

## *Stable isotopes and geochemistry as exploration indicators*

**G. R. GREEN and J. TAHERI**  
*Tasmania Department of Mines*

### ABSTRACT

*The footwall volcanic sequences to massive sulphide mineralisation at the Hellyer and Hercules mines show an increase in whole-rock  $\delta^{18}\text{O}$  values from <7 to 10‰ in the alteration pipe, to values of up to 13.8 and 15.7‰ respectively in more distal rocks. These data are consistent with alteration by a fluid with a  $\delta^{18}\text{O}$  value close to the seawater value of 0‰ with a decline in temperature away from the focus of mineralisation. At Hellyer a similar zonation of increasing  $\delta^{18}\text{O}$  values away from ore and upward through the section appears to persist in the post-ore basalts. At Hercules the situation is more complex, with decreasing  $\delta^{18}\text{O}$  values, increasing Mn contents of chlorite, and enrichment of whole-rock K, Rb, S and base metals, together with Na, Ca and Sr depletion occurring progressively up section towards the old East Hercules copper prospect, 300 m east of the mine. These geochemical signatures are similar to those associated with the focus of alteration in the footwall, and may indicate that the hangingwall rocks are prospective for Hercules-style mineralisation. In areas relatively unaffected by Devonian granite-related hydrothermal overprinting, the higher  $\delta^{18}\text{O}$  values require the interaction of the rocks with considerable quantities of seawater at low temperatures (<150°C), and indicate that sub-sea floor hydrothermal alteration has taken place.*

*Areas of relatively low  $\delta^{18}\text{O}$  rocks warrant more intensive exploration, but other techniques are required for more detailed prospect definition. A distinctive style of alteration of plagioclase phenocrysts to carbonate  $\pm$  K-feldspar is developed adjacent to footwall alteration pipes at both mines, and has also been reported at Rosebery (Green et al., 1981) and Que River (McGoldrick and Large, 1992). Chlorite geothermometry offers promise as a target indicator in the relatively undeformed Que-Hellyer Volcanics, but the compositions of chlorites at Hercules have been reset during deformation. The oxygen isotope compositions of hydrothermal carbonates also offer promise, particularly where the fluid  $\delta^{18}\text{O}$  value can be constrained independently by fluid inclusion geothermometry.*

*Many barren pyritic alteration zones can be distinguished on the basis of relatively low (<5‰)  $\delta^{34}\text{S}$  values.*

*A combination of careful petrography, fluid inclusion work, and oxygen and sulphur isotope data has confirmed the dominantly Devonian magmatic association of Au-Sn-Cu-As mineralisation in the Lakeside-Sterling Valley area.*

### INTRODUCTION

Western Tasmania provides a unique opportunity to study a variety of styles of volcanic-associated mineralisation with differing degrees of deformation, metamorphic grade (prehnite-pumpellyite to lower greenschist), overprinting by later magmatic-related alteration, and wall rocks (felsic to mafic composition; lavas and volcanoclastic rocks). However this geological spectrum presents a challenge to the explorer wishing to develop the most effective exploration strategy. Although EM was responsible for the discovery of the Que River and Hellyer orebodies, some ores (zinc-rich and pyrite-poor), with certain geometries (fragmented) and alteration styles (silicification), may not give an EM response (Bishop and Lewis, 1992).

The approach of the Isotope and Alteration Studies component of the Mount Read Volcanics Project has been to provide an integrated approach to the study of rock alteration around massive sulphide deposits, involving petrography, mineralogy, stable isotope and whole-rock geochemistry, and fluid inclusions, with the dual aims of:

1. Defining the extent of alteration haloes around massive sulphide deposits and developing techniques to map palaeotemperatures within the volcanics, and;
2. Developing criteria to enable the distinction between rock alteration associated with polymetallic massive sulphide ore and barren pyritic mineralisation.

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## TECHNIQUES: APPLICABILITY AND LIMITATIONS

### OXYGEN ISOTOPES

For recent detailed reviews of the literature on stable isotopes and applications to ore deposits and petrology the interested reader is referred to the Mineralogical Society of America volume *Reviews in Mineralogy* (Volume 16, 1986) and the Mineralogical Association of Canada *Short Course Handbook* (Volume 13, 1987).

Stable isotope analyses are expressed as the permil (parts per thousand) difference of the ratio of the heavier to lighter isotope in a sample from that in a standard. For oxygen isotopes this is written as:

$$\delta^{18}\text{O}_{\text{sample}} = \left[ \left( \frac{^{18}\text{O}/^{16}\text{O}}{\text{sample}} / \frac{^{18}\text{O}/^{16}\text{O}}{\text{standard}} - 1 \right) * 1000\text{‰} \right] \quad (1)$$

where the standard is V-SMOW seawater.

Similar definitions apply to other elements, e.g. C, S, H, N, B etc.

#### Mineral Applications

The oxygen isotope compositions of minerals can be used as geothermometers in situations where co-existing minerals formed in mutual equilibrium and have not subsequently undergone isotopic exchange, or in cases where the oxygen isotope composition of a hydrothermal fluid from which a mineral formed can be determined independently, or be reasonably inferred.

The temperature dependence of oxygen isotope fractionation between two minerals, or a mineral and water can be frequently expressed by:

$$1000 \ln \alpha_{X-Y} = A * 10^6 / T^2 + B \quad (2)$$

where  $\alpha_{X-Y}$  is the ratio  $(^{18}\text{O}/^{16}\text{O})_X / (^{18}\text{O}/^{16}\text{O})_Y$ ,  
A and B are constants,  
temperature T is in °K.

Because fractionation factors are usually close to unity:

$$1000 \ln \alpha_{X-Y} \approx \Delta_{X-Y} = \delta^{18}\text{O}_X - \delta^{18}\text{O}_Y \quad (3)$$

The  $\delta^{18}\text{O}$  value of fluids in the Earth's crust varies substantially: seawater has a value of 0‰, magmatic fluids have values generally in the range +5 to +8‰, and meteoric waters mostly range from -15 to 0‰ depending on geographic location, the lower values typifying high latitude or high altitude areas. Over the past twenty years, oxygen and hydrogen isotope studies have been used extensively in the identification of the nature of fluids responsible for hydrothermal mineralisation, and have contributed substantially to a revolution in concepts of ore genesis.

Numerous studies of volcanogenic massive sulphide deposits have shown that the  $\delta^{18}\text{O}$  value of fluids which formed deposits, ranging in age from Archaean to Tertiary, is generally close to the seawater value of 0‰. Fluids precipitating calcite in chimneys and mounds in a

sulphide-forming submarine geothermal system on a sedimented spreading rift, the Guaymas Basin, Gulf of California, have  $\delta^{18}\text{O}$  values ranging from -0.8 to 4‰ (Peter and Shanks, 1992).

In the case of samples from the Mount Read Volcanics,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of Cambrian hydrothermal vesicle- and vein-forming calcites can be used as a semi-quantitative geothermometer, assuming a fluid  $\delta^{18}\text{O}$  value of 0‰ using the equation:

$$\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}} = 2.78 * 10^6 / T^2 - 2.89 \quad (4)$$

where T is in °K.

Similar equations have been calibrated for other carbonate minerals. More confidence in the method can be obtained in cases where the fluid  $\delta^{18}\text{O}$  value has been established by determining the temperature of formation of one or a few members of a suite of samples by an independent technique (e.g. chlorite geothermometry or fluid inclusions). Extreme care must be taken in the selection of samples, firstly in the identification of Cambrian hydrothermal assemblages and secondly in avoiding samples where recrystallisation of carbonate minerals in the presence of a fluid phase may have resulted in resetting of the  $\delta^{18}\text{O}$  value. A rough check on the validity of results may be obtained by calculating the  $\delta^{13}\text{C}$  value of the  $\text{H}_2\text{CO}_3$  in the fluid by the equation:

$$\delta^{13}\text{C}_{\text{H}_2\text{CO}_3} = \delta^{13}\text{C}_{\text{calcite}} + 8.914 * 10^8 / T^3 - 8.557 * 10^6 / T^2 + 18110 / T - 8.27 \quad (5)$$

In submarine basaltic hydrothermal systems the fluid  $\delta^{13}\text{C}$  value is generally close to 0‰ (Muehlenbachs, 1986). In the Guaymas Basin calcite  $\delta^{13}\text{C}$  values are much lower, consistent with deposition from a fluid with a value of about -11‰, reflecting roughly equal carbon inputs from seawater (0‰) and oxidised organic matter from the sediments (-21‰) (Peter and Shanks, 1992). An additional contribution from magmatic  $\text{CO}_2$  (-7‰) cannot be ruled out either from these data. Carbonates from Tasmanian VMS deposits appear to have carbon derived from a mixed seawater-magmatic source ( $\delta^{13}\text{C} = -5$  to +0.6‰; Khin Zaw and Large, 1990).

#### Whole-Rock Applications

For a rock undergoing isothermal alteration in a closed system, in which there is negligible transfer of water between the fluid phase and the rock, the  $\delta^{18}\text{O}$  value of a rock after water-rock interaction can be expressed as (Taylor, 1979):

$$\delta^{18}\text{O}_r^f = \frac{\delta^{18}\text{O}_r^i + (\delta^{18}\text{O}_w^i + \Delta_w^r) w/r}{1 + w/r} \quad (6)$$

where the superscripts i and f refer to the initial and final conditions respectively, and the subscripts r and w refer to the rock and water respectively. w/r is the atomic ratio of oxygen in the fluid phase to that in the rock, which is approximately equal to twice the water/rock mass ratio.

$\Delta_w^r$ , which closely approximates the oxygen isotope fractionation factor between rock and water (Equation 3), is

a function of temperature and the mineralogical composition of the rock, and is given by the expression:

$$\Delta_w^r \approx \delta^{18}O_r - \delta^{18}O_w \quad (7)$$

Equation (7) can be recast in terms of the water/rock ratio:

$$\frac{w}{r} = \frac{\delta^{18}O_r^f - \delta^{18}O_r^i}{\delta^{18}O_w^i - (\delta^{18}O_r^f - \Delta_w^r)} \quad (8)$$

Under open system conditions, in which each aliquot of water makes a single pass through the system and does not have the opportunity to further interact with the rock, the above expression becomes:

$$\frac{w}{r} = \ln \left\{ \frac{\delta^{18}O_w^i + \Delta_w^r - \delta^{18}O_r^i}{\delta^{18}O_w^i - (\delta^{18}O_r^f - \Delta_w^r)} \right\} \quad (9)$$

For VMS systems where a considerable proportion of the water is discharged into the ocean, open system conditions (Equation 9) might prevail. Under conditions of burial diagenesis in which the fluid may have been in prolonged contact with the rock and recycled several times, the closed system case (Equation 8) might provide a better approximation. The assumption of isothermal water/rock interaction involved in the models is clearly somewhat naive, but it should be realised that whole-rock oxygen isotope data reflect the *integrated history* of interaction, and as such provide broad constraints on temperature of alteration and amounts of fluid involved.

Where the water/rock ratio is very large, such as in the hydrothermal feeder zone below a VMS deposit, Equation 6 and the corresponding statement for an open system reduce to:

$$\delta^{18}O_r^f \approx \delta^{18}O_w^i + \Delta_w^r \quad (10)$$

In this case the final  $\delta^{18}O$  value of the rock is a function only of the isotopic composition of the water, the mineralogy of the rock, and the temperature of alteration, and is independent of the original isotopic composition of the rock.

For most felsic rocks  $\Delta_w^r$  can be approximated by the fractionation for alkali feldspar-water (O'Neil and Taylor, 1967), but in rocks rich in minerals with fractionation factors very different from the feldspars (e.g. chlorite or magnetite), the fractionation factors should be calculated individually. Spreadsheet programs have been developed to do this from quantitative X-ray diffraction analyses. For studies with the aim of detecting the outer subtle alteration haloes around VMS deposits, areas of strong overprinting alteration (e.g. that associated with Devonian granite-related mineralisation, rocks with later veining etc.) should be avoided. Experiments on the kinetics of oxygen isotope exchange and studies of geothermal systems (e.g. Cole and Ohmoto, 1986; O'Neil, 1987) show that most minerals (e.g. feldspars, micas, chlorite) re-equilibrate readily under hydrothermal conditions, but that quartz generally preserves its original  $\delta^{18}O$  values and carbonate minerals may exchange oxygen isotopes if they undergo recrystallisation in the presence of a fluid phase. Because of this recalcitrance of quartz to

isotopic exchange, a correction to raw  $\delta^{18}O$  data is required for rocks with significant proportions of pre-hydrothermal quartz (e.g. phenocrysts).

In the Hokoroku district of northern Honshu, Japan, the area of the most important cluster of Kuroko deposits, the effectiveness of the oxygen isotope technique was demonstrated. The Fukazawa deposit consists of a cluster of three major and several small massive sulphide lenses, totalling about 6 million tonnes of ore in an area of  $1.5 \times 0.5$  kilometres. The ore zones are surrounded by distinctive mineralogical alteration zones: a central sericite-chlorite zone extending up to 0.5 km away from ore in footwall rocks, flanked progressively by a montmorillonite zone, 1–3 km wide, and a zeolite zone. Each of the zones is characterised by a unique range in whole-rock oxygen isotope values:  $16.9 \pm 2.7$  ‰ (1 $\sigma$ ) for the zeolite zone,  $11.1 \pm 2.5$  ‰ for the montmorillonite zone, and  $6.7 \pm 1.3$  ‰ for the sericite-chlorite zone (Green *et al.*, 1983). Somewhat surprisingly there is no major break in either the clay-zeolite or oxygen isotope zonation at the ore horizon (although whole rock Na<sub>2</sub>O depletion is restricted to footwall rocks near ore) and low  $\delta^{18}O$  values extend at least 300 m above the ore horizon in the centre of the sericite-chlorite zone. The data were interpreted to reflect both a longevity of hydrothermal discharge in the ore zone and alteration by fluids with a  $\delta^{18}O$  value of 0‰ at temperatures varying from 25° to 120°C in the zeolite zone, to 200° to 300°C in the sericite-chlorite zone. The significance of these results to greenschist facies metavolcanic terranes, such as the Mount Read Volcanics, is that the clay-zeolite mineralogical zonation would be destroyed, but provided that metamorphism took place under low water-rock ratio conditions the whole-rock oxygen isotope zonation would be preserved.

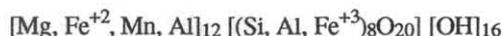
## CHLORITE GEOTHERMOMETRY

Two types of thermometers exist:

- (a) Empirical thermometers
- (b) Thermodynamically calculated thermometers.

### *Empirical thermometers*

The chemical formula for chlorite can be expressed as:



where the first group of cations are octahedrally co-ordinated in the structure and the second group are tetrahedrally co-ordinated by oxygen.

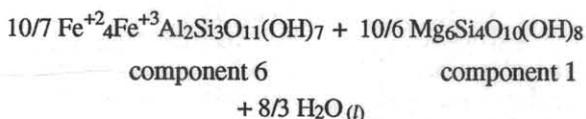
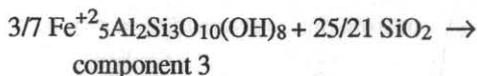
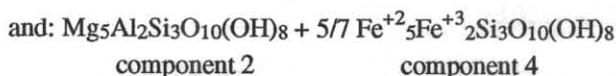
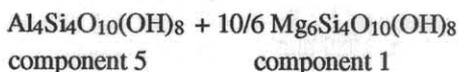
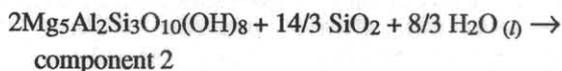
Based on studies of active geothermal fields in the Los Azufres area, Mexico and the Salton Sea area, California, Cathelineau and Nieva (1985) and Cathelineau (1988) noted an excellent correlation between the content of tetrahedrally co-ordinated aluminium of hydrothermal chlorites and temperature, with a regression co-efficient of 0.97 over the temperature range 130° to 325°C. Cathelineau (1988) noted that his thermometer applied in a general way to chlorites formed at temperatures as high as 350°C at Larderello, Italy and diagenetic chlorites formed at temperatures as low as 100° to 140°C in Colorado and the North Sea.

However his geothermometer is calibrated most precisely between 200° and 300°C, and only one data point exists below 170°C. Cathelineau also assumes that all iron is

present in the divalent state. This is likely to lead to over-estimation of the amount of tetrahedrally co-ordinated Al, and consequently of temperature, particularly of chlorites formed at temperatures of less than 200°C.

### *Thermodynamically calculated thermometers*

Walshe (1986) developed a geothermometer based on the consideration of chlorite as a solid solution of six components, the thermodynamic properties of which were either known or could be reasonably estimated. His model specifically calculates the ferric iron and water contents of chlorite from electron microprobe analyses from the following equilibria, and from a formulation of the Gibbs-Duhem equation:



The technique involves solution of non-linear equations and is computer intensive but, apart from the estimation of thermodynamic data for the six components, the model rests on only one assumption: *co-existence in equilibrium of chlorite and quartz*. General experience of the chlorite model is that there is very good agreement between temperatures derived from it and other methods of temperature estimation, particularly in reduced hydrothermal systems at  $T > 250^\circ\text{C}$ , and under these conditions there is also usually good agreement with the Cathelineau and Nieva (1985) Al (IV) method. Under lower temperature, more-oxidised conditions, the Walshe model is preferred because it is more rigorous.

Care must be exercised with both methods in metamorphic terrains particularly where chlorite has an opportunity to re-equilibrate (i.e. exchange silica) with quartz during prograde or retrograde metamorphism. In addition, reliable results are usually only achievable with hydrothermal chlorites. The rocks from the Mt Cattley-Hellyer area are unusual in the Tasmanian context in that undeformed vesicle chlorites enable these conditions to be met.

### FLUID INCLUSIONS

During processes of crystal growth, recrystallisation or fracture healing, small proportions of the fluid medium may be trapped as fluid inclusions. Fluids may be trapped either during crystal growth in growth irregularities to form primary fluid inclusions, or at some later time by processes of recrystallisation or fracture filling to form secondary fluid inclusions. Pseudosecondary fluid inclusions are those formed along fractures during the growth of a crystal. Most fluid inclusions range in size from 3 to 20  $\mu\text{m}$ .

Compositions of fluid inclusions vary widely. The major solvents are  $\text{H}_2\text{O}$  and less commonly  $\text{CO}_2$  and the major solute ions include Na, K, Ca, Mg, Cl,  $\text{SO}_4$  and  $\text{HCO}_3$  with Li, B, Al, Fe, F, Mn, and Si being minor solute ions. Major constituents in inclusions with organic liquid or gas include  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , as well as a variety of high molecule weight compounds.

Fluid inclusions normally have a vapour or gas bubble which may move constantly under the effect of a thermal gradient or of gravity. The volume coefficients of thermal expansion for minerals are less than the water by up to 3 times. Therefore upon cooling, a fluid inclusion which has been formed as homogeneous fluid at elevated temperatures will shrink more than the host mineral, and when the total vapour pressure of the fluid is more than the pressure in the inclusion a bubble will nucleate and grow. The process can be reversed simply by heating the fluid inclusion to the temperature at which the bubble disappears (i.e. homogenisation temperature).

The salinity of fluid inclusions (wt.% NaCl equivalent) can be estimated by freezing the fluid inclusions and measuring the depression of the freezing points of the inclusions. This is just an estimate, as other solute ions such as Mg and Ca, which may also be present in the fluid, can affect the freezing point significantly. There are many methods (non-destructive and destructive) to determine the compositions of the fluid inclusions, and these have been explained in detail by many workers (e.g. Roedder, 1984).

In general, fluid inclusions can be utilised to define the possible environment of ore formation (e.g. epithermal, mesothermal), and in studies of physicochemical conditions of ore-forming fluids. They can also be used in igneous and metamorphic terrains, in oil exploration, in active geothermal systems, and in many other fields.

## RESULTS

### HELLYER

Prior to mining, the Hellyer massive sulphide orebody contained some 15.6 million tonnes of massive sulphide ore grading 0.3% copper, 6.8% lead, 13.0% zinc, 160 g/t silver and 2.2 g/t gold (Aberfoyle Ltd Annual Reports 1990, 1991). The ore is hosted by the Que-Hellyer Volcanics, a unit of predominantly andesitic to basaltic composition with subordinate dacite which includes lavas, hyaloclastites, shallow intrusives and minor epiclastic rocks (Corbett and Komysan, 1989; Corbett, 1992; Waters and Wallace, 1992). In the mine area (McArthur and Dronseika, 1990), the orebody is underlain by plagioclase-phyric andesite lava and epiclastics. The ore horizon is marked by a unit of polymict breccia, sandstone and shale up to 10 m thick, the hangingwall volcanoclastic sequence, which laps onto the massive ore. Succeeding basaltic pillow lavas, peperites and minor chert are about 220 m thick and are overlain by 100 m of black pyritic shale and siltstone of the Que River Shale. The ore is cut by a vertical fault with horizontal displacement of 130 metres.

A well-developed footwall alteration zone extends for at least 550 m below the ore and consists of a central stringer zone, comprising from the centre outward: a siliceous core, chlorite, chlorite-sericite and sericite facies surrounded by the sericite-quartz dominated stringer envelope zone (Gemmell and Large, 1992). Alteration extends through the

hangingwall basalt in the form of a fuchsite-carbonate±barite zone which broadens somewhat immediately below the Que River Shale (Jack, 1989). Ductile deformation is locally intense in the orebody and in the stringer envelope zone and the stringer zone outside the siliceous core, but elsewhere deformation is of a semi-brittle nature and is generally minor. This minimal deformation and the low-grade prehnite-pumpellyite facies metamorphism (Offler and Whitford, 1992) make Hellyer an ideal case study.

Whole-rock oxygen isotope analyses of some 64 samples of drill core selected for a parallel study of geochemical variation (Jack, 1989), together with analyses of samples of footwall rocks supplied by J. B. Gemmell from exploration drill holes up to 2300 m from the deposit, show a number of parallels with the zonation around the Kuroko deposits. Within 200 m laterally of the orebody there is a total variation in whole rock  $\delta^{18}\text{O}$  values from 6.2 to 16.7‰. The data are consistent with alteration by a seawater-dominated hydrothermal fluid with a  $\delta^{18}\text{O}$  value close to 0‰. The footwall andesites have  $\delta^{18}\text{O}$  values of  $11.28 \pm 0.92\text{‰}$  (one standard deviation, number of samples  $n = 20$ ), with progressively lower values reported from the stringer envelope zone of  $9.81 \pm 1.76\text{‰}$  ( $n = 8$ ) and the stringer zone  $8.28 \pm 1.25\text{‰}$  ( $n = 10$ ). In the hangingwall basalt there is a similar distinction between samples from the fuchsite-carbonate zone ( $\delta^{18}\text{O} = 10.57 \pm 1.16\text{‰}$ ,  $n = 12$ ) and other basalts ( $\delta^{18}\text{O} = 11.8 \pm 2.18\text{‰}$ ,  $n = 9$ ). There is no marked increase in  $\delta^{18}\text{O}$  values across the ore horizon in any of the holes sampled.

Two samples from the Que River Shale 250 m laterally from ore have values of 15.4 and 15.6‰, similar to values from unaltered sedimentary rocks. This may indicate that the commencement of deposition of the shale marked the end of activity in the Hellyer hydrothermal system, but more analyses from rocks closer to ore would be needed to confirm this. Some supporting evidence for this postulate is that the highest  $\delta^{18}\text{O}$  values from the hangingwall basalt occur at the top of the unit, consistent with a decline in temperature of alteration. Regionally the highest  $\delta^{18}\text{O}$  values in footwall volcanics are recorded in rocks 1400 to 2300 m from the Hellyer orebody ( $\delta^{18}\text{O}$  range of 12.0 to 13.8‰, mean = 13.09‰, standard deviation = 0.53,  $n = 10$ ). These data indicate the regional extent of alteration; to produce such high  $\delta^{18}\text{O}$  values from normal basaltic to andesitic rocks with initial values in the order of 6 to 7.5‰ requires considerable input of low temperature fluid with a seawater isotopic composition.

The results indicate the potential utility of the use of oxygen isotope data in screening areas worthy of more detailed exploration. However, because of the relatively small gradients in  $\delta^{18}\text{O}$  values in more distal areas other techniques are needed for detailed targeting. Possible techniques include chlorite geothermometry and isotopic studies of carbonates, the latter providing relatively precise temperatures in the range 25° to 350°C. Assuming a fluid  $\delta^{18}\text{O}$  value of 0‰, early (pre-cleavage) vein and amygdale carbonates show a general temperature increase from about 120°C at the top of the hangingwall basalt to around 160° to 200°C towards the base of the fuchsite-carbonate zone and near the margins of the stringer zone. Vesicle-filling hydrothermal chlorites in the Que-Hellyer Volcanics display a distinctive fanning habit and grey-blue interference colours. Similar chlorite also occurs in pyroxene pseudomorphs. Such chlorites generally give temperatures

in good agreement with the carbonate data at liquid-vapour pressure using the program of Walshe (1986). Chlorite occurring in the cleavage has green or brown interference colours. These chlorites give consistent temperatures of 280° to 310°C at 1 kilobar pressure. A combination of the two techniques has considerable promise in the mapping of palaeotemperatures of alteration in these relatively undeformed rocks.

A further useful exploration criterion, indicating proximity to a footwall stringer system, is the presence of K-feldspar carbonate replacements of plagioclase phenocrysts, which in drill hole HL14 extend up to 50 m laterally from the stringer envelope zone. McGoldrick and Large (1992) have recorded similar, but more extensive alteration in the footwall at the Que River Mine, where it is associated with anomalous gold, barium and antimony values. However this alteration style is apparently not always present. Within the K-feldspar-carbonate zone and extending beyond it in HL14 are pyrites with anomalously high  $\delta^{34}\text{S}$  values of +12.7 to +32.0‰ (analysed by R. N. Woolley for this study and reported in Jack, 1989 and Gemmell and Large, 1992).

## HERCULES

The Hercules Mine produced 3.12 million tonnes of ore grading 5.7% lead, 17.8% zinc, 0.47% copper, 180 g/t silver and 2.94 g/t Au from discovery in 1891 to closure in 1986. The ore occurs in a number of lenses extending along strike for some 800 m, straddling the contact between thick plagioclase-phyric pumiceous mass-flow deposits in the footwall and overlying black slate (Allen and Hunns, 1990). Quartz-feldspar bearing breccia and sandstone overlie the slate and are succeeded by pumiceous mass-flow units with feldspar phenocrysts identical to those in the footwall. This stratigraphic arrangement is similar to that at Rosebery. Tabular felsic intrusive bodies are common and appear to occupy significant fault zones. In contrast to Hellyer, the ore lenses are aligned parallel to subvertical cleavage, and are sharply discordant to open to tightly folded bedding. In addition to massive sulphides much of the ore-grade mineralisation is disseminated. The rocks hosting and surrounding the ore are commonly altered to chlorite and a variety of carbonate minerals, with textures ranging from disseminated oolites, through colloform types to large (to about 300 mm) spheroids which predate cleavage development. These bodies appear to be of syn-diagenetic origin (Fitzgerald, 1974) and the disseminated sulphides may, at least in part, represent replacement of this carbonate, or of feldspar, as suggested by Khin Zaw and Large (1992). The origin of the mineralisation is however controversial: recent interpretations range from a replacement origin during Devonian deformation (D. G. A. M. Aerden, pers. comm.), through sub-sea floor replacement during diagenesis, to structurally remobilised lenses of originally massive exhalative massive sulphide (Lees and Howarth, 1989).

The footwall alteration is strongly zoned: beneath a silicified zone closely associated with ore is an alteration pipe cored by quartz-chlorite-pyrite±chalcopyrite which passes outward to quartz-sericite-pyrite±sphalerite±galena with a halo of quartz-sericite rich rocks containing K-feldspar±carbonate replacements of plagioclase, texturally identical to those at Hellyer (Green, 1990; Eastoe *et al.*, 1987). Alteration in the hangingwall rocks is more poorly defined. There are a number of old copper and lead-zinc prospects associated with quartz-sericite or chloritic alteration. Some of these appear to be associated with the margin of the porphyries.

Whole-rock oxygen isotope data show a similar range to that at Hellyer from 6.8 to 15‰, with the lowest  $\delta^{18}\text{O}$  values of 6.8 to 10.0‰ in rocks from the alteration pipe, through 11.2‰ 750 m NE of the mine, to 14.0 to 15.5‰ 100 to 250 m further north. In footwall rocks within 100 m of the pipe margin 600 m west and 350 m vertically below the orebody heavy values of 15 and 15.6‰ are present. Surprisingly a trend of decreasing  $\delta^{18}\text{O}$  values from 12.8 to 6.8‰ upward through the sequence over a horizontal distance of 250 m was noted in hangingwall rocks east of the Hercules orebody. This trend correlates with an increase in alteration towards the old East Hercules copper prospect, and is also marked by an increase in Na, Ca and Sr depletion and enrichment in K, Rb, S and base metals, although the oxygen isotopes provide the broadest halo. The Mn content of chlorites increases progressively from 0.9 to 1.3% over the same interval. The alteration affects all rock types, including the porphyry intrusives.

Eastoe *et al.* (1987) regarded this mineralisation as Devonian in age, but samples of pyritic chlorite-rich rocks from the dumps show evidence of a pre-deformational age (e.g. pressure shadows adjacent to pyrite). Eastoe *et al.* (1987) carried out systematic analyses of chlorite in the footwall rocks. Chlorite is manganese-rich, and there are a variety of Mg/Mg + Fe ratios from 0.3 to 0.75, with relatively iron-rich chlorite (0.35) in the centre of the pipe and an increase in Mn towards ore. Further chlorite analyses were carried out in this study in an attempt at geothermometry. A restricted range of temperatures of 300° to 320°C, calculated at a pressure of one kilobar, reflects metamorphic conditions. Apart from chlorite in late quartz tension veins which gives lower temperatures, all of the chlorite is aligned in the cleavage.

Furthermore the sulphur isotope composition of samples from this hangingwall alteration zone (11 to 19‰) is indistinguishable from that in the Hercules orebody and footwall. This similarity of geochemical characteristics led Green (1986) to postulate that the East Hercules mineralisation might represent a product of Cambrian hydrothermal remobilisation from a buried massive sulphide at depth. An equally probable explanation, permissible if porphyry intrusion closely followed deposition of the enclosing rocks, is that hydrothermal activity in the Hercules area was a protracted process, thus providing indirect evidence for the diagenetic replacement model of mineralisation. Either way, the area of prospectivity is enhanced by these data.

## BOCO

In the Boco Siding area 13 km northeast of Rosebery, a moderately pyritic, pre-cleavage sericite-quartz alteration zone extending along strike for about one kilometre occurs in a sequence of felsic lavas and pyroclastic rocks with a very minor component of epiclastic rocks, which locally contain small amounts of probable exhalative pyrite. No significant base or precious metal mineralisation has been discovered in the area.

The rocks display some of the geochemical features typical of a footwall alteration zone associated with massive sulphide mineralisation, such as strong depletion in Na, Ca and Sr, and moderate enrichment in S and Mg. In contrast to the situation at Hellyer and Hercules there is little difference in the  $\delta^{18}\text{O}$  values of altered and unaltered rocks, with a total range of 9.7 to 11.8‰. The sulphur isotope values are distinctly lower than those at Hercules, with a range of pyrite  $\delta^{34}\text{S}$  values of -1.2 to 4.7‰. This is similar to the values for

some other apparently barren pyritic deposits in the Mount Read Volcanics such as Basin Lake, Chester and the Cattley Range prospect (Collins, 1981; Green, 1986; Solomon *et al.*, 1988; Green, unpublished data). In the latter occurrence, the lead isotope values are consistent with a Cambrian age for the mineralisation (Carr, 1990), suggesting that while lead isotopes provide a useful guide to the age of alteration, they do not necessarily indicate mineralisation of an economic grade.

The data are compatible with alteration by a fluid of seawater origin but at lower temperatures (<200°C) than those required to inorganically reduce seawater sulphate or to transport sufficient base metals together with  $\text{H}_2\text{S}$  to form an orebody. This would account for the low  $\delta^{34}\text{S}$  values in the deposit, in that the sulphur was probably leached from the surrounding volcanic rocks.

## LAKESIDE

The discovery of gold mineralisation at the Henty Prospect prompted intensive exploration along the Henty Fault Zone. Our investigation of the Lakeside Prospect (Taheri and Green, 1990) was undertaken because of a possible volcanogenic component of the mineralisation in the area (Polya *et al.*, 1986), and to study the metallogenically rare gold-tin-copper-arsenic association. Several small to medium sized Pb-Ag to polymetallic Sn-Au bearing deposits occur adjacent to the fault in the Mt Farrell area, where the fault separates the Mt Black Volcanics to the west from the Farrell Slates and the Murchison Volcanics to the east (McNeill and Corbett, 1992). The rocks to the west of the Henty Fault are predominantly chloritised feldspar-phyric andesite and dacite, and are silicified near the fault. The Farrell Slates mainly consist of grey to black slate, shale, greywacke and volcanoclastic arenite. The rocks are commonly deformed and are brecciated.

The mineralisation associated with the Henty Fault Zone in the Mt Farrell area post-dates Devonian cleavage development and may be divided into two broad categories:

1. Pb-Ag dominated deposits hosted by the Farrell Slates. The deposits occur as sub-parallel lenticular fissure lodes and veins in shears striking from NNW to NNE (e.g. New North Mt Farrell Mine).
2. Polymetallic Sn-Au bearing mineralisation which occurs as disseminations, fissure fillings and stringers adjacent to the Henty Fault in the Farrell Slates (e.g. Lakeside Prospect) or in the Mt Black Volcanics (Sterling Valley Sn-As prospect).

The mineralisation appears to be directly associated with the intrusion of the Granite Tor Granite at a shallow depth in the Devonian. A WSW-trending granite ridge extends from the Granite Tor Granite to the Pine Hill Granite, and possibly as far west as the Heemskirk Granite (Leaman and Richardson, 1989). A number of tin and tourmaline-bearing deposits, as well as Pb-Zn-Ag vein deposits, occur within the zone of the granite ridge. Based on recent interpretations of gravity data by Leaman and Richardson (1989) and Archer (1989), the Sn-Au mineralisation occurs above the crest of the ridge where the granite lies at a depth of about 1 km, whereas Pb-Ag dominated deposits occur where the granite surface is at a greater depth. High-angle reverse movement of the Henty Fault synchronous with the intrusion of the granite (Berry, 1989) probably created permeable ore channels in the area.

Mineralisation at the Lakeside Prospect may be divided into four different stages.

Stage 1: pyrite + pyrrhotite + arsenopyrite.

Stage 2: the mineralisation is divided into two substages:

2a: arsenopyrite + cassiterite + chlorite,

2b: chalcopyrite + stannite + gold

with quartz, tourmaline and fluorite being the common gangue minerals for the both substages.

Stage 3: galena + sphalerite, and

Stage 4: chlorite + carbonates + pyrite.

The mineral contents and/or proportion of the different ore minerals changes with increase in depth. Pyrite, galena, sphalerite, stannite and chalcopyrite contents decrease at depth, whereas cassiterite and pyrrhotite contents increase. The main mineralising events appear to have resulted from boiling of a CO<sub>2</sub>-bearing fluid at a temperature of around 340°C, although only dilute CO<sub>2</sub>-rich fluid inclusions interpreted to be the vapour condensate of a fluid which had undergone phase separation. The  $\delta^{18}\text{O}$  values of quartz, together with the fluid inclusion data, constrain the water  $\delta^{18}\text{O}$  values for the early stages of mineralisation at 7.2 to 9.1‰, indicative of Devonian magmatic fluids. The reduced character of the fluid and high temperature of the mineralisation particularly favoured tin transport through Cl complexes. The temperature may have been sufficiently high for Cl complexes to have played a major role in Au transport, although the neutral complex H<sub>2</sub>Au(HS)<sub>2</sub> is at least equally probable (Hayashi and Ohmoto, 1991). Boiling would have been an effective depositional mechanism from either of these species under these conditions, and the concentration of gold was probably optimised at the Lakeside Prospect.

The Sterling Valley Sn-As mineralisation in the Mt Black Volcanics has characteristics indicative of its being a deeper analogue of the mineralisation at the Lakeside Prospect. The gold content is lower and pyrrhotite is a more common mineral. Topaz, closely associated with fluorite, is present. A recent preliminary fluid inclusion investigation by J. Taheri shows that at least four separate generations of fluids, with homogenisation temperatures up to 390°C and salinities of up to 15 wt.% NaCl equivalent, were involved in the mineralisation. Berry's (1989) structural synthesis of syn-mineralisation reverse faulting followed by sinistral strike-slip faulting is consistent with the two deposits being displaced units of an original single-sheeted vein system developed on both sides of the Henty Fault. If so, the extent of the left lateral displacement on the fault can be constrained at about 1100 metres.

Sulphur isotope studies (e.g. Solomon *et al.*, 1969) and the zonation of hydrothermal alteration assemblages in the Murchison Volcanics east of the fault (Polya *et al.*, 1986) have been interpreted to indicate a syn-volcanic Cambrian origin for the mineralisation. Sulphur isotope compositions reflect the gross mineralogical zonation of the area.  $\delta^{34}\text{S}$  values of +11.9 to +16.5‰ in the Ag-Pb deposits flanking the granite ridge are similar to those in the Rosebery and Hercules volcanic-associated deposits. Hence the Pb-Ag deposits could contain recycled Cambrian sulphur. However  $\delta^{34}\text{S}$  values of +5.2 to +12.0‰ (80% of values between +7 to +10‰) for the Sn-Au deposits above the ridge crest suggest a substantial component of magmatic sulphur for these deposits.

The lead isotope compositions from the vein deposits along the Henty Fault Zone in the Mt Farrell area (Gulson and Porritt, 1987; Carr, 1988) have higher  $^{206}\text{Pb}/^{204}\text{Pb}$  than Cambrian VMS deposits, and plot either within the field of the Devonian mineralisation or between the Cambrian and the Devonian fields of Gulson and Porritt (1987). The values from the Lakeside Deposit are the most radiogenic and are consistent with a Devonian magmatic source.

In summary, the mineral zoning, petrographic observations, fluid inclusion, sulphur, oxygen and lead isotope data indicate that the mineralisation along the Henty Fault zone in the Mt Farrell area is related to the intrusion of the Granite Tor Granite, although a country rock input for S and possibly some of the Pb and Au might be important.

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