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Carbonate Isotopic and Major Element Geochemical Exploration Technique

Mt Isa District

ISAMINE

HILTON

North West Lakes

Quartzite

Stony Ck

Native Bee

Isa South

Mt Novit

Report to

MIM Exploration Pty Ltd

C. L. Waring

November 22, 1991

Summary

Isotopic geochemical exploration is most suited to broad scale system definition, because it can detect changes in dolomite isotopic ratios further from mineralisation than any other geochemical technique in the Mt Isa district.

- All dolomite samples from Mt Isa district prospects show major $\delta^{18}\text{O}$ depletion close to Cu mineralisation. Any economic Cu target in the Mt Isa district is also expected to have a large associated $\delta^{18}\text{O}$ depletion halo.
- The isotopic survey proposed is capable of detecting a $\delta^{18}\text{O}$ halo to mineralising hydrothermal systems at a great distance through barren rock (measured >1km, potentially >2kms).
- System definition includes a measure of the size of system. The $^{18}\text{O}_{\text{Dol Sh}}$ depletion halo is directly related to the size of the hydrothermal system that may produce Cu mineralisation. For an economic Cu target there is a **minimum** size $\delta^{18}\text{O}_{\text{Dol Sh}}$ depletion alteration halo directly related to the requirement for sufficient fluid-rock chemical reaction to cause Cu precipitation.

In practice, the characteristics of $\delta^{18}\text{O}_{\text{Dol Sh}}$ distribution enable distinction between the periphery of a major mineralising system from a small scale system. The isotopic method provides a means of categorising sparse dolomite-chalcopyrite veining into small scale systems, or the margins of a much larger perhaps economic systems.

- Isotopic geochemical methods eliminates the “Nugget Effect” (irregular distribution) associated with standard geochemical analysis for Cu (Au). An isotopic anomaly is likely to be much more extensive and **regular** surrounding Cu mineralisation than Cu itself.
- Spurious analyses due to metamorphic effects may be distinguished from isotopic patterns associated with mineralisation.
- Specific areas from Quartzite, Hilton North, and Mt Novit are indicated which suggest potential for economic Cu mineralisation.

1. Introduction

This study is designed to extend the understanding of the previously defined Mt Isa Cu related $\delta^{18}\text{O}$ anomaly, such that carbonate isotopic analyses can be used reliably for exploration purposes.

Prior isotopic analyses were typically from the dolomitic alteration hosting the Cu-orebodies (Smith *et al.* 1978, Heinrich *et al.* 1989, Waring 1990), with a minority of analyses from texturally unaltered dolomitic shale (Waring 1990). These analyses were sufficient to define the full range of ^{18}O depletion surrounding Cu mineralisation (Waring 1990), but not the areal extent or fine subtleties of the spatial distribution. This program addresses these deficiencies and other problems which may be encountered during general application of isotopic exploration techniques.

TABLE 1.	Year Reported	ISAMINE North	S outh	HILTON	NWL	SC, NB, Novit, Qtz, IS.
Smith <i>et al.</i> 1978	1978	23				
Heinrich <i>et al.</i> 1989	1986	29	15			
Valenta 1989	1987			8		
Waring 1990	1986		93		8	
Hannan 1991	1990-91		26			
Waring 1991 (This Study)	1990-91	102	142	78	36	185

Table 1. is a compilation of all carbonate isotopic data sources and locations for the Mt. Isa district.

1.1. Summary of Results from Previous Carbonate Isotopic Work

Initial carbonate isotopic data from the 1900 Cu orebody, northern 200 Cu orebody and adjacent 8, 11 Pb-Zn orebodies (Smith *et al.* 1978) were interpreted in the context of separate early, sedimentary accumulation of Pb-Zn ore and late post - metamorphic emplacement of Cu ore. "These values are interpreted as reflecting isotopic changes induced in original marine carbonates by isotopic exchange during lower greenschist metamorphism" (Smith *et al.* 1978).

Concurrent studies by Heinrich *et al.* (1989), and Waring (1990) also concluded that Cu orebody carbonate isotopic values are the result of interaction with the Cu ore forming hydrothermal fluid.

Heinrich *et al.* (1989) suggested that this ore-forming fluid was syn-metamorphic and formed the Cu orebodies through a multi-stage interaction based on fluid inclusion data. Cu orebody carbonate and silicate isotopic data (Heinrich *et al.* 1989, Waring 1990) suggest concurrent equilibrium formation from a hydrothermal fluid. Multi-stage models (Heinrich *et al.* 1989) are not excluded by the carbonate isotopic data.

Carbonate isotopic data from apparently unaltered dolomitic shales near Lake Moondarra and from exploratory drill holes south of the Cu orebody showed that there is a progressive, consistently large shift from isotopically heavy (20–22‰, ^{18}O enrichment, high $\delta^{18}\text{O}$ values) background dolomitic shales to isotopically light (10–12‰) carbonates associated with Cu ore (Waring 1990). This defined $\delta^{18}\text{O}$ difference of ~10‰ is the basis of the inferred dolomite ^{18}O depletion halo surrounding the Cu orebodies.

Dolomite veins and adjacent dolomitic shales close to, or included within the silica-dolomite alteration envelope have isotopic values that are indistinguishable (Waring 1990). However, further from Cu ore and visible effects of silica-dolomite alteration (recrystallisation and brecciation) there is a difference in $\delta^{18}\text{O}$ between dolomite veins (lighter) and adjacent dolomitic shales of 1.5‰ at 500–700m from Cu ore (Waring 1990). These dolomitic shales up to 1km from percentage Cu mineralisation may show no other indication of proximity to Cu mineralisation (elevated Cu ppm range, or visible dolomite veining) and yet they are partially depleted in ^{18}O due to interaction with the mineralising hydrothermal fluid.

Within the orebody samples, Waring (1990) suggested a trend towards heavier dolomite $\delta^{18}\text{O}$ values going from south to north from a combination of data sources (Waring 1990, and Heinrich *et al.* 1989). An apparent discrepancy between the data sets (Waring 1990) has subsequently been identified as an error in application of acid fractionation factors (Andrew *pers. comm.* 1990) for the Heinrich *et al.* (1989) data. Consequently all Heinrich *et al.* (1989) data has been adjusted by subtracting 1.9‰ for $\delta^{18}\text{O}$. This correction weakens the increasing orebody dolomite $\delta^{18}\text{O}$ south to north trend significantly, although the inferred southern hydrothermal input is further supported by mineralogical data (Waring 1990).

ISAMINE Dolomite Isotopic Data

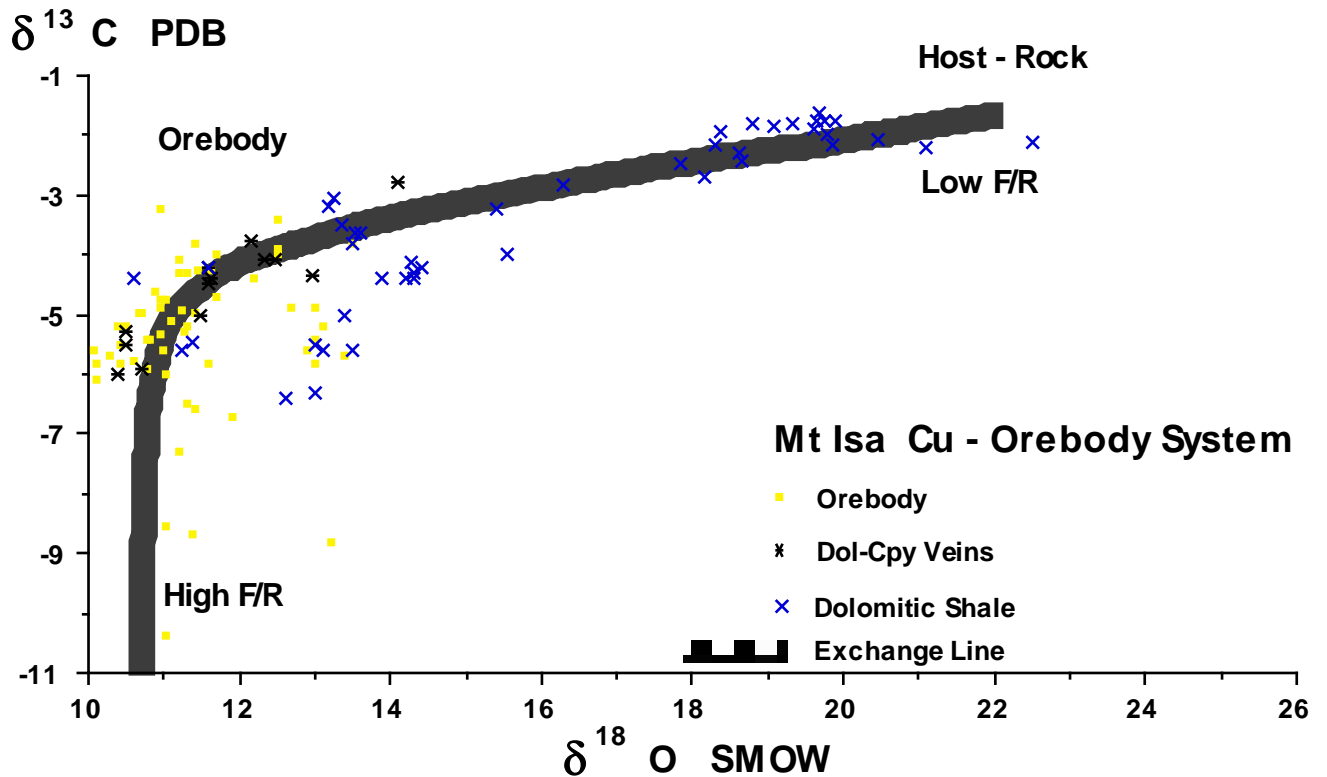


Figure 1.1 ISAMINE environs carbonate isotopic data, from Waring (1990), and corrected Heinrich *et al.* (1989) prior to this study.

This study is aimed at ascertaining whether the same relationships are apparent for other known Cu mineralisation and prospect areas in the Mt Isa district, and how knowledge of the intricacies of the isotopic ^{18}O depletion halo could be used directly in exploration.

1.2 Analytical Method, Correction Procedures and Problems

Mt. Isa district carbonate rocks have been analysed at the University of Queensland Isotope Laboratory by Kim Baublys under the guidance of Dr Sue Golding, and at Monash University, by Dr Ian Cartwright. Details of the analytical procedure are presented in Appendix 1.

An analytical scheme has been designed to give carbonate major element compositions in addition to isotopic analyses. Carbonate major element data is a useful quantitative measure of carbonate abundance, composition and mineralogy. This may be used to help interpret isotope data, and to apply appropriate isotope analytical data corrections due to variable composition and mineralogy. Carbonate major element analysis procedure is designed to suppress chlorite and biotite dissolution whilst achieving quantitative carbonate dissolution prior to AA analysis.

Semi-quantitative X-Ray Diffraction mineral determinations of selected whole rocks from the same dataset includes a biased normalisation procedure, to account for generally weaker

phyllosilicate and exaggerated carbonate measured peak heights relative to the principal quartz reflection.

Three independent CO₂ values (yield from isotopic analysis, implied stoichiometric CO₂ from carbonate major element analysis, and calculated from XRD carbonate abundances) are derived to enable comparison of the different analytical methods.

The full revised dataset with isotopic correction factors, calculated carbonate speciation and composition, XRD mineralogy, sample location and description is presented in the spreadsheets "ISOTOPE".

2. Geological Framework for Interpretation of Isotopic Data

A knowledge of the general Mt Isa district geology and Cu orebody system (Perkins 1984, Heinrich *et al.* 1989, Waring 1990) is assumed for the following discussion of specific aspects which relate to this Isotopic investigation.

2.1 Sample Definition and Petrography

Currently only unoxidised and unleached dolomitic rocks can be analysed with confidence of obtaining primary isotopic values. This limits sampling to drill hole coverage and underground exposure. Sampling of weathered rock and analysis of primary(?) quartz is being investigated concurrently with this study.

There are three basic types of sample used here.

Composite samples are representative of the average rock composition over a long interval of approximately 20m. Core is cut in half, or quarters. One half or quarter of the entire length of core is taken, crushed, split, and a small representative sample is sent for analysis.

Whole Rock (WR) These are spot samples which typically consist of an entire section of $\frac{1}{2}$ core approximately 30cms long, which is representative of the lithology for tens of metres on either side of the sample. Sample spacing down an individual drill hole is approximately 40 - 80m unless there is significant lithological change, or zones of varying vein or deformation intensity. These zones are sampled with greater frequency, particularly for vein / wall-rock relationships. Other features such as light-dark banding in the dolomitic shales are also occasionally sampled. These samples would constitute **whole rock portions (WRP)** with each portion designated as either WRP-D for dolomitic samples or WRP-C for calcitic samples.

Vein (V) These samples consist of vein carbonates only. Wall rock is excluded from the sample. If vein / wall-rock relationships are sought, the WR sample is typically a small sample adjacent to the vein. V-C, and V-D are used to designate vein calcite and vein dolomite.

The underlying goal of the sampling strategy is to maximise spatial coverage, both in areal extent and depth down drill holes for the least number of samples that give a representative sampling. In this respect isotopic values vary less than other geochemical techniques, and require fewer analyses to be representative.

An initial experiment comparing whole rock (minus carbonate, + essentially silicate) $\delta^{18}\text{O}$ above and below the limit of oxidation showed significant differences between the samples. This is presumably because of isotopic exchange with ground water, oxidation, and changes to phyllosilicate mineralogy in near surface samples.

However, if a quartz - only sample could be produced by mineral separation from rock chip samples at a reasonable cost, then surface or near surface rock chip geochemical surveys prior to deep drilling may prove to be a major addition to existing, lesser standard geochemical discriminates.

2.1.1 Composite and Whole-Rock Samples

Most Mt Isa Group rocks are suitable for whole rock isotopic sampling, providing there is some carbonate present. Background carbonate isotopic values (19-22‰ $\delta^{18}\text{O}$, -1- -2 ‰ $\delta^{13}\text{C}$) appear to be independent of stratigraphic position, and have been effectively homogenised isotopically during consolidation, and diagenesis (dolomitisation). Mt Isa Group meta-sedimentary rocks usually contain significant modal dolomite, which varies from greater than 50% for parts of the Native Bee Siltstone to <10% for Breakaway Shale and lower Moondarra Siltstone. Rare siderite also occurs as a diagenetic (?) cement in the more siliciclastic portions of the lower Moondarra Siltstone (Stony Ck, Fi 231). Calcite occurs as a minor disseminated component of dolomitic shale, as distinctive light coloured bands and segregations, and also in veins or vein networks.

Light-coloured calcite segregations form bedding-parallel bands, or sometimes bedding disruptive features that vary in size from 2mm to 10cms wide, with sharp or diffuse boundaries. Calcite in these bands is typically sparry and coarser grained than dolomite in the surrounding rock. Adjacent to strongly developed calcite bands, the rock consists of fine-grained dolomite, phlogopite/biotite, \pm quartz, \pm chlorite. Pyrrhotite laths are also commonly present close to the margin of calcitic bands. Some of these calcitic bands have previously been described in sedimentological terms as ridge and rill structures (Neudert 1984), or as a metasomatic effect, possibly related to mineralisation. The distribution of these calcitic bands together with phlogopite in unmineralised Mt. Isa Group rocks throughout the district, would suggest formation during metamorphism rather than as a sedimentary or metasomatic feature.

Composite samples were taken in conjunction with whole-rock spot samples to gauge the degree of isotopic homogeneity down a drill hole. Composite samples give an effective average composition from which subtle trends in decreasing $\delta^{18}\text{O}$ may be apparent. These trends are masked by the greater “noise” associated with whole rock spot samples, particularly for areas distant from the homogenising effects of the mineralising hydrothermal fluid.

For example, initial sampling (~6 values) and analysis of ISA SOUTH drill hole Ze 541, indicated a regular decrease in $\delta^{18}\text{O}$ from 17‰ near surface, to 13‰ at a depth of 447m, suggesting a depletion pattern analogous to parts of the ISAMINE system. Further spot sampling and inclusion of composite samples showed that there was a high degree of isotopic heterogeneity (see data plot on 25400mN section) in contrast to the isotopically homogenous nature of the ISAMINE system. This false anomaly is attributable to open system metamorphic decarbonation (section 2.2).

2.1.1 Hydrothermal Dolomite Veins vs Metamorphic Calcite Veins

Dolomite, calcite and quartz veins occur irregularly throughout Mt Isa Group rocks, depending on proximity to mineralising hydrothermal systems, and intensity of metamorphic reaction.

Dolomite veins are spatially associated with Cu mineralisation, and often contain minor chalcopyrite close to the Mt Isa Cu orebody system, and at Cu prospects throughout the district. Calcite veins commonly occur in Mt Isa group rocks devoid of mineralisation, and occasionally in the vicinity of Pb-Zn and to a lesser extent Cu mineralisation. Dolomite veins are generally distinguishable from calcite veins on the basis of morphology, grain size, and colour.

Dolomite veins typically have a ptygmatic (meandrine) form caused by syn-tectonic cleavage formation and heterogeneous carbonate dissolution in rock adjacent to the vein. Successive vein forming episodes often cause overprinting of one dolomite vein on another, relatively earlier vein, within a single deformation event. Calcite veins are much closer to planar 2D lensoidal features that typically have parallel sides and are interpreted to be almost totally dilational veins. The relative contribution of dilation versus wall-rock assimilation to dolomite vein formation is difficult to determine, but appears to be considerably higher than for calcite veins.

Dolomite vein grain size is typically saccaroidal with extreme examples of individual grains reaching greater than 1.5cms across. Calcite vein grain size is often microcrystalline.

Colour is perhaps the easiest vein criteria to see in hand specimen. Calcite veins are always white. Dolomite veins are typically off-white to grey, and sometimes display a blueish tinge. Weathered dolomite vein samples show a creamy to brownish colour due to the surface oxidation of the FeCO_3 component.

Exceptions to these generalisations are the rare calcite-dolomite-chalcopyrite veins above the Buck Quartz Fault and talc zones south of 33000mN. Minor calcite inclusions occur in dolomite from the silica-dolomite alteration.

These distinctions are important when dolomite veins imply proximity to Cu mineralisation, and calcite veins are due to district wide metamorphism, albeit heterogeneous.

Figure 2.1 a An anastomosing dolomite vein set. Although vein margins are planar they cannot be rejoined in contrast to a purely dilational vein. The white grains circled are calcite. Sample U250 ISAMINE South.

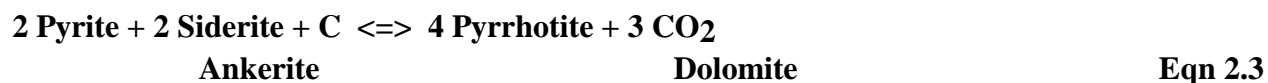
Figure 2.1 b Dilational calcite veins occupying a fold hinge zone. Adjacent to the small fold a zone of intense calcitic micro-veining is developed. This texture is often referred to as “birdswing texture”.

Figure 2.1 c A bedding disruptive calcitic band, showing minor pyrrhotite within the coarser grained calcitic band. Stony Ck Sh 142.

Figure 2.1 d A section of core with a strong calcite band (white) adjacent to strong phlogopite development (pale brown). Stony Ck Sh 142.

2.2 Metamorphism

Unlike the upper greenschist to amphibolite grade metamorphic rocks to the west of the Mt. Isa Fault, the meta-sedimentary rocks east of the Mt. Isa Fault show little obvious metamorphic mineral growth indicative of moderate regional metamorphic grade. However, some subtle indications of metamorphic decarbonation reactions are present that indicate minimum metamorphic grade. One reaction is particularly useful in this respect ;



To demonstrate that these reactions proceeded during isochemical metamorphism independently from hydrothermal Cu system metasomatism, evidence for these reactions were sought from unaltered areas away from Mt. Isa mine. Features suggestive of this reaction have been found from all areas examined; the Isa South area (east of Native Bee), North West Lakes (north and west of Lake Moondarra), and through the Mt. Isa - Hilton strip.

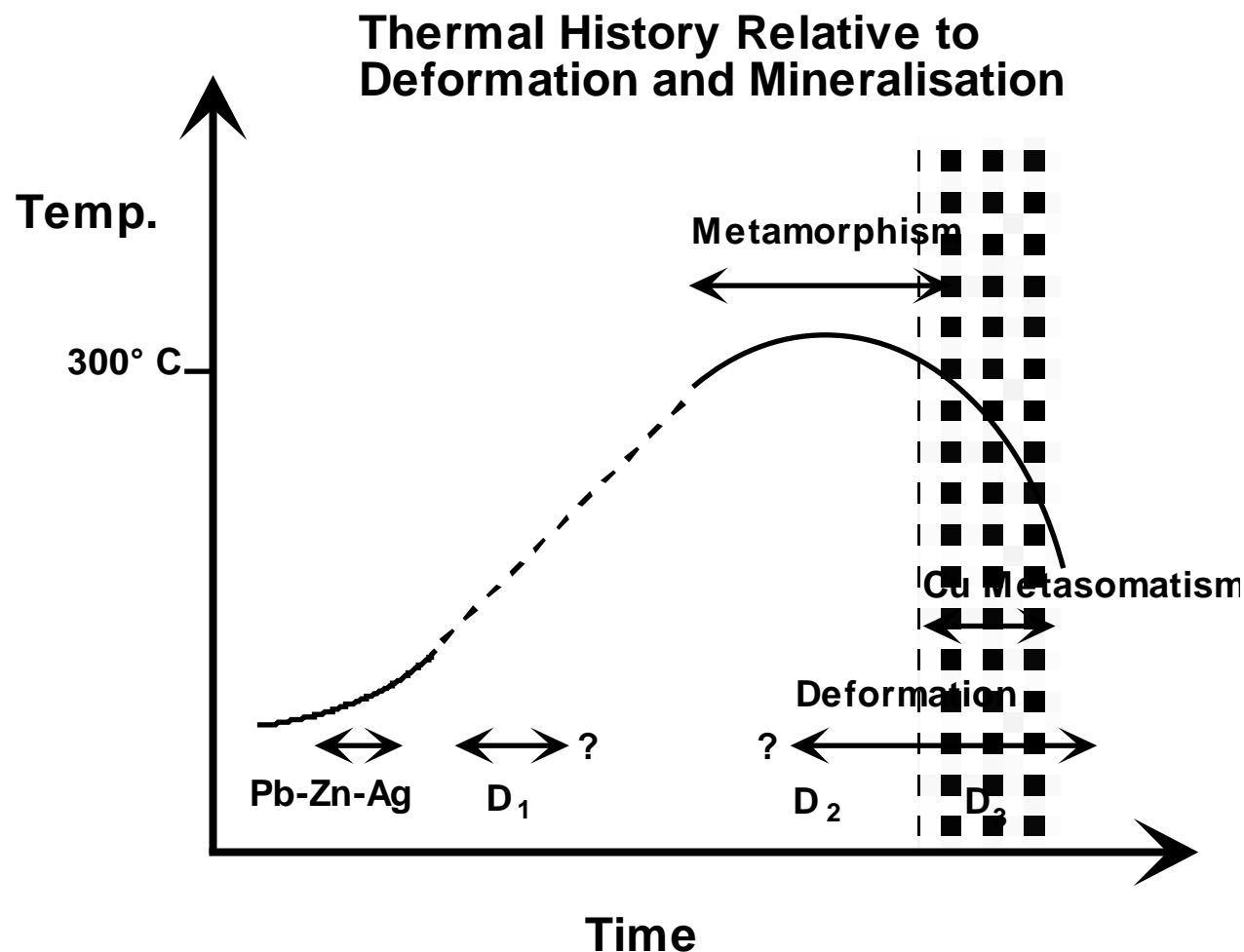
A simulation of metamorphism using a K-feldspar bearing dolomitic shale with 1wt% H₂O has been used to determine the minimum temperature of phlogopite formation by means of a series of calculated temperature stepped mineralogical equilibrations (Waring 1990 a, b). Clinocllore and traces of talc are produced throughout the 250-350°C temperature range. Phlogopite does not form at temperatures less than 332°C. If ankerite is substituted for dolomite, the reaction temperature is lowered by 10°C and biotite, rather than phlogopite, is formed.

Close to Mt. Isa mine and within the central Pb-Zn orebody sequence the distinctive calcitic bands and pyrrhotite laths are also commonly present. In addition to these widespread metamorphic features there are unusual mineral assemblages found only in association with Pb-Zn mineralisation. A stratabound biotite/stilpnomelane/magnetite assemblage, and a white-mica/chlorite/albite assemblage occur amongst stratiform pyrite and Pb-Zn-Ag mineralisation, but do not occur in dolomitic Urquhart Shale adjacent to the southern margins of silica-dolomite Cu alteration. The biotite/stilpnomelane/magnetite assemblage is interpreted to be a metamorphic product of Fe-carbonate/K-feldspar rich, Pb-Zn related portions of the Urquhart Shale. The white-mica assemblage pseudomorphously overprints the biotitic assemblage, and is interpreted to be the product of metasomatism related to interaction with evolved, syntectonic hydrothermal fluids associated with Cu-mineralisation.

At Stony Ck (6kms north-east of Mt. Isa mine) there is further evidence for isochemical metamorphism earlier than Cu mineralisation. Abundant calcite bands are displaced by microfaults and shears, both of which host dolomite-chalcopyrite veins similar to those found peripheral to the Mt. Isa Cu orebodies. The absence of any zonal or symmetrical alteration surrounding these structures, and many intensely calcite banded intervals without obvious

deformation, suggest that the calcite bands are overprinted by the deformation and Cu mineralisation, and are not an alteration effect.

Peak metamorphic temperatures probably exceeded 330°C. This is the upper limit of the wide range (~120°C) of corrected fluid-inclusion temperatures for Cu mineralisation (Heinrich *et al.* 1989). The weight of pseudomorphous, and cross-cutting evidence indicates that Cu mineralisation is distinctly later, and retrogressive, relative to peak regional metamorphism. Figure 2.2



2.2.1 Mt. Isa District Prospect Isotopic Data The Distinction Between Metamorphic Effects and Cu-Related Hydrothermal Systems

Prior to this study very few carbonate or quartz $\delta^{18}\text{O}$ analyses had been taken from the Mt. Isa district away from ISAMINE, and none from Cu prospects within the Mt. Isa district. A few background Urquhart Shale values are available (Waring 1990), and a few silicate analyses from around Lake Moondarra are provided by Windsor (1983). The whole-rock silicate analyses, excluding quartz fault fill, in Windsor (1983) are unreliable because of probable contamination from isotopically exchanged phyllosilicates present in surface samples. The conclusions drawn from Windsor (1983) therefore have no reliable or supportive isotopic evidence.

The full carbonate isotopic data set for Mt. Isa district Cu prospects is plotted (Figure 2.2.1 a) relative to the isotopic exchange line defined for ISAMINE (Waring 1990). Samples have been sub-divided into the broad categories of calcite or dolomite vein samples (V-C, V-D), or whole-rock dolomitic shale (WR). The full range of this data-set is much greater than that for the ISAMINE samples (Figures 2.2.1 a, 3.1 a), extending to 12 positive $\delta^{13}\text{C}$ WR values, 5 V-C and 10 WR with $\delta^{13}\text{C}$ values less than -10‰, and also 2 V-C and 5 WR samples with a $\delta^{18}\text{O}$ value less than 9‰.

These extraneous data require an explanation other than a simple Cu bearing hydrothermal fluid-host rock interaction such as the ISAMINE exchange line. The effects of greenschist grade metamorphism is an obvious possibility compatible with the petrographic interpretation of calcite veins as being metamorphically derived. Other alternatives of differing hydrothermal system(s), with or without mineralisation, and low-temperature diagenetic carbonate formation are also possibilities for some data.

Dolomite veins from Cu prospects around the district all plot very closely to the ISAMINE exchange line (Figure 2.2.1 a), and are likely to have formed from the same style of Cu bearing hydrothermal fluid-host rock interaction as the ISAMINE analogy. Calcite veins and some unusual whole-rocks have a much wider and apparently non-systematic distribution relative to Cu bearing hydrothermal systems.

Close examination of the calcite vein data and wall-rock relationships is possible by using two examples without any apparent effect of Cu mineralisation. These are drill holes ISA Sth Ze541 and HILTON Nth K920. Figure 2.2.1 b shows all isotopic data for these drill holes with the calcite vein samples joined to the adjacent whole-rock samples by a line. These whole-rock samples are usually taken from the few centimetres next to the vein and the second closest sample is typically a few more metres away. There is a distinct difference in the vein wall-rock relationships between the two spatially separated drill-holes, yet for each drill-hole there is an internal consistency within each data set.

HILTON Nth K920 data shows a pattern of calcite veins' $\delta^{18}\text{O}$, ~1.3‰ lighter than the adjacent wall-rock, with $\delta^{13}\text{C}$ only 0.1-0.2‰ lighter than wall-rock. Each vein sample wall-rock pair has a flat parallel vector in $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ space implying interaction with, or formation from, a low CO_2 ($\pm \text{CH}_4$) fluid. Although ISAMINE samples have a similar flat vein - wall-rock isotopic vector (low CO_2) vein samples are dolomitic and are considerably lighter, by 5-10‰, than background values. Four of the six calcite veins from K920 have $\delta^{18}\text{O}$ values greater than 19‰ which is extremely heavy for vein carbonate samples in the Mt. Isa district and are similar to background values. Another difference between the ISAMINE mineralising hydrothermal system and K920 is the degree of $\delta^{18}\text{O}$ heterogeneity as measured by the $\delta^{18}\text{O}$ gradient ($\Delta \delta^{18}\text{O}$ per 100m). ISAMINE samples are extremely homogeneous with a $\delta^{18}\text{O}$ gradient of less than 2‰/100m reflecting the large-scale pervasive nature of the fluid - rock interaction. By contrast K920 is relatively heterogeneous with 8 of the 18 samples having an $\delta^{18}\text{O}$ gradient greater than 2‰. K920 calcite

vein samples are likely to be locally derived (high absolute $\delta^{18}\text{O}$ values, high $\delta^{18}\text{O}$ gradient) from the initial onset of metamorphic dehydration and decarbonation reactions (low CO_2).

ISA Sth Ze541 shows quite a different calcite vein - wall-rock relationship. Most calcite veins are similarly lighter (depleted in the heavier isotope ^{18}O , ^{13}C) than the surrounding wall-rock, although there is less consistency than K920 in the degree of the depletion, and a much greater contribution made by $\delta^{13}\text{C}$ depletion. Two pair of calcite vein wall-rock samples display extremely heavy $\delta^{13}\text{C}$ values greater than 3‰. This effect producing high $\delta^{13}\text{C}$ values is unusual occurring in <5% of samples.

A possibility to account for the high $\delta^{13}\text{C}$ values is interaction with a heavy carbon-species rich external fluid (metamorphic or hydrothermal). Interaction and isotopic exchange with an external fluid is likely to produce much more homogeneous $\delta^{13}\text{C}$ values than the observed wide range. Extreme variation in Fluid/Rock may give a much wider range, but is inconsistent with the observed extremely heavy $\delta^{13}\text{C}$ samples being whole-rock calcitic shales rather than vein samples.

One feature common to all high $\delta^{13}\text{C}$ samples is their low carbonate content (10 wt% carbonate or less), and often detectable (XRD) phlogopite/biotite/muscovite. These factors are indicative of metamorphic decarbonation reactions proceeding nearly to completion (high progress of reaction ξ , Eqn 2.2).

High $\delta^{13}\text{C}$ values are also interpreted to be attributable to the isotopic distillation effects of a high progress of metamorphic reaction. Mass balance dictates that if isotopic fractionation occurs during a metamorphic reaction producing lighter calcite- CO_2 , then the residual carbonate must get heavier. During progressive metamorphism residual carbonate and successive vein calcite- CO_2 generations will get heavier due to the loss out of the system of light CO_2 . At the onset of metamorphism this effect will be masked, because only a small amount of CO_2 has been produced relative to the amount of residual carbonate, and conversely with a high progress of reaction the distillation effects will be amplified, as is the case for these samples.

To further complicate the situation there will be effects of variable exchange of this evolved, light high CO_2 metamorphic fluid with residual carbonate. For example one stratigraphic zone may be high in K-feldspar, and siderite/ankerite, whilst surrounding shale may be more dolomitic. The progress of metamorphic reaction in the Kf- FeCO_3 zone will be comparatively much higher than surrounding dolomitic shale so varying degrees of isotopic distillation will have occurred. Any vein sample isotopic composition will be determined not only by the isotopic value of immediately adjacent wall-rock but the degree of metamorphism in the source region for the metamorphic fluid and the degree of isotopic exchange with wall rocks along the fluid pathway.

An interesting indicator of the degree of vein - wall-rock isotopic exchange is the apparent similarity between adjacent wall-rock samples centimetres to several metres away from a calcite vein, which are in turn distinctly different to samples 10 to 50 metres away. Calcite vein samples do not show a consistent isotopic shift from these wall-rock samples. This pattern suggests that for

these samples (139, 251, 447m) calcite veins formed from an external metamorphic fluid, some of which was derived from further away than the immediate few metres surrounding the vein.

TABLE 2.2.1	Vein Type	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Gradient $\Delta\delta^{18}\text{O} / 100\text{m}$	X CO₂	Progress of Mm Reaction ξ
ISAMINE Cu – Ore	Dolomite	9 – 12‰	-10 – -4‰	< 2	Low <0.02	na
ISAMINE Host Dol Sh	Dolomite	10 – 17‰	-6 – -1‰	< 2	Low	na
Hilton K920	Calcite	11 – 20‰	-6 – -1‰	Heterogeneous 0 - 17	Low- Medium	Low
ISA South Ze541	Calcite	13 – 20‰	-7 – +9‰	Heterogeneous 0 - 12	High	High

Table 2.2.1 is a compilation of comparative features which enables distinction between a Cu mineralising hydrothermal system and metamorphic effects.

Figure 2.2.1 a

Figure 2.2.1 b

3. The Mt Isa District Cu-Ore System Carbonate $\delta^{18}\text{O}$ Anomalies

Figure 3. shows the location of all Mt Isa district carbonate isotopic samples, and the 54 cross-sections constructed.

All dolomite samples from Mt Isa district prospects show major $\delta^{18}\text{O}$ depletion close to Cu mineralisation. Any economic Cu target in the Mt Isa district is also expected to have a large associated $\delta^{18}\text{O}$ depletion halo, in proportion with target size.

3.1. ISAMINE

160 prior carbonate isotopic analyses (see Section 1.) established many of the relationships of the ISAMINE dolomite $\delta^{18}\text{O}$ depletion anomaly. This study further defines the spatial extent of the ISAMINE $\delta^{18}\text{O}$ anomaly with 244 analyses from all peripheral drill-holes which were available to sample, and from Cu orebody zones previously unsampled.

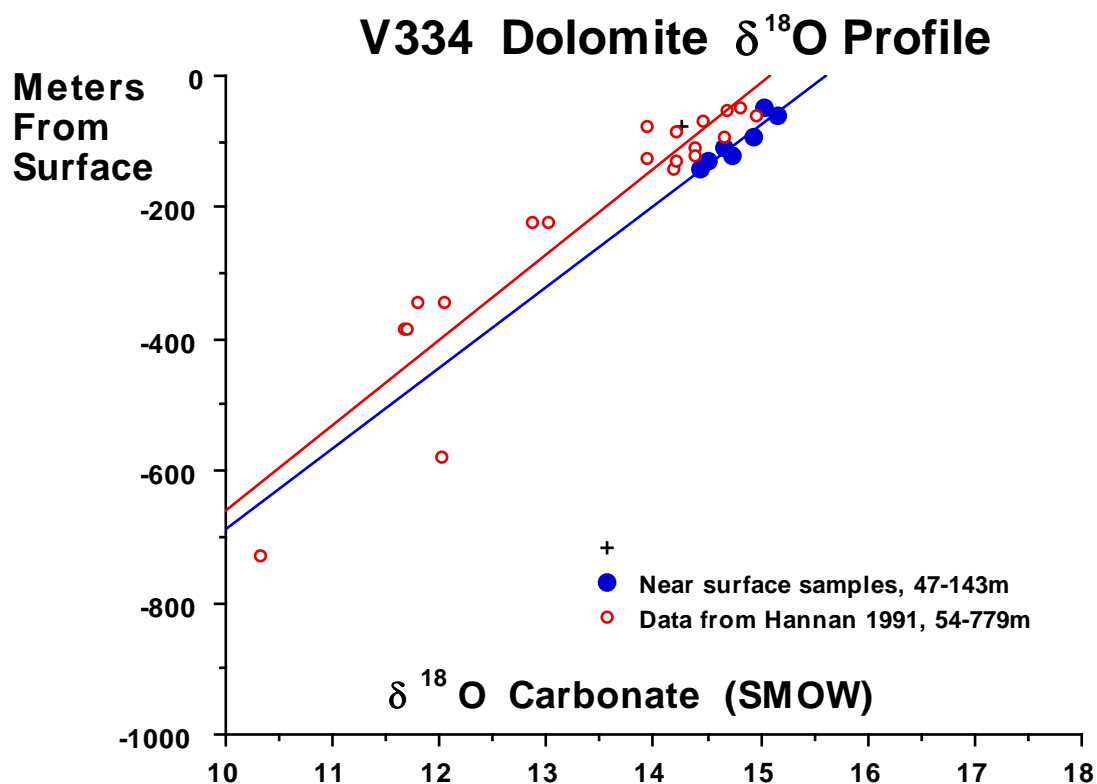
The dolomite $\delta^{18}\text{O}$ depletion anomaly is now sufficiently well defined to construct contours on many ISAMINE cross-sections, and a contoured surface plan (Figure 3.1). Surface contours were constructed from near surface drill hole data projected to the surface, and from cross-section contour extrapolation to the surface. Contours are representative of dolomitic shale values. Where only vein samples were analysed, an inferred shale value could be determined because of the regular relationship between dolomitic veins and wall-rock. Veins are lighter than dolomitic shale by 1- 1.5‰ at 500-1000m from ore, and are approximately equal close to ore (Waring 1990).

There are some striking features apparent from the contoured sections and plan.

- The surface $\delta^{18}\text{O}$ anomaly surrounding the Cu orebody system is enormous, at 9 * 2 kms.
- The surface $\delta^{18}\text{O}$ anomaly and depth profile approaching the Cu orebodies is extremely regular.
- The contour plan and cross-sections reveal extreme depletion approaching some major faults, the Mt Isa Fault Zone, Buck Quartz Fault, S48 family of SW-NE faults, Racecourse Shear, and Urquhart Shear. These faults are interpreted to have acted as major channels for the Cu mineralising hydrothermal fluid. The Mt Isa Fault appears to be the primary structure, with the other faults subordinate. The $\delta^{18}\text{O}$ anomaly is bracketed in the west by the Mt Isa Fault, and to the east by S48 and the Urquhart Shear. A surface zone of maximum $\delta^{18}\text{O}$ depletion occurs asymmetrically on the western side and adjacent to the Racecourse Shear approximating a projection of the 200 and 500 Cu orebodies to the surface. At depth this zone broadens adjacent to the contact with the underlying greenstone, and envelopes the lower 1100, 1900, 3000, and 3500 orebodies.

$\delta^{18}\text{O}$ Gradient

Profiles of the isotopic gradient from the surface to the southern 1100 Cu orebody are calculated for the southern exploratory drill hole Q152, (0.76‰ per 100m) and for 4200mN section (0.38‰ per 100m, Waring 1990). This relationship is confirmed by data collected from the intervening drill hole V334 (Hannan 1991). Near surface dolomitic shale isotopic values from V334 are extremely homogeneous. They show a small but significant regular depletion (0.7‰ per 100m) approaching Cu mineralisation within the narrow interval 47.0 - 143.4m down hole. V334 near surface values are a reliable guide to the overall profile to the 1100 orebody.



Spot gradients are calculated where possible for all carbonate isotopic analyses by comparison with adjacent analyses. These data are presented in the accompanying tables. Samples very close to one another are likely to show a spurious large isotopic gradient, and are therefore presented merely as a difference rather than a rate of change.

Data from ISAMINE show a remarkable homogeneity, with spot $\delta^{18}\text{O}$ gradients universally $<2\%$.

MIFZ (ISAMINE Far Hanging-Wall) Mineralization Style and Potential Targets

The distribution of Cu mineralisation through this area is correlated with a narrow zone of intense steeply west dipping anastomosing shearing related to the nearby MIFZ. Less deformed upper Mt. Isa Group rocks further to the east away from the MIFZ show little surface indication of Cu mineralisation. This high strain zone close to the MIFZ is expected to host a slightly different style of mineralization to the vein network developing up dip from a basement fault contact that is observed for the 1100 Ob. Within the high strain zone, narrower (E-W) lensoidal higher Cu grade zones, with an elongate form stretched along the lineation, plunging $\sim 60^\circ$ to the south may have formed. These hypothetical "orebodies" may form at any level, from near surface to close to the basement contact, although near surface Magazine Shale, and lower Urquhart Shale (?) are more favourable hosts than the intervening Kennedy Spear Siltstone.

Current surface mapping and observation allows some speculation on the petrogenesis of these rocks (Dr Paul Pearson pers. comm. 1991). Bedding close to the MIFZ has been folded by D2? into an open syncline. Further deformation during D3? has tightened up the folds, sheared out some portions of fold limbs generally with a west block up sense of displacement, and increased the fold plunge angle due inhomogeneous strain through the general high strain zone. Synchronous deformation and silicification associated with Cu mineralisation may also have contributed to the strain inhomogeneity and fold plunge reversals. Further deformation continued after Cu mineralisation.

MIFZ Primary Mineralisation Targets

- A.** Small perched primary Cu targets above the Parroo Fault, analogous to the 650 Ob style are inferred (Figure 1.2). Cu mineralisation is expected to be much more sheared and elongate than the 650 Ob, but may also be associated with an adjacent steeply west dipping fault/shear zone. Application of the Bell (1989) 650 Ob plunge reversal model, for perched targets, may be appropriate for this zone. However, the greater degree of strain adjacent to the MIFZ, and oblique shear sense may give greater asymmetry (shallower southward plunge and steeper shorter northern fold axes). Development of a vein network is favoured by a high bedding/cleavage angle, developed through this zone, due to the shallow dips of the D2? broad syncline.
- B.** Another possible primary Cu target occurs on the margin of the sub-vertical high strain zone, slightly further away from the MIFZ, but also close to major fault/shear zones. This style is more like the usual 1100 Ob style of mineralisation, and is close to the basement fault contact.

The carbonate $\delta^{18}\text{O}$ values are consistently low (10-12‰), compared with a background Urquhart Shale dolomite value of $\sim 21\text{‰}$. They have been depleted in ^{18}O in a manner similar to the 1100 Orebody System. N358WH#1 has values of $\sim 10\text{-}11\text{‰}$, and Xw450WD#1A has values of $\sim 10\text{-}12\text{‰}$ which are comparable with the $\sim 9\text{-}10\text{‰}$ range for the southern "footwall 1100" exploratory

drill holes, ~10-12‰ range for the 34200mN orebody section, and 11-13‰ values from 35030 section. Too few analyses are currently available to confirm the apparent slight increase in carbonate $\delta^{18}\text{O}$ northwards within the area adjacent to the MIFZ, that has been identified within the 1100 Orebody System.

The consistent depletion patterns for the 1100 Orebody System and this area adjacent to the MIFZ are indicative of pervasive Cu mineralising hydrothermal fluid flow through the ore zones and adjacent rock. The hangingwall isotopic depletion is an extension of the overall "halo" surrounding the known Cu Orebody System. Both areas are likely to have an ultimate source for the mineralising fluid as the Mt. Isa Fault Zone (yet to be confirmed). From the south to north flow pattern demonstrated for the 1100 Orebody System, areas close to the fluid source, where the Mt. Isa Group rocks are in direct contact with the MIFZ are particularly prospective (31500- 32500mN) within the long narrow area adjacent to the MIFZ.

3.2. HILTON

A small number of carbonate isotopic analyses are available for Hilton mine from Valenta (1988). $\delta^{18}\text{O}$ values range from 13 - 19‰ for a wide variety of sample types, in and around the highly deformed zone of Cu mineralisation overprinting 1-3 Pb-Zn-Ag hanging-wall orebodies (Valenta, 1988). A 12 Level underground drill hole, R504 is collared in Breakaway Shale 600m to the foot-wall of 7 Pb-Zn-Ag orebody, and passes into 400m of upper Moondarra Siltstone. Isotopic samples from R504 are a little irregular and relatively heavy ($\delta^{18}\text{O}$ 17 - 20‰), except for one sample closest to Cu mineralisation which has an $\delta^{18}\text{O}$ of 15.6‰. This sample and the Cu zone samples give an indication of small-scale irregular depletion associated with Cu mineralisation. The slight variation in $\delta^{18}\text{O}$ from R504 is likely to be due subtleties of metamorphism, indicated by the positive $\delta^{13}\text{C}$ values and calcite/biotite in some samples.

Hilton Periphery

Many of the Hilton North and South samples show significant $\delta^{18}\text{O}$ depletion close to either the MIFZ or the Hangingwall Fault. Other major faults intersected in drilling such as the Spring Ck Fault or the Barkly Shear Zone do not appear to deplete ^{18}O in nearby dolomite to the same degree (K920, F320, F350). However like R504, $\delta^{18}\text{O}$ quickly increases away from these structures. There may be significant Cu mineralisation in the Hilton South area close to the Hangingwall Fault, but from $\delta^{18}\text{O}$ distribution it is likely to be similar to Hilton Cu mineralisation rather than a tip of an Isa style system.

Hilton C320 and F320 appear to be analogous to the Native Bee drill holes F328 and S330. In both cases the drill hole close to and parallel to the major structure (Native Bee F328 - Satellite Fault, Hilton C320 - MIFZ/Barkly Shear) is strongly depleted, but quickly changes to a patchy depletion pattern away from the major structure.

In both cases there has not been sufficient "diffuse" fluid flow through dolomitic rock (ie vein network) to give the chemical changes required for significant chalcopyrite deposition. Interconnected subordinate structures with significant dilational capacity need to be identified.

The isotopic pattern from L101 Spring Ck is a little different to other Hilton drill holes, in that the two lowest $\delta^{18}\text{O}$ values are at the bottom of the drill hole slightly further away from the Spring Ck and Hangingwall faults. There is also an unusually high degree of dolomite veining throughout the hole, and particularly for Breakaway Shale. These factors are encouraging for location of prospective sites in more favourable host units (Urquhart Shale, Moondarra Siltstone), with a wide extensional structural site. Although encouraging, the isotopic values higher in the drill hole are slightly erratic and heavier than at Isa, and are not a direct analogy for peripheral parts of the Isa system.

3.3. North West Lakes

North West Lakes and Stone Axe prospects were drilled because of surface outcrops of megacrystic dolomite-quartz bodies which were thought to analogous to the silica-dolomite alteration surrounding the Cu orebodies. These dolomite-quartz bodies are all close to the Spillway Fault, are generally hosted by Spear Siltstone, and often have albitic breccias at the margins. Intervening shale appears essentially unaltered and does not have dolomite recrystallisation and micro-veining present in the outer Isa silica-dolomite.

Although isotopic values are strongly ^{18}O depleted in the dolomite bodies, this depletion does not extend far beyond. Isotopic contours are extremely tight, yet are also regular.

North West Lakes carbonate bodies appear to be large scale discrete dilational fracture fill features which do not have significant hydrothermal fluid - wall rock interaction. Without the chance of chemical interaction / reaction with the wall rock the hydrothermal fluid will not change chemically and precipitate sulphides efficiently. The size of the dolomite bodies is a little misleading as an indication of the scale of the system, because dolomite will deposit in response to the pressure drop associated with fracturing, whereas chalcopyrite solubility is relatively insensitive to pressure decreases.

3.4. Quartzite

Four deep holes have been drilled through an upper Mt Isa Group sequence, away from a collar position close to the Mt Isa Fault at an even spacing through the Quartzite block (between ISAMINE and HILTON).

The northern Quartzite drill hole Uw 886 is similar in many ways to the style of the Hilton holes to the north. It passes through Kennedy and Spear Siltstones before intersecting Urquhart Shale at a depth of approximately 1km, close to the major Hangingwall Fault and Barkly Shear zone. Isotopic values of samples close to the Hangingwall Fault are strongly depleted, yet rapidly increase a small distance from the fault, suggesting rather restricted discrete fluid flow in the fault zone and limited interaction with the surrounding dolomitic shale.

Ww 728 has a small number of slightly depleted (15 -18‰) Urquhart Shale samples, which are 500m from the surface. Although Ww 593 is 1300m south of Ww 728 the cross-sections for these

two drill holes could be overlain. Ww 593 intersects Urquhart Shale with some dolomite veining at a depth of 1200-1400m and has a pattern of generally homogeneous stronger isotopic depletion (13 analyses $\delta^{18}\text{O}$ 14 -15‰) than the shallower Ww 728.

There are 4 unusual samples with an $\delta^{18}\text{O}$ greater than 15‰ with a $\delta^{13}\text{C}$ of -3 to -4‰. If these samples were reflecting less altered dolomitic shales then the $\delta^{13}\text{C}$ values should be heavier than they are. These samples may reflect isotopic changes occurring with metamorphism which have been incompletely homogenised by hydrothermal interaction. Alternatively, minor open system hydrothermal interaction has allowed significant further decarbonation reaction and CO_2 loss. An indication of increased metamorphic or pseudo-metamorphic reaction is the close proximity of phlogopite zones in Ww 593.

Ww728 and Ww593 appear to have intersected a broad zone of isotopic depletion associated with a large scale hydrothermal system, potentially hosting significant Cu mineralisation.

However, realistic targets in this zone are likely to be greater than 1500m beneath the surface and economically less attractive.

Further to the south Zw 295 has a single light $\delta^{18}\text{O}$ value (12.8‰) at 295.6m closest to the surface and 500m from the Mt Isa Fault Zone. Four other samples range from 17-20‰ regularly increasing $\delta^{18}\text{O}$ away from the MIFZ. Zw 295 isotopic distribution is similar in style to Ww 728, although depletion is far less extensive.

Isotopic values reported from Spear Ck Kf 512, and Kingfisher We 955 are indicative of metamorphic effects.

Surface definition of isotopic contours between ISAMINE and HILTON may identify the best site for more intensive follow-up work, although depth to Cu targets will remain problematical.

3.5. Stony Ck

The dominant style of Cu mineralisation at Stony Ck is characterised by broad zones of dolomite-chalcopyrite veining in lower Moondarra Siltstones. This dolomite veining is very similar to dolomite-chalcopyrite veining seen around the margins of the Mt Isa Cu ore system. At Stony Ck these zones appear not to intensify, and merge into a high grade Cu zone. Space restrictions suggest that sizeable high grade Cu zones are unlikely to be found with the intense drill coverage surrounding the best Cu intersections. Minor disseminated chalcopyrite often occurs in the Warrina Park Quartzite and the upper siliciclastic portions of the underlying Surprise Ck formation. Dolomite-chalcopyrite veins in lower Moondarra Siltstone, appear to change character depending on the host lithology, to a quartz chalcopyrite alteration zone in the siliciclastic units. Often there is no discrete dilational vein which can be identified, rather the cross-cutting alteration zones have silicified the quartzites and deposited minor chalcopyrite by reaction with the carbonate (? not observed directly) cement between detrital quartz grains.

Away from the main area of Cu mineralisation (+ 2kms) drill hole Fi 231 has intersected an unaltered equivalent of the same stratigraphic interval. Samples of fresh rock from Fi 231 have a measured high proportion of siderite in the siliciclastics and probably also minor siderite in the dolomitic shale. This siderite forms a cement between the sand grains during diagenesis in the more porous siliciclastics. Siderite is isotopically extremely heavy ($\delta^{18}\text{O}$ 20-26‰) and could not form from the same hydrothermal fluid that caused the isotopically light dolomite-chalcopyrite mineralisation in Zh 013, Ai993.

Diagenetic siderite is a cause for localisation of Cu mineralisation in the lower Moondarra Siltstone and Warrina Park Quartzite rather than an effect. Siderite assists in the formation of Cu mineralisation in two ways. 1. reaction with the hydrothermal fluid will directly lower the solubility product for chalcopyrite and cause deposition. 2. indirectly siderite reaction metamorphically at lower temperatures than dolomite, will induce greater reaction with consequent production of biotite/phlogopite, calcite and CO_2 , evident from the abundant calcite phlogopite banding in Sh 142 and other drill holes distal to Cu mineralisation. Increased volatile production generates a CO_2 rich metamorphic fluid which is lost from the system. Derivation of a metamorphic open system may then induce localisation of external hydrothermal fluids through the higher permeabilities offered by an already defined metamorphic vein network. At Stony Ck dolomite-chalcopyrite veins are observed overprinting and replacing calcite veins.

Dolomite isotopic data from mineralised drill holes show a pattern of ^{18}O depletion similar to all other Cu occurrences in the Mt Isa district. Isotopic values from the top of Ai 993 show that the $\delta^{18}\text{O}$ gradient approaching mineralisation is greater than at ISAMINE and upper Sh 142 1.5kms north is essentially close to background (17-18‰) with lower values metamorphically affected. This would suggest that the Stony Ck. system is at least 100 times smaller than Mt Isa, and little scope exists for economic targets within the confined Stony Ck. area (south of Fi 231).

3.6. Native Bee

All 4 drill holes sampled from Native Bee (S330ED #1, F328 #1A, P430SED #1, M415ED #1) showed the expected $\delta^{18}\text{O}$ isotopic depletion pattern associated with Cu mineralisation. Half of the whole rock samples from P430 and M415 did not contain any carbonate for isotopic analysis. These samples were often highly deformed, biotitic, (sometimes talcose), and siliceous containing significant pyrrhotite and minor chalcopyrite. They are representative of a high strain zone close to the Satellite Fault / Mt Isa Fault.

There is a rough correlation between higher Cu grade zones, and proximity to the Satellite Fault. However better Cu grades are adjacent to the Satellite Fault high strain zone rather than in it. Carbonate adjacent to the siliceous high strain zone is highly depleted in ^{18}O . The weakly Cu mineralised interval of F328 from 610-950m is homogeneously and strongly depleted in $\delta^{18}\text{O}$. S330 is also strongly depleted in parts, but does not show the pervasive depletion of F328, P430, and M415.

There are also a small number of unusual carbonate isotopic analyses from S330 and M415 that show extreme ^{18}O depletion coupled with extremely heavy $\delta^{13}\text{C}$. These carbonates are likely to represent a 2 stage process of metamorphic decarbonation, followed by interaction with a hydrothermal fluid. The heavy $\delta^{13}\text{C}$ is due to interaction with an isotopically heavy carbon bearing fluid, possibly hydrothermal methane, or the residual of extreme CO_2 distillation. Many more samples are likely to have also been affected, but heavy $\delta^{13}\text{C}$ values are not recorded in most carbonates because of the generally low CH_4 or CO_2 to reservoir carbonate-C mass ratio. These heavy $\delta^{13}\text{C}$ samples from Native Bee are low modal carbonate samples that record interaction because of their higher CH_4 or CO_2 to carbonate mass ratio. Initial decarbonation is likely to produce significant scatter of carbonate $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ dependent on degree of decarbonation and degree of exchange with exogenous high CO_2 metamorphic fluids. Some extreme values may be possible for very low abundance residual carbonate.

There are 5 analyses from S330 which plot away from the hydrothermal fluid - host rock exchange line (Figure 1.1) and these are unreliable indicators of Cu mineralisation. They are those $\delta^{18}\text{O}$ values that are less than 9‰ and positive $\delta^{13}\text{C}$ values. The remaining $\delta^{18}\text{O}$ values increase away from the greenstone contact close to the Sybella Fault, from 12.7‰ to 16.9‰ near surface, except for a light vein and fault sample. This steep increase away from the greenstone contact and the F328 - Satellite Fault zone coupled with the S330 erratic values are indicative of the periphery of a small-scale hydrothermal system.

“Best case” small economic targets might fit on the greenstone contact just outside the high strain zone (11800mE, 2300RL).

3.7. Isa South

Four drill holes from Isa South were sampled. Two of these drill holes ZE541ED #1 (Isa Sth #2), and FF050ED #1 (Isa Sth #4) appeared from the log and during core sampling to be completely barren holes drilled through calcitic and phlogopitic Moondarra Siltstone. The remaining two VF622SED #1 and UE258ED #1 were known to contain minor chalcopyrite in the Surprise Ck formation close to the greenstone contact.

The initial isotopic results from ZE541 were particularly encouraging. There was a consistent major $\delta^{18}\text{O}$ depletion from ~17‰ near surface, to 13‰ at 447.5m. The remaining 6 samples from 521.4m to 724.8m were biotitic/pyrrhotitic, and did not contain any carbonate. This isotopic profile looked remarkably similar to Q152 (the southern most intersection of Isamine Cu mineralisation) until intensive follow-up sampling showed that the depletion was erratic and caused by metamorphism, rather than interaction with a hydrothermal fluid (see section 2.2).

3.8. Mt Novit

Isotopic values from Mt Novit appear to be determined by proximity to one or more of the major north-south faults through the area except for E412. Mt Novit stratabound pyrite Pb-Zn mineralisation is not consistently depleted in $\delta^{18}\text{O}$ and its presence seems irrelevant to the adjacent dolomitic shale isotopic values.

The most southern drill hole through the Mt Novit area E412 passes through metamorphosed Moondarra Siltstone to the west of the Mt Isa Fault, through a pyritic Mt Novit horizon and into the MIFZ. E412 was drilled essentially to test the Pb-Zn grade of the Mt. Novit horizon. It intersected a zone of chalcopyrite mineralisation at 405.8m to 410.5m, which is within a wider zone of tremolite which may be either metamorphic or metamorphosed dolomite alteration.

Carbonate isotopic values from E412 are strongly depleted close to Cu mineralisation and further up the drill hole away from the Mt Isa Fault and the Mt Novit horizon. This pattern is different to other Mt Novit isotopic relationships. The small range in $\delta^{18}\text{O}$ for these samples is remarkable given the wide range in lithologies that were sampled. It suggests proximity to a significant size hydrothermal system with potential for Cu ore. Intensive isotopic sampling, petrology, and structural analysis should better define Cu targets in this area.

4. Application of Stable Isotopic Techniques to Exploration

Isotopic geochemical exploration is most suited to broad scale system definition, because it can detect changes in dolomite isotopic ratios further from mineralisation than any other geochemical technique. Close to ore, within 200 m, standard geological criteria are most useful for target definition.

In practice fresh rock is required for sampling.

1. A geochemical survey is proposed that would sample the full areal extent of Mt Isa Group rocks to identify isotopic anomalies associated with previously undetected buried Cu mineralisation.
2. Follow-up close spaced RAB/RC sampling of near surface fresh rock to define any $\delta^{18}\text{O}_{\text{Dol Sh}}$ surface anomalies identified in Stage 1. Cull spurious anomalies.
3. Deep drilling if warranted, to test the defined target.
4. Close spaced isotopic sampling of initial deep drilling will characterise the style of the target.

Hypothetical $\delta^{18}\text{O}$ Anomalies Associated with an Economic Cu Target

The $\delta^{18}\text{O}_{\text{Dol Shale}}$ anomaly surrounding Cu mineralisation at Mt. Isa (22×10^6 tonnes Cu metal) is approximately 8kms long N-S, by 1.6kms wide at the surface, and has a depth extent of at least 1km. At a hypothetical ground surface 500m above the present ground surface a smaller anomaly of approximately half the size is expected to be projected.

The size of an $\delta^{18}\text{O}_{\text{Dol Shale}}$ anomaly associated with a minimum size economic Cu target may be approximated by scaling down the known Mt. Isa anomaly. If an economic target is $\frac{1}{10}$ th the size of the Mt Isa Cu system (2.2×10^6 tonnes Cu metal) then it might produce an $\delta^{18}\text{O}_{\text{Dol Shale}}$ surface anomaly 3.5kms by 0.6kms from mineralisation at a depth of 0.6kms. With mineralisation at a depth of 1km the $\delta^{18}\text{O}_{\text{Dol Shale}}$ anomaly should be detectable with a grid spacing of 1km N-S and 200m E-W.

However alternate less elongate anomaly forms produced by fault intersections or other scenarios for dilation are just as plausible. This hypothetical exercise is merely one of the many situations possible for an economic Cu target. It is very useful as a guide to the required optimum sample spacing.

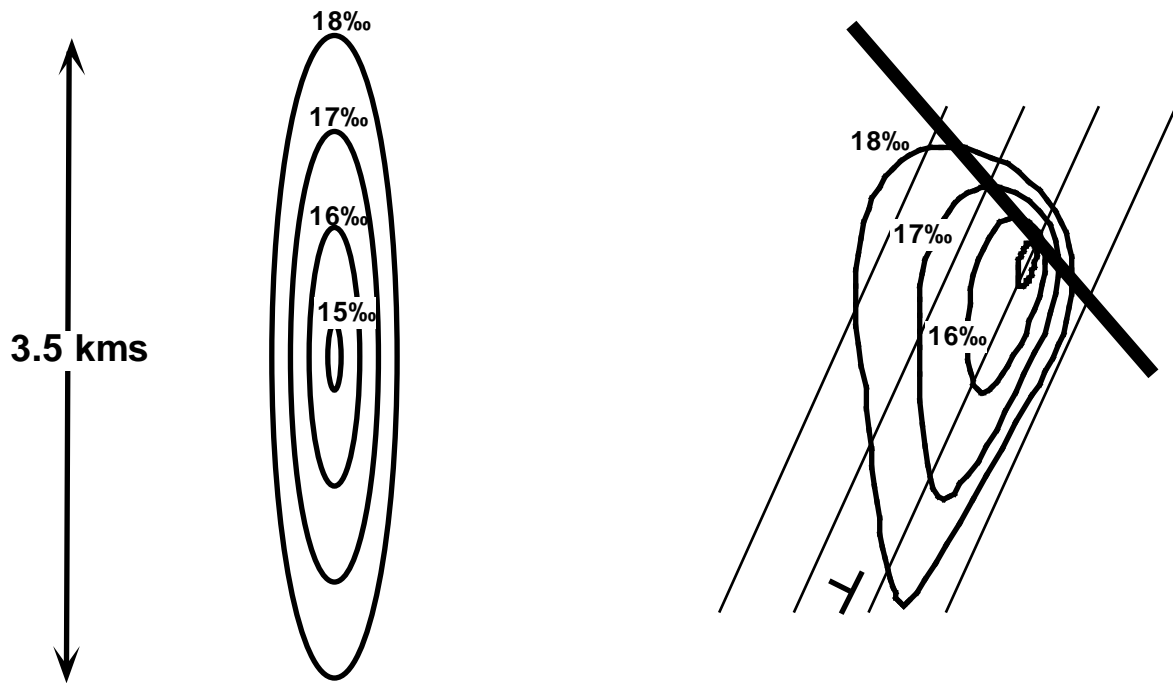
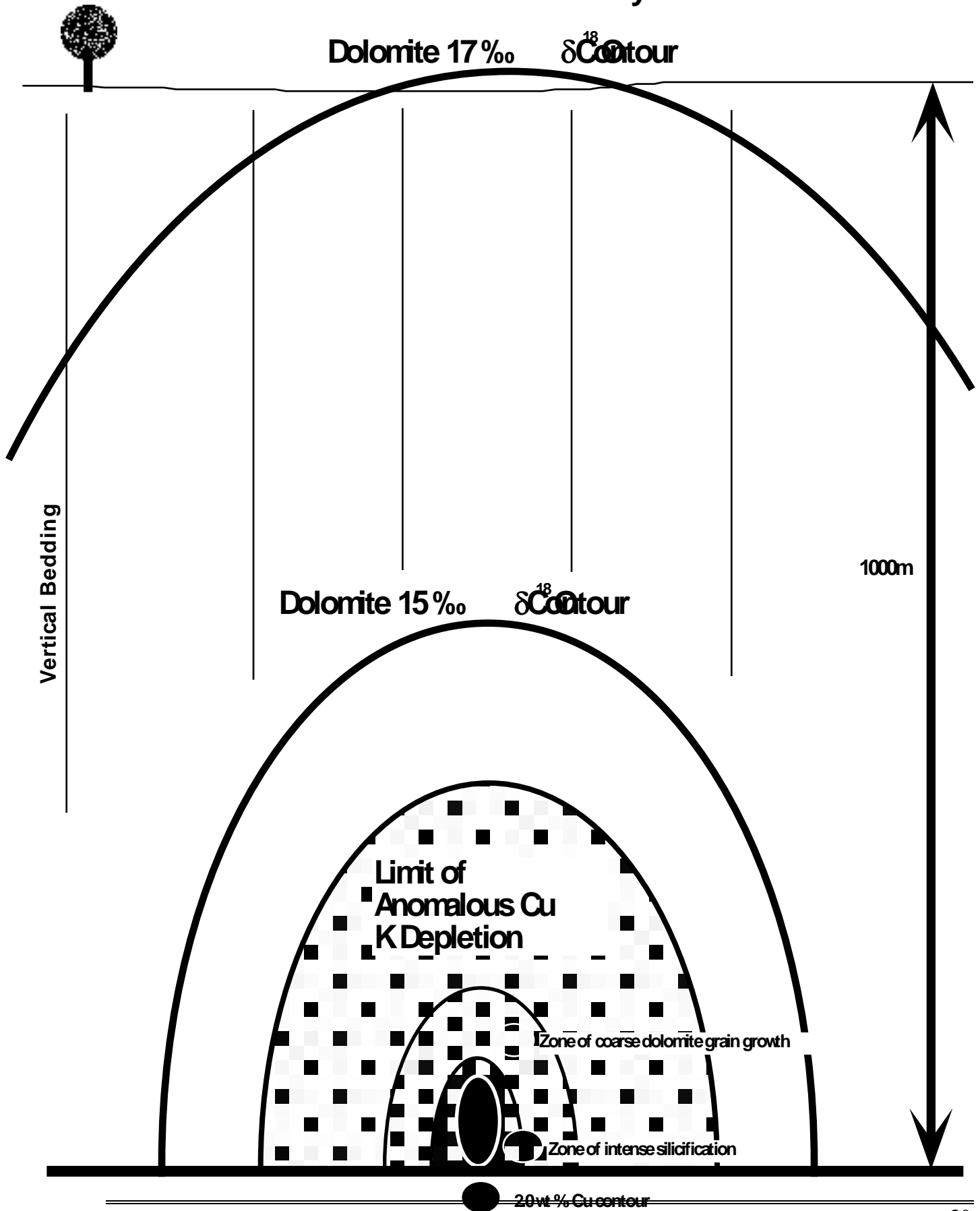


Figure 4. Surface contours of hypothetical isotopic anomaly forms, for a hydrothermal system one tenth the size of the Mt Isa Cu system, with Cu ore at a depth of 600m.

Schematic Cross-Section

Relative Halo Size for a System
0.1 Times the Size of the Isa System



Sample Definition, Spacing and Technique

Carbonates are a virtually ubiquitous (except minor portions of Moondarra Siltstone) component of Mt. Isa Group metasediments and are an ideal sample medium for isotopic analysis. Carbonates are the preferred sample mineral for isotopic analysis because it is one third to one quarter the price of current quartz analyses and provides more information with the automatic inclusion of $\delta^{13}\text{C}$ values. Even if residual quartz in oxidised and leached rock is demonstrated to retain its primary isotopic signature (investigation underway, memo 4/5/91), it may be more cost effective to drill a shallow RAB hole and sample fresh rock dolomite than to analyse for quartz $\delta^{18}\text{O}$. Quartz $\delta^{18}\text{O}$ measurement may be applicable (if the technique is demonstrated) in areas of deep leaching where drilling costs for fresh rock markedly rise.

Stage 1. Reconnaissance Coverage of Prospective Lithologies

Fresh Rock Sample Collection (RAB / RC drilling)

Suitable samples of near surface fresh rock (retaining dolomite/ \pm calcite) can be obtained for most samples without deep leaching from an extension of current “bedrock” (oxidised and leached rock) geochemical RAB drilling practice by hammering down an extra few meters at minimal cost.

A trial sampling for fresh rock using the RAB drilling rig over the Speedway prospect area (west of powerhouse) was successful in penetrating to fresh rock and providing suitable sample material at a depth of 11-12m. Current “bedrock” sampling typically provided an oxidised and leached rock sample from a depth of 8 - 16m, except for a narrow zone along the Leichhardt River. Fitting a down hole hammer allowed further penetration of an additional 2 - 4m and fresh rock chips. These fresh rock chips are easily discernible from oxidised and leached rock chips further up the drill hole because they are not coated with mud. Leached rock chips retain water which forms a surficial pale green-grey mud in contrast to dry clean black fresh rock chips.

Samples must consist of fresh rock chips only.

There is typically a mixture of chips from the bottom of the hole due to dilution from above. The fresh rock chips must be hand picked from the mixed sieved fraction to provide a clean uniform sample of only fresh rock chips. A uniform sample material of only fresh rock will be useful for providing additional geochemical data to compare with the existing large data set of weathered rock geochemical data. This would not be possible from a variably mixed sample.

Hand picking of fresh rock chips by a field assistant will take 5 - 10 minutes per sample, and may be done whilst waiting for the drill to relocate and penetrate to bedrock. At least 400gms of fresh rock chips should be collected for each sample.

Those areas in which there is deep leaching RC drilling will be required for both bedrock and fresh rock geochemical sampling.

Sample Spacing

Those areas already covered by leached rock chip geochemical data will need to be resampled for this isotopic geochemical program. The likely size and form of an $\delta^{18}\text{O}$ anomaly associated with economic Cu mineralisation allows much wider sample spacing than for standard bedrock geochemical surveys. Without knowing exactly what the target and anomaly form is, a conservative sample spacing of 500m by 500m along existing grids should detect an isotopic anomaly associated with an economic target if present. Sample positioning on adjacent east-west grid lines, should be staggered to provide a minimum 250m spacing north-south per kilometer.

$\delta^{18}\text{O}_{\text{Dol Sh}}$ Detailed Anomaly Definition

Specific areas, which for structural or geochemical reasons have a higher degree of prospectivity, or are already known to be isotopically anomalous have a slightly different requirement. Further isotopic analyses need to define the fine scale form of the isotopic anomaly, rather than mere presence or absence of isotopic depletion. Knowledge of anomaly form can be used to better site deep drill holes.

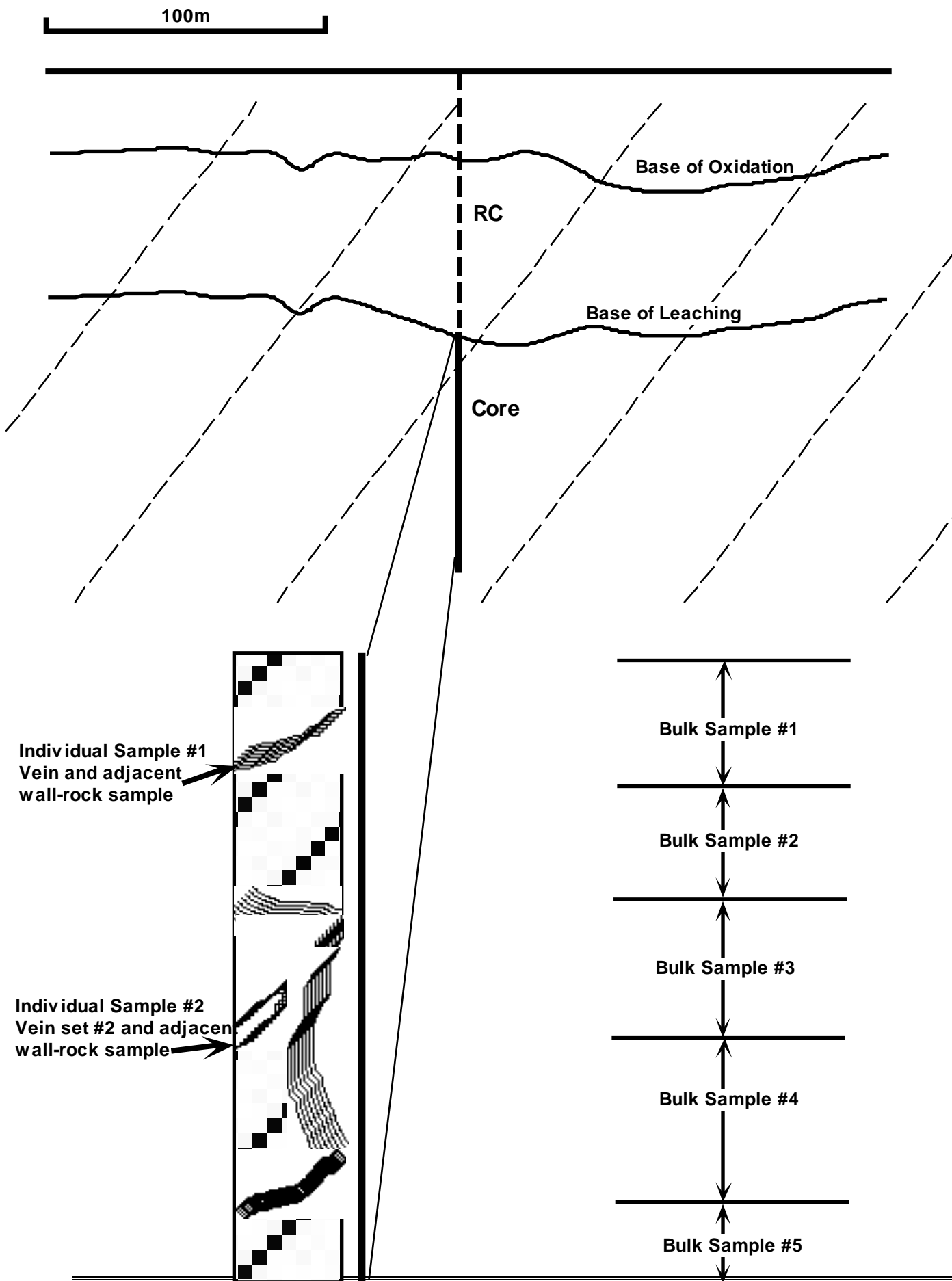
Sample spacing will need to be determined for each area depending on the geological situation, form and style of the anomaly detected in initially. For the Lena prospect area a 200m sample spacing may be appropriate.

Shallow Diamond Drilling (100-150m) of $\delta^{18}\text{O}_{\text{Dol Sh}}$ Anomalies.

Before drilling a deep diamond drill hole on the basis of one or two $^{18}\text{O}_{\text{Dol Sh}}$ depleted samples, false anomalies due to metamorphic effects should be eliminated. This is often not possible without close spaced comparative sampling.

A method of anomaly characterisation is proposed that should eliminate spurious anomalies based on one or two widely spaced near surface values. In addition, the approximate size of the target hydrothermal system and depth of the target may be determined under favourable circumstances, by drilling a shallow diamond drill hole for close spaced sampling.

Proposed Drilling and Sample Style



Both bulk sampling of $\pm 20\text{m}$ intervals, and spot samples of vein and wall rock pairs should be taken from half core.

Analytical Scheme

1. All samples should be inspected by a geologist to ensure that they consist of fresh rock only. Each sample should also record along with its location, a basic description, geological formation, **and stratigraphic position within each formation.** This information will be vital for determining the stratigraphic distribution and significance of sideritic, pyritic or potassic zones.
2. The samples should be split with 100 - 200gms crushed to a pulp at the Mt Isa chemical laboratories, with the remaining chips placed in **secure** storage for future reference.
3. Each pulp should be split again, with the option available for one half sent to a commercial laboratory for a full range of major element analyses (i), and the other half sent to the University of Queensland Isotope Laboratory for a carbonate major element analysis, and a carbonate isotopic analysis (ii).
 - (i) If additional geochemical data is required, a broad suite of elements already analysed for standard bedrock geochemical surveys should be adopted, ensuring the inclusion of Si, Al, Ca, Mg, Fe, Mn, Na, K, Cu, Co, Pb, Zn, Ag, Au, S, C, $\pm\text{CO}_2$, $\pm\text{P}$, $\pm\text{Ba}$, $\pm\text{As}$, $\pm\text{Tl}$.
 - (ii) Sample pulps sent to U of Q for isotopic analysis including carbonate major element analysis cost \$78 each. Spot analyses requiring sample preparation at U of Q cost \$93 each. Approximately 5% of samples will require an XRD at \$85 each, for definition of siderite etc.
4. Interpretation of geochemical data requires reference to the the existing isotopic database to best determine the significance of isotopic data, with respect to known mineralisation and hypothetical structural / geochemical targets.

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Appendices

A Analytical Procedure and Practice for Whole Rock Isotopic, Carbonate Major Element and XRD Analyses

A 1. Isotopic Analytical Method and Practice

The standard method of extracting CO₂ from carbonates (McCrea, 1950) at 25°C using anhydrous phosphoric acid, takes from a few weeks to several months to produce complete yields, when the carbonate attacked is iron-rich dolomite, ankerite or siderite (Rosenbaum and Sheppard, 1986). Complete reaction of the carbonate eliminates possible errors due to partial dissolution. Consequently, a modification of the phosphoric dissolution method has been used to extract CO₂ from the Isa dolomites, at elevated temperatures, where the time necessary for complete CO₂ evolution is greatly reduced. The technique utilised at the University of Queensland differs only slightly from that used by Rosenbaum and Sheppard (1986). At U of Q, the samples are heated, reacting with the phosphoric acid at a temperature of 50°C.

Trials of CO₂ extraction at 75°C for ferroan dolomites and siderites are continuing. Complete carbonate dissolution is required, to ensure correct application of literature acid fractionation values, particularly for mixed carbonates.

A 1.1. Isotopic Acid Fractionation Correction Procedure

The liberation of CO₂ from carbonates using phosphoric acid, only liberates two-thirds of the oxygen. There is consequently a temperature dependent fractionation between the extraction products. Knowing the isotopic composition of the evolved CO₂ and the fractionation factor $\alpha_{(\text{CO}_2 - \text{Carb})}$, where

$$\alpha_{(\text{CO}_2 - \text{Carb})} = \frac{\frac{^{18}\text{O}}{^{16}\text{O}} (\text{CO}_2)}{\frac{^{18}\text{O}}{^{16}\text{O}} (\text{Carb})}$$

it is possible to calculate the oxygen isotopic composition of the original carbonate. Such fractionation factors have been determined experimentally against total oxygen extraction techniques for a variety of carbonates at 25°C (Sharma and Clayton 1965, Becker 1971, Clayton and Mayeda 1963, data in Becker and Clayton 1976, Land 1980, Chivas unpubl. data in Golding pers. comm. 1986, and Rosenbaum and Sheppard 1986). Recently, Rosenbaum and Sheppard (1986) have shown the temperature (to 150°C), and compositional dependence of this fractionation for dolomite, ankerite and siderite.

The results of the isotopic analyses of dolomites from Mt Isa are reported using the standard “ δ ” notation, where δ is defined by

$$\delta = 1000 \left(\frac{R_{sample} - 1}{R_{standard}} \right) \quad \text{and}$$

R is the isotope abundance ratio of the rarer to the more common isotope (ie $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$). Using the approximation (Friedman and O'Neil, 1977)

$$1000 \ln \alpha_{ij} \cong \delta_i - \delta_j \equiv \Delta_{ij}, \quad \text{when } \Delta_{ij} \rightarrow 0 \quad \text{a}$$

comparative table of the various literature CO_2 phosphoric extraction fractionation factors may be constructed in δ notation, (attached diagram).

At U of Q, samples are measured in the mass spectrometer relative to an internal CO_2 gas standard, that was produced from a calcite at 25°C using the same phosphoric acid technique. Thus any correction to measured values should account for the difference in the fractionation of the samples liberated CO_2 , compared with the calcite standards' fractionation of liberated CO_2 . Acid extraction fractionation factors need to account for both the dependence on the temperature of evolution, and the changes due different carbonate species.

The literature values are shown schematically in the attached diagram, where there is a $\sim 1.0\text{‰}$ $\delta^{18}\text{O}$ difference between the CO_2 evolved from calcite and dolomite at 25°C (Sharma and Clayton 1965, Land 1980). The temperature dependence of the CO_2 extraction fractionation also appears to be different between dolomite/ankerite (2.44‰, Rosenbaum and Sheppard, 1986) and calcite (2.0‰, Monash) for the temperature interval 25°C to 90°C . The assumption that CO_2 extraction fractionations for dolomite/ankerite, and calcite, are the same, is unjustified.

A problem remains in the choice of literature values, because of the inconsistency between the results of the two studies that compare calcite and dolomite CO_2 extraction fractionation at 25°C (Sharma and Clayton, 1965; Land, 1980), as shown in the diagram. The calcite and dolomite fractionation values of Sharma and Clayton (1965) are significantly less (0.32‰ Cc, 0.58‰ Dol) than the respective calcite and dolomite fractionations of Land (1980). However, both data sets show a significant difference between the calcite and dolomite 25°C CO_2 extraction fractionations, at 0.84‰ (Sharma and Clayton 1965) and 1.10‰ (Land 1980).

Some of the discrepancy between the quoted carbonate fractionations may be due to compositional variation (Land, 1980), but this probably accounts for less than 0.2‰ based on data in Rosenbaum and Sheppard (1986).

The values of CO_2 extraction fractionation for dolomite at 25°C are similar for Land (1980), at 11.62‰ (quoted in δ notation, $10^3 \ln \alpha_{\text{CO}_2\text{-Carbonate}}$), and Rosenbaum and Sheppard (1986) at 11.72‰. Therefore for consistency, a correction factor based on the dolomite CO_2 extraction fractionation at 90°C of 9.28‰, and dolomite CO_2 extraction fractionation at 25°C of 11.72‰ (Rosenbaum and Sheppard 1986) in conjunction with a calcite CO_2 extraction fractionation at 25°C of Land (1980), 10.52‰, is adopted. This results in an addition correction factor of 1.24‰, to be applied to dolomites reacted at 90°C and compared with an internal calcite standard reacted at 25°C .

Comparison of $\delta^{18}\text{O}$ values for 3 identical samples analysed independently at Monash (90°C extraction), and at University of Saskatchewan (Kerrich *pers. comm.* 1989) at an extraction temperature of 50°C, gave near identical corrected values, with a discrepancy of only 0.16‰, 0.01‰, and 0.03 - 0.10‰ for a repeated sample (Waring 1990, Table 5.3). However, 6 analyses from approximately ^{34}S 4200mN section (Heinrich *et al.*, 1989), of outer silica-dolomite and marginal shales all have ~1.5‰ heavier $\delta^{18}\text{O}$ dolomite values than other ^{34}S 4200mN orebody section samples analysed at Monash. These are not identical samples, but an apparent systematic inter-laboratory discrepancy of ~1.5‰ is significant.

Ensuing communication with Anita Andrew has established that an error was made in application of CO_2 extraction fractionation factors for the carbonate $\delta^{18}\text{O}$ values reported in Heinrich *et al.* (1989). All of the "new" CSIRO dolomite data (not values reprinted from Smith *et al.*, 1978) should have 1.9‰ deducted from the values reported in Heinrich *et al.* (1989) to make them comparable with the Waring, (1990) dolomite $\delta^{18}\text{O}$ data, and the current carbonate $\delta^{18}\text{O}$ data.

The new mixed carbonate data requires even greater care with isotopic CO_2 extraction fractionation factors. Typical dolomite - calcite carbonate mixes found in Mt. Isa Group rocks have been extracted together to give one isotopic value, which must have an appropriate mixed carbonate acid fractionation factor applied for the elevated temperature of concern. Both of these factors may be interpolated from literature values, shown in the attached diagram. The accompanying spreadsheet "ISOTOPE" has these factors built in. Raw data and temperature of extraction are entered and an appropriate correction factor is determined and applied. If at any stage in the future, new literature values are chosen, these may be entered in the heading position and all values will automatically be recalculated.

$\delta^{18}\text{O}$ Corrected Data (L Cc₂₅) =

$$\begin{aligned} \delta^{18}\text{O Raw Data (S+C Cc}_{25}) &+ \text{Mole Frac Dol} * (\text{Cc}_{25} - \text{Dol}_{50}) + \text{Mole Frac Cc} * (\text{Cc}_{25} - \text{Cc}_{50}) \\ &+ \text{Mole Frac Sid} * (\text{Cc}_{25} - \text{Sid}_{50}) + \text{Mole Frac Mag} * (\text{Cc}_{25} - \text{Mag}_{50}) \\ &+ (\text{S+C Cc}_{25} - \text{L Cc}_{25}) \end{aligned}$$

The equation above for a mixed carbonate 50°C CO_2 extraction may be read as the corrected mixed carbonate $\delta^{18}\text{O}$ value relative to the Land (1980) calcite 25°C extraction fractionation is equal to the quoted raw $\delta^{18}\text{O}$ value relative to the Sharma and Clayton (1965) calcite 25°C extraction fractionation plus the mole fraction dolomite of the carbonate present times the Land (1980) calcite 25°C extraction fractionation less the Rosenbaum and Sheppard (1986) dolomite 50°C extraction fractionation, plus terms for calcite, siderite, and magnesite if present.

A 1.2 Carbonate Major Element Analytical Method and Practice

The initial carbonate major element analyses included in the interim report (6 / 7 / 90), were analysed by dissolving the carbonate fraction of the whole rock powder in a 1:1 HCl solution, and then determining the major element composition by atomic absorption spectroscopy. These results are not reproducible. Two reasons for this are that there was not strict temperature or time control on the carbonate dissolution. At higher temperatures of approximately 70°C over twice as much

chlorite is dissolved than at 50°C, and for dissolution times of less than an hour incomplete carbonate dissolution occurs. These initial data also appear to have overestimated the soluble Ca content of the rocks by 25% compared to later data, without explanation at this stage.

An investigation of the procedure by Bill Dixon (U of Q), instigated by CLW, revealed that approximately 30% of the chlorite present, and 100% of the pyrrhotite present, dissolved into the 1:1 HCl, after about an hour at 70°C. For samples with significant chlorite or pyrrhotite this level of unaccounted dissolution introduced a significant error into the recalculated carbonate values. Original carbonate species and compositional data (6 / 7 / 90) should be disregarded. Chlorite dissolution needs to be suppressed whilst maintaining 100% carbonate dissolution, and accounting for pyrrhotite.

A new procedure will now be applied to all future carbonate major element analyses, from the Native Bee samples onwards in the analytical program. The new procedure essentially fixes the

- **temperature of dissolution at 55°C ±5°C,**
- **HCl acid strength is weaker at a 1:4 dilution, and**
- **time for dissolution is set at 1 hour.**

These settings give 100% carbonate dissolution, and suppress chlorite (and biotite/phlogopite) dissolution to less than 1% MgO from 100% chlorite samples.

Pyrrhotite is still dissolved. To account for pyrrhotite dissolution, all future carbonate major element - isotopic analyses will also record the H₂S yield during phosphoric acid dissolution. Most samples are dominantly pyrrhotitic rather than pyritic, and pyrrhotite is far more soluble than pyrite in phosphoric or hydrochloric acid. From the H₂S yield, assuming 100% pyrrhotite dissolution, a stoichiometric amount of pyrrhotite FeO is then possible to deduct from the total major element HCl dissolution FeO, to give the carbonate only FeO.

A 1.2. Carbonate Calculation Procedure

Some assumptions are made to allow a recalculation of the constituent carbonate species and composition from a major element oxide chemical analysis. These are ;

- that the metal oxides being measured are only derived from carbonate dissolution (or are accounted for),
- that there is 100% carbonate dissolution,
- that there are only two carbonate species present (thermodynamically stable),
- that those species are either dolomite plus calcite, or dolomite plus siderite-magnesite,
- and that if calcite is present it has a fixed composition equal to the average microprobe analysed calcite south of the mine, and if siderite-magnesite is present dolomite has a fixed low iron composition (3 mole %).

In general these assumptions are quite reasonable. The first of these assumptions is probably the worst for the initial dataset because of significant phyllosilicate dissolution (70°C with 1:1 HCl), and unaccounted pyrrhotite dissolution. Specific drill holes such as Kingfisher #1 which are

phyllosilicate rich and carbonate poor are prone to error from non carbonate dissolution, which is minimal from the "normal" abundant dolomite \pm calcite drill holes such as Vg 436. Future analyses will have virtually no non-carbonate dissolution error. Assumptions regarding speciation are necessary to resolve ambiguity and appear to be sound when compared with the XRD mineral modes.

Wt % Oxide \emptyset Wt % Carb and Carb Tot. \emptyset Mole Frac Carb \emptyset Carb Speciation

\emptyset if $\sum \text{Fe+Mn+MgCO}_3 < \text{CaCO}_3$ then Dol + Cc (fixed comp.)

\emptyset if $\sum \text{Fe+Mn+MgCO}_3 (+3\%) > \text{CaCO}_3$ then Dol (fixed comp.)+ Sid-Mag

\emptyset if $\sum \text{Fe+Mn+MgCO}_3 > \text{CaCO}_3$ but $< \sum \text{Fe+Mn+MgCO}_3 (+3\%)$ then Dol

The above figure is a schematic of the recalculation procedure, in which the speciation criteria are basically set by considering whether there is an excess of $\sum \text{Fe+Mn+MgCO}_3$ over CaCO_3 or a deficiency. An excess is taken to indicate that there is dolomite plus siderite-magnesite, and a deficiency dolomite plus calcite.

A 1.3 Semi-Quantitative X-Ray Diffraction Method and Practice

X-Ray diffraction traces of some selected whole rock samples were run for a number of reasons. To provide a full mineralogy of unusual fine-grained rocks and as background suite of least altered rocks. XRD's are necessary to determine the feldspar and phyllosilicate mineralogy and abundance. Feldspar mineralogy and abundance is important in determining the early diagenetic history of the rock and it's pre-disposition to hydrothermal mineralization. Phyllosilicate mineralogy and abundance is more important in determining the late metamorphic and hydrothermal history. The XRD's also provide an independent modal mineralogy as a check on the carbonate major element analyses, speciation, and for future mineral modes derived from whole rock major element analyses.

To detect and quantify the minor amounts of feldspar and phyllosilicates present the XRD traces must be examined very carefully and all minor peaks allocated and measured prior to the normalisation procedure. Even with the best normalisation procedure and measurement the detection limit is still approximately 5%, with a $\pm 5\%$ error. Figures quoted for minerals present at less than 5% are really only an indication that the mineral is suspected to be present. However, if the figures for CO_2 abundance in the background Urquhart Shale (Stone Axe CEC Vg 436) are compared from the isotopic extraction yield vs the calculated XRD data there is remarkable agreement, much better than the $\pm 5\%$ figure quoted above. Half the values are within 1% and the other half within 2.5%!!!

A 1.3. XRD Normalisation Procedure

The raw data gained from XRD peak height measurement requires a normalisation procedure to give percentage modal mineralogical abundances. To account for the variable strength of different minerals' diffraction peaks a suppression or enhancement factor relative to the quartz 001 peak was

determined. Each of the detected minerals was made into a synthetic bi-minerallic 50 / 50 wt% mixture with quartz. XRD's of these mixtures were then measured to determine the strongest XRD peak and its height relative to the principal quartz peak height. These relative peak heights are then used to give factors by which the rock peak heights are multiplied during normalisation. For example the measured dolomite 104 peak height is multiplied by 0.5 and the muscovite 002 peak height is multiplied by 3.0. Factors for each mineral are listed above the mineral in the spreadsheet ISOTOPE.

A 1.4 Comparison of CO₂ Analytical Values

Comparison of three independent measures of CO₂ allows speculation regarding the source of error for the different datasets. There is an apparent systematic error of over estimation for the carbonate major element analyses compared with the values from the isotopic extraction yield and XRD datasets. This discrepancy is thought to be primarily attributable to phyllosilicate and pyrrhotite dissolution (discussed above), that will be minimised in all future analyses. Other known sources of error include weighing errors during calculation of the CO₂ isotopic extraction yield. The sample weights for isotopic analysis were only roughly determined because they were previously only required to provide an appropriate amount of CO₂ for isotopic analysis. In future the CO₂ and H₂S yield will be determined as accurately as the gas evolution and measurement will allow.

CROSS-SECTIONS

ISAMINE

HILTON

North West Lakes

Quartzite

Stony Ck

Native Bee

Isa South

Mt Novit

All cross-sections are at a scale of 1 : 10,000

Original cross-sections were redrawn at a scale of 1 : 2,500 from MIM cross-sections at various scales.

CARBONATE ISOTOPIC DATA

ISAMINE

HILTON

North West Lakes

Quartzite

Stony Ck

Native Bee

Isa South

Mt Novit