TRACE METALS AND VOLATILES ZONING IN ACTIVE GEOTHERMAL SYSTEMS

Isabelle Chambefort[1] and John H. Dilles[2]

[1]GNS Science, Wairakei Research Centre, Taupo, New Zealand

[2] College of Earth, Oceanic and Atmospheric Sciences, Oregon State University, USA

i.chambefort@gns.cri.nz

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ABSTRACT

New insights concerning chemical zoning in active geothermal systems of the Taupo Volcanic Zone refine the chemical footprint of both dilute meteoric-dominated and potential magmatic-hydrothermal fluids. Whole rock lithogeochemical analyses (via 4-acid digestion with Au super trace) of altered rocks and in situ major and trace element analyses on white mica at the Ngatamariki, Rotokawa, and Ohaaki geothermal systems, show major variation with depth, due to the influence of past hydrothermal activity (i.e. at Ngatamariki where a shallow intrusion degassed at 0.7Ma), natural variability of the reservoir rocks, and current active fluid-rock interactions. Whole rock concentrations of Au, Tl, Bi, Sn, Ag, Se, Te, generally increase upward toward the paleosurface, where they are 10-100 times greater than near the intrusions that may be the source of metals. At Ngatamariki, samples distal to or post-dating this magmatic-hydrothermal alteration consistently contain less Au, Ag, As, Sb, Bi, and Te than samples of rock affected by the intrusion-related alteration, highlighting the intrusive complex as the likely source of the metals. In contrast to the pre-modern Ngatamariki enrichment, active geothermal fields do not show enrichment in Bi, Se, Mo and Te, and only rarely are enriched in Ag and Tl but show clearly zoning in As, Au, Sb, Sr, Li and Cs.

Major and trace element analyses of the white micas are dependent on temperature, water/rock ratio and fluid composition. White micas composition varies from illite to muscovite or phengite with depth with increase in K and Al. Clay trace element content is independent of the illite stoichiometry, and volatile and trace metal element contents correlate well with the whole rock chemical footprint. 'Shallow' illite is enriched in As, Te, Cl, S, Li, and B, whereas deeper samples show enrichment in Ba and Tl.

Variation in trace and volatile contents between the different site results from the host rock, heat source and magmatic derived fluids.

1. INTRODUCTION

New Zealand generates over 730 MW of electricity per annum from renewable geothermal energy in the Taupo Volcanic Zone (TVZ). The current conceptual model assumes that the deep heat source is a partial molten zone in the crust below 10 km, but it remains to be determined how deep magmatic processes and shallow geothermal systems are linked, and the fluid-rock interaction at the magmatic-hydrothermal transition. New insights into the nature and presence of magma bodies in the crust are needed to provide fundamental information to underpin geothermal research. Recent geophysical investigations have suggested that observed low resistivity plumes underneath some TVZ geothermal fields are likely to be associated with fluid rising via large basement structures or shallow intrusive systems (Bertrand et al., 2012; 2013).

Recent mineralogical investigations, largely driven by ore deposit research, have focused on the magmatic-hydrothermal transition and have developed new techniques to characterise the evolution of hydrothermal systems in a volcanic arc setting (Halley et al., 2015). Variation in trace element contents of hydrothermal alteration minerals are directly influenced by uprising magmatic fluids, carrying with it magmatic-like trace elements (e.g. arsenic, lithium, thallium). Thus, trace element variations in minerals can be used in resource exploration as a vector toward active or fossil heat source.

This work characterises the major and trace element variations of the Taupo Volcanic Zone geothermal systems. The chemical zoning of Ngatamariki fossil magmatic-hydrothermal system, is used as a proxy of the influence of potential 'active' intrusion(s) underneath TVZ geothermal systems.

This work seeks to answer the following fundamental questions:

1- Can chemical variations due to the interaction of exsolved magmatic fluids be recognised in hydrothermal alteration minerals and geothermal fluids? 2- Can deep mineral chemistry be used as a vector in geothermal exploration to target degassing magmatic intrusions for drilling deep geothermal wells?

2. GEOTHERMAL SYSTEMS

Three geothermal fields were selected based on their geological framework, volcanic stratigraphy and magmatic history, sample accessibility and geophysics assessment: Ngatamariki, Ohaaki and Rotokawa Geothermal Fields (Fig. 1). Illite and whole rock samples were selected from Ohaaki – Braodlands and Rotokawa Geothermal Fields to study clay composition using Ngatamariki relict alteration zoning as a proxy for magmatic 'signature'. Both fields are high-temperature gas-rich systems.

2.1 Ohaaki and Rotokawa Geothermal Fields

Both geothermal systems present a deep magnetotelluric anomaly representing the potential feed zones (Bertrand et al., 2012). Both are located along the eastern margin of the TVZ rifting arc, and are hosted by greywacke basement at depth and thick succession of rhyolitic volcanic and volcaniclastic. At Rotokawa there is also significant andesite (up to 1000 m thick). Hydrothermal alteration is typical of TVZ geothermal system, mainly due to dilute chloride reservoir water and dominated by temperature-dependant clay succession from deep illite to shallow smectite. Both systems have shallow acid bicarbonate and steam-heated horizon.

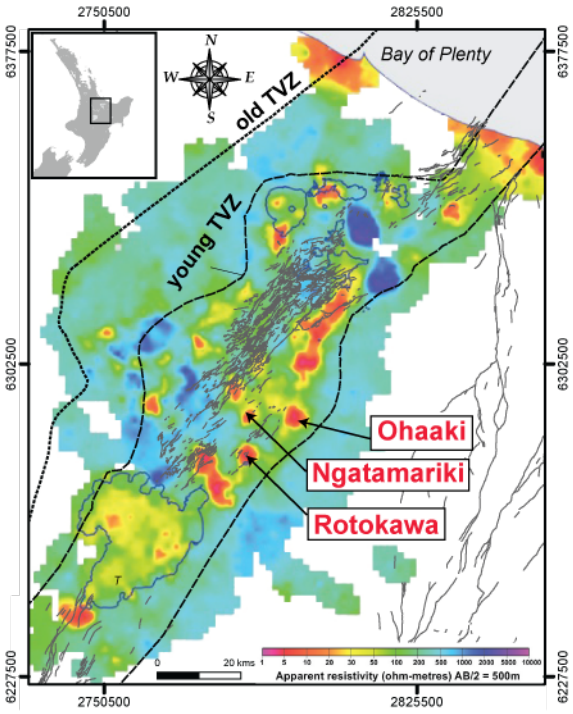

Figure 1: Map of the Taupo Volcanic Zone with the locations of the studied geothermal fields as defined by anomalously low electrical resistivity (Bibby et al., 1995). The boundaries of the old and young TVZ are from Wilson et al. (1995). Active faults are from the GNS active fault database (GNS Science Active Fault Database http://www.gns.cri.nz/Home/Products/Databases/Active-Faults-Database-of-New-Zealand.

2.2 Ngatamariki Geothermal Field

Ngatamariki Geothermal Field is the most recently developed field in the TVZ (commissioned in 2013). It comprises a deep, hot (260-285°C) geothermal reservoir overlain by two separate groundwater aquifers. Host rocks are predominantly similar to most of TVZ geothermal systems, rhyolitic pyroclastic and lava, with volcaniclastic sediments and deep buried andesitic units, but differ in the North part of the field where an intrusive complex has been intercepted by drillings (Chambefort et al., 2014, 2015a). At least three intrusive bodies (emplaced between 0.55 and 0.71 Ma) have been encountered at Ngatamariki, representing a unique feature in the TVZ intersected by drilling to date. Drilling of NM4 in 1985 intercepted a quartz diorite and a microdiorite. A core of the diorite was recovered and was described by Wood (1986) and Browne et al. (1992). The microdiorite and the quartz diorite occur below -2000 masl. During recent drilling of NM8 and NM9 in 2011 and 2012, the intrusions were intercepted again and a tonalite body was encountered below ~-2700 masl. Chambefort et al. (2014) gave a full description of the rocks.

The northern part displays mainly relict high-temperature hydrothermal alteration due to the emplacement, cooling and degassing of the intrusive complex (Fig. 2; Chambefort et al., 2015b). Subtle potassic alteration consisting of biotite + magnetite ± K-feldspar mantles the intrusive complex, and grades upward into texturally destructive quartz + white clay mica + pyrite (phyllic-type) alteration with massive silicification and hydrothermal breccias. Potassic and phyllic zones are crosscut by hypogene advanced argillic alteration containing pyrophyllite ± andalusite ± topaz ± rare alumino-phosphates and fluorine-bearing minerals, as well as localized residual vuggy quartz (Chambefort et al., 2015b). Sparse near-paleosurface (top of the Tahorakuri Formation sedimentary succession) kaolinite and dickite suggest possible shallow hypogene acid alteration. The most northerly wells, NM1, NM4, NM8 and NM9 have evidence of mineral overprinting due to lower temperatures than the magmatic-hydrothermal alteration assemblage.

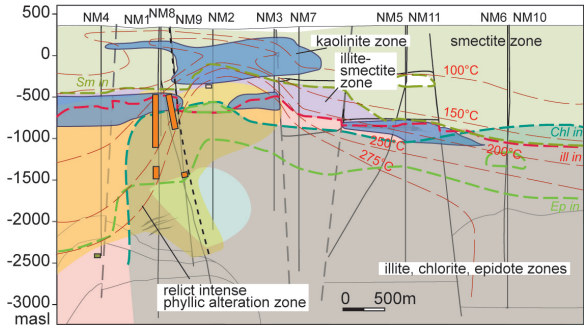

Figure 2: NNW-SSE hydrothermal alteration cross-section of the Ngatamariki Field. Modified from Chambefort et al. (2015a,b).

3. ANALYTICAL METHODS

Whole rock and mica clay, major and trace element analyses, were conducted on 104 samples from the Ngatamariki (n=25), Ohaaki (n=33) and Rotokawa (n=46) Geothermal Fields. These samples were mainly from drill core to avoid any mixing issues that can arise from the use of drill cuttings. New results are added to already existing whole rock data in the litterature from Ohaaki, Wairakei, Te Kopia, Horakei Korako and Kawerau fields (Bignall, 1994; Christenson, 1987; Krupp and Seward, 1987; Mitchell, 1989; Sanders et al. 2013 and Simmons and Browne, 2000).

Samples from Ohaaki and Rotokawa were selected based on XRD data and from drill core samples in the 'illite' zone and shallow steam-heated zone. Samples from Ngatamariki targeted the northern part of the field focussing on the area of magmatic-hydrothermal alteration linked to the fossil hydrothermal system (Chambefort et al., 2014, 2015b).

Whole rock major and trace element geochemical analyses were realised by ALS Chemex in Vancouver Canada. Major elements and gold were analysed by ICP-MS, carbon and sulfur by combustion furnace, resistive elements by lithium borate fusion, base metals by four acid digestion, and gold-related trace elements by aqua regia digestion.

Micas clay were examined by backscattered electron (BSE), secondary electron microscopy (SEM) imaging and electron dispersive spectroscopy (EDS) on polished mounts to identify and texturally characterised the clay prior to electron microprobe analyses. The major element composition of white micas were determined using the Cameca SX100 electron microprobe at the College of Earth, Ocean and Atmospheric Sciences of Oregon State University, with a 30 nA current, 15 kV accelerating potential and 5 μm beam diameter. The trace element composition of white mica was determined using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a VG ExCell quadrupole ICP-MS

system and NewWave DUV 193 nm ArF Excimer laser system, with He as the sweep gas at the W.M. Keck Collaboratory for Plasma Mass Spectrometry at Oregon State University. General analytical conditions were similar to those of Loewen and Kent (2012) and employed laser spots 40 μm in diameter and pulse rates of 5Hz for 20 ns, for 110 s. ^{29}Si was used as the internal isotopic standard, and GSE-1G as the calibration standard. Analyses were quantified with reference to multiple replicate analyses of NIST 612, BCR-2G and BHVO-2G standard glasses under similar ablation conditions.

4. TRACE ELEMENTS LITHOGEOCHEMISTRY

Whole rock compositions are compared with existing whole rock trace element contents from Bignall (1994), Christenson (1987), Krupp and Seward (1987), Mitchell (1989), Sanders et al. (2013) and Simmons and Browne (2000) for Orakei Korako, Ohaaki-Broadlands, Rotokawa, Reperoa, and Wairakei geothermal fields (Fig. 3). The samples were generally selected from the silicic pyroclastic rocks, the Ngatamariki intrusions, shallow sedimentary succession, and the deep andesites.

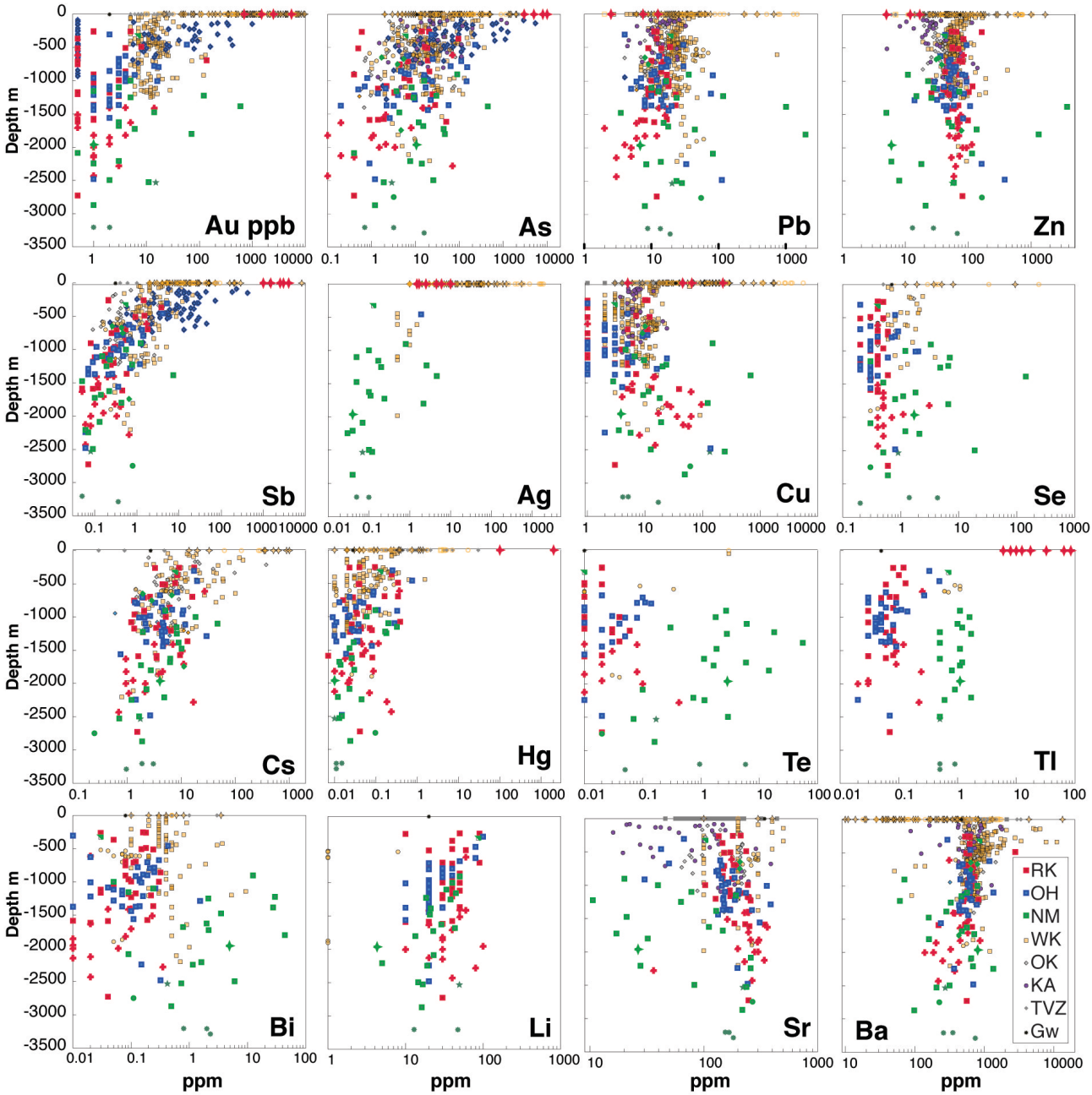

Figure 3: Whole rock compositions in log ppm versus vertical depth for TVZ geothermal systems. Data for Au is in ppb. Symbols reflect the different references; colours reflect the different fields. Red crosses represent Rotokawa andesite samples and green stars are the Ngatamariki intrusive complex (Modified from Chambefort et al., 2015b; Abbreviations: Gw: greywacke, KA: Kawerau, NM: Ngatamariki, OH: Ohaaki, OK: Orakei Korako, RK: Rotokawa, TVZ: Taupo Volcanic Zone fresh rhyolite (Deering et al., 2008), and WK: Wairakei).

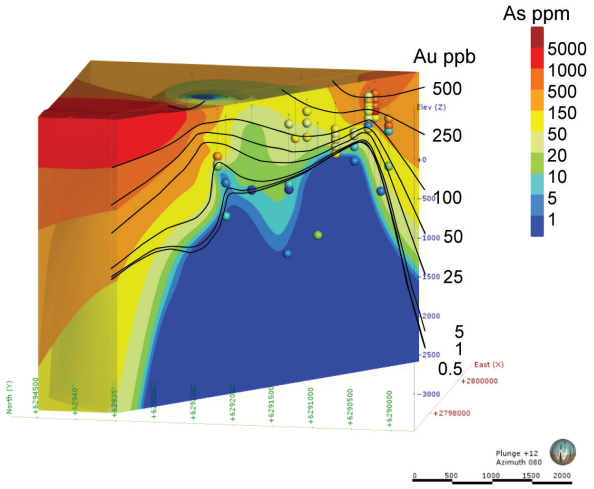

Figure 4: 3D representation of the As (colour coded), and Au (contour lines) zoning of the Ohaaki Geothermal Field.

Overall surface samples from mudpools and sinters are the most enriched in Au, Ag, Hg, Cu and Pb, suggesting that these metals are transported directly to the surface with less deposition at depth. Only Ohaaki samples show a clear enrichment in Au at depth, similarly to what is observed for Ngatamariki fossil hydrothermal chemical footprint.

5. WHITE MICA CLAY CHEMISTRY

5.1 Major element composition and substitutions

Mica clay major and trace element content was assessed for the three fields. The structural formula of each analysis was realised based on a muscovitic composition ($K_2Al_4[Si_6Al_2O_{20}](OH,F)_4$) with 22 O equivalents. Illite ($(K_{1.3}(Al,Fe,Mg)_4[Al_{1.3}Si_{6.7}]O_{20}(OH,F)_4$) differs from muscovitic mica in that it is more hydrous, has a lower tetrahedral charge, contains less K and usually has a significant content of octahedral Mg and Fe3+ (Wilson, 2013). The composition of the white micas for Ngatamariki, Ohaaki and Rotokawa are shown in Figures 5a, b, and c.

For the purpose of this study only samples in the 'illite' zone defined by XRD or reflectance spectrometry where selected in similar silicic whole rocks. Figure 5 thus shows mainly the variation in composition of the geothermal 'illite'.

The composition of the white mica is resulting from several substitutions producing the 'phengitic' and 'illitic' compositions (Rosenberg, 2002, Meunier and Velde, 2004, Wilson, 2013).

$\rightarrow [(Al^{3+})^{VI}+(Al^{3+})^{IV} \leftrightarrow (Fe^{2+}, Mg^{2+})^{VI}+(Si^{4+})^{IV}]$

$\rightarrow (Fe^{3+})^{VI} \leftrightarrow (Al^{3+})^{VI}$

$\rightarrow [(K^{+})+Al^{3+})^{IV} \leftrightarrow (Si^{4+})^{IV}+[C]$

$\rightarrow (Na^{3+}) \leftrightarrow (K^{+})$

Geothermal illite varies between phengitic muscovite to almost muscovite and phengitic illite. Some 90 % of samples from Ngatamariki and Ohaaki have an Al_{tot} (apfu) between 5 and 5.9 (Fig. 5a,b), with a significant increase in K toward high Al content muscovitic illite and depth (Fig. 6). Consistently the phengitic substitution is more common in the shallow part of the system (high Mg# = Mg/Mg+Fe+Mn). Rotokawa illite is less aluminous and potassic with Al_{tot} ranging from 4.7 and 5.3 apfu (Fig. 5c).

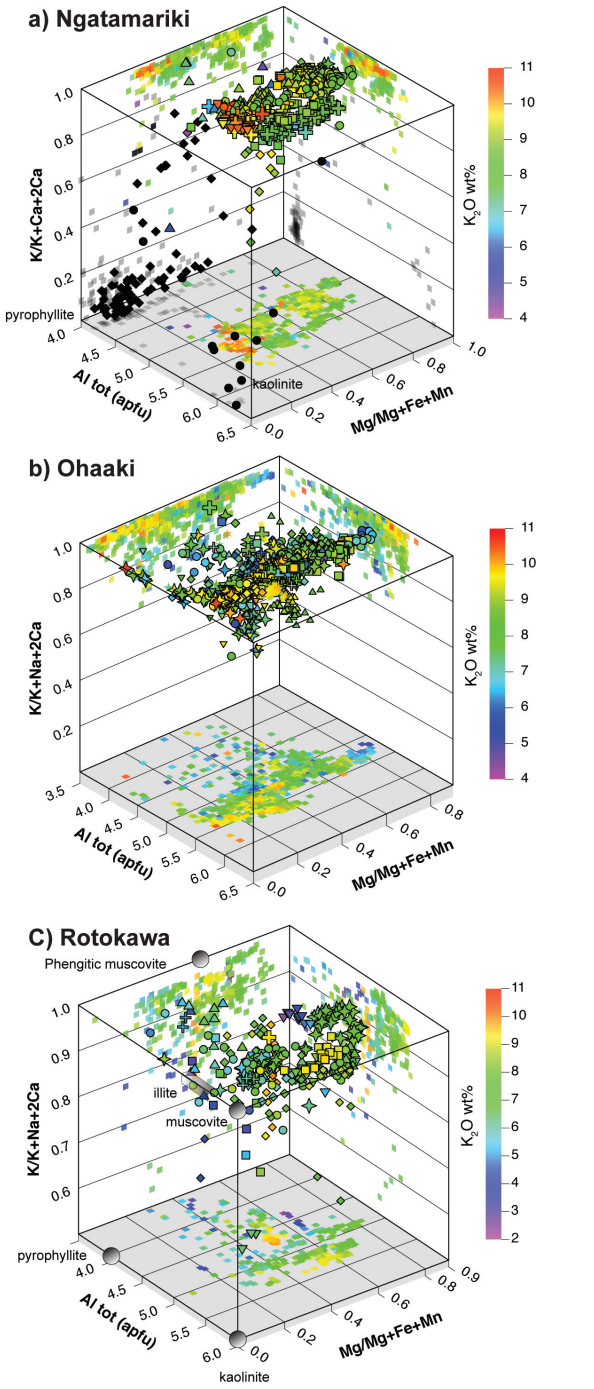

Figure 5: Mica clay composition of a) Ngatamariki, b) Ohaaki, and c) Rotokawa geothermal fields representing in function of their atoms per formula units (apfu) and coloured coded by K_2O wt.%.

Ngatamariki samples present at depth a trend in composition between muscovitic, phengite and pyrophyllite (Fig. 5a), in agreement with the presence of high temperature acid alteration closer to the intrusive complex.

Trace elements are strongly variable in the mica clays, however clear spatial zoning can be observed for Ngatamariki and Ohaaki, and is less distinct for Rotokawa. Figure 6 shows enrichment in Cs and Sb for Ohaaki illite toward the surface as well as As, Li, Pb, Tl, W, and Cu. Similar zoning is observed at Ngatamariki, but it less clear at Rotokawa where the influence of the andesitic host rock

compare to rhyolite is likely to be responsible for some of the variations in trace metal contents.

6. DISCUSSION

Chemical zoning in modern geothermal systems and relict magmatic-hydrothermal alteration haloes in the TVZ can be drawn from this study. As previously described by Simmons and Browne (2000), As, Sb and Au are strongly correlated and enriched toward the surface in fossil and modern geothermal systems. Active geothermal systems show a clear enrichment toward the surface in Hg, Li and Cs, even at Ngatamariki, suggesting any enrichment linked to the 0.5 Ma hydrothermal event has been remobilised by active systems.

Fresh TVZ rhyolites and lithologies above the paleosurface at Ngatamariki are inherently poorer in trace metals (Johnson et al., 2013; Chambefort et al., 2015b), thus the content in metals observed at Ngatamariki (although sub-economic) are due to the circulation of magmatic derived fluids from the intrusive complex. Above the intrusions at Ngatamariki Zn, Pb, Se, Sn are enriched and this is comparable to the zonation (although not the grade) of these elements seen around porphyry Cu systems (Halley et al., 2015).

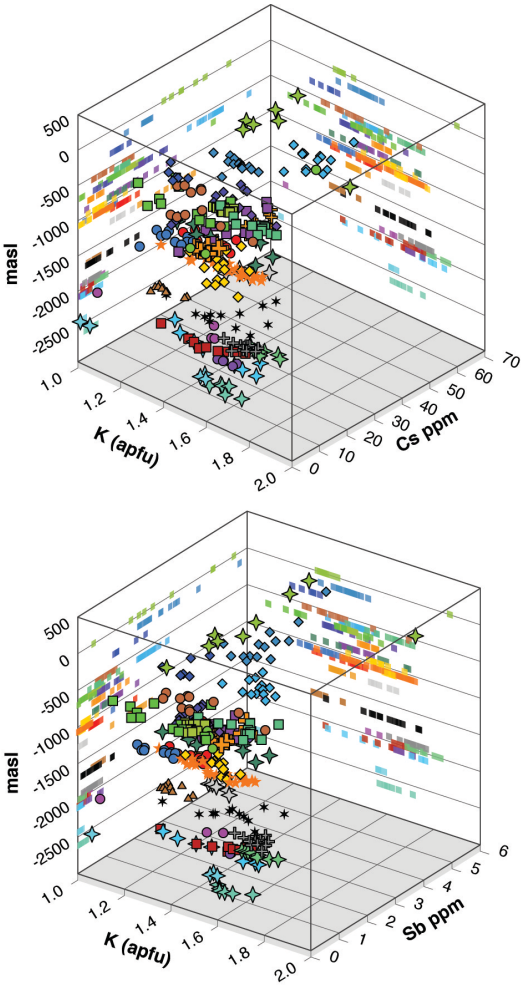

Figure 6: Major and trace element composition of Ohaaki clay mica shown as a function of sample depth.

Similarly enrichment in Bi, Ag, Te, Li, Sb, Tl, As and Au, and depletion in Sr, Al, Na and Sc are characteristic of the chemical zoning due to the magmatic intrusion near the paleosurface where intense acid alteration is occurring (e.g. Halley et al., 2015, Hedenquist et al., 2000). This shallow zoning and enrichment in more volatile metals is more characteristic of acid-sulfate epithermal systems (where Te, S, Se, and As are generally enriched). This zoning is expected at the apex of any degassing intermediate to silicic in composition magma intrusion in the crust, where system are fluid-dominated with large input of magmatic components (e.g. Henley and Ellis, 1983; Hedenquist and Lowenstern 1994, Giggenbach, 1997; Seward and Barnes, 1997; and others).

The similarity between the zoning observed at Ngatamariki and particularly Ohaaki is likely to suggest that some of the enrichment in metals are linked to a deep undrilled degassed intrusive system.

7. CONCLUSIONS

In this study we present for the first time the chemical zoning of TVZ active geothermal systems associated with the natural state of a system pre-utilisation. By comparing the results with the zoning observed in the high-temperature magmatic-hydrothermal altered rocks above Ngatamariki intrusive complex, we can now have a better idea of the effect of a magmatic intrusion on hydrothermally altered rock chemistry in the Taupo Volcanic Zone. The similarity between the chemistry observed in the older Ngatamariki system and the present-day Ohaaki system, lead to the conclusion that some of the metal enrichment may come from a degassing intrusion underneath Ohaaki, and possibly Rotokawa.

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