PALEOHYDROLOGY OF THE GOLDEN CROSS VEIN SYSTEM

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SUMMARY - Fluid inclusion and stable isotopic analyses of carbonates and quartz establish that there are three fluids represented in the Empire Vein structure at Golden Cross. The first fluid is a more near-surface meteoric fluid which has undergone little or no isotopic exchange with the surrounding rocks. The second fluid comprises a deep geothermal fluid of probable meteoric origin but which has exchanged oxygen isotopes with the rock through which it has passed at elevated temperatures. The third fluid is of magmatic origin. In most cases the latter two fluids have been significantly diluted by mixing with the first fluid.

1. INTRODUCTION

The Golden Cross epithermal gold-silver deposit is located in the Hauraki gold district in the Coromandel range of New Zealand (Figure 1). This important district has yielded in excess of 10^6 kg of gold-silver bullion over the past 120 years (de Ronde and Blattner, 1988). Detailed discussion of the regional and local geology are included in Skinner (1983), de Ronde (1986), and de Ronde and Blattner (1988).

The Empire structure is the manifestation of the upflow zone of a major fossil geothermal system and is hosted in a through-going fault zone that trends N15E and generally dips steeply to the NW. In addition to quartz, most of the ore-bearing veins also contain variable amounts of adularia, calcite, clays, and sulfides (mainly pyrite) as banded and brecciated vein material that is typical of high-flow geothermal systems. The purpose of this study was to examine the paleohydrology of this fossil system in terms of sources of components and paths of fluid migration.

2. SAMPLE DISTRIBUTION AND DATA

For this study 147 samples (39 quartz, 108 carbonate) were analysed for fluid inclusion homogenization and freezing point depression temperatures, and for carbon and oxygen isotopes. Included in this study are data from M Simpson (1996), C Simpson (1996), and de Ronde and Blattner (1988). Two samples were sent to the laboratory of Y Sano (University of Hirsohima, Japan) for He isotope determinations.

The fluid inclusion population of most samples is dominated by liquid + vapour inclusions; these contained approximately 20% vapour at room temperature. In a few samples, there exist liquid + vapour inclusions containing variable proportions of vapour (indicative of boiling). Heating and freezing measurements were performed in replicate for most samples resulting in precision of ±0.1 °C for freezing measurements and ±1°C for heating measurements. Modal homogenization temperatures for individual samples studied range from 145°C to 230°C, but the majority of the data fall between 185 °C and 205 °C. Freezing point depression temperatures ranged from slightly positive values to -2.2 °C; the majority of values fall between -0.1 °C and -0.9 °C, corresponding to between 0 and 1.5 weight percent NaCl equivalent.

Stable isotope measurements of oxygen and carbon were made on calcite and both ore-stage and late-stage quartz; uncertainties are ±0.1‰ for all measurements. $\delta^{13}C$ values of calcite range between -2.0% and -9.9% (PDB) and $\delta^{18}O$ values range between 3.4% and 15.4% (VSMOW). $\delta^{18}O$ values of quartz fall between 7.3% and 11.2‰ (VSMOW).

Fluid inclusion modal homogenization temperatures are plotted as a function of calcite and quartz stable isotope data in Figure 2. Isocompositional curves of fluids in equilibrium with quartz and calcite also are plotted, based on equilibrium fractionation factors (Friedman and O'Neil, 1977). The majority of the carbonate samples are in equilibrium with a fluid having an oxygen isotopic composition near -4.5‰, though they range from -6‰ to -3‰, and a carbon isotopic composition near -7‰. There are a number of samples (discussed below) that depart from these means and are in equilibrium with a fluid(s) having higher $\delta^{18}O$ and $\delta^{13}C$ values. Data for quartz are presented in Figure 2c. Although there is a significant spread in the data (-1‰ to -6‰), most samples appear to be in equilibrium with a fluid having $\delta^{18}O$ near -3‰.

Two samples of fluid inclusions from vein calcite were analysed for their rare gas ratios for comparison with rare gas data from active geothermal systems in the Taupo Volcanic Zone. $^4He/^{20}Ne$ abundances of the

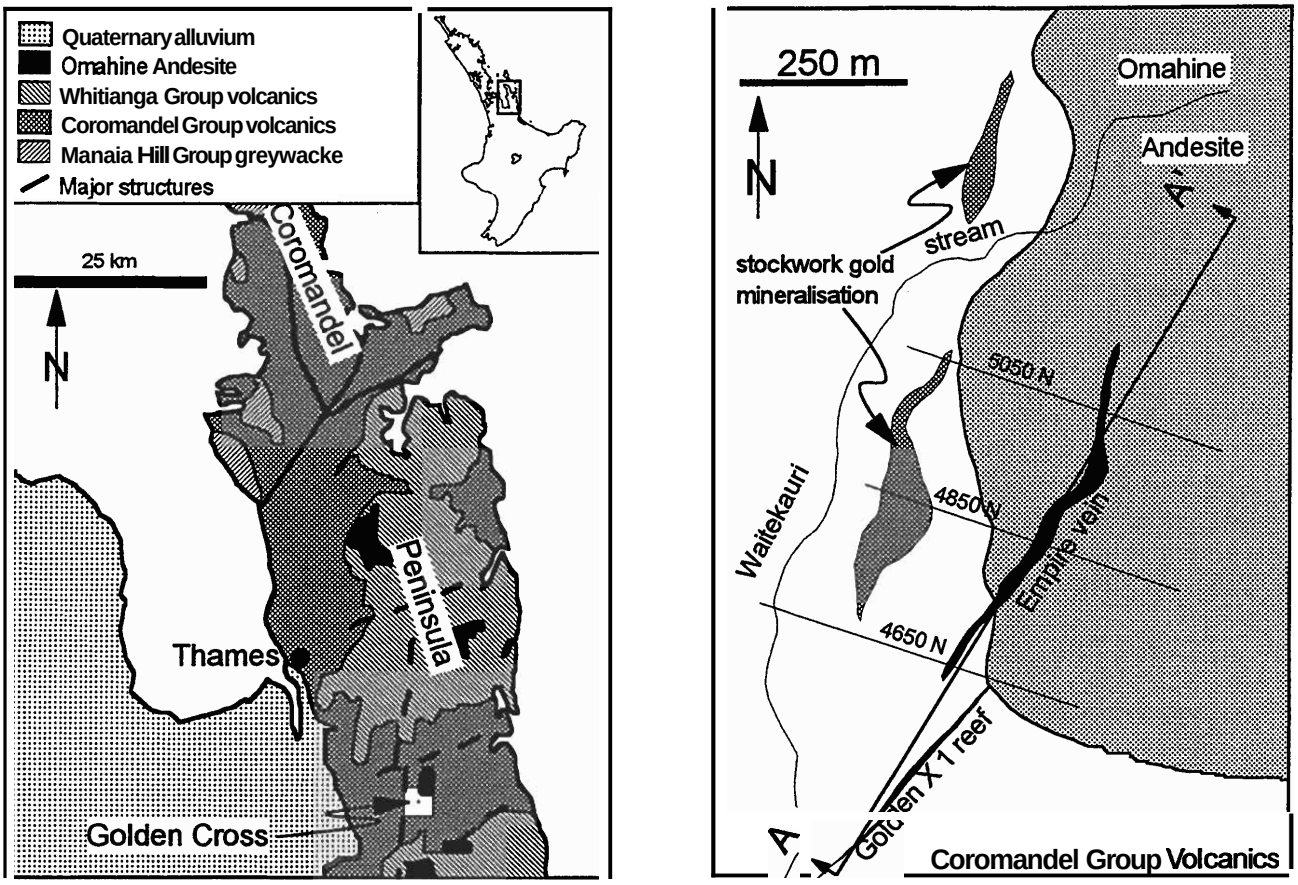

Figure 1. a) Location map and generalized geology of the Coromandel Peninsula (simplified from CRJ Simpson, 1996); b) Surface geology at the Golden Cross mine showing location of veins (projected to surface) and cross section of Figure 5.

samples were between 2 and 4; $^3He/^4He$ ratios (R/Ra) on two samples were 4.4 and 8.6 (Y. Sano, pers. comm 1996).

3. ORIGINS OF HYDROTHERMAL CALCITE

Calcite solubility (and consequently. deposition) is a complex function of several parameters, including pH, temperature, calcium ion activity, and fugacity of CO_2. These have been discussed in detail by Holland and Malinin (1979), Fournier (1985) and Simmons and Christenson (1994) and only will be summarized here. Calcite deposition can be effected by three mechanisms: hydrolysis (i.e. replacement) reactions, heating, and boiling. Where calcium-bearing aluminosilicates are invaded by CO_2-bearing fluids, the ensuing reactions often yield calcite and clay minerals (Giggenbach 1981). Because all of the calcite discussed in this paper formed in relatively open space, boiling and heating are the two primary mechanisms controlling calcite deposition considered here. Platy textures, as documented by Simmons and Christenson (1994) in several geothermal systems, are likely the result of high degrees of supersaturation and consequent rapid growth of crystals during boiling events following the reaction:

$$2HCO_3^- + Ca^{+2} = \text{calcite} + H_2O + CO_2.$$

Evaluation of the effectiveness of boiling on calcite precipitation requires a knowledge of changes in the relative distribution of the various aqueous species. As shown by Simmons and Christenson (1994), calcite typically becomes supersaturated during the early stages of boiling due to increasing pH as CO_2 is lost from solution. However, *extensive* boiling and consequent adiabatic cooling leads to undersaturation and possible redissolution of the early-deposited calcite.

Owing to the inverse solubility of calcite (Ellis, 1959), a second depositional mechanism that warrants discussion inolves conductive heating of a calcite-saturated solution. Although this process could not be viewed as being sustainable in a convecting hydrothermal system, suitable conditions could prevail during transient periods, such as those occurring during thermal collapse and decay of a system. In this case, shallow, bicarbonate-rich steam heated fluids such as those encountered at Ohaaki (Hedenquist, 1990) could temporarily invade higher temperature environments, potentially flooding available open space with carbonate minerals.

In principle, it is possible to determine the difference between these two modes of origin for calcite in vein systems by utilizing fluid inclusion and stable isotopic data on the calcites. Although both supergene and hypogene fluids are meteoric in their ultimate origin (O'Neil and Silberman, 1974), deeply-circulating water

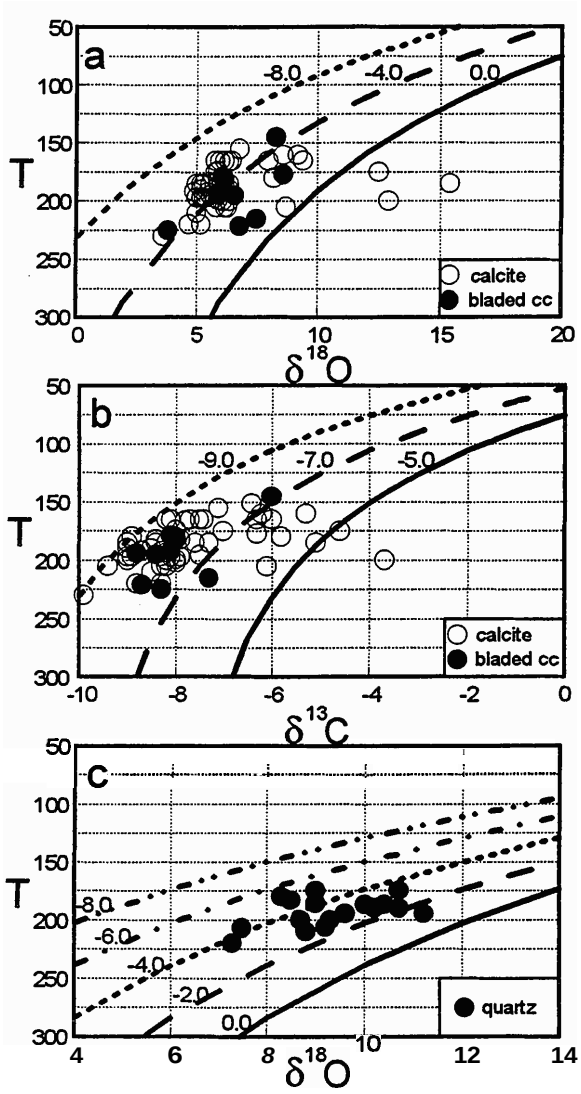

Figure 2. Measured homogenization temperature vs. isotopic composition of minerals from the Empire structure. a,b = calcite; c = quartz.

will exchange oxygen with the rock through which it passes at elevated temperatures and will evolve isotopically toward higher $\delta^{18}O$ values. Steam-heated waters, on the other hand, consist primarily of unexchanged meteoric waters. A third possible component is that of magmatic water, which would contribute oxygen with much higher $\delta^{18}O$ values, in the range of +6 to +10‰.

There may or may not be differences in the C isotopic composition of hydrothermal carbonates as a function of the source carbon. Descending waters may have different sources (or be less modified) than ascending thermal waters. Potential carbon sources include atmospheric CO_2 (-7 to -9‰), organic carbon (*ca.* -25‰), reduced igneous carbon (-15 to -30‰), oxidised igneous carbon (ca. -4‰), and marine carbonates (ca. 0%). Because there are no reported marine carbonate rocks in the section, the latter is not a likely source for any of the carbon in the Golden Cross hydrothermal system. All of the other sources potentially could contribute to the carbon budget at Golden Cross.

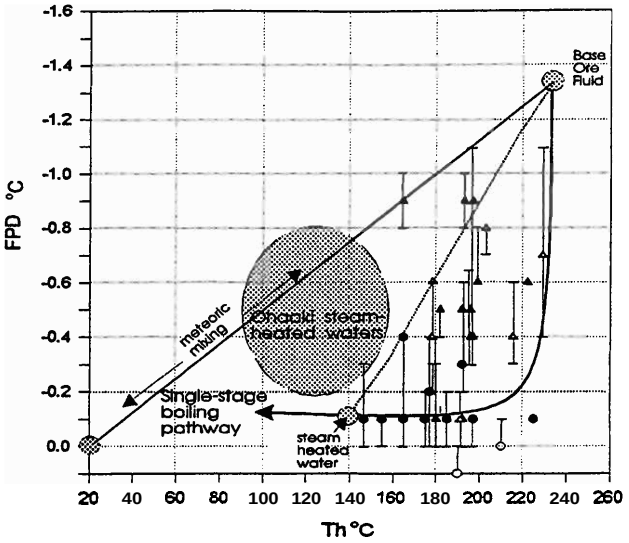

Figure 3. NaCl-equivalent salinity vs. homogenisation temperature for fluid inclusions. Mixing between deep fluid and meteoric water and boiling trend shown by straight line and arrow, respectively.

4. DISCUSSION

Overall, salinities of the inclusions are quite low (Fig. 3), comparable to salinities reported for many other epithermal vein systems (e.g. Bodnar et al., 1985) and active geothermal systems (Christenson, 1987; Hedenquist, 1986; Simmons and Christenson, 1994). Mixing lines drawn between ambient meteoric water of nil salinity and a base ore fluid of 240 °C and bulk salinity of *ca.* 0.7 molal, and between a steam heated water at 140 °C and the ore-stage fluid provide constraints on the temperature - composition relations for the parent fluids. However, most data fall below these mixing relationships suggesting that simple 2-component mixing is probably not the dominant process affecting reservoir fluid compositions.

The narrow temperature range over which the freezing point depression varies (Fig. 3) is more consistent with boiling being the dominant reservoir process. A major portion of the freezing point depression observed in these samples is likely to be due to aqueous CO_2 rather than salts and is supported by crushing tests, and by comparison of the data to a single-stage adiabatic boiling pathway (Fig. 3). Rapid degassing of CO_2 in the earliest stages of boiling very rapidly lowers the FPD, resulting in the steep trajectory of the curve from the base fluid position. Both the range of FPD in individual samples and the overall distribution of data point to boiling as the likely mechanism controlling the P-T-X of the fluid. In addition, reaction path modelling of Broadlands-Ohaaki fluids using REACT (Bethke, 1992) shows that they are strongly undersaturated with respect to calcite (e.g. log Q/K for well BR16 = -1.35), and that simulated conductive heating of these fluids does not lead to precipitation of calcite, but rather dolomite, owing to their relatively high Mg concentrations.

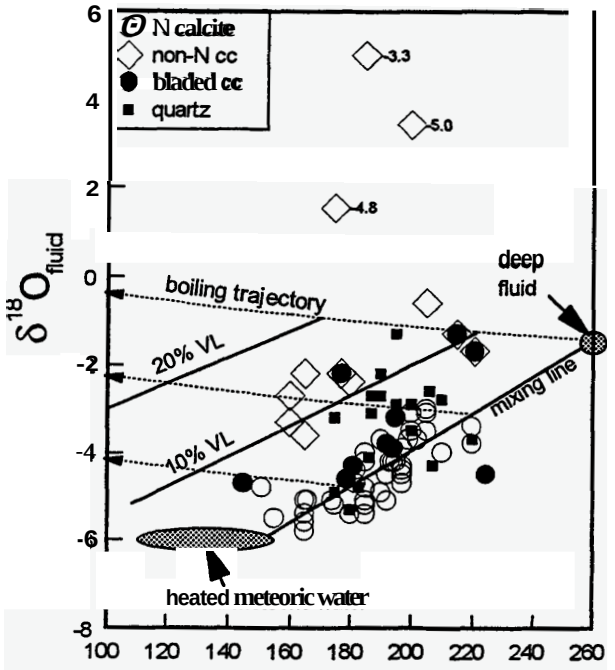

Figure 4. Calculated oxygen isotopic data vs. homogenization temperature for vein samples. Two major fluid components are deep geothermal fluid and steam-heated meteoric waters. Boiling of mixed waters is shown by dashed arrows. Three samples plot significantly above the main set of data and may represent significant magmatic contributions to the fluid from which these samples were deposited. $\delta^{13}C$ values of those samples are shown. VL = vapour loss as a result of boiling.

The majority of the calcite samples are in equilibrium with a fluid having an isotopic composition near -4.5 ‰ ($\delta^{18}O$) and -8% ($\delta^{13}C$), but there are a significant number that indicate equilibrium with other fluid(s). This requires either evolution of a single fluid or mixing of two (or more) different fluids to yield the observed compositions. There are no distinctive paragenetic features that separate the outlying samples from the Main group. Both groups contain bladed samples, very late vuggy calcite, and more massive calcite. Therefore, no clear temporal distinction in fluid composition can be inferred. Within the main group, variations in $\delta^{18}O$ values are probably related to mixing of deep ascending fluids with meteoric waters marginal to the main upflow of the system. Similar variability on the scale of a few permil is observed in presently active geothermal systems as a result of mixing of deep fluids with entrained shallower fluids (e.g. Kawerau; Christenson, 1987; Broadlands-Ohaaki, Hedenquist, 1990).

In addition to differences in $\delta^{18}O$ values, most of these non-N calcites also have higher $\delta^{13}C$ values. There is no simple way to generate these enriched compositions (of both isotopes) from a single fluid. The most attractive possibility for generating the observed higher $\delta^{13}C$ values is the input of heavier carbon of magmatic origin. The elevated helium isotope values are supportive of magmatic gas input to the hydrothermal system.

Figure 4 is a plot of the calculated oxygen isotopic composition of the fluid vs. homogenization temperature. In addition to calcite, quartz data also are plotted. Several features of Figure 4 are notable. The distribution of bladed calcite samples is not significantly different from that of non-bladed samples, suggesting that there is no difference isotopically in these morphologic types. An interesting feature is the apparent mixing trend developed for both quartz and calcite vein minerals, which has endmember components having $\delta^{18}O$ values of -2.0% at ca. 260 °C and -6.0% at ca. 140°C respectively. These characteristics are similar to those described by Hedenquist (1990) for the present-day Ohaaki system, and by Hedenquist and Brown (1989) for the Waiotapu field.

Calculated isotopic composition of the water (oxygen) from which calcite and quartz were deposited and fluid inclusion homogenization temperatures are depicted as a function of location in Figures 5a and 5b. The isotopic calculations are based on equilibrium fractionations between calcite or quartz and water (Friedman and O'Neil, 1977) at the temperature of deposition as determined by fluid inclusion data. This cross-section is along the main Empire structure, the main fluid conduit during hydrothermal activity.

The data fiom the Golden Cross vein calcites and quartz do not show a clear plume structure. Given the complexity of the system, it is unlikely that such a structure could be identified easily without more detailed sampling and paragenetic controls (because of the probable shifts in the locus of upflow). However a few tentative conclusions may be inferred from the existing set of data. The highest temperatures recorded in fluid inclusions are those on or near section 4650N. To the north along the vein structure, temperatures generally decrease, as does the amount of calcite (Figure 5). To the south along the vein, exposures and data are sparse, although calcite veining is reported to be abundant. The calculated oxygen isotopic fluid compositions show signficant scatter along the vein structure, but the most ^{18}O-rich fluids that have been identified lie on this same 4650N section. These data suggest that at least one major locus of fluid upflow during the time of calcite deposition was near 4650 section. It is possible (perhaps likely) that this upflow zone extends down to the south along the centre of the major calcite flooding zone, but connot be constrained with the existing set of data.

5. ORIGIN OF THE VEIN COMPONENTS

The data described above indicate that the P-T-X parameters of the system that precipitated the late,

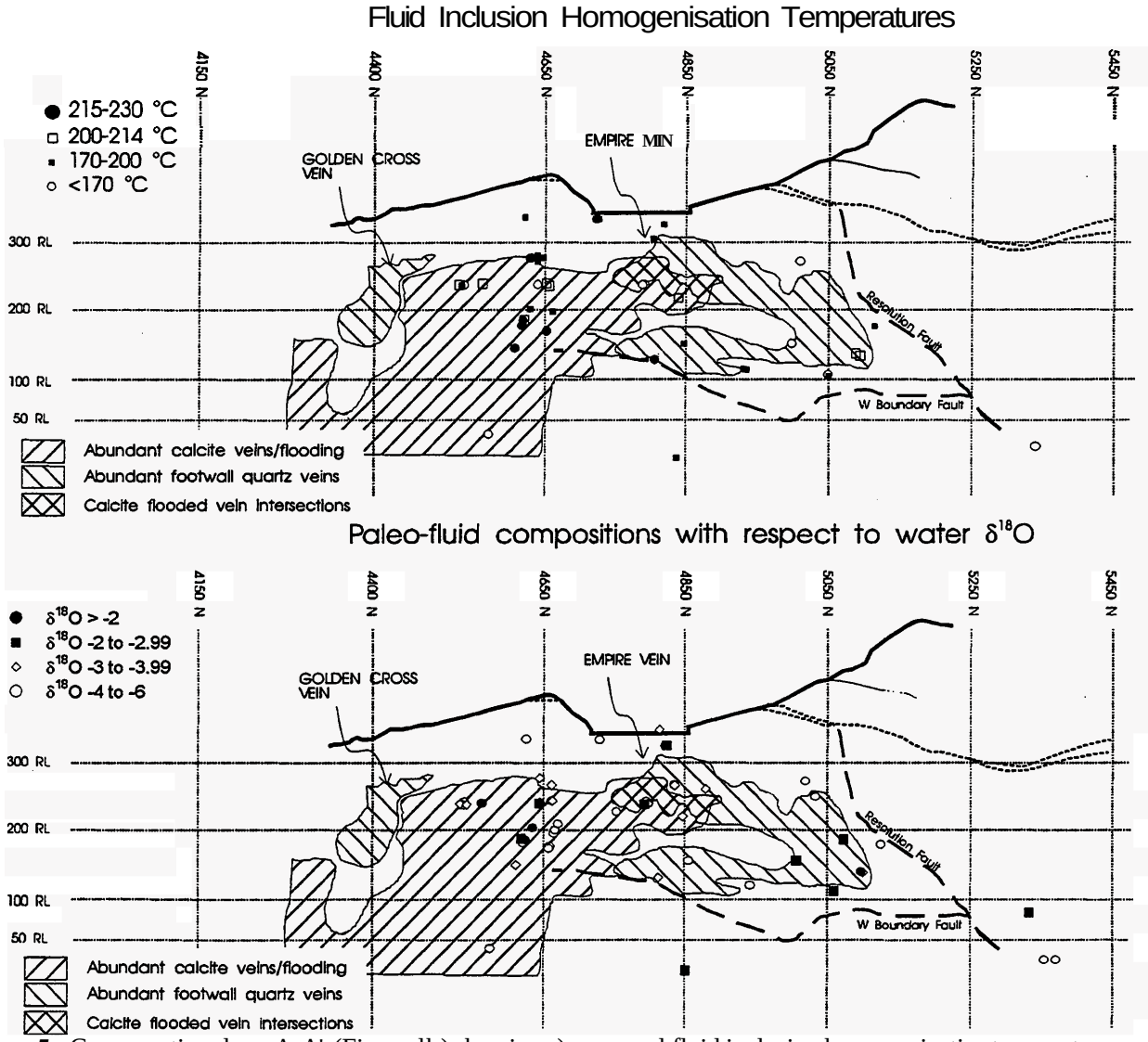

Figure 5. Cross-section along A-A' (Figure 1b) showing a) measured fluid inclusion homogenization temperatures and b) calculated oxygen isotope composition of the fluid from which minerals were deposited.

massive calcite in the southern portion of the Golden Cross system were not appreciably different from those extant during deposition of the ore. It seems clear that the fluids were at or near the boiling point, and that boiling was probably directly responsible for precipitation of much of the calcite. This is considerably different from the range of conditions existing in geothermal aquifers containing steam-heated fluids, which are most often well below boiling-point for their respective depths (Hedenquist, 1990).

The isotopic signatures of the fluids from which the ore-stage quartz was precipitated are virtually indistinguishable from those of the later calcite, and both show evidence of mixing of a deeper, isotopically shifted fluid with a presumably shallower fluid having a more meteoric composition. The situation is similar to what is observed in active geothermal systems such as Broadlands (Simmons and Christenson, 1994) where deep, oxygenexchanged geothermal fluid is upwelling and mixing with marginal non-oxygen-exchanged meteoric steam-heated water. The origin of the water in both fluids at Golden Cross is ultimately meteoric, but the deeper fluid has evolved through water-rock isotope exchange to significantly higher $\delta^{18}O$ values.

The origin of most calcites at Golden Cross can most easily be explained by combined mixing/boiling processes. The flux of CO_2 represented in the precipitation of the later calcite is large, and is unlikely to have been supplied in total by descending bicarbonate waters, but rather requiring input of deep-sourced CO_2. (perhaps representing a separate (i.e. later), hydrothermal pulse?). The origins of this pulse could be linked to adjacent magmatic activity, as indicated by the elevated $\delta^{13}C$ and $\delta^{18}O$ values of some samples. The size and geometry of the calcite vein(s) are consistent with substantial pressure transients, such as those which would attend hydrothermal eruptions, leading to the focussed depostion of calcite in these large fractures. The absence of quartz from the late veins is consistent with findings of Glover and Mroczek (ms, 1996) which point to this phase being kinetically inhibited from precipitating at temperatures below ca 220 °C.

For those samples falling off of the mixing line, both $\delta^{13}C$ and $\delta^{18}O$ values are elevated (Figure 4). The most satisfactory explanation for the elevated $\delta^{13}C$ values of the samples is a third fluid source, possibly magmatic (Hedenquist and Browne, 1989). The $\delta^{13}C$ values of the CO_2 in the deeper fluid could be shifted by input of relatively small amounts of magmatic CO_2, while little effect would be observed in the fluid $\delta^{18}O$ values. In addition, there are three carbonate samples that were deposited from fluids having the highest $\delta^{13}C$ and $\delta^{18}O$ values; these values are significantly above the values for the boiled deep fluid and appear to reflect high percentages of magmatic volatile input for both carbon and oxygen.

6. SUMMARY

In summary, we believe that the fluids responsible for the epithermal mineralisation at the fossil geothermal system at Golden Cross comprise a mixture of three distinct fluids: a deep geothermal, isotopically exchanged meteoric fluid, a shallower, unexchanged meteoric fluid, and a magmatic fluid. Although the locus of upflow probably varied over time, at least one major upflow zone during the later stages of the geothermal system was present near the 4650N portion of the vein system.

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