the Pilbara Craton and the Rodall Complex. The lowestmost Thrussell Group unit is a thick sequence of the oxidized red bed, Coolbro Sandstone. Conformably overlying the Coolbro Sandstone is the carbonaceous shale of the Broadhurst Formation. The Nifty Cu deposit is hosted in the upper Broadhurst Formation. Local mine sequence stratigraphy consists of the footwall beds, Nifty member, pyritic marker bed, and hangingwall beds. The footwall beds consist of chloritic and pyritic shales. The Nifty member is a thick package of interbedded fine-grained, laminated, pale grey, dolomitic mudstone and blue-black, carbonaceous shale. The uppermost units of the Nifty member contain higher concentrations of pyritic shale, pseudomorphs of evaporitic minerals, and minor dolomitic mudstone. Overlying the Nifty member is the pyritic marker bed, which consists of 1-22m of frambooidal pyrite in carbonaceous shale. Hangingwall beds consist of carbonaceous and pyritic shales, and finely laminated dolomitic and calcareous siltite shale units.

The Paterson Orogen is a mobile zone between Archean and Palaeoproterozoic continental blocks and has experienced several events of compressional to tranpressional orogeny. Five deformation events are recognised at Nifty. D<sub>1</sub> include rare variably oriented folds of unknown significance. D<sub>2</sub> produced regional folding and cleavage during north-east, south-west compression. Folds are doubly plunging with axes trending north-east, south-west. D<sub>2</sub> deformation has been dated at 717±5Ma (Reed, 1996). D<sub>3</sub> is an upright folding and faulting event that folds S<sub>D2</sub>. Associated with D<sub>3</sub> is a north-north-east striking, slaty cleavage that is less well developed than S<sub>D2</sub>. D<sub>4</sub> is a complex folding
event with sub-horizontal axial planes and fold axis coaxial to D2. A brittle deformation event, D3, has also been recognised and this event has resulted in fault offsetting of the ore body.

12.4.2 Mineralisation Features

The Nifty Cu deposit occurs as a structurally controlled, chalcopyrite-quartz-dolomite replacement of carbonaceous and dolomitic shale. The main phase of Cu mineralisation occurred during D3 deformation and is associated with a zoned sequence of hydrothermal alteration. Six mineralisation textures were observed; veins, vein networks, breccia matrix, and a progressive sequence of isolated chalcopyrite spots and blebs, to bedding parallel bands, and finally replacement of host rock. Early framboidal pyrite with later chalcopyrite,濑状 pyrite, sphalerite, and galena are the dominant sulphide species. Minor Pb and Zn mineralisation occurs in galena and sphalerite and is preferentially concentrated in the silicified pyritic shale of the lowermost hangingwall beds, pyrite marker bed, and uppermost footwall beds. Galena and sphalerite overprint framboidal pyrite and are associated with bedding parallel silicicic replacement of carbonaceous shale by quartz, pyrite, and chalcopyrite. The distribution of Pb and Zn closely matches that of Cu except that it occurs above the main Cu mineralisation.

Nifty has a simple sulphide mineralogy. The earliest formed sulphide occurs as framboidal pyrite in the footwall beds, pyrite marker bed and hangingwall beds. Another early sulphide is fine-grained sphalerite that is concentrated as lenses in carbonaceous shale above the upper carbonated bed. During the main mineralisation phase galena, sphalerite chalcopyrite and pyrite where precipitated. Chalcopyrite is the only Cu-sulphide observed at Nifty. Sphalerite and galena are preferentially concentrated in pyritic area of the uppermost footwall beds, pyrite marker bed, and lowermost hangingwall beds. Sphalerite and galena are rare in high chalcopyrite areas. Pyrrhotite was not observed during this study however it has been reported in trace concentrations by WMC Resources Ltd. petrologists. No bornite, chalcocite or digenite have been observed or recorded in the primary sulphide ore body.

12.4.3 Alteration

The earliest alteration occurs as thin bands of E1-Fe-Mg Carbonate in hangingwall shales close to the contact with the pyrite marker bed. A diagenetic timing is interpreted for E1-Fe-Mg Carbonate. Two main stages of alteration of occur at Nifty, A pre-D3, unmineralised, siliciaceous alteration, E2-Green Quartz, with minor chlorite + pyrite + haematite + sericite + sulphomelanes, replaces interbedded carbonaceous shale and dolomitic mudstone beds of the upper and lower unit of the Nifty member. The second phase of alteration (syn-D3) is associated with Cu mineralization and occurs as a zoned quartz-dolomite system. The most distal alteration texture consists of a subset K-silifspar metasomatic halo that occurs in hangingwall shales above the ore body. Inward of the K-silifspar halo, carbonaceous and pyritic shale beds are overprinted by cataclastic pyrite, quartz, chalcopyrite, galena and sphalerite. In shales close to these areas, pyrite frambois are pseudomorphed by sphalerite and galena. The
preferential concentration of Pb and Zn in this region is likely to be because of two features 1) this unit is further from possible fluid conduits and therefore fluids reaching this horizon are likely to be cooler, and 2) that the unit has high concentrations of available sulphur. The sulphur depleted fluid on encountering the high concentrations of pyrite utilised this sulphur source to precipitate galena and sphalerite. A narrow horizon of high Ba concentration occurs at the top of the upper shale and base of the pyrite marker bed where Ba has been mobilised from the ore zone and precipitated as barite. Inward is a progressive sequence of interbedded/handed S3-stage hydrothermal Dolomite and unaltered shale beds. The S3-stage hydrothermal Dolomite-Dolomite alteration first appears as spots and veins with 2-
4mm light grey alteration margins in the footwall followed by coalesced spots. An Fe-rich variant of hydrothermal dolomite occurs and minor S3- Chlorite Shale occurs on the distal margins of the Fe-rich quartz-dolomite altered rocks. Further inward and proximal to the highest ore grade is S4-stage Silicified Dolomite and this grades into S5-Black Silica in the centre of the ore body. S5 alteration consists of fine-grained quartz + chalcopyrite + apatite + carbonaceous material and replaces host rock and earlier siliceous alteration and in zones of the most intense siliceous alteration host rock textures have been obliterated. Cu grade has a strong positive correlation with intensity of alteration.

12.4.4 Deposit Geochemical Criteria
A geochemical zoning of Cu→Ba→Pb-Zn→K occurs at Nifty. Cu is confined to zones of quartz-
dolomite alteration and the concentration is Cu is proportional to silicification. Background concentration of Ba in unaltered shales is approximately 130ppm and within S3, S4 and S5 altered zones the concentration of Ba is approximately 70-190ppm. An interval of high Ba concentration (as barite) occurs within the uppermost upper shale and pyrite marker bed and this coincides with a zone with high concentrations of evaporite pseudomorphs. A zone of high K, Th and Pb occurs in hangingwall shales above the Cu ore body. These elements are depleted in S4 and S5 silicified zones suggesting the dissolution of fine-grained feldspars in Nifty member shales and the precipitation in the hangingwall. Mass balance calculations suggest that the concentrations of Al2O3, TiO2 and Zr have remained approximately constant and that there have been increases in most elements with greatest increase of Cu, SiO2, As, Zn, Pb, P2O5 occurring in both shale and dolomitic mudstone.

12.4.5 Genetic Model
During regional D8 compression, fluids were expelled along basement decollagament and D8 thrust faults into the dolomitic and carbonaceous shale of the Nifty member. The Cu-bearing hydrothermal fluid was hot, saline, reduced and moderately acidic. The hydrothermal fluid contained minor concentrations of CH4 and the dominant sulphur species in the fluid was H2S. The hydrothermal fluid reacted with dolomitic beds of the Nifty member resulting in an increase in fluid pH. Minor changes in temperature (370°C-320°C) and logf2 (−31 to −75) may have contributed to the formation of the deposit. During mineralisation, host rocks were altered in a zoned quartz-dolomite system with the
outer zone experiencing dolomite alteration and the centre zone, of highest Cu-mineralisation, siliceous alteration.

12.4.6 Fluid conduit

The location of the mineralising fluid conduit and related thrust fault at Nifty is uncertain because and the lack of drilling deep between the primary and secondary mineralisation and into the footwall below the primary Cu deposit. A further complication in identifying the fluid conduit is that its subsequent deformation is likely to have resulted in fault reactivation and offsetting of early faults. Elevated fluid temperatures will cause a thermal perturbation close to the fluid conduit. Equilibrium fractionation $\delta ^{18}O$ values are influenced by temperature due to and therefore an estimate of the conduits location is provided by low $\delta ^{18}O$ values. A trend of $\delta ^{18}O$ close to the northern limb suggesting that this area may have been hotter. Figure 12.2 shows two thrusts and these faults have been labelled R & T Faults (also see Fig. 3.2). The location of the mineralising fluid conduit is speculative and more drilling close to the northern limb of the deposit, may clarify the exact location and orientation of this conduit.

The proposed genetic model suggests that a decollement acted as the fluid conduit. Another potential conduit is the arkose sands of the Coolburo Sandstone and these would form an efficient aquifer for the passage of fluids from deep in the basin. If fluids were transported in the Coolburo Sandstone then it is likely that they would have been oxidised and at the conditions modelled for Figure 12.2 the Fluid would be capable of carrying high concentrations of dissolved Cu. Precipitation of Cu would occur at a redox boundary and the contact between oxidised Coolburo Sandstone and reduced Broadhurst Formation would provide a suitable boundary. This mechanism is similar to that proposed for Zambian-style Cu deposits (Mendelsohn, 1961; Deehow and Jensen, 1965; Cunningham, 1986; Sweeney et al., 1986; Ahnelt, 1989; Kirkham, 1989; Plumb et al., 1980; Blake, 1987; Richardson and Moy, 1998; Pirson, 1970; Richards et al., 1985) and the Rainbow Cu prospect (Haynes et al., 1993). However in the case of Nifty, the deposit is not at a redox boundary and the Fluid is not highly oxidised.

In modelling basinal brines that formed sediment-hosted Cu deposits, Sverjensky (1989) suggested that fluids in a sandstone aquifer could overwhelm the reaction capacity of the aquifer by destroying all K-feldspar or coating it with reaction products such as kaolinite or quartz. A consequence of this reaction occurring is that the chemistry of the quartz sandstone aquifer would change progressively toward the initial basinal values. This mechanism would allow Nifty hydrothermal fluids to utilise the Coolburo Sandstone as an aquifer and would result in initial and final fluids having different compositions. $\delta _2$ Green Quartz and the weak hematite association of this alteration texture may represent initial fluids before the reaction capacity of the aquifer became overwhelmed and $\delta _1$-SS the initial basinal composition.
Another option is that Nifty hydrothermal fluids did not interact with the Coolbrook Sandstone. This may occur if the Coolbrook Sandstone thins or has undergone a facies change basinward, or the unit has been faulted out. The nearest outcrop of Coolbrook Sandstone is located approximately ten kilometres to the south of Nifty. There is no evidence that the Coolbrook Sandstone occurs in close proximity to Nifty. Deep diamond drill holes have penetrated the deposit to a depth up to 400 m and these drill holes have not encountered Coolbrook Sandstone. Hickman and Clarke (1994) noted in the western and northwestern parts of the Broadhurst map sheet that the Coolbrook Sandstone was 300-400 m thick and to the south-east thinned to 2000 m. The unknown occurrence, extent, and composition of the Coolbrook Sandstone below Nifty or further basinward and the role that this unit may have played as an aquifer is uncertain. A definitive answer as to the nature of the fluid conduit cannot be made because of uncertainties associated with the mineralising fault, decollement location, and composition of the basement.

12.5 Implications for Exploration

This section briefly outlines major implications of this study for exploration in the Yeneena Supergroup and especially the Throssell Group. The Paterson Orogen is a poorly understood region because of the thick cover sequences and this suggests reliance on remote methods such as geophysics.

12.5.1 Regional Scale Targeting

The Paterson Orogen is a highly mineralized and yet poorly explored area. The presence of world-class Cu concentrations at Nifty and Maroochydore and the similarities between Nifty and Mount Isa-style mineralisation suggest that the basin has high potential for yield further Cu deposits. WMC Resources Ltd. exploration focused on a sediment-hosted stratiform copper model that is no longer valid for the Paterson Orogen given evidence from this study. WMC Resources Ltd. focused on searching for Cu–Pb–Zn mineralisation at redox boundaries at the Coolbrook Sandstone and Broadhurst Formation contact and on the basin’s western margin. Nifty mineralisation does not occur at this redox boundary, the hydrothermal fluid is reduced rather than highly oxidised, and mineralisation is associated with D₁ deformation. The majority of mineralised prospects in the Paterson Orogen outcrop or occur under shallow cover. Cu mineralisation at Nifty, Maroochydore, and minor Cu occurrences at Warrabarry and Telfer, are associated with D₂ deformation. These features suggest that outcropping or shallowly covered areas in close proximity to D₂ fold and fault structures have high potential as exploration targets.

Carbon and oxygen isotopes results indicate that 1) Nifty is clearly distinguishable from the host rock field and from other mineralised occurrences, 2) that Nifty isotope data has similarities with Telfer data, 3) isostructural modelling of Nifty carbon and oxygen data suggests that the fluid from which carbonate precipitation occurred has a magmatic signature, and 4) oxygen isotopes show a depletion toward ore similar to the depletion pattern observed at Mount Isa (Wiring, 1987). Carbon and oxygen
Fluid inclusion, isotopic and geochemoical data suggests there is potential for an igneous source of Nifty hydrothermal fluids. This conclusion was not favoured during this study because of the absence of an appropriately aged intrusive body, instead an interpretation of hot fluids leaching material from igneous derived basement is favoured. The potential for an intrusive-related fluid-flow event however, should not be discounted and the circular geophysical feature in the Grevillea area should be considered a potential Teller-style target.

12.5.2 Local scale exploration

Cu mineralization at Mount Isa occurs as a series of ore bodies (500, 600, 1100, 3000 and 3500) along the greenstone contact that acted as the fluid conduit. The similarities of Nifty to Mount Isa-style Cu-mineralisation suggests that the Paterson Orogen has potential for other Cu ore bodies below the existing primary ore body. Although the exact location and orientation of the Nifty hydrothermal fluid conduit is uncertain, the preferential concentration of mineralisation in the keel and north limb of the Nifty syncline suggests that local exploration should concentrate on 1) dolomitic and carbonaceous shales host rocks below the existing ore body, 2) at depth, to the north of the current open pit (east of TND3), and also at the northern limit has minor potential. D3 thrust faults and associated folding to the south of Nifty are also potential exploration targets. Primary sulphide mineralisation is associated with a zoned alteration system. The first indication of ore is the occurrence of the spotty alteration texture of ST-Hydrothermal Quartz-Dolomite and HBB-Alteration margin veins. Alteration typically occurs along bedding and favours dolomitic mudstone units.

12.6 Summary

Geologic, paragenetic, stable isotope, and fluid inclusion data suggest that Cu mineralisation at Nifty occurred during D2 deformation where hot, saline, moderately acidic, and reduced fluids ascended thrust faults from deep in the Yeneena Basin. Fluid expulsion was driven by over-pressureing association with the accretion of D2 thrust sheets. The process of Cu mineralisation is best explained by fluids entered the carbonaceous and dolomitic shales of the Nifty member and Cu precipitated due to an increase in pH and FO2. During mineralisation a zoned hydrothermal, quartz-dolomite alteration halo formed. The Paterson Orogen holds high potential for additional Cu mineralisation.