

# CLAY MINERALOGY, OXYGEN ISOTOPE GEOCHEMISTRY, AND WATER/ROCK RATIO ESTIMATES, TE MIHI AREA, WAIRAKEI GEOTHERMAL FIELD, NEW ZEALAND

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**Abstract**—Diocahedral clays from an active continental geothermal system have been studied to assess their usefulness as proxies of paleo-hydrological and thermal conditions in the subsurface. Drill cuttings from Well WK244 in the Te Mihi area of the Wairakei Geothermal Field, New Zealand, were analyzed to determine the mineralogical, morphological, and isotopic characteristics of hydrothermal clays in these samples. Mixed-layer illite-dioctahedral smectite (I-S) and R0 chlorite-trioctahedral smectite are the main clay minerals, with I-S clays varying downward from R1 to R3 ordering and 50 to >90% illite over 160 m. The proportion of illite in I-S correlates positively with downhole temperature ( $r = 0.98$ ) and I-S morphology changes from high aspect ratio ribbons, laths, and hairy fibers to pseudo-hexagonal plates with depth. Swelling clay percentages determined using the methylene blue method show a strong positive correlation with %S in I-S ( $r = 0.91$ ), validating use of methylene blue as a rapid field tool for characterizing the smectite to illite transition in this active geothermal environment. The oxygen isotopic composition of I-S ( $\delta^{18}\text{O}_{\text{I-S}}$ ) decreases systematically with depth, and mostly reflects a progressive increase in subsurface temperature during clay formation. Estimates of water/rock ratios calculated using  $\delta^{18}\text{O}_{\text{I-S}}$  values display stratigraphic variability that corresponds to variations in permeability. Oxygen isotopic measurements of I-S are a useful tool for understanding reservoir and permeability evolution in such geothermal systems and their related fossil analogs.

**Key Words**—Clay Minerals, Hydrothermal, Geothermal, Illite-smectite, Methylene Blue, pXRD, New Zealand, Oxygen Isotopes, SEM, Taupo Volcanic Zone, Wairakei, Water/Rock Ratio.

## INTRODUCTION

The transition from smectite to illite through mixed-layer illite-smectite (I-S) clays is well documented in upper crustal environments that have been affected by hydrothermal alteration, low-grade metamorphism, burial diagenesis, and contact metamorphism (Inoue *et al.*, 2005). Variables affecting the development of this clay transitional series are time, temperature, fluid chemistry (including availability of K), and water/rock ratios (Hower *et al.*, 1976; Nadeau and Reynolds, 1981; Whitney, 1990; Altaner and Ylagan, 1997). The compositional dependence of I-S clays on these variables permits their use as tools for physicochemical evaluation in a variety of geologic environments.

Several studies have described the isotopic systematics of structural oxygen in smectite, illite, and I-S in diagenetic and pedogenic environments (*e.g.* Savin and Epstein, 1970; Yeh and Eslinger, 1986; Longstaffe and Ayalon, 1991; Ryan *et al.*, 1998; Vitali *et al.*, 2002) and during laboratory experiments (James and Baker, 1976;

Savin and Lee, 1988; Bechtel and Hoernes, 1990). Fewer studies have examined active geothermal environments (*e.g.* Ohaki-Broadlands – Eslinger and Savin, 1973; Kakkonda – Inoue *et al.*, 2004). The present study adapted methods described in the aforementioned studies to examine the oxygen isotope systematics of the Te Mihi area of the Wairakei geothermal field, and suggests how such data can be used to characterize the properties and evolution of such geothermal resources.

### Geologic setting

The Taupo Volcanic Zone (TVZ) is a 200 km long, 30–50 km wide, SSW–NNE trending area of active rifting within the North Island of New Zealand, with NW–SE extension rates ( $7\text{--}16 \text{ mm y}^{-1}$ ) increasing northward toward the Bay of Plenty (Cole, 1990; Harrison and White, 2006). This extension is a continental expression of the Tonga–Kermadec oceanic backarc spreading center, resulting from the westward subduction of the Pacific Plate. As a result, the North Island of New Zealand has experienced rhyolitic volcanism for ~12 million years, with active andesitic and rhyolitic volcanism now confined to the TVZ (Stratford and Stern, 2006).

The Wairakei geothermal field, which is situated ~8 km northeast of Taupo in the southerly region of the TVZ, was globally the first liquid-dominated geothermal resource to be exploited for electricity generation. The

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DOI: 10.1346/CCMN.2013.0610304

subsurface geology at Wairakei comprises ~2.5 km of Pliocene–Pleistocene volcanoclastic, volcanic, and lacustrine deposits resting on a downfaulted block of Jurassic greywacke (Rosenberg *et al.*, 2009).

The Te Mihi area constitutes the westernmost division of the Wairakei geothermal field (Figure 1). This area is interpreted as a major zone of convective upflow, as indicated by discharge fluids containing some of the highest gas contents, temperatures, and chloride contents within the Wairakei field (Harvey and Browne, 1991). Samples for this study were obtained from production Well WK244, which was drilled to a depth of 1100 mRF (meters below rig floor), with no cuttings returned below 811 mRF. Downhole lithologies intersected by Well WK244 are identical to those intersected by WK245 (see cross-section in Rosenberg *et al.*, 2009) and have been described by Rosenberg *et al.* (2009) and the Institute of Geological and Nuclear Sciences (pers. comm.). In ascending stratigraphic order, these lithologies include: the Karapiti IIB (rhyolite lava); Waiora W<sub>3–4</sub> (tuffaceous sandstone, mudstone); Waiora W<sub>5</sub> (ignimbrite, tuff); Rautehuia Breccia (muddy lithic volcanoclastic breccia); Huka Falls Formation (HFF, tuffaceous lacustrine sediments); Oruanui Formation (ignimbrite); and post-26 ka surficial deposits (unaltered

coarse tuff). The Rautehuia Breccia is considered a basal sub-unit of the Huka Falls Formation (Rosenberg *et al.*, 2009). Significant circulation losses during drilling of Well WK244 indicate the presence of highly permeable zones within the Waiora and Karapiti IIB units (Rosenberg *et al.*, 2009; GNS, pers. comm.).

## ANALYTICAL METHODS

### Clay fraction

Nineteen samples of drill cuttings were crushed to <~2 mm and dispersed ultrasonically in distilled water. The <~10 µm supernatant of dispersed samples was transferred to 30 cm high, 1000 mL glass columns and the <2 µm fraction separated using settling times determined by Stokes Law. Each sample underwent re-suspension and collection of the <2 µm fraction four times. 50 mL of 6% sodium hypochlorite was added to glass beakers containing the <2 µm fractions to assist with flocculation and to oxidize organic matter. The samples were then placed in a water bath overnight at ~60°C and subsequently washed with distilled water *via* centrifugation. Separate aliquots of each Na-saturated <2 µm fraction then underwent Ca and K saturation, followed by additional washing with distilled water. All

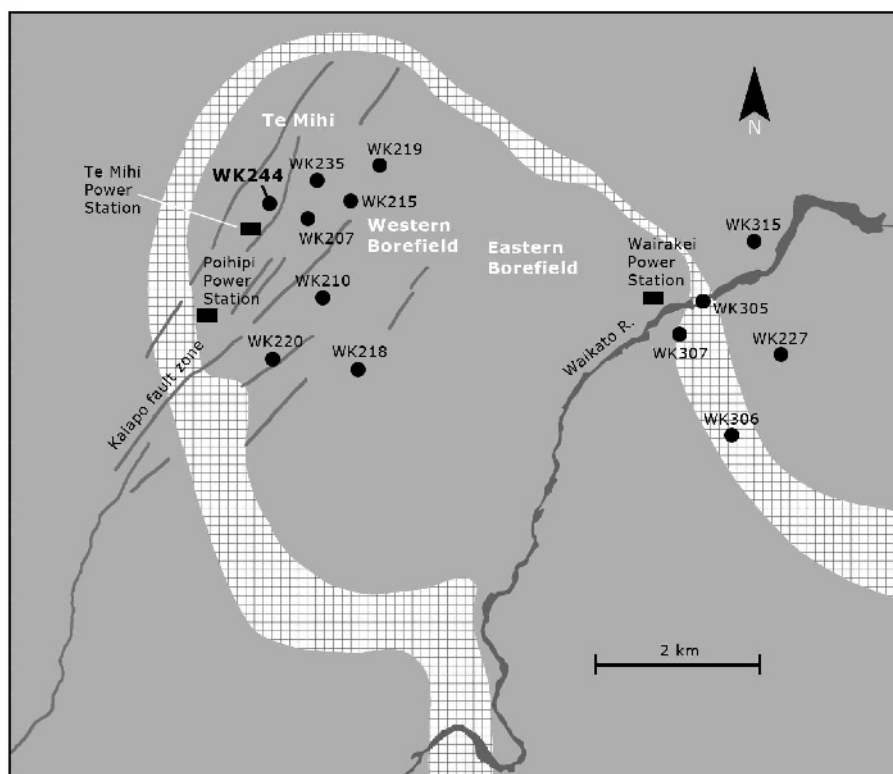


Figure 1. Map of the Wairakei geothermal field showing selected wells (circles) and deviation path of WK244, power-plant locations (rectangles), dominant faults in the Te Mihi area (gray lines), the Waikato River, and the resistivity boundary of the geothermal system (cross-hatched) (modified after Rosenberg *et al.* (2009) and Bixley *et al.* (2009)).

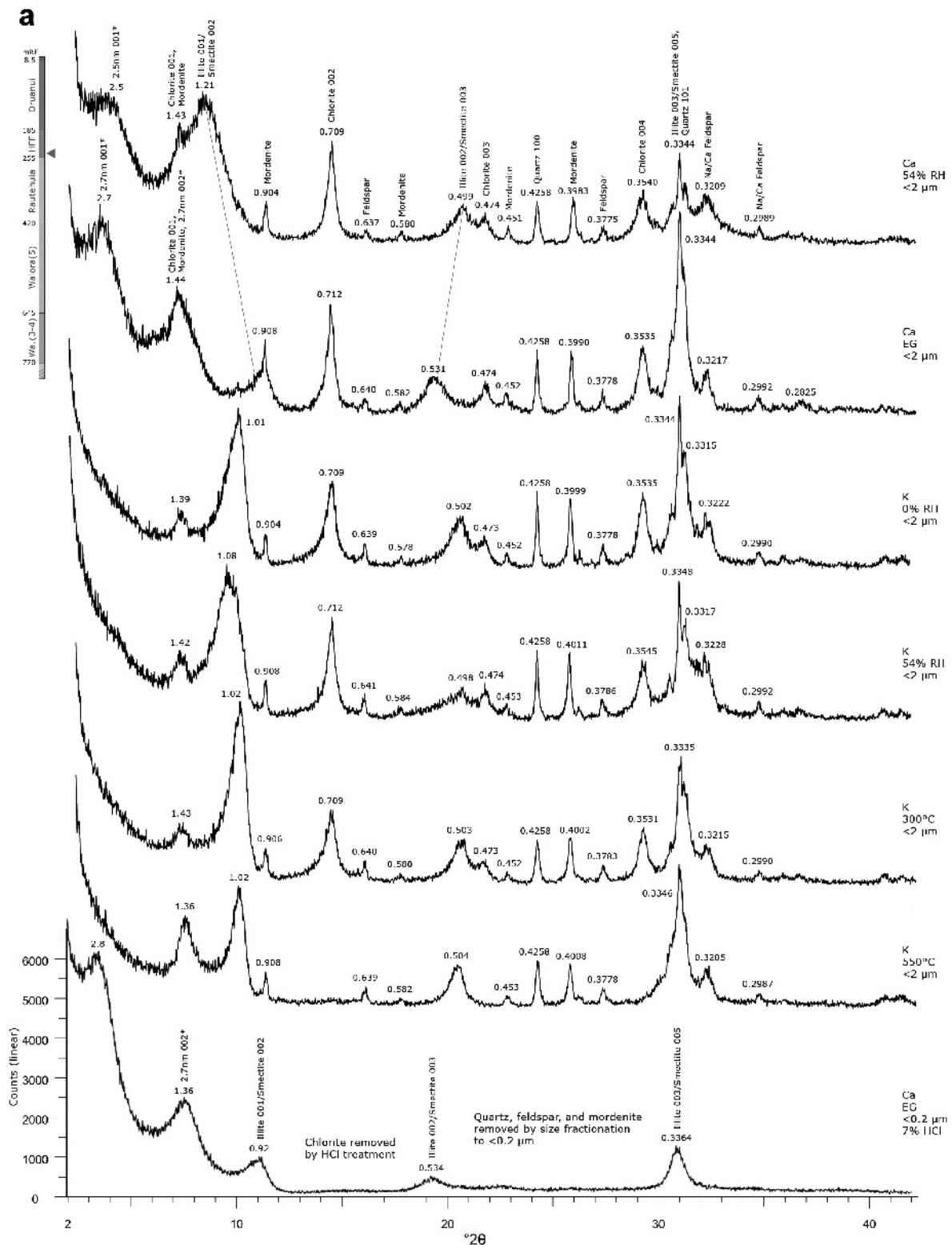
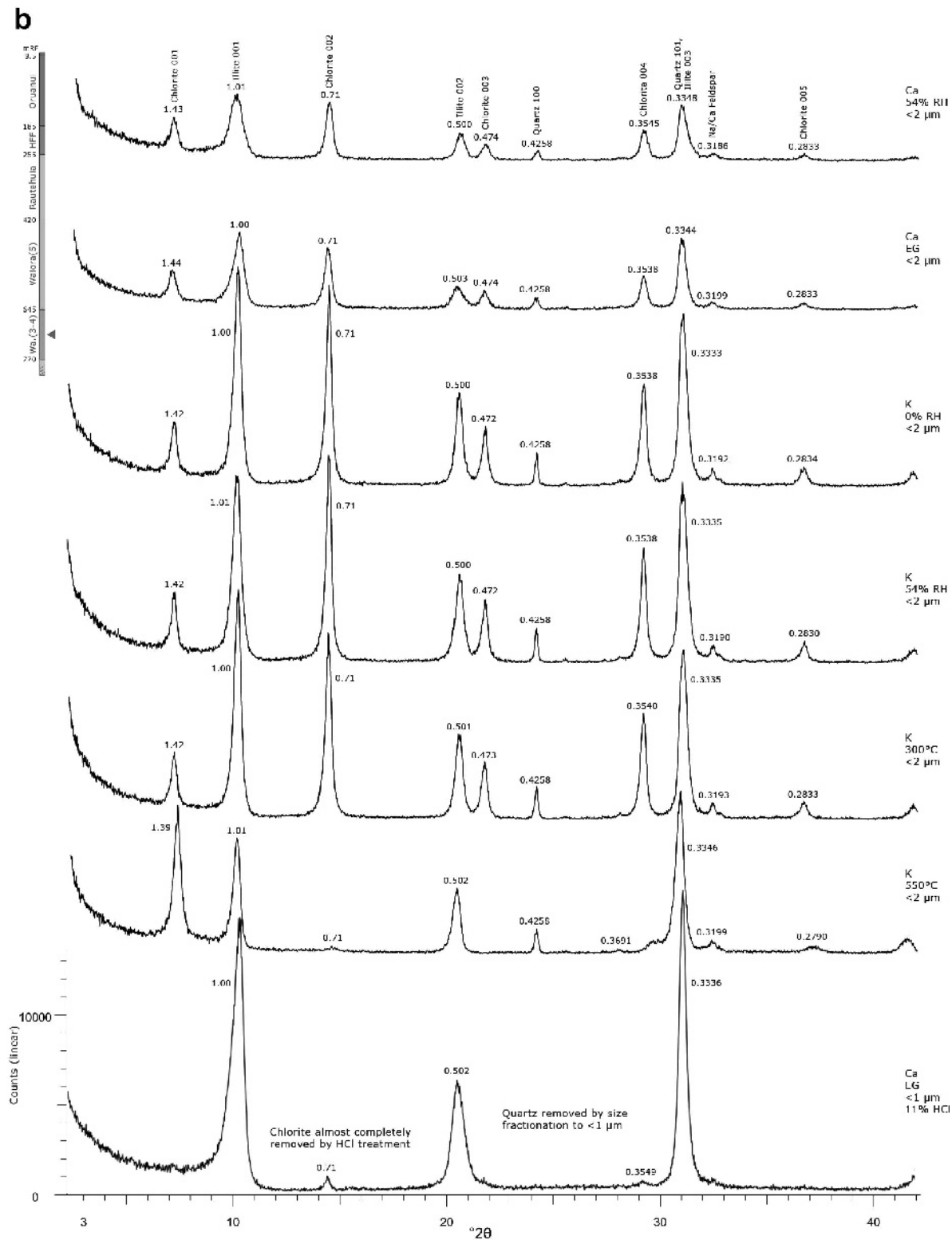


Figure 2. Representative pXRD patterns for oriented clay-size fractions of drill cuttings from (a) 245 mRF and (b) 710 mRF in WK244. Size fractions, cation saturation, and treatment (ethylene glycol (EG), humidity, heating, acid) are indicated adjacent to each XRD pattern. All scans were corrected to the quartz 100 peak (0.4258 nm) except <math><1/<0.2 \mu\text{m}</math> fractionations where no quartz was present. Stratigraphic columns showing sample locations (arrows) are provided to the top left of the diagram.



aliquots were then freeze dried. Ceramic tile mounts (~30 mg) of the freeze-dried Ca- and K-saturated samples were prepared using suction to obtain a preferred basal orientation of the clay minerals for powder X-ray diffraction (pXRD).

While some <2  $\mu\text{m}$  size fractions consisted almost entirely of clay minerals, others also contained non-phyllsilicates. To remove non-phyllsilicates, finer size fractionations (<1, <0.5, and/or <0.2  $\mu\text{m}$ , as required) were obtained by centrifugation of the <2  $\mu\text{m}$  fraction, following Jackson (1969). Glass slides of these size fractionations were prepared using the pipette method for examination by pXRD. Once a separated fraction consisting of only clay minerals was obtained, heated HCl (7% or, if required, 11%) was used to reduce or eliminate the presence of chloritic clays, as described by Ayalon and Longstaffe (1990). This acidification does not affect the isotopic composition of the remaining silicate mineral residues (Longstaffe, 1986). Pure I-S and/or illite samples were obtained by the end of this process (Figure 2).

#### XRD and SEM

The ceramic and glass mounts of the clay samples were analyzed at the Laboratory for Stable Isotope Science (The University of Western Ontario) using a high-brilliance Rigaku Rotaflex RU-200B series diffractometer, equipped with a rotating anode (CoK $\alpha$  source operated at 160 mA and 45 kV) and a graphite monochromator. Scans were performed at 2°2 $\theta$ /min with a step size of 0.02°2 $\theta$ . K-saturated samples were analyzed at 0% and 54% relative humidity, and additionally after heating at 300 and 550°C (for 3 h and 2 h, respectively). Ca-saturated samples were analyzed at 54% relative humidity and after glycolation. A randomly oriented front-pack mount of each Ca-saturated sample was also prepared and analyzed from 58 to 78°2 $\theta$  at 5°2 $\theta$ /min to determine 060 band positions. Calculated XRD data of Moore and Reynolds (1997), adapted for CoK $\alpha$  radiation, were utilized to determine phase proportions and ordering of mixed-layer clays (illite-smectite and chlorite-smectite); *NEWMOD*© software (Reynolds, 1985) was used to confirm these determinations. The % illite (%I) values were considered to be accurate within  $\pm 5\%$ .

The non-clay mineralogy was determined for unfractionated, powdered rock material at the Wairakei Research Centre, New Zealand, using randomly oriented front packs and a Philips X'Pert X-ray diffractometer equipped with CoK $\alpha$  radiation. Each sample was scanned from 2 to 80°2 $\theta$  at 1.2°2 $\theta$ /min, with a total step count of 3900. Scans were interpreted using Bruker *DiffracPlus*™ *EVA* evaluation software at the University of Western Ontario.

To identify phases present in small amounts,  $\mu\text{XRD}$  analysis of individual grains was performed using a Bruker™ D8 Discover diffractometer, equipped with a

CuK $\alpha$  source (40 kV, 40mA), theta-theta geometry, Gobel mirror parallel optics system, and a general area detector diffraction system. Samples were mounted on an XYZ stage oriented to target predetermined points (with an accuracy of 12.5  $\mu\text{m}$ ; Flemming, 2007). Crystal morphologies and mineral-mineral relationships for samples from each depth interval were examined using an Hitachi S-4500 field emission SEM with a Quartz XOne EDS system at Surface Science Western, The University of Western Ontario, and a JEOL JSM-7400F high-resolution field emission SEM at the Laboratory for the Study of Calcified Tissues and Biomaterials, at the Université de Montréal.

#### Oxygen isotope analysis

The oxygen isotopic compositions of illite-smectite and illite ( $\delta^{18}\text{O}_{\text{I-S}}$ ) were analyzed at the Laboratory for Stable Isotope Science, The University of Western Ontario, Canada. About 8 mg of each sample was placed in spring-loaded sample holders, and heated while pumping under vacuum overnight at 150°C to remove sorbed and interlayer water. The samples were then loaded into Ni-reaction vessels under dry nitrogen, and heated while pumping under vacuum at 150°C for an additional 3 h to eliminate any remaining non-hydroxyl water from the system. Structural oxygen was then liberated using chlorine trifluoride; this oxygen was then reacted with incandescent carbon to produce carbon dioxide gas, following Clayton and Mayeda (1963), as modified by Borthwick and Harmon (1982). Isotopic measurements were conducted using a Prism II, dual-inlet, triple-collecting stable isotope ratio mass-spectrometer. The results are reported in  $\delta$ -notation relative to Vienna Standard Mean Ocean Water (VSMOW). Analyses of NBS-30 ( $n = 6$ ) and KGa-1 ( $n = 3$ ) produced  $\delta^{18}\text{O}$  values of  $+5.1 \pm 0.1\%$  and  $+21.5 \pm 0.1\%$ , respectively, which compares well with their accepted values of  $+5.1\%$  and  $+21.5\%$ , respectively. Duplicate analyses of samples ( $n = 10$ ) were reproducible to better than  $\pm 0.2\%$ . No significant difference was observed in  $\delta^{18}\text{O}$  values between samples that underwent treatment with sodium hypochlorite and those that did not ( $n = 7$ ).

#### Bulk-rock swelling clay percentages

Methylene blue (MeB) is an organic dye that is preferentially incorporated into the interlayer sites of smectitic clays, and can be used for rapid, semi-quantitative determination of the smectitic component of a crushed rock sample. The method set out by Harvey *et al.* (2000) for active geothermal environments was utilized in this study as follows. Dry-crushed samples were fractionated through a <3  $\phi$  (0.125 mm) sieve. 1 g of the recovered material was added to a well stirred and warmed (~50°C) 10 mL solution of 1% H<sub>2</sub>SO<sub>4</sub>. A 3.74 g/L MeB solution was then titrated into the sample in 1 mL aliquots until all expandable clay interlayers were saturated. Interlayer saturation was tested by pressing a



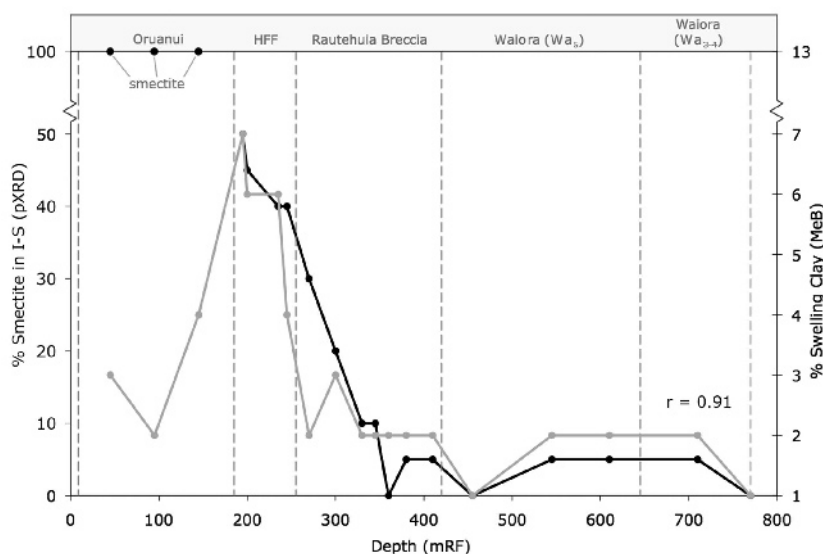


Figure 3. Smectite proportions in I-S and occurrence of end-member smectite and illite (black data series; primary Y axis) as determined by powder XRD analyses and bulk rock %swelling clay estimates (gray data series; secondary Y axis) as determined by MeB methods. The two data series (exclusive of samples from the Oruanui Formation) exhibit a strong positive correlation ( $r = 0.91$ ).

drop of the solution onto filter paper after the addition of each MeB aliquot. Once sample saturation is achieved, excess MeB in solution creates a diagnostic blue halo about the spot where the solution droplet touched the filter paper. All samples were analyzed in duplicate.

## RESULTS AND DISCUSSION

### Clay and zeolite mineralogy

The pXRD analysis of the  $<2 \mu\text{m}$  size fraction indicates progressive illitization with increasing depth (Figure 3). Smectite is present in all samples from the Oruanui Formation ( $<185 \text{ mRF}$ ). The I-S transition occurs between 195 and 360 mRF within the Huka Falls Formation and the Rautehulia Breccia. This I-S transition is similar to that observed in the nearby Wairakei Well WK207, where it occurs between 146 and 297 mRF (Harvey and Browne, 1991). The total interval thickness over which the I-S transition occurs is similar in Wells WK244 and WK207 (165 and 151 m, respectively), but the actual depths are  $\sim 50\text{--}60 \text{ m}$  deeper in WK244. This difference is a result of hotter downhole conditions in Well WK207 (as reported by Harvey and Browne, 1991) relative to WK244.

The composition of mixed-layer illite-dioctahedral smectite in WK244 changes from  $I_{0.5}$  to  $I_{>0.95}$  over the 165 m interval. Compositions of  $I_{\geq 0.95}$  are present between 360 and 770 mRF within the Rautehulia Breccia, the Waiora, and the boundary zone between the Waiora and the Karapiti IIB Rhyolite. The I-S has R1 ordering at  $I_{<0.85}$  and R3 ordering at  $I_{\geq 0.85}$ . A strong positive correlation ( $r = 0.98$ ) exists between illite proportions in the I-S and downhole temperature (Figure 4) ( $57\text{--}221^\circ\text{C}$ ; Contact Energy, pers. comm.). Linear regression of these

data yields the following I-S ‘geothermometer’ for the Te Mihi area:

$$T (^{\circ}\text{C}) = (I - 0.30839)/(0.00296) \quad (1)$$

where  $I$  is the fractional component of illite in the mixed-layered I-S. Chi and Browne (1991) reported a similar relationship for other boreholes in the Wairakei geothermal field (Figure 4). Such empirical ‘geothermometers’ can be very useful for intra-field geothermal prospecting as they provide subsurface temperature estimates for comparison with other wells in a given field, before reliable downhole measurements are available. However, they do not necessarily reflect the original formation temperatures of the clay minerals and they are generally insensitive to field-wide thermal changes that have occurred since clay formation.

Swelling clay percentages obtained for bulk samples using MeB organic-dye testing range from  $\sim 7$  to  $<1\%$  in Well WK244. Swelling clay phases within the bulk rock are predominantly pure smectite and the smectitic component of I-S (the contribution from smectite interlayers within trioctahedral clays is considered negligible). The downhole trend of decreasing swelling clay percentage from the upper Huka Falls Formation to the boundary of the Karapiti IIB Rhyolite shows a strong positive correlation with decreasing %S in I-S, as determined by pXRD ( $r = 0.91$ ; Figure 3). This pattern suggests that the abundance of hydrothermal I-S is approximately constant at all depths  $\geq 195 \text{ mRF}$ , an observation supported by illitic clay abundance estimates from pXRD of bulk samples. This strongly suggests that the swelling component in these samples is contained mostly in I-S. The slight decoupling between the two datasets probably arises from the

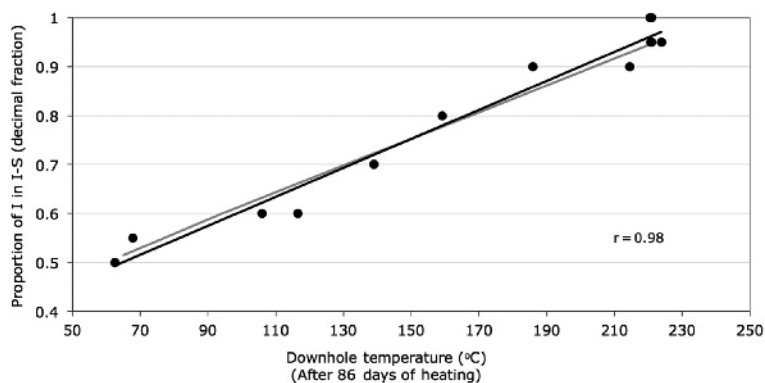


Figure 4. Illite proportions in I-S vs. downhole temperatures (Contact Energy, pers. comm.). The I-S geothermometer proposed for WK244 (black line; linear regression,  $r = 0.98$ ) is very similar to the I-S geothermometer (gray) determined previously for the Te Mihi area (Chi and Browne, 1991; with data from Harvey and Browne, 1991).

assumption of a constant abundance for I-S across the sample intervals. Overall, the comparison of the two methods shows that the MeB method is useful for rapid, field-based estimation of %S in I-S within the Te Mihi area, and perhaps other similar geothermal settings.

The pXRD data for glycolated and dehydrated samples suggest that R0 chlorite( $>0.95$ )-smectite is also generally present throughout the sampled portion of Well WK244. In addition, poorly developed diffractions observed throughout the Oruanui Formation may indicate the additional presence of a chloritic (possibly detrital) trioctahedral clay.

The XRD and SEM results indicate a depth/temperature-dependent sequence of zeolites in Well WK244. Clinoptilolite is present in the shallowest sample studied (45 mRF). Mordenite appears within the lower Oruanui and Huka Falls formations. Laumontite and wairakeite are present at depths greater than 410 and 455 mRF ( $>220^{\circ}\text{C}$ ), respectively.

#### Clay morphologies

The commonly used terminology for describing illite/I-S morphologies (e.g. Guven, 2001) is adopted herein. Lath and fibrous morphologies are characterized by mineral length/width aspect ratios of 3–50 and  $>50$ , respectively, and flexible laths and fibers are referred to as ribbons and filaments or hairs, respectively.

Smectite occurs in a typical ‘cornflake’-type morphology (e.g. Keller *et al.*, 1986) in all samples from the Oruanui Formation (Figure 5a). The appearance of I-S ribbons and hairs at 145 mRF indicates the presence of minor illitic clay not detected by pXRD.

Within the Huka Falls Formation and Upper Rautehuia Breccia (corresponding to samples from 195–345 mRF), I-S appears as laths, ribbons, fibers, and hairs (Figure 5b,c), with flexibility negatively correlated to crystal thickness. These high-aspect-ratio morphologies could arise from illite supersaturation and rapid mineral growth rates paired with relatively low diffusion rates (e.g. in a low-porosity environment; Inoue and Kitagawa, 1994).

Alternatively, they could reflect inhibition of mineral growth in the *b* crystallographic direction (due to organic or inorganic functional groups reacting with exposed hydroxyl ligands on the illite (010) crystal face; Surdam *et al.*, 1984; Guven, 2001).

Experimental studies have shown that high-aspect-ratio illites are metastable (Bauer *et al.*, 2000; Champion, 1989; and Lanson and Champion, 1991), and eventually coalesce and transform through Ostwald ripening into flakes and end-member pseudo-hexagonal plates – a phenomenon previously documented in hydrothermal systems (e.g. Keller *et al.*, 1986; Inoue *et al.*, 2004; Meunier, 2005). In Well WK244, I-S laths and fibers have coalesced into flakes with ‘scalloped’ edges, probably because of the variable lengths of the amalgamated laths and fibers (Figure 5c,d,e). This ripening process seems to have progressed with increasing depth within the Huka Falls Formation and Upper Rautehuia Breccia (Figure 5c,d,e).

At greater depths in Well WK244, within the Waioara Formation, high-aspect-ratio morphologies were not observed and pseudo-hexagonal crystallites prevail (Figure 5f). Greater porosities in the Waioara Formation probably contributed to an increased fluid flux, which may well have facilitated the ripening process from laths/fibers to platelets.

#### Oxygen isotopic systematics

The  $\delta^{18}\text{O}_{\text{I-S}}$  values in Well WK244 decrease systematically with depth, from +5.4 to +0.5‰ (Figure 6). This pattern is consistent with increasing temperature of clay formation.

Hydrothermal fluids in Wairakei originate from local meteoric water with a  $\delta^{18}\text{O}$  of  $\sim -6\text{‰}$  (Eslinger and Savin, 1973; Giggenbach, 1995) but are enriched in  $^{18}\text{O}$  during heating by isotopic exchange with host rocks in the Wairakei subsurface. However, assuming present downhole temperatures for clay formation and using the oxygen isotope illite-smectite–water geothermometer of Savin and Lee (1988), calculated  $\delta^{18}\text{O}_{\text{water}}$  values appear

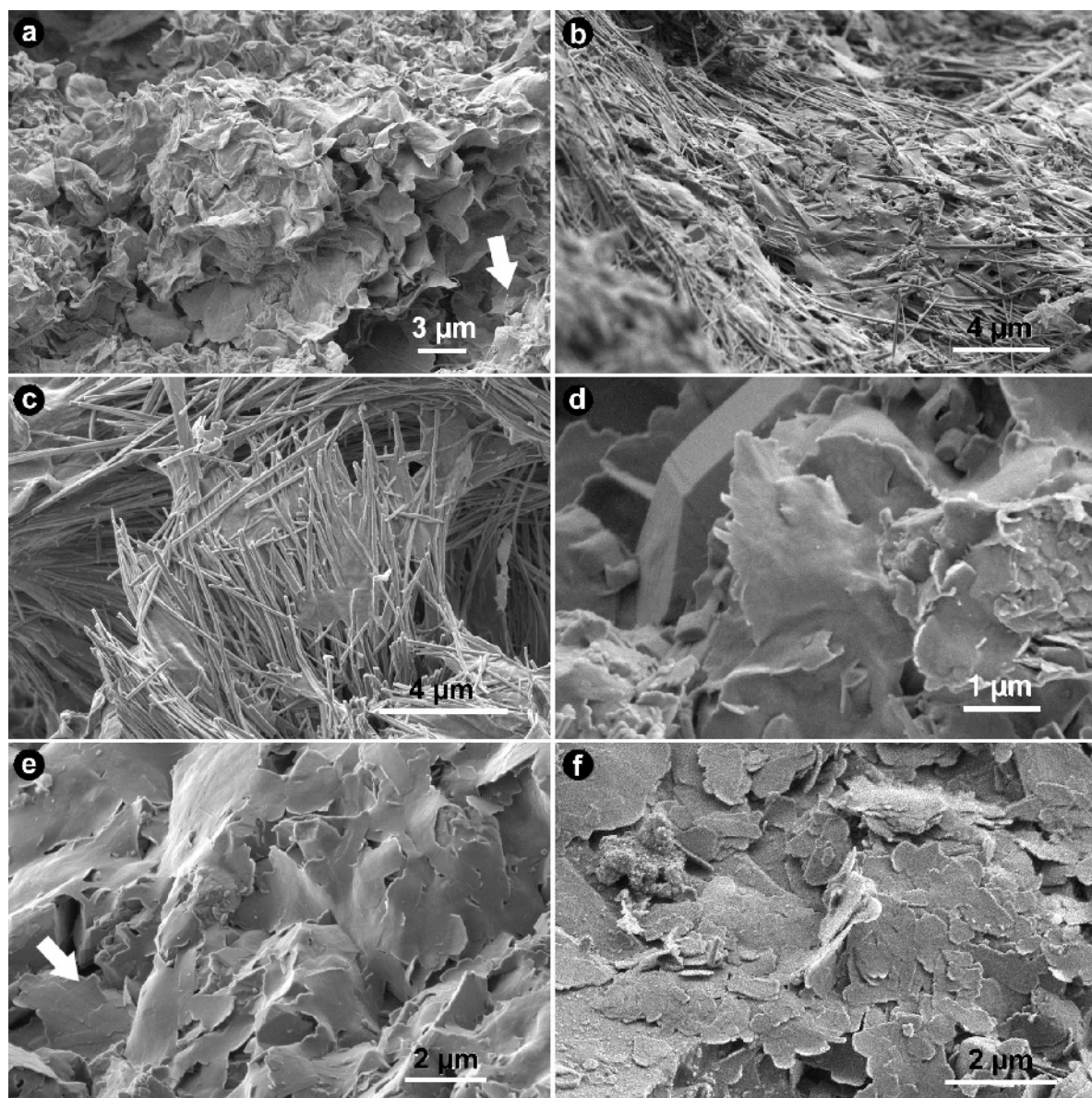


Figure 5. SEM images of hydrothermal clays from Well WK244 in the Te Mihi area, Wairakei geothermal field. Mineralogical identifications were made using morphological characteristics, EDS, and  $\mu$ XRD. (a) 'Cornflake'-textured dioctahedral smectite from the Oruanui Formation, 145 mRF. Submicron illite filaments extending from coalesced flakes are visible in the bottom right quarter of the image (arrow). (b) Strands of 'hairy' illite coalescing into flakes near the center of the image, 195 mRF. (c) Coalescence of hairs and ribbons of illite, 195 mRF. (d) Flakes of coalesced illite ribbons of varying original length displaying scalloped edges, 235 mRF. (e) Flakes of well coalesced illite ribbons, 345 mRF. Evidence of amalgamated ribbons is provided by scalloped edges and faint ribbon impressions on flake surfaces (arrow). (f) Well developed pseudo-hexagonal illite platelets, 610 mRF.

to be as low as  $-12.6\%$  in the upper portions (195–300 mRF) of Well WK244. Such compositions are unlikely, and suggest instead that shallower parts of this system were hotter during clay formation. This observation is supported by the presence of R1 and R3 ordered I-S within this interval (Table 1), for which minimum temperatures of 100 and 200°C, respectively, are normally required (Nadeau and Reynolds, 1981).

Heat transfer by convecting fluids is the primary control on thermal gradient in geothermal systems, with maximum subsurface temperature generally governed by the thermal buffering properties of the  $H_2O$  liquid-vapor transition. Active geothermal systems commonly exhibit temperature-depth profiles that approach the 'boiling point with depth' (BPD) curve of water – implying hydrostatic control on pressure in the upper few hundred



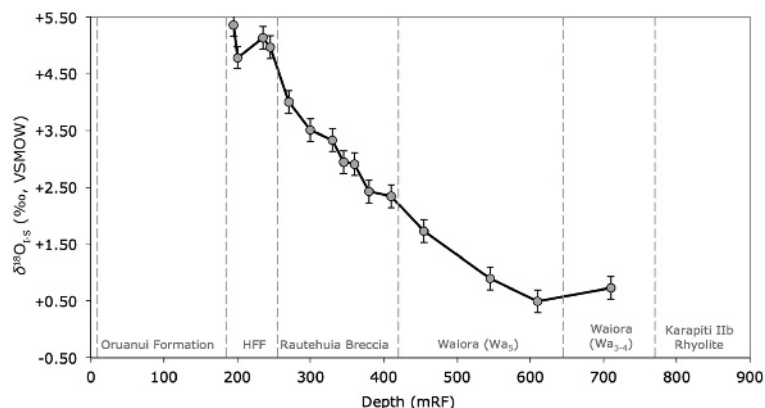


Figure 6. Oxygen isotopic composition of I-S in WK244. Error bars shown for the  $\delta^{18}\text{O}$  values are  $\pm 0.2\%$ .

meters and, thus, a hydrothermal system that is connected (through permeable networks) to the surface (Haas, 1971). In Well WK244, the temperature change from 345 to 195 mRF follows a remarkably linear trend (Figure 7), which is inferred to represent increasing interaction between cool groundwater and hydrothermal fluids up-section. Temperatures throughout this interval have been adjusted upward toward the BPD curve using 345 mRF as a pivot point. Constraints governing this correction were that: (1) the minimum  $\delta^{18}\text{O}_{\text{water}}$  value was fixed at  $-6\%$ , and (2) a linear trend was required for the adjusted depth-temperature profile on the assumption that mixing with cooler groundwaters also attenuated temperature increases in the upper 330 m at the time of clay formation (Figure 7). With this adjustment, agreement was produced with the expected thermal thresholds for R1 and R3 ordered I-S, which were first observed at 195 and 330 mRF, respectively.

Other support for a reduction in temperature and fluid pressures between the time of clay formation and present conditions is provided by overprinting of previously established propylitic assemblages in Wairakei by lower temperature and/or pH phases (Rosenberg *et al.*, 2009). Radial anhydrite present on open pore surfaces at 545 mRF in Well WK244 may have formed in a recent boiling zone below the Rautehuia Breccia, as documented elsewhere in the Wairakei (Bixley *et al.*, 2009; Rosenberg *et al.*, 2009) and Kakkonda, Japan, (Muramatsu *et al.*, 2000) geothermal fields. The occurrence of clinoptilolite at 45 mRF, well below its typical occurrence at  $>60^\circ\text{C}$  in the Wairakei geothermal field (Braithwaite, 2003), provides further evidence of temperature depression at the current time in the upper portions of Well WK244.

Measured temperatures below 345 mRF are within  $\sim 15\text{--}40^\circ\text{C}$  of the boiling-point curve (Figure 7).

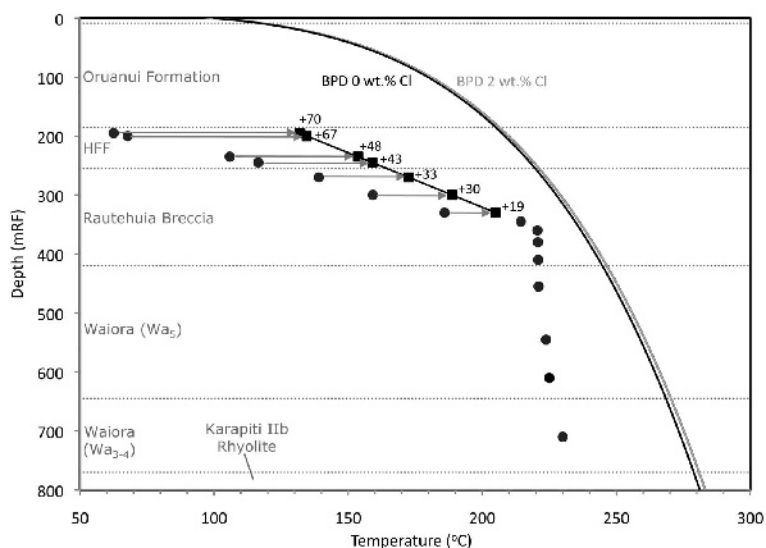


Figure 7. Measured downhole temperatures (filled circles) in Well WK244. Temperature-corrected values (squares) have been fitted to a linear trend, which lies closer to the 'boiling point with depth' (BPD) curve for water (Hass, 1971). Hydrothermal fluids at Wairakei generally contain 1–2 wt.% Cl (Giggenbach, 1995; Kissling *et al.*, 1996).

Wairakite, which is commonly used as an indicator of temperatures above 210°C (Browne and Ellis, 1970; Steiner, 1977), first appears in Well WK244 at 455 mRF and a present temperature of 221°C. Based on these observations, the present authors have assumed that the illite<sub>>0.9</sub>-smectite is close to thermal equilibrium under present conditions. No temperature adjustments were made for samples from 345 to 710 mRF.

Using the adjusted temperature profile,  $\delta^{18}\text{O}_{\text{water}}$  values calculated using the I-S data range from -6.0 to -2.7‰ and have a mean of -4.1‰ (Table 1), 0.8‰ higher than the average  $\delta^{18}\text{O}_{\text{water}}$  value of Wairakei reservoir fluids reported by Clayton and Steiner (1975).

#### Water/rock ratios in Well WK244

Estimates for water/rock (W/R) ratios in the study area can be calculated using both closed- and open-system models. In the former case, a package of fluid makes an infinite number of passes through a convective system; in the latter case, the package of fluid makes only a single pass. Fluids in natural geothermal systems operate between these two end-members, with many documented systems behaving more like closed systems (Taylor, 1977). However, some consider that the hydrological system at Wairakei may be an exception, given its relatively large W/R (by mass) ratio of 4.3 (Clayton and Steiner, 1975) and its considerable natural fluid discharges of 400 kg/s (Banwell, 1963).

#### Closed system

Water/rock ratios under closed-system conditions for the Kakkonda geothermal field using  $\delta^{18}\text{O}_{\text{I-S}}$  values were estimated by Inoue *et al.* (2004), who developed a simplified model for clay formation based on dissolution of volcanic glass of albitic composition (similar to the volcanic rocks dominating Wairakei) followed by precipitation of I-S (beidellite composition for the smectitic layers). This model was applied in the present study and the mineral compositions, as described in equation 2 (see Inoue *et al.*, 2004 for details), to the present samples from the Te Mihi area:

$$\text{W/R (atomic)} = \frac{[\delta^{18}\text{O}_i^r - \delta^{18}\text{O}_f^w - (0.6435 - 0.126I)\Delta_{\text{I/S-w}}]/(\delta^{18}\text{O}_f^w - \delta^{18}\text{O}_i^w)}{2} \quad (2)$$

where  $\delta^{18}\text{O}_i^r$  is the isotopic composition of unaltered (initial) rock;  $\delta^{18}\text{O}_i^w$  and  $\delta^{18}\text{O}_f^w$  are the isotopic compositions of unreacted (initial) and reacted (final) water, respectively;  $\Delta_{\text{I/S-w}}$  is the difference between  $\delta^{18}\text{O}_{\text{I-S}}$  and  $\delta^{18}\text{O}_f^w$ ; and  $I$  is the fractional proportion of illite in I-S. Values of  $\delta^{18}\text{O}_i^r$  and  $\delta^{18}\text{O}_i^w$  for the Wairakei geothermal field were assumed to be +7.5 to +9.7‰ (Clayton and Steiner, 1975) and -6.0‰ (Eslinger and Savin, 1973), respectively. Values of  $\delta^{18}\text{O}_f^w$  were taken from Table 1, as described earlier. W/R (atomic) ratios, as given by equation 2, were then converted to W/R (mass) ratios, assuming a starting material of albitic composition.

The calculated W/R (mass) ratios for Well WK244 range from 1.2–1.6 to 5.3–6.5 and have an average of  $2.6 \pm 0.3$ . This average lies between the previously suggested ratios for the Wairakei geothermal field of 2 (Stewart, 1978) and 4.3 (Clayton and Steiner, 1975). Such relatively high ratios are consistent with the high permeability of some host rocks at Wairakei. Henley and Ellis (1983) suggested that W/R (mass) ratios in Wairakei are near the maximum for a convecting geothermal system; such ratios for other active geothermal systems are commonly (though not exclusively; Christidis, 1998)  $< 2$  (Inoue *et al.*, 2004; Larson and Taylor, 1986; White *et al.*, 1992).

The calculated W/R ratios can be divided into two groups that correspond well with the variations in relative permeability of the formations intersected by Well WK244. In this area, ‘high’ vs. ‘low’ permeability is identified by the extent of drilling fluid losses during production drilling (GNS, pers. comm.; Rosenberg *et al.*, 2009). The Huka Falls Formation and Rautehuia Breccia (Group 1, Figure 8) have average W/R (mass) ratios of 1.4–2.5, excluding samples at 195 and 200 mRF (for which the largest temperature corrections had to be made). Such W/R ratios are consistent with the lower permeability of these lacustrine and volcanoclastic units, which are considered to be aquitards within the Wairakei geothermal field. The lowest values occur in the mid to lower portions of the Rautehuia Breccia, which is more massive and compacted than its upper portions (Rosenberg *et al.*, 2009; Bixley *et al.*, 2009). The high W/R ratios calculated for the upper half of the Huka Falls Formation may be related to shallow steam zones that are known to occur within this unit (Rosenberg *et al.*, 2009).

The highly permeable ignimbrite, tuff, and tuffaceous sandstone and mudstone of the Waiora Formation in the Te Mihi area (Group 2, Figure 8) have greater calculated W/R ratios (2.5–5.9) than Group 1. This unit contains the main producing hot aquifers at Wairakei. The lithological boundary between the Rautehuia Breccia (*i.e.* lower Huka Falls Formation) and the upper Waiora Formation is gradational (Rosenberg *et al.*, 2009), which may explain the corresponding gradient in W/R ratios (Figure 8).

#### Open system

Open-system W/R ratio calculations assume the unlikely scenario that a unit of water makes a single pass through the hydrothermal system. Nevertheless, such calculations can be used to provide a lower limit for W/R ratios in convective hydrothermal systems.

Water/rock ratios calculated for a closed system can be adapted to an open-system model using the equation provided by Taylor (1977):

$$\text{W/R} = \ln[(\text{W/R})_{\text{closed}} + 1] \quad (3)$$

As expected, the calculated W/R ratios for the open-system model yield a very subdued version of the pattern obtained for the closed-system model (Figure 8).

Table 1. Temperature, pXRD, isotopic, and MeB data for samples from Well WK244. % Illite and interlayer ordering were determined following Moore and Reynolds (1997) and confirmed using *NEWMOD*© (Reynolds, 1985). The  $\delta^{18}\text{O}_{\text{fluid}}$  values were calculated using the oxygen isotope illite-smectite–water geothermometer of Savin and Lee (1988). Water/rock (mass) ratios were calculated using the closed-system model described by Inoue *et al.* (2004).

Depth	Formation	Measured temperature (°C)	Corrected temperature (°C)	% Illite	R	% Swelling clay (MeB)	$\delta^{18}\text{O}_{\text{mineral}}$ (‰, VSMOW)	$\delta^{18}\text{O}_{\text{fluid}}$ (‰, VSMOW)	W/R closed system (avg.)	W/R open system (avg.)
45	Oruanui	15		—		<3%				
95	Oruanui	18		—		<2%				
145	Oruanui	30		—		<4%				
195	Huka Falls	63	132.06	50	R1	<7%	+5.4	-5.6	12.2	2.2
200	Huka Falls	68	134.5	55	R1	<6%	+4.8	-6.0	—	—
235	Huka Falls	106	153.67	60	R1	<6%	+5.1	-4.2	2.4	1.4
245	Huka Falls	116	159.07	60	R1	<4%	+5.0	-4.1	2.2	1.3
270	Rautehuia	139	172.58	70	R1	<2%	+4.0	-4.2	2.5	1.4
300	Rautehuia	159	188.78	80	R1	<3%	+3.5	-3.7	2.0	1.3
330	Rautehuia	186	205.00	90	R3	<2%	+3.3	-3.0	1.5	1.1
345	Rautehuia	214		90	R3	<2%	+2.9	-3.0	1.6	1.1
360	Rautehuia	221		>95	R3	<2%	+2.9	-2.7	1.4	1.1
380	Rautehuia	221		95	R3	<2%	+2.4	-3.2	1.8	1.2
410	Rautehuia	221		95	R3	<2%	+2.4	-3.2	1.8	1.2
455	Waioa W5	221		>95	—	<1%	+1.7	-3.9	2.5	1.4
545	Waioa W5	224		95	R3?	<2%	+0.9	-4.6	4.2	1.7
610	Waioa W5	225		95	R3?	<2%	+0.5	-5.0	5.9	1.9
710	Waioa W3-4	230		95	R3?	<2%	+0.8	-4.6	3.9	1.6
770	Karapiti 2B	—		>95	—	<1%				

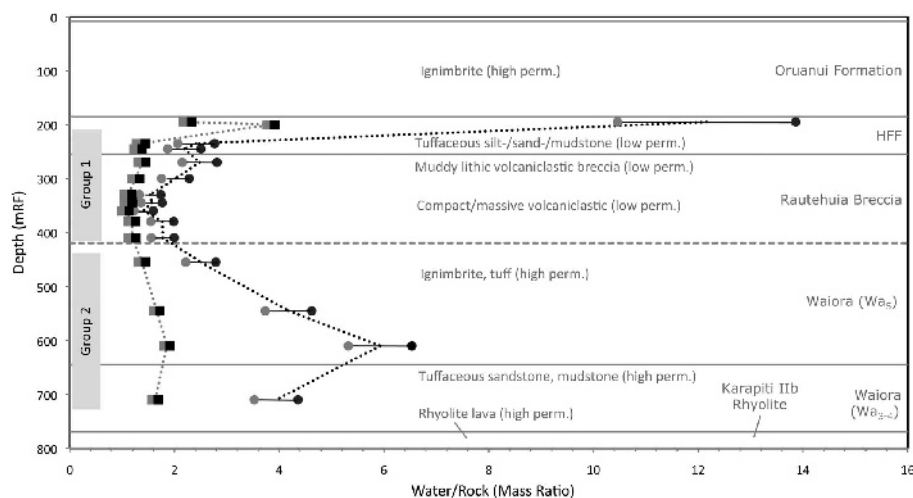


Figure 8. Calculated W/R ratios as a function of depth in Well WK244. Values for closed (circles) and open (squares) system models are shown for upper (black) and lower (gray) estimates of  $\delta^{18}\text{O}_i$  (Clayton and Steiner, 1975). Closed-system calculations follow Inoue *et al.* (2004) and assume that a unit of water makes an infinite number of passes through the hydrothermal system. Open-system calculations following Taylor (1977) assume that a unit of water makes a single pass through the hydrothermal system. Average W/R ratios are illustrated as black (closed system) and gray (open system) dotted lines. Horizontal lines denote lithological boundaries, with the dashed horizontal line representing a gradational boundary.

## CONCLUSIONS

Mixed-layer I-S in Well WK244 from the Te Mihi area, Wairakei geothermal field, displays a systematic change from R1 to R3 ordering and from 50 to >90% illite over a 160 m interval within the Huka Falls Formation and associated Rautehuia Breccia. High-aspect-ratio hairs and ribbons of illitic clay have coalesced through Ostwald ripening to form flakes and pseudo-hexagonal platelets, with the degree of ripening increasing with depth. Estimates of the swelling clay percentage obtained using the methylene blue method show a strong positive correlation with %S of I-S ( $r = 0.91$ ) as determined by pXRD. This result further validates use of the methylene blue method for delineating illitization sequences and estimating temperatures in active geothermal environments. Values of  $\delta^{18}\text{O}_{\text{I-S}}$  become progressively lower with depth, reflecting increasing temperature of clay formation. W/R ratios calculated using  $\delta^{18}\text{O}_{\text{I-S}}$  values and clay-formation temperatures show significant variability that corresponds well with permeability differences among the units that host this geothermal system.

The general agreement between calculated W/R ratios and empirically documented variations in host-rock permeability in Well WK244 suggests that oxygen isotopic compositions of hydrothermally produced I-S, combined with determinations of % illite layers and ordering, are useful in delineating hydrogeologic variability and thermal evolution in such environments. The W/R ratios calculated assuming both open and closed systems for the Wairakei field provide reasonable upper and lower limits for actual conditions at depth. While the open-system model is probably unrepresentative of

conditions persisting in active geothermal environments, the possibility of such lower limits should not be overlooked for systems operating at high fluid fluxes, such as Wairakei.

## ACKNOWLEDGMENTS

The authors acknowledge K. Law, L. Munro, J. Potter, and G. Yau for their assistance at the Laboratory for Stable Isotope Science (The University of Western Ontario, Canada); the Institute of Geological and Nuclear Sciences and Contact Energy for supplying samples; K. Elliston, M. Elliston, B. Mountain, G. Bignall, A. Rae, and B. Carey of the Wairakei Research Center for on-site assistance; and K. Coverdale, A. Libbey, B. Libbey, P. Haughian, M. Haughian, and F. Haughian for their continued support. This manuscript benefited from thoughtful reviews and suggestions by Dr Atsuyuki Inoue and Dr Joseph W. Stucki. This work was supported by a Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery grant and Canada Foundation for Innovation and Ontario Research Fund (ORF) infrastructure awards to F.J. Longstaffe, and also made possible, in part, through release time provided to F.J. Longstaffe under the Canada Research Chairs Program. This is 'Laboratory for Stable Isotope Science' Contribution #285.

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(Received 13 August 2012; revised revised 24 April 2013; Ms. 699; AE: W. Huff)