THE APPLICATION OF CHLORITE GEOTHERMOMETRY TO HYDROTHERMALLY ALTERED ROTOKAWA ANDESITE, ROTOKAWA GEOTHERMAL FIELD

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Keywords: Rotokawa Andesite, geothermal, chlorite geothermometry, chlorite crystallinity, geohydrology, fluid inclusion microthermometry, hydrothermal alteration petrography.

ABSTRACT

Chlorite is a common hydrothermal alteration product in rocks hosting Taupo Volcanic Zone geothermal systems. It typically replaces ferromagnesian minerals (pyroxene, biotite, hornblende) and volcanic glass, or occurs via direct precipitation in open spaces (vugs, veins, etc.). The Rotokawa Andesite is widespread across the Rotokawa Geothermal Field, between 800 m and 1800 m depth, and up to 2 km thick. It is typically moderately to strongly altered to a hydrothermal mineral assemblage dominated by chlorite. To minimise the influence of variable host-rock chemistry on chlorite composition we investigate the use of the chlorite geothermometer on hydrothermally altered Rotokawa Andesite rocks. Independent estimates of reservoir temperature were obtained from chlorite geothermometry, chlorite crystallinity (from XRD analyses) and fluid inclusion microthermometry (from vein samples in chlorite-altered host rock) and compared with measured downhole temperatures from well completion tests.

The results show that chlorite geothermometry at Rotokawa provides reasonable estimation of reservoir temperatures. Deviations from downhole measured temperatures, where substantiated by fluid inclusion evidence and interpretation of hydrothermal mineral assemblages, confirm that downhole measured temperatures commonly mask thermal variations and validates the use of these petrographic techniques to establish geothermal fluid paths.

1. INTRODUCTION

The interaction between fluids and the host rocks in an active hydrothermal setting produces a range of alteration minerals that reflect the physicochemical conditions during the time of mineral precipitation. Chlorite, a common hydrothermal alteration product belonging to the phyllosilicate group of minerals, is a hydrated magnesium, iron aluminosilicate with a wide composition range, 

\[ (\text{Mg,Fe}^2+,\text{Fe}^{3+},\text{Mn},\text{Al})_6[(\text{Si},\text{Al})_2\text{O}_5](\text{OH})_4 \]

It forms in low- to moderate-grade metamorphic rocks at temperatures up to 450°C and pressures of a few kilobars (Cathelineau and Nieva, 1985). In a hydrothermal environment it typically forms through the replacement of ferromagnesian minerals and volcanic glass or via direct precipitation in open cavities (i.e., veins, vugs, etc.).

Chlorite composition is dependent on formation temperature, fO₂ and pH of the hydrothermal solution and bulk composition of the host rock, in particular the Fe/(Fe + Mg) ratio (de Caritat et al., 1993). Previous workers have used variations in chlorite chemistry as an empirical and thermodynamic geothermometer to determine temperature gradients in hydrothermal systems (Cathelineau and Nieva, 1985; Walshe, 1986). At Los Azufres, Cathelineau and Nieva (1985) examined hydrothermal chlorite in andesites to minimise the influence of fluid and rock chemistry, and enhance that of fluid temperature on chlorite composition. An excellent positive correlation between formation temperature and tetrahedral Al⁴⁺ occupancy was demonstrated. Further, Cathelineau (1988) combined data from the Salton Sea geothermal system and defined the relationship between temperature and tetrahedral Al (Al⁴⁺) in chlorite with the following expression:

\[ \text{AI}^4\text{O}_2(\text{°C}) = 321.98(\text{AI}^4\text{O}_2) - 61.92 \]

This was calibrated for 130° – 310°C temperatures, but extrapolation to higher temperatures is likely to be valid given the agreement of data from Larderello where chlorite forms at ~350°C (Cathelineau, 1988).

In this study we test the reliability of the chlorite geothermometer on chlorite from the Rotokawa Andesite affected by hydrothermal alteration. We focus on this formation to minimise the influence of variable host-rock chemistry on chlorite composition. However, it is important to recall a review by de Caritat et al. (1993) who cautioned that the geothermometer is unsatisfactory over a wide range of temperature, chlorite composition and coexisting mineral assemblages, and that its use is ill-advised as a sole method for estimating reservoir temperatures.

The Rotokawa Andesite occurs across the Rotokawa Geothermal Field, between 800 m and 1800 m depth. It is up to 2 km thick and typically has moderately to strongly developed hydrothermal mineral assemblages, dominated by chlorite, but also calcite, illite, quartz, pyrite and epidote.

Chlorite crystallinity, via clay separate X-Ray Diffractometry (XRD) analysis, is defined as the degree of ‘ordering’ within the crystal lattice and, for illite crystallinity, has been applied with limited success as an indicator of metamorphic grade in low-grade, metasedimentary rocks (Frey, 1987; Arkai and Ghabrial, 1997). Chlorite crystallinity values (expressed as ChC) are determined by measuring the peak width at half the peak height of either the 7Å or 14Å reflections. Decreasing ChC values correspond to increasing metamorphic grade (i.e., temperature and pressure). Here, its applicability as a geothermometer will be compared with the chlorite geothermometry temperatures.

Drill core samples were collected from several wells across the Rotokawa Geothermal Field (Figure 1) from wells that have encountered a range of downhole temperatures within the andesite. Thin section petrography was undertaken to document hydrothermal alteration assemblages and chlorite occurrences. Samples were then selected for Electron Probe
Micro-Analysis (EPMA) and XRD analyses. Lastly, fluid inclusion microthermometry experiments were carried out on any quartz, calcite and anhydrite vein material spatially associated with chlorite alteration. This provided a third estimate of formation temperature to compare against chlorite geothermometry and chlorite crystallinity. It is important to bear in mind that for many samples the temporal relationship between chlorite alteration and the veining event was not known.

By obtaining three independent estimates of reservoir temperature (chlorite geothermometry, chlorite crystallinity and fluid inclusion microthermometry) and comparing these with measured downhole temperatures, insights into how reservoir temperatures have changed with time can provide important insights into geothermal reservoir geohydrology and its evolution.

The formation consists of porphyritic andesite lavas and breccias. The intensity of hydrothermal alteration commonly obscures identification of the phenocryst assemblage (particularly the ferromagnesian component) that typically comprises between 20 – 40% of the rock. Least-altered samples show an assemblage dominated by plagioclase, clinopyroxene, magnetite and subordinate biotite and orthopyroxene. The groundmass is comprised of fine, interlocking plagioclase laths and dusty ilmenite/magnetite.

3. HYDROTHERMAL ALTERATION

Hydrothermal alteration affects the andesite to varying intensities, from weak to intense. The alteration mineralogy (Table 1) is dominated by chlorite, quartz, leucoxene, calcite, albite and epidote, with accessory adularia, pyrite and hematite. XRD clay separate analyses confirm that chlorite occurs in all andesite samples, but there is also interlayered chlorite-smectite and corrensite in a few (RK4 1430, RK5 2212, RK5 2653). Other clay minerals present in some samples in trace to abundant quantities are smectite and illite.

In all 23 samples, chlorite occurs in common to abundant quantities, as selective replacement of primary ferromagnesian minerals (i.e., pyroxene and biotite), pervasive replacement of the rock groundmass, and as cavity-fill (i.e., vugs and veins). In vugs and veins chlorite coexists with quartz, calcite and hematite, as well as epidote, and in some samples, pyrite, prehnite, wairakite and anhydrite.

The presence of epidote in most samples (i.e., 17 of 23 samples) implies reservoir temperatures at the sample depths >240°C (Steiner, 1977). However, higher temperatures are implied by the presence of actinolite-tremolite in five samples (RK4 2001, RK5 2212, RK5 1871A, RK22 2430, RK27 1854), indicating temperatures >300°C (Browne, 1978).

There is petrological evidence that the hydrothermal minerals affecting most samples are mixed assemblages that have precipitated under different fluid conditions. For example, epidote is partially altered to calcite in some samples (e.g., RK5 2002, RK5 2212) and actinolite-tremolite is partially replaced by chlorite (RK4 2001, RK8 2219, RK21 1871A). Illite, smectite and/or calcite replaces epidote, chlorite (RK5 2002, RK5 2212, RK9 1749, RK24ST1 1820, RK27 1854) and albite (RK5 1786, RK22 2430). Illite typically indicates reservoir temperatures >220°C (Browne, 1978). The presence of smectite (RK4 1430, RK5 2002, RK5 2212, RK21 1871A) and interlayered chlorite-smectite (RK5 2212, RK5 2653) indicates temperatures no greater than ~200°C (Steiner, 1977). Therefore, the co-existing high- (~220°C) and low-temperature (~<200°C) assemblages (e.g., RK5 2002, RK5 2212, RK5 2653 and RK21 1871A) are likely to indicate varying reservoir temperatures in the parts of the Rotokawa reservoir these samples occurred.
### Table 1. Summary of the alteration intensity and hydrothermal mineral abundances in the sample suite, identified from thin section petrography and clay separate XRD analyses.

<table>
<thead>
<tr>
<th>Well Depth (mRF)</th>
<th>Intensity</th>
<th>chlorite</th>
<th>quartz</th>
<th>leucocene</th>
<th>calcite</th>
<th>albite</th>
<th>epidote</th>
<th>adularia</th>
<th>pyrite</th>
<th>hematite</th>
<th>illite</th>
<th>actinolite-tremolite</th>
<th>Others</th>
</tr>
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<tbody>
<tr>
<td>RK4 1430</td>
<td>strong</td>
<td>A</td>
<td></td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>r</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>chalcopyrite (r), smectite (r), corrensite (r), chlorite-smectite (r), chalcedony (m)</td>
</tr>
<tr>
<td>RK4 1630</td>
<td>strong</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>A</td>
<td>m</td>
<td>r</td>
<td>m</td>
<td>r</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>chalcedony (m)</td>
</tr>
<tr>
<td>RK4 1830</td>
<td>intense</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>bornite (r), anhydrite (r)</td>
</tr>
<tr>
<td>RK4 2001</td>
<td>strong</td>
<td>A</td>
<td></td>
<td>C</td>
<td>m</td>
<td>-</td>
<td>r</td>
<td>-</td>
<td>-</td>
<td>r</td>
<td>C</td>
<td>-</td>
<td>chalcopyrite (r)</td>
</tr>
<tr>
<td>RK5 1591</td>
<td>strong</td>
<td>C</td>
<td>m</td>
<td>C</td>
<td>C</td>
<td>-</td>
<td>r</td>
<td>r</td>
<td>-</td>
<td>r</td>
<td>m</td>
<td>-</td>
<td>anhydrite (r)</td>
</tr>
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<td>C</td>
<td>-</td>
<td>C</td>
<td>r</td>
<td>r</td>
<td>-</td>
<td>-</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>-</td>
<td>chalcedony (C), chalcopyrite (m)</td>
</tr>
<tr>
<td>RK5 2002</td>
<td>strong</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>m</td>
<td>C</td>
<td>r</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>smectite (r)</td>
</tr>
<tr>
<td>RK5 2212</td>
<td>strong</td>
<td>A</td>
<td>-</td>
<td>C</td>
<td>m</td>
<td>C</td>
<td>r</td>
<td>m</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>chalcedony (m), smectite (r), chlorite-smectite (r), biotite (?)</td>
</tr>
<tr>
<td>RK5 2653</td>
<td>moderate</td>
<td>A</td>
<td>C</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>C</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>chlorite-smectite (m), chalcopyrite (r)</td>
</tr>
<tr>
<td>RK6 1863</td>
<td>intense</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>day</td>
</tr>
<tr>
<td>RK6 2280</td>
<td>intense</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>m</td>
<td>C</td>
<td>r</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>A</td>
<td>-</td>
<td>pyrrhotite (r)</td>
</tr>
<tr>
<td>RK8 1595</td>
<td>intense</td>
<td>C</td>
<td>A</td>
<td>C</td>
<td>r</td>
<td>A</td>
<td>C</td>
<td>-</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>wairakite (C), pyrrhotite (r), biotite (r), sphalerite (r)</td>
</tr>
<tr>
<td>RK8 2219</td>
<td>weak to moderate</td>
<td>C</td>
<td>m</td>
<td>C</td>
<td>r</td>
<td>m</td>
<td>m</td>
<td>-</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>RK8 2727</td>
<td>weak</td>
<td>C</td>
<td>m</td>
<td>C</td>
<td>-</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>pyrrhotite (r), prehnite (?)</td>
</tr>
<tr>
<td>RK9 1749</td>
<td>strong</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>C</td>
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<td>A</td>
<td>r</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RK21 1871A</td>
<td>weak</td>
<td>A</td>
<td>r</td>
<td>-</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>r</td>
<td>-</td>
<td>smectite (r)</td>
</tr>
<tr>
<td>RK21 1871B</td>
<td>strong</td>
<td>A</td>
<td>m</td>
<td>C</td>
<td>C</td>
<td>r</td>
<td>m</td>
<td>r</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>chalcedony (r)</td>
</tr>
<tr>
<td>RK22 2430</td>
<td>intense</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>A</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>-</td>
<td>r</td>
<td>r</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RK24 ST1 1820</td>
<td>moderate</td>
<td>A</td>
<td>C</td>
<td>C</td>
<td>A</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>r</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RK25 2200A</td>
<td>intense</td>
<td>A</td>
<td>m</td>
<td>C</td>
<td>-</td>
<td>m</td>
<td>C</td>
<td>m</td>
<td>m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>anhydrite (C)</td>
</tr>
<tr>
<td>RK25 2200B</td>
<td>intense</td>
<td>A</td>
<td>m</td>
<td>C</td>
<td>C</td>
<td>m</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>RK27 1854</td>
<td>strong</td>
<td>A</td>
<td>m</td>
<td>C</td>
<td>C</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>r</td>
<td>anhydrite (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RK27 2147</td>
<td>strong</td>
<td>A</td>
<td>m</td>
<td>C</td>
<td>m</td>
<td>r</td>
<td>A</td>
<td>-</td>
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</tbody>
</table>

Key: A = Abundant (>10%); C = Common (1-10%); m = Minor (0.1-1%); r = Rare (<0.1%); - = absent

### 5. ELECTRON PROBE MICROANALYSIS

#### 5.1 Chlorite Chemistry and Al\(^{IV}\) Geothermometry

EPMA of twenty-two andesite samples was done using a JEOL 830 Superprobe, equipped with a SphinX 133 Si (Li) energy dispersive spectrometer, housed at the University of Auckland. Standard operating conditions involved using a 10 μm beam that measured for 100 s, with a current of 120 nA and an accelerating voltage of 15 kV.

Chlorite in hydrothermally altered Rotokawa Andesite is a Mg-Fe chlorite belonging to the clinochlore – chamosite solid-solution series. Using the Cathelineau (1988) geothermometer, the average Al\(^{IV}\) temperatures calculated for each Rotokawa chlorite sample range between 199° and 310°C. Generally these temperatures are lower than the respective downhole measured temperatures (Figure 2). However, the 2σ standard deviations presented with each average Al\(^{IV}\) temperature highlight the variability of chlorite composition within each sample. These average temperatures are calculated from all chlorite modalities in each sample (i.e., replacement and vein/vug chlorite), and hence do not consider the multiple generations of chlorite that may have precipitated under different physicochemical conditions.

![Figure 2: Comparison of calculated Al\(^{IV}\) temperatures and measured downhole well temperatures. Error bars show the 2σ standard deviations.](image)

The proportion of smectite interlayering within chlorite can be assessed from EPMA using the empirical quantification \(X_c\), where pure chlorite has \(X_c = 1\) and pure smectite has \(X_c = 0\) (Bettison and Schiffman, 1988). López-Munguira et al. (2002) showed that chlorites with \(X_c\) values as low as 0.81...
were without interlayered smectite. For our study XRD analyses demonstrate that Rotokawa chlorites with $X_c$ values as low as 0.85 are free of any interlayered smectite, and we regard all analyses with $X_c$ values greater than this as end-member chlorite.

Based on the $X_c$ parameter, six Rotokawa samples contain interlayered chlorite-smectite (RK4 1424, RK5 2212, RK5 2653, RK8 1955, RK8 2219, RK25 2200). Three of these (i.e., RK4 1424, RK5 2212, RK5 2653) are in agreement with the occurrence of interlayered chlorite-smectite or corrensite in trace to minor abundances (Table 1). However, clay minerals were not detected by thin section petrography or XRD analysis in the other three samples (i.e., RK8 1955, RK8 2219, RK25 2200). It is possible interlayered clays are present in these samples, but in such low quantities that XRD was unable to detect their presence. Six other samples also contain chlorite with $X_c$ values <0.85 (RK4 1830, RK4 2001, RK5 1591, RK6 2280, RK22 2430, RK24 1820), however both petrography and XRD analysis (Table 1) show these to also contain illite, commonly intergrown with chlorite, and it is likely the EPMA analyses were contaminated by illite adjacent to the chlorite analysis spot.

5.2 Chlorite crystallinity and $Al^{IV}$ geothermometry

Clay-separate (<2 μm) XRD analyses of twenty-one samples were done with the Panalytical X’pert Pro diffractometer, with CoKα radiation, at GNS Science, Wairakei. Analyses were performed on oriented clay samples, and subsequent air dried samples were glycolated at 60°C for at least 8 hours. Standard operating conditions were 45 kV and 30 mA. XRD spectra were recorded from 2° to 45°2θ with a scan step of 0.02°2θ at 1.6 s/step.

The 14Å reflection from the XRD spectra provides the chlorite formation temperature from an XRD analysis using the algorithm:

$$T(°C) = 333.49 - 50.126* R$$

where $R$ is the $ChC_{(001)}/ChC_{(002)}$ ratio. The error of this calculated temperature is provided by the standard deviation of the calculated $Al^{IV}$ temperatures, being ±10°C 1σ or ±20°C 2σ.

Despite its use as an indicator for metamorphic grade, the relationship between chlorite crystallinity and $Al^{IV}$ geothermometry shows a poor correlation with $ChC_{(001)}/ChC_{(002)}$, and no correlation with $ChC_{(002)}$. However, the $ChC_{(001)}/ChC_{(002)}$ ratio does have a good linear correlation with the $Al^{IV}$ geothermometry temperature ($R^2=0.71$; Figure 3). This correlation is encouraging for estimating the chlorite formation temperature from an XRD analysis using the algorithm:

$$T(°C) = 333.49 - 50.126* R$$

where $R$ is the $ChC_{(001)}/ChC_{(002)}$ ratio. The error of this calculated temperature is provided by the standard deviation of the calculated $Al^{IV}$ temperatures, being ±10°C 1σ or ±20°C 2σ.

6. ROTOKAWA GEOHYDROLOGY

Physical downhole measurements that are made post-drilling, during geothermal well completion tests (i.e., temperature, pressure and spinner), provide vital information on the geothermal resource encountered by the well. However with respect to recording true formation temperatures, important data can be lost or obscured by either the well having poor permeability and being slow to heat-up, or the occurrence of various downhole phenomena such as internal circulation and/or cross-flows (Grant and Bixley, 2011).

The use of chlorite geothermometry, in unison with a suite of other petrographic tools (hydrothermal mineral assemblages, fluid inclusion microthermometry), provides alternative methods for estimating natural state formation temperatures in the well (i.e., temperatures of the reservoir that existed prior to drilling the well). These estimates may provide valuable reservoir temperature information that may be masked in completion testing temperature profiles. In addition, comparisons with the completion test profiles may indicate where parts of the reservoir have remained thermally stable, or alternatively cooled or heated during the history of the geothermal system.

In RK4, generally the estimated $Al^{IV}$ temperatures from each sample are consistently less than the interpreted natural state temperatures (Figure 4). The two deeper samples (1830, 2001) have the closest estimates, with $Al^{IV}$ temperatures within 50°C of the interpreted natural state temperature (Figure 4). However, $Al^{IV}$ temperatures for the two shallower samples (1430, 1630) are well below the natural state temperatures (Figure 4). In sample 1430 the $Al^{IV}$ temperature mode is between 170°-190°C, more than 100°C below the natural state temperatures (~300°C) for that depth. Such $Al^{IV}$ temperatures are more compatible with the clay mineral assemblage contained in this sample (smectite and corrensite; Figure 4), rather than the natural state temperature. This suggests that the reservoir temperature at this depth is either lower than the interpreted natural state temperature, or the natural state temperatures are true temperatures and the temperatures estimated from the geothermometer and clay mineral assemblage are recording an earlier thermal regime that has yet to equilibrate with the higher temperatures. This may be indicated in the deeper sample (1630) which also shows cooler $Al^{IV}$ temperatures, relative to the natural state temperatures, but have fluid inclusion homogenisation temperatures that are equivalent to the natural state thermal regime (Figure 4).

New Zealand Geothermal Workshop 2011 Proceedings
21 - 23 November 2011
Auckland, New Zealand
Figure 4: Temperature versus depth plots for RK4, RK5, RK6 and RK8. The plots show the depth range for Rotokawa Andesite (green shading), down hole measured temperature profiles (orange curve), feed zone locations (red asterisks), chlorite geothermometry and fluid inclusion homogenisation temperatures (as histograms) and summarises thin section and XRD petrography for each sample.
Figure 5: Temperature versus depth plots for RK22, RK24, RK25 and RK27. The plots show the depth range for Rotokawa Andesite (green shading), down hole measured temperature profiles (orange curve), feed zone locations (red asterisks), chlorite geothermometry and fluid inclusion homogenisation temperatures (as histograms) and summarises thin section and XRD petrography for each sample.
An isothermal profile in the Rotokawa Andesite is evident from the interpreted natural state temperatures for RK5 (Figure 4), suggesting the likelihood of interzonal flow between feedzones in the well (Grant and Bixley, 2011). There is a reasonable correlation between chloride geothermometry, fluid inclusion microthermometry and natural state temperatures for samples 1786 and 2002 (Figure 4). The AI\textsuperscript{IV} temperatures for these samples appear to be bimodal, with the hotter mode (320° – 330°) corresponding to the natural state temperatures. It is possible that these samples are affected by variable thermal regimes and this is suggested by the petrography with the occurrence of illite and smectite, respectively in samples 1786 and 2002. Discrepancies between AI\textsuperscript{IV} and natural state temperatures occur in the three other RK5 samples (1591, 2212, 2653), particularly sample 2212 where geothermometry temperatures are ~150°C below the natural state temperature (Figure 4). Similar to sample RK4 1430, this RK5 sample also contains smectite and interlayered chloride-smectite, occurrences that are close to compatible with the AI\textsuperscript{IV} temperatures. It is possible that reservoir temperatures at this depth, close to a major feed zone (Figure 4), are significantly cooler than the natural state temperatures, and the feed zone is supplying fluids into the well that are cooler than that indicated for that depth. Alternatively, the chloride geothermometry and hydrothermal mineral assemblage at this depth reflect a cooler thermal regime that has yet to equilibrate with the present natural state temperatures.

For both the northern wells, RK6 and RK8, the thermal profiles indicate conductive heating through the Rotokawa Andesite (Figure 4). In RK6, fluid inclusion microthermometry from a sample (1602) collected from the Tahorakuri Formation, above the Rotokawa Andesite (Figure 4), and the chloride geothermometry for andesite sample 1863, both indicate temperatures slightly below the natural state temperatures (i.e., within 30°C). Fluid inclusion data from the deep sample (2280) is comparable to the natural state temperatures, but the chloride geothermometer underestimates the reservoir temperatures. Petrographic examination of this sample shows it to have intense hydrothermal alteration to illite, which partially replaces chloride. This replacement manifests as illite interlayering within chloride that may compromise the quality of the EPMA data from which the AI\textsuperscript{IV} temperatures are derived. Regardless, replacement of chloride by illite involves a hydrolysis reaction with a fluid with lower pH and implies the geothermal fluid characteristics have changed at this depth, from near neutral to slightly acidic.

Despite the chloride geothermometer in the deepest RK8 sample (2727) indicating reservoir temperatures consistent with the conductive temperature gradient (Figure 4), the indications for the two shallower samples (1955, 2219), are that temperatures in the northern parts of the field have declined. For sample 1955, fluid inclusion microthermometry and chloride geothermometry tend to indicate hotter temperatures than the natural state temperatures (Figure 4). In sample 2219 it is the fluid inclusion microthermometry that indicates hotter reservoir temperatures, whereas the AI\textsuperscript{IV} temperatures are cooler than the natural state temperatures. Nevertheless, the occurrence of hydrothermal actinolite-tremolite in sample 2219 that is partially replaced by chloride, implies reservoir temperatures have declined from >280°C (Browne, 1978).

For RK22, the 2430 sample indicates cooler AI\textsuperscript{IV} temperatures (i.e., -50°C cooler), than the natural state temperature at this sample depth (Figure 5). Geothermometry temperatures (mode temperature: 280° – 300°C) are consistent with the occurrence of hydrothermal actinolite-tremolite. However, petrographic examination of this sample also indicates an intense calcite overprint, suggesting that CO$_2$-bearing fluid(s) were heated and caused calcite precipitation in the host-rock at this depth.

An isothermal profile is indicated through the Rotokawa Andesite in RK24 (Figure 5). The natural state temperatures at the sample (1820) depth (i.e., 330°C) are equivalent to the anhydrite fluid inclusion heating temperatures (320° – 330°C) (Figure 5). However, both the Al\textsuperscript{IV} mode (280° – 290°C) and the calcite fluid inclusion heating temperatures (290° – 300°C) are less than the natural state conditions (Figure 5), suggesting temperatures at this reservoir depth have varied. Petrographic evidence shows calcite and illite are both part of an overprinting assemblage, which implies varying fluid chemistry (i.e., pH and CO$_2$ contents) and possibly temperature.

Widespread AI\textsuperscript{IV} temperatures with a bimodal distribution are represented in the RK25 sample (2200) (Figure 5). The hottest temperature mode (320° – 330°C) is comparable to the calcite fluid inclusion heating temperatures (330° – 340°C), which are both similar to the natural state temperature (320°C; Figure 5).

Two intervals of Rotokawa Andesite were encountered by RK27, with both samples (1854, 2147) from the lower interval (Figure 5). For 1854, chloride geothermometry and calcite fluid inclusion microthermometry temperatures are similar to the natural state temperatures (Figure 5). Quartz fluid inclusion microthermometry temperatures are widely distributed between 210° – 310°C, possibly implying variable fluid compositions at this depth resulting in the illite and calcite overprint seen in petrography (Figure 5). The deeper sample 2147 has AI\textsuperscript{IV} temperatures that appear to underestimate the natural state temperatures, but the calcite fluid inclusion microthermometry suggests hotter temperatures (Figure 5).

7. CONCLUSIONS

It is apparent from the results of this study that chloride geothermometry can provide useful formation temperatures when comparing samples of similar lithology, from the same hydrothermal system.

There is reasonable correlation between chloride geothermometry and chloride crystallinity, when using the Ch$_{\text{CO}_2}$/Ch$_{\text{CO}_3}$ ratio, from the 14Å and 7Å reflection peaks. This correlation is potentially useful as chloride formation temperatures can possibly be derived from whole-rock XRD clay separate analyses rather than chloride EPMA data, which are ultimately more expensive and time-consuming to obtain.

When used in conjunction with other petrographic techniques, such as fluid inclusion microthermometry and interpretation of hydrothermal mineral assemblages, it provides valuable information about the geothermal reservoir that can be masked or obscured in completion test temperature profiles. This possibly occurs in RK4 and RK5 where indications are that cooler inflows, not evident in downhole temperature profiles, occur at the top of and
within the, andesite in RK4 and RK5, respectively. It can also provide insights into how parts of the reservoir have evolved, especially where cooling has occurred, as apparent in the northern part of the field near RK8.

ACKNOWLEDGEMENTS
This study is co-funded through FRST project PROJ-20199-GEO-GNS and MRP Ltd. MRP also provided access to drillcore and completion test data, and permission to publish and present this data. Thank you.

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