

THE OCCURRENCE, DISTRIBUTION AND XRD PROPERTIES OF HYDROTHERMAL CLAYS AT THE GOLDEN CROSS EPITHERMAL Au-Ag DEPOSIT, NEW ZEALAND

M.P. SIMPSON¹, J.L. MAUK¹ AND S.F. SIMMONS²

¹Department of Geology, The University of Auckland, Auckland, NZ.

²Geothermal Institute, The University of Auckland, Auckland, NZ.

SUMMARY - Hydrothermal clays display distinct zonation around veins in the Empire zone of the Golden Cross epithermal Au-Ag deposit. At shallow levels the main clays are interstratified illite-smectite (I/S) and tentatively identified chlorite-conensite which grade downwards into illite and chlorite, respectively. Minor interstratified I/S at depth corresponds to areas of low permeability. The overall zoning pattern of interstratified I/S and illite presumably reflect a former deposit-scale increase in temperature with depth and towards veins; local variations in clay mineralogy, additionally reflect varying intensities of water-rock interaction. The interpretation of clay mineral transitions must be coupled with other geothermometric data to derive the fullest possible interpretation of the thermal, chemical and hydrologic regimes of fossil geothermal systems.

1. INTRODUCTION

Low sulfidation epithermal vein deposits are an important source of precious metals and are surrounded by distinct zones of hydrothermal alteration (Hayba et al., 1985). Alteration is typically described in terms of mineral assemblages (i.e. silicic, argillic and propylitic), but these names do not fully describe the occurrence and distribution of individual alteration minerals. This paper describes the occurrence, distribution and XRD properties of hydrothermal clays that surround mineralised quartz veins in the Empire zone of the Golden Cross low sulfidation epithermal deposit, New Zealand.

2. GEOLOGICAL SETTING

The Golden Cross deposit (Figure 1) occurs within the Coromandel Peninsula, the central subaerial sector of a 200 km long by 35 km wide continental volcanic arc, known as the Coromandel Volcanic Zone (CVZ) (Adams et al., 1994). The CVZ is built on a block faulted basement of late Jurassic greywackes that are exposed on the northern and northwestern sides of the peninsula. This basement is overlain by a sequence of early Miocene to Pliocene andesites and subordinate dacites of the Coromandel Group which underlie and interfinger with Late Miocene to Early Pleistocene rhyolites and rhyodacites of the Whitianga Group (Skinner, 1986). Northwest to north-northwest and northeast to east-northeast trending faults transect the CVZ, forming a series of block faults. Most of the east-northeast faults are downthrown to the south (Skinner, 1986).

Historically, gold at the Golden Cross deposit (Figure 2) was extracted from the Golden Cross 1 reef (1895 to 1920) and in more recent times from the Empire zone (1989 to 1997); combined they have produced more than 700,000 oz of gold. The gold bearing veins

in the Empire zone are hosted in several volcanic units of the Coromandel group that include the Waipupu Formation, the Waiharakeke Dacite and the Whakamoehau Andesite (Figures 2 & 3). The oldest is the Waipupu Formation (7.9 to 6.3 Ma), which consists of andesitic lava flows with localised volcanic breccias and lithic-crystal tuffs (Brathwaite and Christie, 1996). The Waipupu Formation in the mine area is represented by four informally named members; 'Monroe', 'Empire', 'Candle' and 'Golden Cross porphyry' (Caddey et al., 1995). This unit is in fault contact with the younger Waiharakeke Dacite (7.2 Ma) that comprises dacitic lava flows and tuff breccia, intercalated with lithic-crystal tuffs (Brathwaite and Christie, 1996). In the mine area this

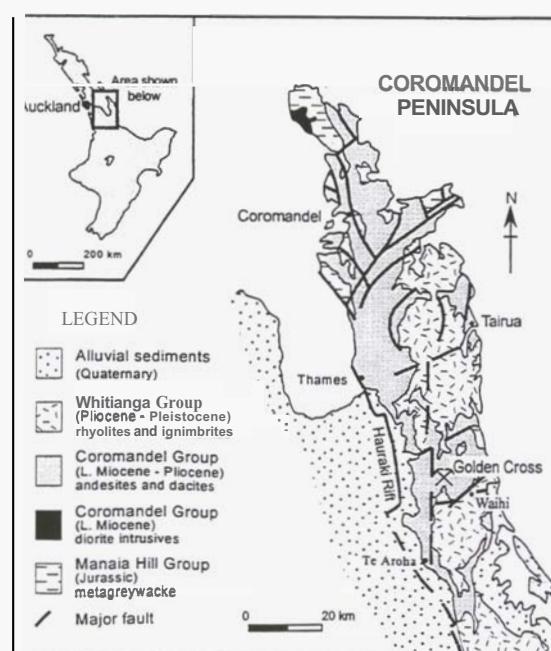


Figure 1. Simplified geological map of the Coromandel Peninsula (after Skinner, 1986).

unit is represented by four informally named members 'lower', 'middle', 'middle member breccia' and 'upper' (Caddey et al., 1995). Unaltered, post-mineral Whakamoehau Andesite (6.7 to 6.6 Ma) consisting of andesitic and dacitic flows and tuff breccia unconformably overlies all the above units (Brathwaite and Christie, 1996).

The **main** structural features in the Empire zone are the Empire and Western Boundary faults (Figures 2 & 3). The Empire fault is a north-northeast-striking, steeply west dipping fault, with over 300 m of reverse displacement. The north-striking, east-dipping Western Boundary fault forms the western limit of open pit stockwork veins, although the sense of movement and amount of displacement are uncertain (Keall et al., 1993).

Mineralisation in the Empire zone occurs in two discrete ore zones; the underground Empire vein system and the open pit stockwork (Figures 2 & 3). The Empire vein system, developed along the Empire fault is comprised of the Empire hanging wall vein and shallow-dipping subsidiary footwall veins. The open pit stockwork in the hanging wall of the Western Boundary Fault formed at higher elevations (Keall et al., 1993).

Pervasive alteration surrounds the veins and encompasses an area of 3 km x 1.5 km x 0.8 km (de Ronde and Blattner, 1988). Quartz, clays, and pyrite are ubiquitous mineral phases with adularia enveloping the Empire vein system and veins of the open pit stockwork (Simpson, M. et al., 1995; de Ronde and Blattner, 1988). These are overprinted and replaced by calcite, siderite and clays with quartz veins cut and diluted at depth by late massive calcite veins (Simpson, M. et al., 1995).

Hydrothermal alteration and vein mineralisation from stratigraphic relationships is inferred to have occurred between 7.9 and 6.7 Ma (Brathwaite and Christie, 1996), and is consistent with an unpublished age of 6.9 Ma for adularia.

3. METHODS

Selected 'samples of hydrothermally altered volcanic rock were collected from drill core along three cross sections (4650, 4850 and 5050m N) perpendicular to the strike, and along the length of the Empire vein system (Figure 2). Alteration minerals were studied by thin section petrography, X-ray diffraction and SEM analysis. A suite of 122 samples examined by XRD analysis were initially crushed into a fine homogeneous powder using a mortar and pestle. Clay mineral separates were prepared by dispersing the crushed rock into distilled water with the 12.0 µm fraction collected by gravitational settling and mounted on glass slides. Oriented clay mounts were successively analysed under air dried, ethylene glycol solvated, and heated (550°C for 1 hour) conditions. All samples were analysed using a Philips PW 1050/25

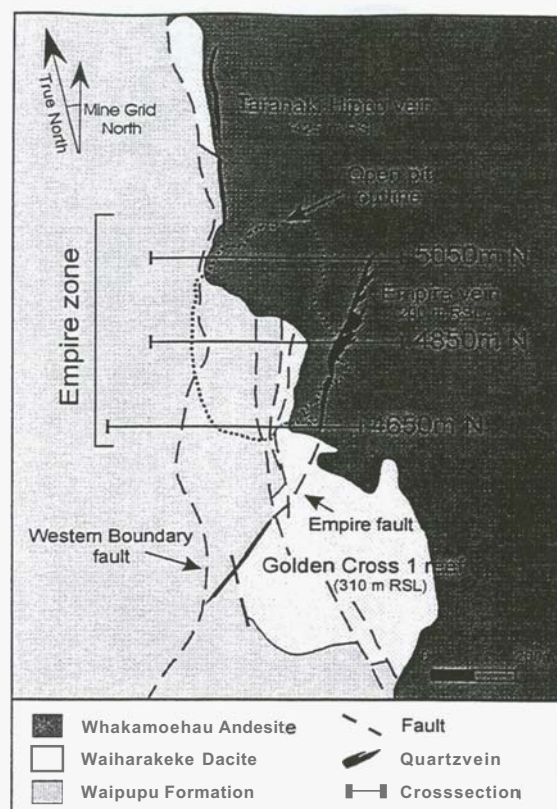


Figure 2. Surface geology map of the Golden Cross deposit(modified from Caddey et al., 1995).

diffractometer utilising CuK α radiation. Interpretation of XRD diffractogram profiles are based on the data of Moore and Reynolds (1997).

4. RESULTS

Several hydrothermal clay types occur in the Empire zone and include chlorite, interstratified illite-smectite (I/S), illite, kaolinite and minor smectite.

Chlorite:- Chlorite is a common alteration mineral forming between 2 to 20 percent of the rock by volume (Figure 3). Chlorite occurs as a replacement mineral of hypersthene, augite and plagioclase phenocrysts. It is also a significant replacement mineral of the groundmass where it is intergrown with fine-grained quartz. Open space deposited chlorite that fills cavities, vesicles and veinlets, displays variable crystal morphology from microcrystalline to coarsely crystalline radiating masses of acicular crystals. Optically, in plain polarised light the chlorite is typically pale to dark green, although commonly it has murky brown patches which suggest the presence of another clay.

X-ray diffraction profiles of chlorite are characterised by peak reflections at -14.2, 7.10, 4.74, and 3.558. The 7.10 and 3.558 peaks of chlorite superimpose on the 7.16 and 3.588 peaks of kaolinite, and therefore heating at 550°C for 1 hour was used to distinguish between these minerals. Heating of chlorite results in dehydroxylation of the hydroxide sheet which is seen

in XRD profiles as an increase in intensity and shift of the 14.2Å peak to between 14.1 and 13.8Å, with the 7.10, 4.74, and 3.55Å peaks weakened but not altogether eliminated (Moore and Reynolds, 1997).

Two types of chlorite are distinguished based on the stability of this mineral upon heating (cf. Harvey and Browne, 1991). After heating, type A chlorite yields diffractogram profiles that are characterised by an absence of the 7.10, 4.74, and 3.55Å reflections, with the 14.2Å peak shifting and increasing in magnitude (Figure 4). In contrast, type B chlorite is essentially unaffected by heating, although some structural reorganisation was evident by an increase in magnitude of the 14.2Å peak (Figure 4). The distribution of type A and B chlorite are shown in figure 3. Type A chlorite, which collapsed on heating, occurs at shallow levels (above 280m RSL) on both the 4650 and 4850m N cross sections with type B chlorite extensive at depth. On the 5050m N cross section type A chlorite is ubiquitous with only rare type B chlorite at depth. The contact between type A and B chlorite on both the 4650 and 4850m N cross sections occurs -45 to 85 m below the contact between interstratified I/S and illite.

None of the chlorite peaks shifted on glycolation. Thus, an expandable component is minor or absent, comprising no more than 10 %, given the detection limit of the technique (Moore and Reynolds, 1997). Preliminary SEM observations indicate the presence of discrete corrensite (an ordered 1:1 mixed-layered chlorite/smectite) and chlorite within the same samples (Mauk et al., 1997). Based on optical, XRD and SEM studies we speculate that type A chlorite, is an interstratified chlorite-corrensite that has discrete packages of chlorite and corrensite (cf. Shau et al., 1990), with the latter likely present in amounts of less than 10 percent.

Interstratified illite-smectite:- I/S forms a 50 m thick blanket over the Empire vein system and open pit stockwork (Figure 3). It also occurs at depth on the 4850m N cross section, occupying a wedge shaped body that coincides with the Waiharakeke Dacite 'middle member breccia'. Interstratified I/S is an alteration product of adularia that has replaced plagioclase phenocrysts. Where adularia is absent, plagioclase has directly altered to interstratified I/S. Interstratified I/S is also a rare replacement mineral of mafic phenocrysts and fills interstitial sites in the groundmass. In addition, this mineral is a significant constituent in the matrix cement and clasts of volcanic and hydrothermal breccias.

XRD diffractogram profiles of ethylene glycol solvated interstratified I/S are characterised by second order superstructure reflections comprised of the illite and smectite end members. The absence of the 001* second order superstructure reflection in diffractogram profiles indicates that the interstratification between illite and smectite is random (Reynolds, 1980). The position of the 003*

second order superstructure reflection was used to determine the degree of illite interstratification (Moore and Reynolds, 1997). Accordingly, randomly interstratified I/S contains between 40 to greater than 80 percent illite. The degree of illite interstratification on the 4650 and 4850m N cross sections gradually increased with depth and grades into the underlying illite zone. By contrast, the illite content of interstratified I/S on the 5050m N cross section above 350 m RSL is relatively uniform and consequently the contact between the interstratified I/S and illite zones appears to be sharp. Randomly interstratified I/S also occurs in several samples at depth and its occurrence here coincides with volcanic breccias, hydrothermal breccias and local lenses of less intensely altered rock ('hard bars').

Illite:- Illite is widespread at depth and occurs below the interstratified I/S zone (Figure 3). Illite is an alteration product of adularia that replaced plagioclase phenocrysts. Illite also replaces rare mafic phenocrysts and commonly floods interstitial sites in the groundmass. In addition, illite fills cavities, vesicles and veinlets. XRD analyses reveal that the illite on both the 4650 and 5050 m N sections commonly contains up to 10 percent smectite, whereas the illite from the 4850 m N section lacks smectite and is characterised by sharper basal reflections.

Smectite:- Smectite was identified in the glycolated diffractograms of several samples. XRD analyses show that discrete smectite in places coexists with illite or interstratified I/S. Smectite replaces the groundmass and plagioclase phenocrysts.

Kaolinite:- Kaolinite is a widespread alteration mineral that mostly formed during the late stage alteration history of the system. Late kaolinite predominantly fills veinlets and extends to depths of greater than 0.0 m RSL on all three cross sections. It is most abundant at shallow levels in the open pit (above 385m RSL) as veinlets that commonly have selvages of pyrite. At deeper levels (below 385m RSL) kaolinite veinlets lack pyrite selvages, although many contain grains of pyrite. Kaolinite also replaces plagioclase phenocrysts and the groundmass overprinting all the above clay minerals. In addition, kaolinite appears as thin (<1 mm wide) concordant bands in colloform banded quartz veins of the Empire vein system (Simpson, C. et al., 1995).

The XRD profiles of kaolinite are characterised by major reflections at 7.16 and 3.58Å, and these collapsed upon heating to 550°C for 1 hour. XRD profiles of random bulk rock powder mounts indicate that kaolinite is well crystallised, and has a crystallinity which appears to increase with depth, and towards the Empire vein system.

5. DISCUSSION

Clay minerals at the Golden Cross deposit show a distinct zonation. At shallow levels, the main clays are interstratified I/S and tentatively identified

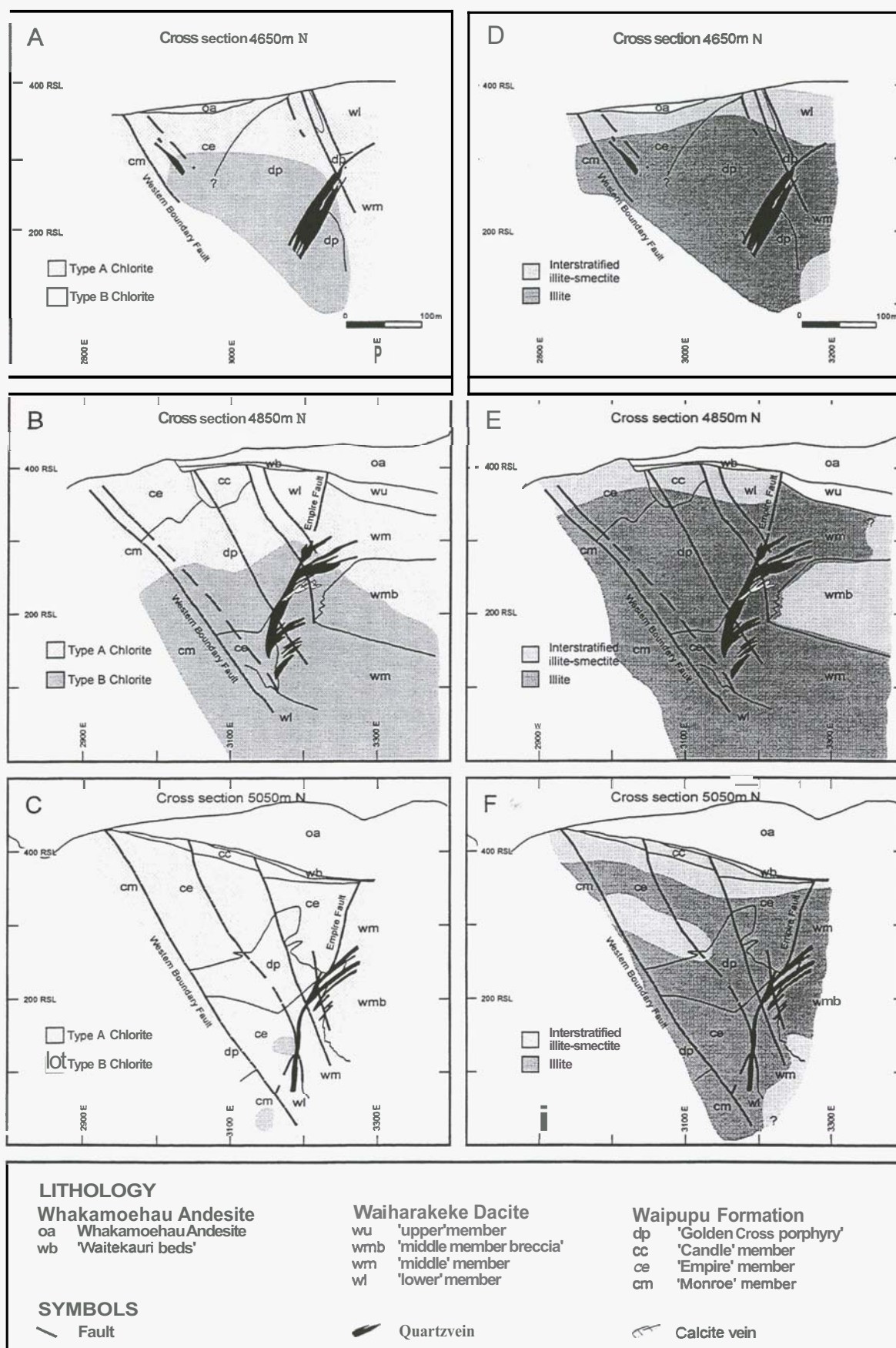


Figure 3. Cross sections 4650, 4850 and 5050m N. A), B) and C) display the distribution of type A (interstratified chlorite-conensite) and type B chlorite. D), E) and F) display the distribution of interstratified illite-smectite and illite.

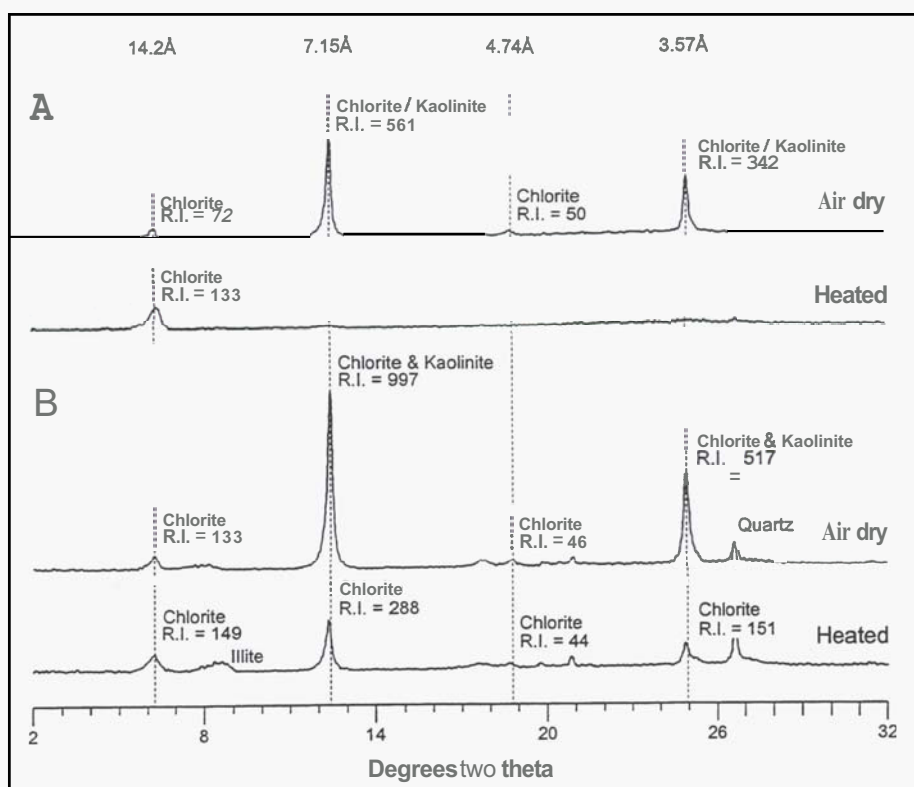


Figure 4. Oriented clay mount air dry and heated (550°C for 1 hour) XRD profiles for type A and B chlorite. **A.** Type A chlorite (interstratified chlorite-corrensite) displays complete structural collapse of the 7.1, 4.7, and 3.58, reflections on heating, with some structural reorganisation indicated by a shift and increase in magnitude of the 13.88, reflection. Kaolinite may also be present in this sample. **B.** A mixture of type B chlorite and kaolinite. The intensity of the 14.2 and 4.78, reflections are essentially unchanged after heating and represent chlorite. Heating has resulted in partial collapse of the 7.12 and 3.578, reflections indicating the thermal decomposition of kaolinite; with the persisting peaks at 7.17 and 3.58Å from chlorite. R.I. = raw intensity.

chlorite-corrensite. These grade downward to illite and chlorite, respectively. However, interstratified I/S also occurs at depth, most notably in the 'middle member breccia' unit of the Waiharakeke Dacite, where adularia is absent (Simpson, M. et al., 1995).

On the one hand the change in clay mineralogy with depth is assumed to reflect increasing paleo-temperatures with depth, as documented at numerous active geothermal systems (e.g. Steiner, 1968; Reyes, 1990). In these systems, smectite is stable to approximately 150°C, interstratified US between 150° and 220°C, and illite above 220°C. Chlorite in drill core from the Wairakei geothermal system, Taupo (Harvey and Browne, 1991) displays similar XRD properties to that found at Golden Cross, with non-collapsed chlorite (heated to 600°C for 1 hour) forming at temperatures greater than 200°C. Although these temperature ranges are widely accepted, a recent evaluation of smectite, US and illite at the Broadlands-Ohaaki geothermal system showed uncertainties in the US geothermometer of $\pm 50^\circ\text{C}$ (Simmons and Browne, 1998). Taken together, these data from active geothermal systems suggest that, based on clay mineral geothermometry, the temperatures at Golden Cross during hydrothermal mineralisation ranged from $>150^\circ\text{C}$ near 350 m RSL

to $>220^\circ\text{C}$ below 300 m RSL. These temperature estimates are consistent with those derived from fluid inclusions in quartz and calcite veins, which homogenise between 137° and 237°C , and show generally decreasing temperatures at shallower levels.

On the other hand, Essene and Peacor (1995) strongly question the use of clay minerals as geothermometers. In some cases, clay mineral transitions clearly reflect changes in chemistry (e.g. Turner and Fishman, 1991) or intensity of water-rock interaction (e.g. Li et al., 1997). At Golden Cross, the presence of interstratified I/S in the 'middle member breccia' unit of the Waiharakeke Dacite and in other relatively unaltered units, most likely reflects low permeability. This would indicate minimum water-rock interaction, and possibly lower temperatures. Here the primary control on clay mineral transitions is best interpreted in terms of permeability.

6. CONCLUSIONS

Clay minerals in the Empire Zone of the Golden Cross deposit show distinct zonation, with higher rank clays at depth and surrounding the former upflow zone of the Empire vein zone. Although the

overall zoning pattern likely reflects deposit-scale changes in temperature, local variations in clay mineralogy are best interpreted in terms of water-rock interaction and permeability. This study shows that interpretations of clay mineral transitions must be coupled with other geothermometric data to derive the fullest possible interpretation of the thermal, chemical and hydrologic regimes of fossil geothermal systems.

7. ACKNOWLEDGMENTS

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8. REFERENCES

- Adams, C. J., Graham, I. J., Seward, D., and Skinner, D. N. B., (1994). Geochronological and geochemical evolution of the late Cenozoic volcanism in the Coromandel Peninsula, New Zealand. *New Zealand Jour. Geol. and Geophys.*, Vol. 37, 359-379.
- Brathwaite, R. L., Christie, A. B., (1996). Geology of the Waihi area, scale 1:50 000: Institute of Geological and Nuclear Sciences of New Zealand, *Geological map 21.1* sheet + 64p.
- Caddey, S. W., McOnie, A. W., and Rutherford, P. G., (1995). Volcanic stratigraphy, structure and controls on mineralisation, Golden Cross Mine, New Zealand. In: *Pacrim Congress 95*, Australasian Inst. Mining and Metallurgy, p. 93-98.
- de Ronde, C. E. J., and Blattner, P., (1988). Hydrothermal alteration, stable isotopes, and fluid inclusions of the Golden Cross epithermal gold deposit, Waihi, New Zealand. *Econ Geol.*, Vol. 83, 895-917.
- Essene, E. J., and Peacor, D. R., (1995). Clay mineral thermometry- a critical perspective. *Clay and clay miner.*, Vol. 43, 540-553.
- Harvey, C. C., and Browne, P. R. L., (1991). Mixed-layer clay geothermometry in the Wairakei geothermal field, New Zealand. *Clays and Clay Minerals*, Vol. 6 14-621.
- Hayba, D. O., Bethke, P. M., and Foley, N. K., (1985). Geologic, mineralogic, and geochemical characteristics of volcanic-hosted epithermal precious-metal deposits. In: Berger, B. R., and Bethke, P. M., eds., *Geology and geochemistry of epithermal systems*. *Rev. Econ. Geol.*, Vol. 2, 129-167.
- Keall, P. C., Cook, W. C., Mathews, S. J., and Purvis, A. H., (1993). The geology of the Golden Cross orebody: Complex veining and evolving mining responses. In: *Proc. 27th Ann. Conf. 1993*, New Zealand Branch AusIMM, pp. 143-160.
- Mauk, J. L., Simpson, M. P., Begbie, M. J., and Keall, P. C., (1997). Styles and conditions of hydrothermal alteration and vein mineralisation at Golden Cross. In: *Proc New Zealand Minerals and Mining Conference*, 119 - 124.
- Moore, M. M., and Reynolds, R. C., (1997). *XRD and the identification and analysis of clay minerals*. Second edition: Oxford University Press, 378p.
- Li, G., Peacor, D. R., and Coombs, D. S., (1997). Transformation of smectite to illite in bentonite and associated sediments from Kaka point, New Zealand contrast in rate and mechanism. *Clay and clay miner.*, Vol. 45, 54-67.
- Reyes, A. G., (1990). Petrology of Philippine geothermal systems and the application of alteration mineralogy to their assessment. *Jour. Volc. and Geotherm. Research*, Vol. 43, 279-309.
- Shau, Y. -H., Peacor, D. R., and Essene, E. J., (1990). Corrensite and mixed layer chlorite/corrensite in metabasalts from northern Taiwan: TEM/AEM, EMPA, XRD and optical studies. *Contrib. Minerals Petrol.*, Vol. 105, 123-142.
- Simmons, S. F., and Browne, P. R. L., (1998). Illite, illite-smectite and smectite occurrences in the Broadlands-Ohaaki geothermal system and their implications for clay mineral geothermometry. In: Arhant, G. B., and Hulston, J. R., (eds). *Water-rock interaction WRI-9*. 691-694.
- Simpson, C. R. J., Mauk, J. L., and Arhant, G., (1995). The formation of banded epithermal quark veins at the Golden Cross Mine, Waihi, New Zealand. In: *Pacrim Congress 95*, Australasian Inst. Mining and Metallurgy, p. 545-550.
- Simpson, M. P., Simmons, S. F., Mauk, J. L., and McOnie, A., (1995). The distribution of hydrothermal alteration minerals at the Golden Cross epithermal Au-Ag deposit, Waihi, New Zealand. In: *Pacrim Congress 95*, Australasian Inst. Mining and Metallurgy, p. 551-556.
- Skinner, D. N. B., (1986). Neogene Volcanism of the Hauraki Volcanic Region. In: *Late Cenozoic Volcanism in New Zealand* (Ed I. E. M. Smith) Royal Soc New Zealand Bull, Vol. 23, 20-47.
- Steiner, A., (1968). Clay minerals in hydrothermally altered rocks at Wairakei, New Zealand. *Clays and Clay Miner.*, Vol. 16, 193-213.
- Turner, C. E. and Fishman, N. S., (1991). Jurassic Lake T'oo'dichi': A large alkaline, saline lake, Morrison Formation, eastern Colorado Plateau.: *Geol. Soc. Amer. Bull.*, Vol. 103, 538-558.