

EVIDENCE FOR MAGMATIC FLUID PULSES INTO THE ROTOKAWA GEOTHERMAL SYSTEM.

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ABSTRACT

Geothermal systems of the Taupo Volcanic Zone (New Zealand) are dominated by meteoric-sourced waters, although rare magmatic fluid input is inferred in some systems (e.g. Ohaaki). Hydrothermal minerals can provide insights on magmatic and/or meteoric fluid origin and controls on fluid flow, with their compositions dependent on host rock and fluid composition, water-rock ratio etc. In this study, EPMA and LA-ICP-MS data, and oxygen, hydrogen and sulphur isotope data for secondary quartz and epidote (in veins, and replacing primary plagioclase and pyroxene) and in relict anhydrite (in epidote-quartz veins) in Rotokawa Andesite has been used to test if the hydrothermal mineral assemblage records the signature of contrasting fluid types in the Rotokawa Geothermal Field.

Hydrothermal epidote at Rotokawa exhibit epidote-clinozoisite substitution, with Fe-rich epidote replacement of phenocrysts and in epidote at vein margins, and Al-rich clinozoisite in vein cores, whilst trace element contents reveal extreme fractionation in REE and Sr abundances.

Oxygen isotopes in epidote and quartz range from -2.9 to 3.3‰, and 9.4 to 13.6‰, respectively. $\delta^{18}\text{O}$ in anhydrite varies from 13.9 to 17.9‰, with respective $\delta^{34}\text{S}$ of 10.1 and 13.0‰. Preliminary interpretations suggest that a variation in major element chemistry of the epidote is linked to fluid-rock interactions with the Fe-rich (andesitic) host rock. Trace element variations are consistent with a fluid-dominated system in the southern part of the Rotokawa geothermal system, and rock-dominated fluid-rock interactions at the time of epidote crystallisation further to the north. Oxygen and hydrogen stable isotopes are heavier in the south-eastern part of the Rotokawa Geothermal Field, and may be related to (episodic?) “pulses” of magmatic fluid into the system, in agreement with the isotopic signature of the hypogene anhydrite in disequilibrium with the present day composition of fluids in the Rotokawa wells.

1. INTRODUCTION

The chemical signature of fluids in geothermal systems is dependent on the host rock composition, water-rock ratio, oxidation and phase state (liquid-vapour-boiling processes), and origin (e.g. derived from meteoric, magmatic, connate sources). Variations in the fluid chemistry of active geothermal systems also reflect processes in the reservoir (e.g. boiling, dilution, mixing etc), and developed fields can be affected by operational processes (i.e. production and/or

injection of fluid). In attempting to resolve fluid evolution and origin in the geothermal system, the chemist and alteration mineralogist must look beyond effects caused by recent resource development and utilisation.

Petrological assessment of hydrothermal alteration paragenesis, and thus mineral disequilibrium, is a key to characterise the origin of the fluid(s) in a geological environment. The alteration mineralogy gives an insight into reservoir conditions as a function of temperature, chemistry and fluid-rock interactions. Minerals (and trapped fluid inclusions) records evidence of variations in the chemistry of the fluids in the active hydrothermal system (assuming that equilibrium is not reached with fluids in the system that have been produced by effects of exploitation).

In this paper, we present major and trace element, and stable isotope chemical data for hydrothermal epidote and other secondary minerals from Rotokawa Geothermal Field. The purpose of our study was to test if variations in the chemistry of the hydrothermal minerals might reveal the nature of fluid-rock interactions, chemistry and origin of hydrothermal fluids in the Rotokawa geothermal system that are responsible for formation of the secondary mineral assemblage. In order to limit variability due to host rock chemical composition, samples were selected only from deep-seated andesite lavas and associated rocks, present across the field. Oxygen, hydrogen for hydrothermal epidote and secondary quartz (in veins, and replacing primary plagioclase and pyroxene), and sulphur isotope data in relict anhydrite, has been used to ascertain if the hydrothermal mineral assemblage records the signature (origin), of fluids in the Rotokawa geothermal system.

2. ROTOKAWA GEOTHERMAL FIELD

2.1 Geology

Rotokawa is a high temperature (>200°C) liquid-dominated geothermal system. Utilisation of the field for electricity generation started in 1997 with a 29 MWe Ormat combined steam turbine and binary plant, and 6 MWe expansion in 2004, and the new Nga Awa Purua power station built in 2010 with a 140 MWe capacity.

The Rotokawa Geothermal field is located ~10km northeast of Taupo and covers an area of 17-28 km². The boundary of the field has been established by resistivity surveys by Hatherton et al. (1966), and Hunt and Harms (1990) (Figure 1A). The field is divided by the Waikato River, and most of the utilisation is located on the south bank. The age of the system has been estimated at ~20,000 years, based on C¹⁴

dating of the latest Oruanui Formation (Vucetich and Howorth, 1976).

Surface manifestations at Rotokawa are extensive, and include breccia deposits associated with numerous hydrothermal eruptions (including at least one centred on Lake Rotokawa, an eruption crater of ~1.5 km diam.), and bedded massive sulphur deposits in the southern part of the Rotokawa Geothermal Field.

Basement rocks at Rotokawa are Torlesse greywacke, which is intersected by six wells between -1770 and -2720 mRL. The basement is overlain by a thick succession of plagioclase-, pyroxene-phyric andesitic lava and breccia, named the Rotokawa Andesite (Figure 1B).

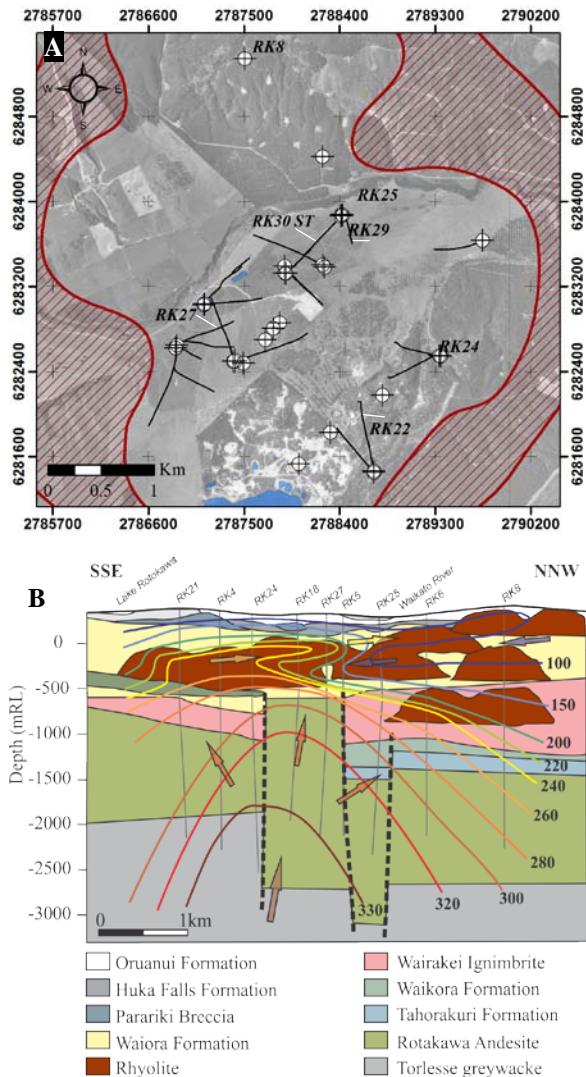


Figure 1: A. Rotokawa Geothermal Field, showing well locations and resistivity boundary (from Risk, 2000). Core samples from labeled wells were incorporated in this study. B. Schematic cross section of the Rotokawa Geothermal Field showing stratigraphy, inferred faults, isotherms and geohydrology (modified from Browne et al., 1992; Rae, 2007; Andersen, 2011).

Above the Rotokawa Andesite is a succession of interbedded volcaniclastic, sedimentary and pyroclastic units of the Tahorakuri and Waikora Formations. This

sequence is covered by the welded, crystal-rich, quartz-bearing Wairakei Ignimbrite member of the ~320 to 340 Ka (Houghton et al., 1995) Whakamaru-group Ignimbrites. The Wairakei Ignimbrite generally has low permeability, except where it is fractured, and is 200 to ~400 m thick across the field. The ignimbrite is covered by the Waiora Formation, which comprises a thick sequence of interbedded pumice-, lithic-, crystal-bearing tuff and breccia, with intercalated with rhyolitic lava and breccia. At shallow level (i.e., <400 mVD) the stratigraphy is covered by interbedded laminated mudstone, siltstone and sandstone of the Huka Falls Formation, with intercalated Parariki hydrothermal eruption breccia in the south part of the field (Figure 1B). Surface deposits consist mainly of pumice-bearing volcaniclastic units associated with the Oruanui Formation, which are covered by superficial tephra and alluvium.

2.2 Alteration mineralogy

Surficial alteration is driven by steam-heated acid-sulphate fluids, and is characterised near Lake Rotokawa by an intensive acidic assemblage to ~200 mVD. Deeper acid-sulphate alteration occurs sporadically to ~1600 mVD (e.g. in RK16) with rare supergene anhydrite, alunite and kaolinite. The alteration assemblage and the well chemistry show that sulphate-and CO₂-rich waters are percolating from shallow aquifer (Hedenquist et al., 1988; Rae, 2007; Bowyer et al., 2008).

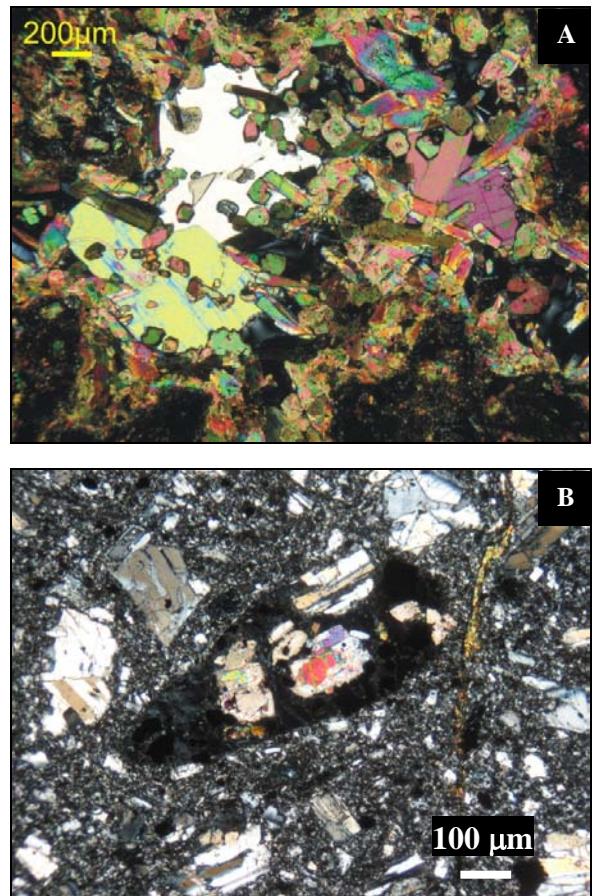


Figure 2: A. RK27-2147mRF, Anhydrite-epidote-chlorite assemblage; B RK24-1820mRF, altered pyroxene to biotite, chlorite, enclosing plagioclase crystals which are partially replaced by anhydrite and calcite.

The main alteration assemblage associated with reservoir conditions is propylitic, and is influenced by hot dilute near-neutral pH chloride fluids. The common hydrothermal mineral assemblage at depth consists of chlorite, epidote-group minerals, calcite, illite, adularia, albite and wairakite. The alteration at depth is mainly controlled by fractures, particularly in the Rotokawa Andesite and greywacke (Rae, 2007; and numerous GNS consultancy well geology reports for Mighty River Power Ltd.).

The chlorite-epidote alteration has overprinted a higher temperature/high rank hydrothermal mineral assemblage which included actinolite and biotite. Occurrence of anhydrite below 2000 mVD (e.g. in RK27, RK30) is unlikely to be supergene in origin, and is overprinted by epidote and calcite (Figures 2A, B).

Examples of disequilibrium and overprinting assemblages are shown in Figure 3, with anhydrite and epidote overprinted by calcite, which is itself overprinted by illite and quartz in a vein cutting the Rotokawa Andesite in this sample.

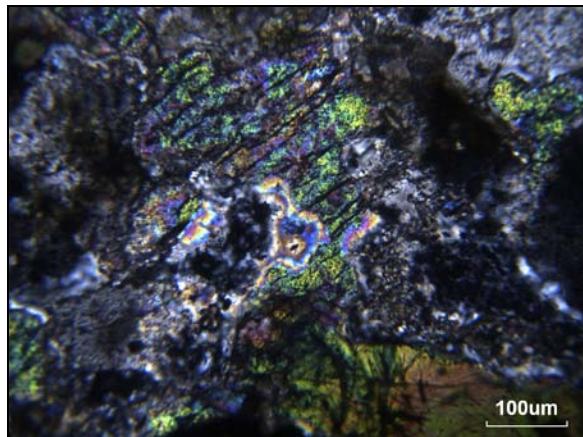


Figure 3: RK30 2223.76 mRF, Anhydrite-epidote, overprinted by calcite, rimmed by quartz, and overprinted by fine grained granular quartz and illite.

3. GEOCHEMISTRY

3.1 Analytical methods

Electron microprobe analyses of hydrothermal epidote were conducted for major elements, using the JEOL JXA-8230 electron superprobe at Victoria University of Wellington (VUW, New Zealand), using a 12 nA current, 15 kV accelerating potential and 2 μ m beam diam. Laser-ablation ICP-MS analyses of trace elements in the epidote were also performed at VUW using an Agilent 7500 ICP-MS octopole, with He as the sweep gas. Laser spots vary between 25 and 50 μ m diam. Analyses were quantified with reference to replicate analyses of BCR2 standard glasses under similar ablation conditions. Comparison of standard analyses suggests accuracy better than 10% (2 σ stdev) for all elements reported.

Stable isotope analyses were analysed at the National Isotope Centre at GNS Science (Lower Hutt, New Zealand). Oxygen and hydrogen data are reported in per mil (‰) relative to V-SMOW, sulphur isotope relative to VCDT with replication of external standards yielded respective 2 σ stdev of ± 0.15 , 1.5 and 0.5 ‰ (n=35).

Samples for analyses were selected in the Rotokawa Andesite from 6 different cores in different wells (RK8-2219mRF, RK22-2275mRF, RK25-2200mRF, RK27-1854 and 2147mRF, RK28-2313mRF and RK29-2083mRF). Only three samples of deep anhydrite were possible to separate for isotope analyses (RK27-1854 and 2147mRF, and RK24-1820mRF).

3.2 Major / trace element content of Rotokawa epidote

Hydrothermal epidote from the Rotokawa geothermal system exhibit epidote-clinozoisite substitution ($16 < \text{Fe}^{\#} < 35$; $\text{Fe}^{\#} = 100 * \text{Fe}^{3+} / (\text{Fe}^{3+} + \text{Al})$; Figure 4A), with Fe-rich epidote replacement of phenocrysts and at vein margins, and Al-rich clinozoisite in vein cores. No systematic variations in major elements are noticeable between well samples / field location.

LIL elements such as strontium are strongly fractionated, with content between 290 and 2288 ppm for Sr (Figure 4B), whilst Pb has variable abundance (ranging from ~8 ppm in epidote from RK25-2200 mRF, to 313 ppm the RK27-1854 mRF sample). REE are strongly fractionated between individual analyses, with similar La/Yb ratios up to 10, although La contents are 0.3 to 231 ppm (Figure 4C). Apparent negative anomalies in HSFE (Zr, Nb, Ta) are probably related to the arc signature of the leached TVZ rocks (Figure 4D). Epidote occurring as a replacement of magmatic (primary) phenocrysts is enriched in trace elements, compared to vein epidote (Figures 4C and D).

3.3 Stable isotopes

Oxygen, hydrogen, sulphur stable isotope compositions have been acquired for hydrothermal epidote, quartz and anhydrite from Rotokawa. Oxygen isotopes in epidote and quartz range from -2.9 to +3.3, and +9.4 to +13.6 $\pm 0.15\text{\textperthousand}$, respectively. Hydrogen composition of Rotokawa epidote ranges between -82 and -72 $\pm 1.5\text{\textperthousand}$. Isotopic compositions of anhydrite from RK27-1854 mRF and RK24-1820 mRF are $\delta^{18}\text{O}_{\text{anh}} = +13.9$ and $+17.9 \pm 0.5\text{\textperthousand}$, with $\delta^{34}\text{S}_{\text{anh}}$ of $+10.1$ and $+13.0 \pm 0.5\text{\textperthousand}$, respectively. Sample RK27-2147 mRF has a sulphur composition of $\delta^{34}\text{S} = +14.9\text{\textperthousand}$, but a lighter oxygen composition of $+0.4\text{\textperthousand}$.

The fluid compositions in equilibrium with epidote and quartz have been calculated using the fractionation equations of Chacko et al. (1999) and Zheng (1993a, b), and primary fluid inclusions homogenisation temperatures from Rae et al. (these proceedings), with $T_{\text{eq}}=300$ °C for the assemblage in equilibrium with epidote, 280 °C for quartz and 360 °C for anhydrite. Large uncertainties exist for the ΔD fractionation between epidote and H_2O at 300 °C, with $\Delta\text{D}_{\text{epidote-H}_2\text{O}} = -49.91$ (Graham et al., 1980), $= -33.59$ (Chacko et al., 1999) and $\Delta\text{D}_{\text{epidote-H}_2} = 440.13$ (Vennemann and O'Neil, 1996).

Figure 5 shows calculated $\delta^{18}\text{O}$ and δD fluid compositions in equilibrium with epidote, and fluid composition in equilibrium with quartz. The majority of the fluid isotopic compositions calculated at 300 °C in equilibrium with epidote are similar to well water isotopic compositions (in particular RK3 and RK4; Figure 5). Two isotopic compositions calculated in equilibrium with epidote in RK27-1854 mRF and RK22-2275 mRF show heavier oxygen composition, with $\delta^{18}\text{O}$ up to $2.3 \pm 0.15\text{\textperthousand}$, trending toward the primary magmatic water composition (Taylor, 1979).

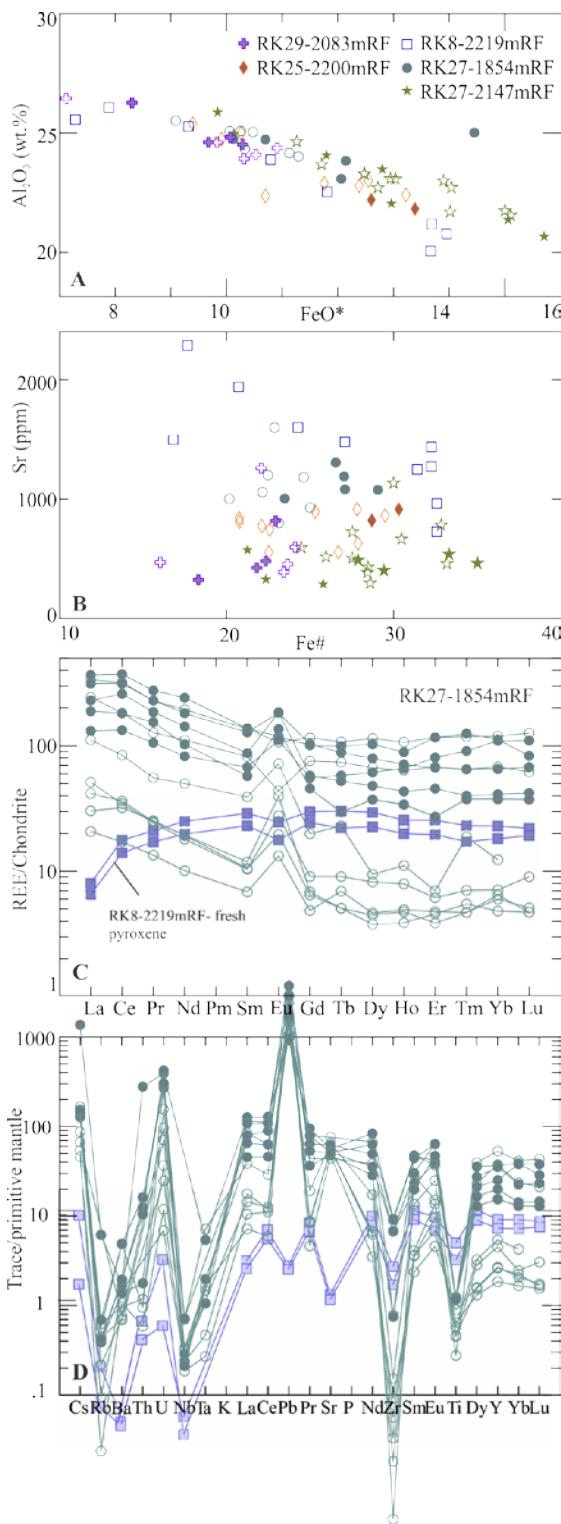


Figure 4: A. FeO^* (FeO total; wt.%) versus Al_2O_3 (wt.%) contents of vein (open symbols) and replacement (closed symbols) epidote from Rotokawa. B. Fe^* versus Sr (ppm) content of RK epidote. C, D. REE and trace element contents normalised to chondrite and primitive mantle (after Sun and McDonough, 1989) respectively, for sample RK27-1854 mRF. Open symbols are vein epidote, closed symbols are replacement epidote, blue squares are fresh pyroxene from RK8-2219 mRF.

$\Delta^{34}\text{S}_{\text{CaSO}_4-\text{H}_2\text{S}}$ from Ohmoto and Rye (1979) is used to calculate the composition of H_2S in equilibrium with anhydrite assuming minimum fractionation between sulphate mineral and sulphate ion in the geothermal fluid. The theoretical calculated composition of H_2S varies between -4 and -9‰. H_2S gas isotopic compositions analysed for RK fumarole, RK4 and RK5 are about +4.5‰ (Giggenbach, 1995).

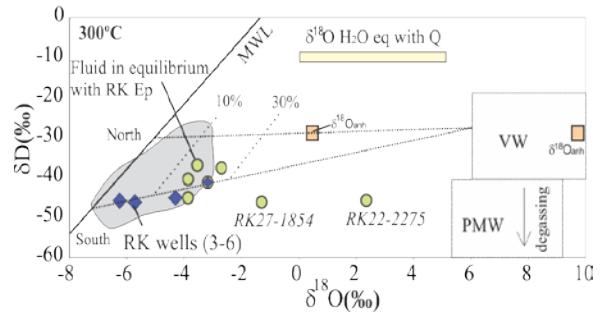


Figure 5: $\delta^{18}\text{O}_{\text{fluid}}$ (‰) versus $\delta\text{D}_{\text{fluid}}$ (‰) for Rotokawa epidote calculated at 300°C. Rotokawa well chemistry (from Hedenquist et al., 1988), $\delta^{18}\text{O}_{\text{fluid}}$ for fluid in equilibrium with quartz and $\delta^{18}\text{O}_{\text{anh}}$, TVZ geothermal fluid isotopic compositions (shaded area), volcanic water (VW; Giggenbach, 1995), and primary magmatic water (PMW; Taylor, 1979) are also indicated.

4. DISCUSSION

The deep source(s) and evolution of geothermal fluids in the Taupo Volcanic Zone have long been debated. The geothermal systems are mainly heated deep groundwater convection cells, but a small (<10%) magmatic fluid component (from a degassing intrusive) has been inferred by several authors (e.g. Giggenbach, 1995; Christenson et al., 2002). The Rotokawa geothermal system is defined as a high gas (medium CO_2 , high H_2S) system, with high Cl (± sulphate-rich) dilute, low salinity fluids that originate from deep boiling, with near-surface dilution and oxidation (Hedenquist et al., 1988). The N_2 , He , Ar composition of Rotokawa gases align along a magmatic-groundwater trend, with RK4 showing the least dilute magmatic signature (Giggenbach, 1986).

The important chemical variations in epidote chemistry seem mainly to be influenced by water-rock interactions, and the fluid composition(s).

The sample from RK8 is the only one with epidote compositions showing a trend between major elements (Ca, Fe, Al) and trace elements (such as Sr). The high Sr content in the distal epidote may be attributable to recycling of Sr in plagioclase, although RK8 epidote are mainly vein type and it is expected that Sr content should be higher in epidote overprinting plagioclase. We suggest that the variation may be associated with variation in fluid chemistry across the field. The La/Yb ratio for all epidote samples is quite similar, i.e. between 0 and 10 (relatively similar to the La/Yb ratio of TVZ mafic/intermediate lavas; Price et al., 1992), although the REE content is variable with low content in REE in vein epidote compared to epidote occurring as a phenocryst replacement. The fractionation

between vein and replacement epidote might be due to dilution of the fluid, and water-rock exchange.

The isotopic compositions of epidote and quartz also show variable compositions, with $\delta^{18}\text{O}$ ranges between -2.9 and 3.3‰. The calculated fluid compositions for the majority of the epidote samples appear to be similar to well discharge water isotopic compositions, which point to the epidote crystallising from fluid in chemical equilibrium with present reservoir conditions. However, two epidote samples (from RK22-2275 mRF and RK27-1854 mRF, respectively) are in equilibrium with less dilute fluids, and have $\delta^{18}\text{O}$ values (+2.3 and -1.4‰) trending toward a partially degassed magmatic composition (Figure 5). Such fluid compositions are similar to fluid composition associated with mineralising fluids characteristic of magmatic-hydrothermal high-sulfidation epithermal deposits (Arribas, 1995), and show low water-rock ratio fractionation.

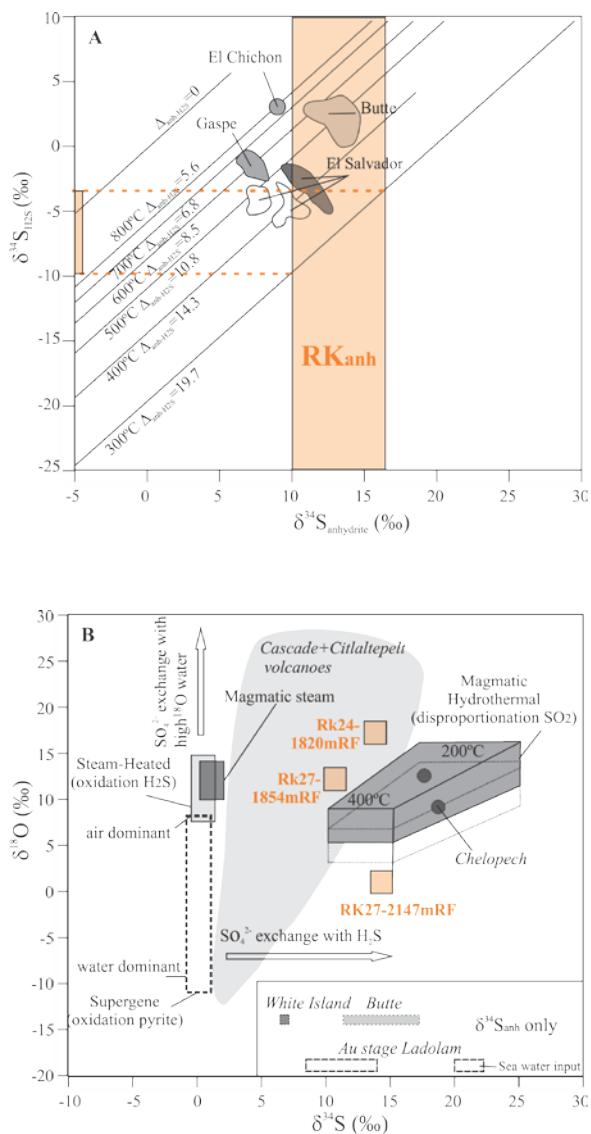


Figure 6: A. $\delta^{34}\text{S}_{\text{anhydrite}}$ (‰) versus $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (‰) diagram (Rye, 2005) showing sulphate-sulphide equilibrium at a range of temperatures (typical magmatic-hydrothermal, porphyry-Cu and surficial environments are also shown). **B.** Figure shows $\text{S}^{34}\text{S}_{\text{SO}_4}\text{-S}^{18}\text{O}_{\text{SO}_4}$ pairs for Rotokawa anhydrite as well as magmatic-hydrothermal, magmatic-steam, steam-heated and supergene environments (Rye, 1995; and Rye et al., 1992). The Cascade and Citaltepetl fields are defined for alunite, jarosite, gypsum and Al-Fe hydrosulphates isotope analyses (Rye, 2005). Hypogene $\delta^{34}\text{S}_{\text{anhydrite}}$ compositions from White Island (Hedenquist et al., 1993), high-sulfidation Ladolam (Gemmell et al., 2004), Chelopech (Jacquat, 2003) and pre-Main stage porphyry-Cu, Butte (Field et al., 2005) are also shown for comparison.

Anhydrite in hydrothermal systems can form in a supergene or hypogene environment, i.e. by oxidation of H_2S via boiling and dilution by meteoric water, or by precipitation from magmatic SO_2 or oxidized magmatic H_2S . Figure 6A shows isotopic compositions for sulphate-sulphide pairs at different temperatures, with $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ in equilibrium with $\delta^{34}\text{S}_{\text{anhydrite}} = -12$ for Rotokawa anhydrite at 360 °C (inferred from fluid inclusion data) being about -5‰. At this temperature, fractionation between sulphide and H_2S is minimal ($\pm 1\text{‰}$; Ohmoto and Rye, 1979), and therefore the calculated value can be used as a corollary to the fluid values. Rotokawa $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ gas in well discharges range between +4.1 and +4.8‰. Consequently, this study concludes that the present reservoir fluid composition at Rotokawa cannot have precipitated the anhydrite seen in core samples from >2000 mVD in several Rotokawa wells.

Figure 6 shows $\delta^{34}\text{S}$ compositional fields for magmatic-hydrothermal and steam-heated supergene environments (Rye et al., 1993; Rye, 1995). We suggest that the signature of the deep-sourced Rotokawa anhydrite is isotopically similar to hypogene anhydrite, associated with magmatic-hydrothermal fluids in high-sulphidation epithermal environments, such as Ladolam or Butte (Gemmell et al., 2004; Field et al., 2005) and differs from the steam-heated (hydrothermal) environment.

Relict alteration phases below 2000 mVD, including anhydrite (e.g. in RK27-1854 mRF and RK24-1820 mRF), are in disequilibrium with present reservoir fluids. Sulphur isotopic compositions show that the deep Rotokawa anhydrite precipitated from magmatic SO_2 , or oxidized magmatic H_2S in a magmatic-hydrothermal environment similar to magmatic-derived ore deposits, which we suggest may be related to intermittent (episodic?) “pulses” of exsolved deep-sourced magmatic fluid into the active geothermal system.

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REFERENCES

Andersen, L.C.: A comparison of buried andesites at Ngatamariki and Rotokawa geothermal fields, Taupo. *MSc University of Waikato*. 283p. (2011).

Arehart, G.B., Christenson, B.W., Wood, C.P., Foland, K.A., Browne, P.R.L.: Timing of volcanic, plutonic and geothermal activity at Ngatamariki, New Zealand. *Journal of Volcanology and Geothermal Research*, v.116, pp. 201-214. (2002).

Arribas, A.Jr.: Characteristics of high-sulfidation epithermal deposits, and their relation to magmatic fluid: *Mineralogical association of Canada Short Course*, v.23, p.419-454. (1995).

Bowyer, D., Bignall, G., Hunt, T.M.: Formation and neutralization of corrosive fluids in the shallow injection aquifer, Rotokawa Geothermal Field. *Geothermal resources Council, Transactions*, v32, pp- 201-205.

Browne, P.R.L., Graham, I.J., Parker, R.J., Wood, C.P.: Subsurface andesite lavas and plutonic rocks in the Rotokawa and Ngatamariki geothermal systems, Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research*, v.51, pp. 199-215. (1992).

Chacko, T., Riciputi, L.R., Cole, D.R., Horita J.: A new technique for determining equilibrium hydrogen isotope fractionation factors using the ion microprobe: Application to the epidote-water system. *Geochimica et Cosmochimica Acta*, v.63, pp. 1-10. (1999).

Field, C.W., Zhang, L., Dilles, D.H., Rye, R.O., Reed, M.H.: Sulfur and oxygen isotopic record in sulfate and sulfide of early, deep, pre-main stage porphyry Cu-Mo and late stage base-metal mineral deposits, Butte district, Montana. *Chemical Geology*, v.215, pp.61-93. (2005).

Gemmell, J.B., Sharpe, R., Jonasson, I.R., Herzig, P.M.: Sulfur isotope evidence for magmatic contributions to submarine and subaerial gold mineralization: Conical Seamount and the Ladolam Gold deposit, Papua New Guinea. *Economic Geology*, v.99, pp. 1711-1725. (2004).

Giggenbach, W.F.: The use of gas chemistry in delineating the origin of fluids discharged over the Taupo Volcanic Zone. *Proc. Symposium 5, International Volcanological Congress*, pp. 47-50. (1986).

Giggenbach, W.F.: Variations in the chemical and isotopic compositions of fluids discharged from the Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research*, v.68, pp. 89-116. (1995).

Graham, C.M., Sheppard, S.M.F., Heaton, T.H.E.: Experimental hydrogen isotope studies: I. Systematics of hydrogen isotope fractionation in the systems epidote-H₂O, zoisite-H₂O and Al(OH)-H₂O. *Geochimica et Cosmochimica Acta*, v.44, pp. 353-364. (1980).

Hatherton, T., MacDonald, W.J.P., Thompson, G.E.K.: Geophysical methods in geothermal prospecting in New Zealand. *Bulletin Volcanologique*, v.29, pp.485-498. (1966)

Hedenquist, J.W., Mroczek, E.K., Giggenbach, W.F.: geochemistry of the Rotokawa Geothermal System: Summary of data, interpretation and appraisal for energy development. *N.Z. DSIR Chemistry Division, technical note 88/6*, 63p. (1988).

Hedenquist, J.W., Simmons, S.F., Giggenbach, W.F., Eldridge, C.S.: White Island, New Zealand, volcanic-hydrothermal system represents the geochemical environment of high-sulfidation Cu-Au ore deposition. *Geology*, v.21, p.731-734. (1993).

Houghton, B.F., Wilson, C.J.N., McWilliams, M.O., Lanphere, M.A., Weaver, S.D., Briggs, R.M., Pringle, M.S.: Chronology and dynamics of a large silicic magmatic system: Central Taupo Volcanic Zone, New Zealand. *Geology*, v.23, pp. 13-16. (1995).

Hunt, T.M. and Harms, C.: Gravity survey of the Rotokawa geothermal field. *Proc. 12th New Zealand Geothermal Workshop*, Auckland, New Zealand. pp. 91-96. (1990).

Jacquat, S.: Etude paragenetique et geochemique du gisement epithermal d'or et de cuivre de type high-sulfidation de Chelopech, Bulgarie: Diplome d'ingenieur geologue, University of Geneva, 172p. (2003).

Ohmoto, H., Rye, R. O.: Isotope of sulfur and carbon, in Barnes, H. L. Ed., *Geochemistry of Hydrothermal deposits*, John Wiley & Sons, pp. 509-567. (1979).

Rae, A.J.: Rotokawa geology and geophysics. *GNS Science consultancy report 2007/83*. 12p. (2007).

Rae, A.J., L.E. Ramirez, L.E., McCoy-West, A.J., O'Brien, J.: The application of chlorite geothermometry to hydrothermally altered Rotokawa Andesite, Rotokawa Geothermal Field. *Proc. 33rd New Zealand Geothermal Workshop*, Auckland, New Zealand. this volume. (2011).

Risk, G.F.: Electrical resistivity surveys of the Rotokawa geothermal field, New Zealand. *Proc. 22nd New Zealand Geothermal Workshop*, Auckland, New Zealand. pp. 121 – 126. (2000).

Rye, R.O.: A review of the stable-isotope geochemistry of sulfate minerals in selected igneous environments and related hydrothermal systems. *Chemical Geology*, v.215, pp. 5-36. (2005).

Rye, R.O., Bethke, P.M., Wasserman, M.D.: The stable isotope geochemistry of acid sulfate alteration. *Economic Geology*, v.87, pp.225-262. (1992).

Steiner, A., Rafter, T.A.: Sulfur isotopes in pyrite, pyrrhotite, alunite and anhydrite from steam wells in the Taupo Volcanic Zone, New Zealand. *Economic Geology*, v.61, pp. 1115-1129. (1966).

Sun, S., McDonough, W.: Chemical and isotopic systematics of oceanic basalts: implications for

mantle composition and processes. *Geological Society of London Special Publications*, v.42, pp. 313-345. (1989).

Taylor, J.P.Jr.: Oxygen and hydrogen isotope relationships in hydrothermal mineral deposit, in Barnes, H. J. Ed., *Geochemistry of Hydrothermal deposits*, John Wiley & Sons, pp. 236-277. (1979).

Vennemann T.W., O'Neil J.R.: Hydrogen isotope exchange between hydrous minerals and molecular hydrogen: I. A new approach for the determination of hydrogen isotope fractionation at moderate temperatures. *Geochimica et Cosmochimica Acta*, v.60, pp. 2437-2451. (1996).

Vucetich, C.G., Howorth, R.: Late Pleistocene tephrrostrigraphy in the Taupo district. *New Zealand Journal Geology Geophysics*, v.19, pp. 51-69. (1976).

Zheng, Y.-F.: Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochimica et Cosmochimica Acta* 57, pp. 1079-1091. (1993a).

Zheng, Y.-F.: Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates. *Earth and Planetary Science Letters*, v.120, pp. 247-263. (1993b).