PROGRESSIVE DEVOLITISATION OF NEW ZEALAND RESERVOIR ROCKS FROM SUB-CRITICAL TO SUPERCRITICAL CONDITIONS

Bruce W. Mountain[1], Isabelle Chambefort[1], and Lucjan Sajkowski[1,2]

[1]GNS Science, Wairakei Research Centre, Taupo 3384, New Zealand

[2]School of Earth and Environment, Victoria University of Wellington, New Zealand

b.mountain@gns.cri.nz

Keywords: *chlorine, experimental geochemistry, water-rock interactions, greywacke, rhyolite, devolitisation.*

ABSTRACT

The source of volatiles such as Cl, S and CO_2 in geothermal systems is an object of frequent debate. Early experiments concluded that they could be derived solely from water-rock interaction. Others infer that some component of magmatic input is necessary. We have conducted experiments to measure the volatiles released during progressive heating of the typical reservoir rocks of the Taupo Volcanic Zone: greywacke (Mountain et al. 2016) and rhyolitic pumice (this study). The experiments aim to simulate the chemical exchange occurring during recharge of the geothermal plume of a reservoir.

The pumice experiment was conducted over a period of 82 days using a high temperature and pressure fluid-rock interaction simulator. Temperature ranged from 20 to 400^{o}C and a maximum pressure of 405 bar. The flow rate was maintained at 1 ml hr^{-1} throughout the experiment.

Up to a temperature of 250^{o}C, only small amounts of Cl were released. Most Cl was released between 250 and 300^{o}C. The integrated ΣCl flux was almost 1200 mg kg^{-1} rock. Sulfur released by the pumice was mostly SO_4 (180 mg kg^{-1} rock) which occurred between 20 and 250^{o}C while H_2S release was minimal (6.5 mg kg^{-1} rock).

These preliminary results show that different geothermal reservoir rocks can influenced the composition of the fluids reacting with them. This can be a possible explanation for some of the chemical observations observed in between geothermal systems of the Taupo Volcanic Zone.

1. INTRODUCTION

The source of volatile elements in the geothermal waters of the Taupo Volcanic Zone (TVZ) is a continuous source of debate. While the water is predominantly meteoric in origin, higher concentrations, when compared with average groundwater, in components such as S, Cl, and CO_2 are characteristic of geothermal waters (Fig. 1). The relative influence of deep magmatic input and crustal recycling via water-rock interaction is still debated, and no convincing models exist for the source, transfer and recycling of the volatiles.

Bégué et al. (2017) suggested that variation in rhyolitic degassing behaviour could explain/contribute to the variation in chlorine observed at the surface between arc versus rift-type systems. These authors suggest the geothermal systems, that appear to have an ‘arc-type’ andesitic fluid contribution, are actually derived from a rhyolite melt in equilibrium with a highly crystalline andesite magma.

Ellis and Mahon (1964) proposed that Cl released from the volcanic rocks during hydrothermal alteration is more than sufficient to explain the concentrations of this element in geothermal waters. Henley and Ellis (1983) estimated using Ellis and Mahon (1964) leaching data that an extra magmatic source was necessary to provide enough Cl in the Wairakei geothermal system. More than 2000 km^3 of rock would be required to be leached to provide sufficient Cl during the lifetime of the system. This value is unreasonable and not supported by the alteration halo around the system. Recent Cl isotope data suggests that the chlorine originates from andesitic or rhyolitic magmatism (δ^{37}Cl ranges -1.0 – 0.8 ‰, Bernal et al., 2014).

New Zealand geothermal systems are hosted by a large volume of rhyolitic volcaniclastics. The thickness of the deposits varies from >3000 m at Wairakei to less than 600 m at Kawerau. Rhyolite is the dominant reservoir rocks at Wairakei, Tauhara, Ohaaki, Ngatamariki geothermal fields and largely control the shallow hydrology in all fields (Fig. 1). Kawerau geothermal reservoir is hosted by the metasedimentary basement.

The aim of this work is to assess the role of these two dominant reservoir rocks. Devolitisation experiments have been conducted to measure S and Cl release during progressive heating. Mountain et al. (2016) reported results of devolitisation of Waotu greywacke (Mountain et al., 2016). The present study reports results from a similar step heating experiment on rhyolite. It aims to test whether the rhyolite can be the source or at least contribute via water-rock interaction to the S and Cl budget in the deep discharge of the geothermal systems. This study revisits the older close-system experiments from Ellis and Mahon (1964) but using a progressive heating with fluid flow approach.

2. METHOD

Pumice sample was selected from Taupo 1.8 Ka plinian fall Unit Y5 (Sample courtesy of M. Rosenberg). Taupo pumice is crystal poor (Fig. 3) with less than 3% pyroxene, plagioclase and magnetite. It has a characteristic high-silica rhyolite composition with 74.0 wt% SiO_2, 13.6 wt% Al_2O_3, 2.7 wt% K_2O and ~ 2 wt% LOI (Barker et al., 2015).

The ΣS and Cl content of the pumice are <50 and ~1600 mg kg^{-1}, respectively. The Cl content is in agreement with melt inclusion and groundmass analyses for TVZ rhyolite and melt inclusions (Johnson et al., 2011; Bégué et al., 2015) and is considered representative of TVZ host silicic reservoir rock.

The rock was crushed and sieved to retain the 0.35 – 0.5 mm size fraction which was cleaned in an ultrasonic bath to remove fine material. The pressure vessel was loaded with 7.54 g of pumice.

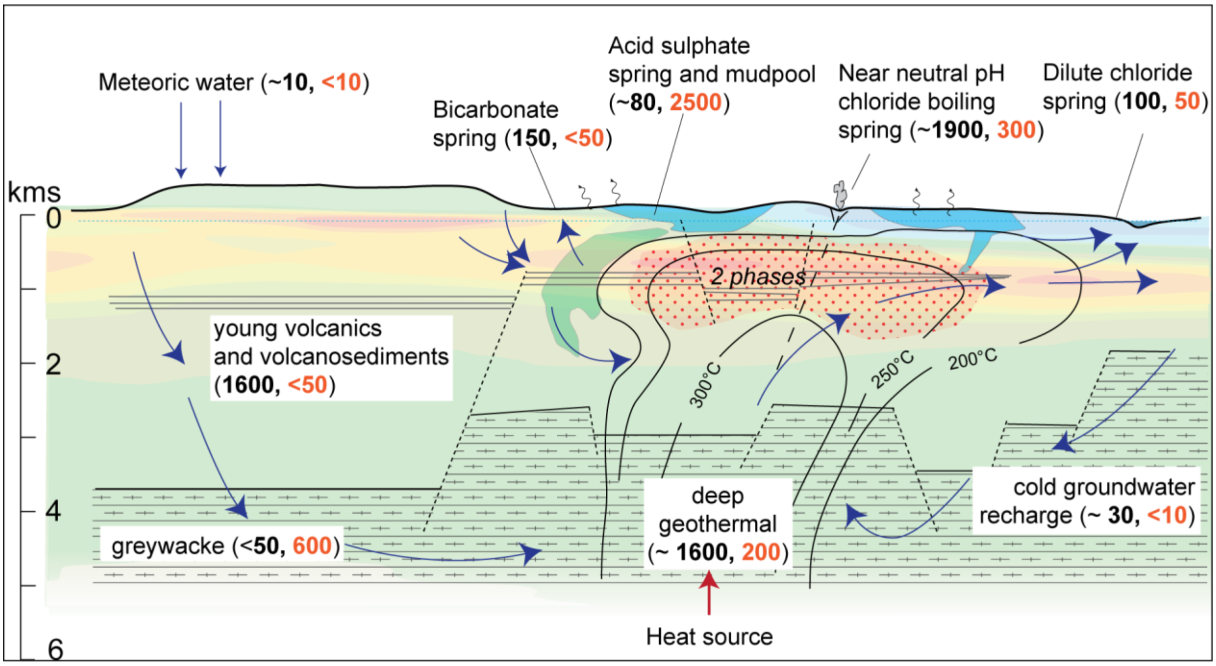

Figure 1: Schematic model of TVZ geothermal systems' chlorine and sulfur reservoirs modified after Henley and Ellis (1983). Numbers in bold represent the average chlorine (black) and Σsulfur (orange) content of the different reservoir components in ppm (mg kg^{-1}) (from Krupp and Seward, 1987; Giggenbach, 1995; Reyes and Trompetter, 2012)

The experiment was conducted using a high temperature and pressure fluid-rock interaction simulator for 82 days. The temperature ranged from 20 to 400°C and a maximum pressure of 405 bar. Figure 2 shows the P-T path for the experiment. The fluid used was doubly-distilled water at a flow rate of 1 ml hr^{-1}. Details on the experimental apparatus can be found in Sonney and Mountain (2013).

Fluid samples were analysed for major cations (Li, Na, K, Mg, Ca, Sr, Mn, Fe, As, Al, B, and SiO_2) by ICP-OES and anions (Cl^- and SO_4^{2-}) by IC. H_2S was determined by the methylene blue method/UV-Vis spectroscopy. The pH was measured using a standard pH meter. Only anion and H_2S results are reported here.

3. RESULTS

Figure 4 shows the Cl concentrations and integrated Cl (ΣCl) flux per kg of rock versus time for the pumice experiment. The starting composition of the inlet fluid is <0.05 mg kg^{-1} Cl.

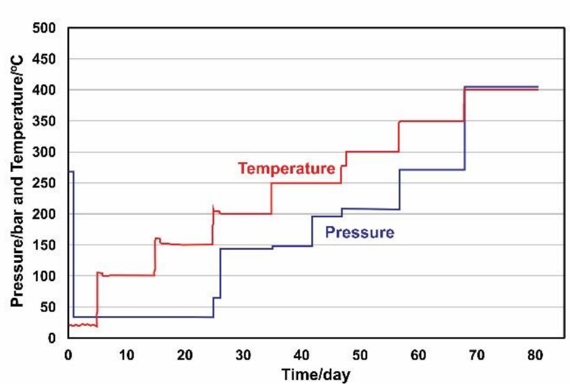

Figure 2: Pressure-temperature path for the pumice devolitisation experiment.

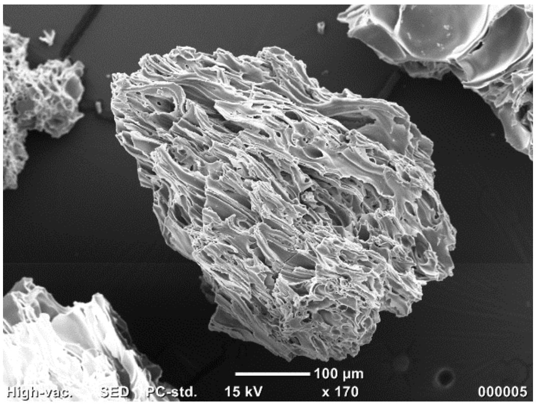

Figure 3: Scanning electron micrograph showing a single unreacted Taupo pumice fragment as used in the experiment.

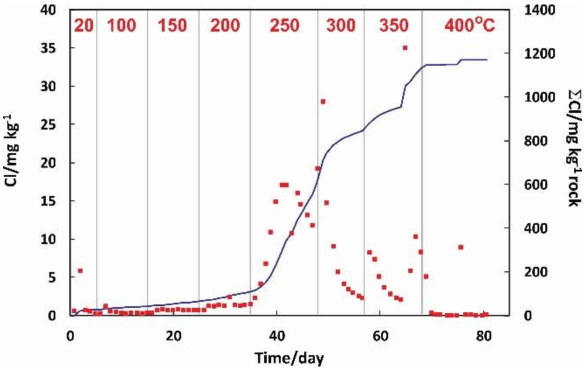

Figure 4. Cl concentrations (red squares) and integrated ΣCl flux per kg of rock (blue line) versus

experimental time. Temperature shown at the top of graph.

Up to the temperature increase from 200 to 250°C, most Cl concentrations lie below 2 mg kg^{-1}. There are small increases between 100 to 150°C and 150 to 200°C but these increases are <0.5 mg kg^{-1}. At 250°C, however, a sudden rapid rise to about 18 mg kg^{-1} occurs over six days which then decreases back to around 12 mg kg^{-1} at which time the temperature was increased to 300°C. At the temperature shifts from 250 to 300°C and 300 to 350°C, significant increases in Cl concentration occur which decline down to about 3 mg kg^{-1} in both cases. This does not occur at the temperature shift to 400°C, after which most Cl concentrations are near detection limit.

The ΣCl flux is relatively small up to 250°C, totalling only about 100 mg kg^{-1} rock. At 250°C this increases rapidly to about 600 mg kg^{-1} rock. During the 300 and 350°C periods, the flux increases to the maximum slightly less than 1200 mg kg^{-1}. After the shift to 400°C, the ΣCl flux remains relatively unchanged.

Figure 5 shows the SO_4 concentrations and integrated SO_4 (ΣSO_4) flux per kg of rock versus time. The starting SO_4 concentration in the inlet fluid is <0.05 mg kg^{-1}.

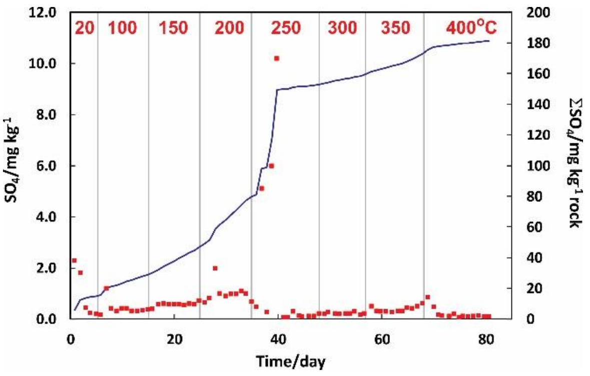

Figure 5. SO_4 concentrations (red squares) and integrated ΣSO_4 flux per kg of rock (blue line) versus experimental time.

A small amount of SO_4 is released at room temperature. As temperature is increased from room temperature to 100, 150 and 200°C, the average SO_4 concentration for the effluent increases by a small amount (<0.5 mg kg^{-1}). After the increase to 250°C, there is a rapid loss of SO_4 with the concentration reaching as high as 10 mg kg^{-1}. This takes a couple of days and then SO_4 concentrations drop back down to near detection limit. Between 250 and 400°C, SO_4 concentrations increase again on average but after the switch to 400°C, SO_4 remains near detection limit.

The ΣSO_4 flux shows a continuous increase up to 250°C to about 80 mg kg^{-1} rock. At 250°C, there is rapid release of SO_4, increasing the total flux to about 150 mg kg^{-1} rock. After this, the ΣSO_4 flux increases marginally to about 180 mg kg^{-1} by the end of the experiment.

Figure 7 shows the H_2S concentrations and integrated H_2S (ΣH_2S) flux per kg of rock versus time. The starting H_2S concentration in the inlet fluid is <0.01 mg kg^{-1}.

Between 100 and 150°C, there is detectable H_2S. This drops to below detection limit at 200°C. There are detectable but small concentrations of H_2S measured at 250°C, however, when temperature shifts to 300 and 350°C, there are measurable concentrations of H_2S averaging about 0.05 mg kg^{-1}. After the temperature increase to 400°C, H_2S concentrations drop to low values.

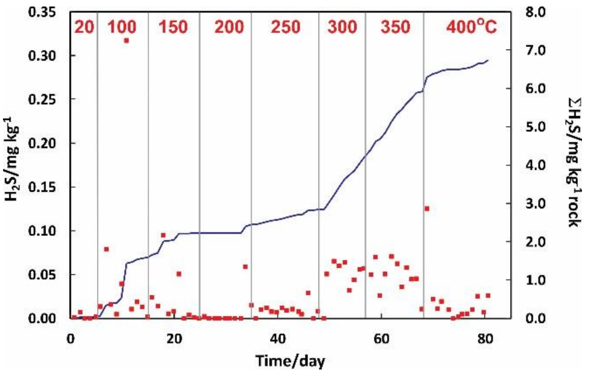

Figure 6. H_2S concentrations (red squares) and integrated ΣH_2S flux per kg of rock (blue line) versus experimental time.

The ΣH_2S flux shows about 1 mg kg^{-1} rock is released by 150°C. This remains relatively constant at about 2.5 mg kg^{-1} until 300°C. After this, H_2S flux increases until the temperature shift to 400°C, at which time the H_2S flux is about 6 mg kg^{-1}. During the 400°C period, the ΣH_2S flux increases only to about 6.5 mg kg^{-1} rock.

4. DISCUSSION

4.1 Comparison with Greywacke

In our previous devolitisation experiment "fresh" greywacke was used to simulate the basement rocks in the Taupo Volcanic Zone (Mountain et al, 2016). Figure 7 shows the ΣCl flux from this experiment plotted with the results from the pumice experiment. The figure shows the midpoint of the ΣCl flux during each temperature period plotted versus inverse temperature in K. Both datasets show trends with varying slope. This suggests more than one mechanism for Cl release instead of a single mechanism whose rate is solely dependent on temperature.

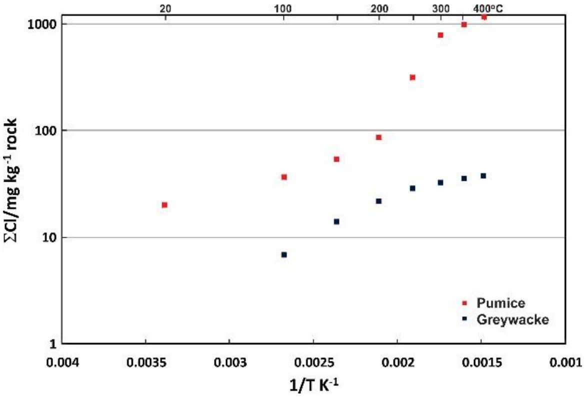

Figure 7. Average integrated Cl flux versus inverse temperature for pumice and greywacke experiments.

The difference between the two rock types is evident with the greywacke releasing only 38 mg of Cl per kg of rock while the pumice releases almost 1200 mg kg^{-1} rock. The large increase of integrated Cl release between 200 to 300°C corresponds to the increase in the "instantaneous" release at

250 – 350°C (Fig. 4). This trend is not present in the greywacke experiment. The higher rate of release between these temperatures cannot be solely explained by increased reaction rate of the volcanic glass; between 100 - 200°C and >300°C a similar temperature dependence is not found. Another possible explanation is a mineral phase change that commenced at 250°C releasing Cl at a faster rate than at other temperatures.

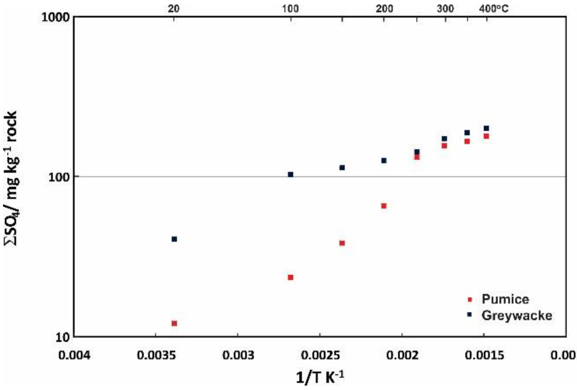

Figure 8. Average integrated SO_4 flux versus inverse temperature for pumice and greywacke experiments.

The ΣSO_4 flux, at low temperature, it is much higher for the greywacke than for the pumice (Fig. 8). This is explained by the dissolution of trace amounts of sulfate minerals in the greywacke. These minerals are not present in the pumice and the SO_4 must be derived from the SO_3 trapped in the volcanic glass. Because the dissolution rate of this glass is slow at low temperature only small amounts of SO_3 are released.

Between 100 and 400°C, the release rate from the greywacke is relatively constant and the integrated flux with each temperature increase is small. This is because most of the SO_4 is released at low temperature with only trace amounts released at higher temperature. In contrast, the amount of SO_4 released by the pumice increases faster due to the increased solubility of the volcanic glass with temperature. At 250°C, the ΣSO_4 flux from the pumice is equal to the greywacke and remains so as temperature increases.

Figure 9 shows the integrated H_2S flux from both the pumice and greywacke plotted versus inverse temperature in K.

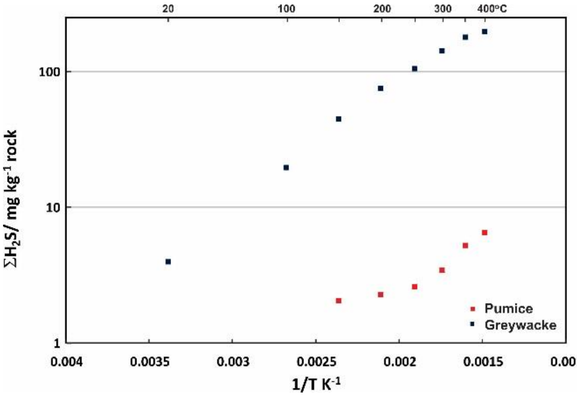

Figure 9. Average integrated H_2S flux versus inverse temperature for pumice and greywacke experiments.

ΣH_2S flux from pumice is low, totalling only 6.5 mg kg^{-1} rock with most evolving at temperatures above 300°C. H_2S release does not follow the SO_4 release, indicating that it is not entirely related to glass dissolution. One possible explanation for the increased release above 300°C is a small amount of SO_4 reduction at higher temperatures.

In contrast, the ΣH_2S flux from the greywacke is about 170 mg kg^{-1} rock and plotting log ΣH_2S flux versus inverse temperature shows an almost straight line dependence. This is indicative of a single mechanism, the most likely of which is the dissolution of pyrite.

4.2 The Role of Greywacke versus Rhyolite Pumice

The implications of the experimental results have bearing on the origin and relative amounts of volatile components in geothermal fluids and to the debate on the contribution of magmatic volatiles.

The ΣS released as sulfate and sulfide from the pumice was about 67 mg kg^{-1} rock. This is greater than the <50 mg kg^{-1} reported in the whole rock analysis. Given the large uncertainties in the calculation this suggests that all the sulfur has been released. The ΣCl released is about 1200 mg kg^{-1} rock while the rock analysis shows 1600 mg kg^{-1}. This indicates that most but not all Cl was released.

In comparison, the ΣCl derived from the greywacke was only 38 mg kg^{-1} while the ΣS was 107 mg kg^{-1}. The concentration in the greywacke for Cl and S are <50 and 600 mg kg^{-1}, respectively. This indicates that most Cl was released but only about 18% of the S.

The greywacke experiment shows that significant amounts of S can be derived from the dissolution of pyrite while the amount of Cl produced is small. In contrast, devolitisation of the pumice produced significant Cl and only a small amount of S. Most release of the volatiles occurs between 250 and 300°C.

In the case of a descending meteoric water, with low concentrations of S and Cl (Fig. 1), no significant amount of these components will be picked up as the fluid passes through rhyolitic volcanic rocks, at least up to temperatures of around 250°C, at which point Cl devolitisation begins. If the fluid remains in volcanic rocks and heats to temperature above 350°C then enough Cl is produced to create the geothermal concentrations found in the TVZ. Sulfur is not significantly enriched. If, however, the volcanic/greywacke interface is encountered before reaching 250°C then Cl sequestration slows but significant S sequestration can begin by dissolution of pyrite in the greywacke. Thus, in the first case, the result is a fluid that is enriched in Cl but low in S. While in the second case, the fluid is enriched in S but low in Cl. The implication is that the S/Cl ratio in the recharge fluid could be controlled by the position of the 200 - 300°C temperature transition relative to the volcanic/greywacke interface.

5. CONCLUSIONS

An experiment has been conducted to measure the release of the volatile components S and Cl from rhyolitic pumice. The stepped temperature profile ran from 20°C to 400°C and up to a pressure of 405 bar. The results were compared with those of a previous experiment that utilised greywacke to simulate the basement rocks of the TVZ.

Up to a temperature of 250°C, only small amounts of Cl were released. Most Cl released was encountered between 250 and 300°C. The integrated ΣCl flux was almost 1200 mg kg^{-1} rock. Sulfur released by the pumice was mostly SO_4 (180 mg kg^{-1} rock) which occurred between 20 and 250°C while H_2S release was minimal (6.5 mg kg^{-1} rock).

This contrasts with the results from the greywacke experiment where only 38 mg kg^{-1} rock of Cl was released over the whole experiment while 170 mg kg^{-1} of H_2S was released.

The contrasting behaviors of the pumice and greywacke to devolalitisation has implications to the source of volatiles in geothermal fluids. It would appear that the amount of Cl contained in the rhyolitic volcanics is sufficient to provide Cl for the fluids without any magmatic input. However, the small concentration of S in the rhyolites is insufficient for systems with high S content such as at Rotokawa, New Zealand. A possible explanation is that the recharge waters are entering the greywacke basement where heat and the presence of pyrite allow the fluid to sequester H_2S.

It is here suggested that descending recharge waters in a New Zealand geothermal system could have their S/Cl ratios controlled by the position of the 200 to 300^{o}C temperature transition relative to the volcanic/basement interface.

ACKNOWLEDGEMENTS

This Research is supported by the Government of New Zealand through the GNS Science DCF Programme New Zealand Geothermal Future.

REFERENCES

Barker, S.J., Wilson, C.J.N., Allan, A.S.R., Schipper, C.I.: Fine-scale temporal recovery, reconstruction and evolution of a post-supereruption magmatic system. Con. Mineral. Petrol., v. 170:5. (2015).

Bégué, F., Gravley, D.M., Chambefort, I., Deering, C.D., Kennedy, B.M.: Magmatic volatile distribution as recorded by rhyolitic melt inclusions in the Taupo Volcanic Zone, New Zealand. From: Zellmer, G. F., Edmonds, M. and Straub, S. M. (eds) The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas. Geological Society, London, Special Publications, 410, p. 71–94. (2015). http://dx.doi.org/10.1144/SP410.4.

Bégué, F., Deering, C.D., Gravley, D.M., Chambefort, I., Kennedy, B.M.: From source to surface: Tracking magmatic boron and chlorine input into the geothermal systems of the Taupo Volcanic Zone, New Zealand. Jour. Volc. Geotherm. Res. (2017). doi:10.1016/j.jvolgeores.2017.03.008.

Bernal, N.F., Gleeson, S.A., Dean, A.S., Liu, X-M, Hoskin, P: The source of halogens in geothermal fluids from the Taupo Volcanic Zone, North Island, New Zealand. Geochim.Cosmochim. Acta, v. 126, p. 265–283. (2014).

Ellis, A.J., and Mahon, W.W.J.: Natural hydrothermal systems and experimental hot-water/rock interactions. Geochim. Cosmochim. Acta, v. 28, p. 1323–1357. (1964).

Henley, R.W., and Ellis, A.J.: Geothermal systems ancient and modern: A geochemical review. Earth Sci. Rev., v. 19, p. 1–50. (1983).

Giggenbach, W.F.: Variations in the chemical and isotopic compositions of fluids discharged from the Taupo Volcanic Zone, New Zealand. Jour. Volc. Geotherm. Res., v. 68, p. 89–116. (1995).

Johnson, E.R., Kamenetsky, V.S., McPhie, J, and Wallace, P.: Degassing of the H_2O-rich rhyolites of the Okataina Volcanic Center, Taupo Volcanic Zone, New Zealand. Geology, v. 39, p. 311–314. (2011).

Krupp, R.E., and Seward, T.M.: The Rotokawa Geothermal System, New Zealand: An active epithermal Gold-depositing environment. Econ. Geol., v. 82, p. 1109–1129. (1987).

Mountain, B.W., Chambefort, I., Sajkowski, L.: Progressive devolitization of New Zealand reservoir rocks from sub-critical to supercritical conditions. 38th New Zealand Geothermal Workshop, Auckland, New Zealand (2016).

Reyes, A.G. and Trompetter, W.J.: Hydrothermal water-rock interaction and the redistribution of Li, B and Cl in the Taupo Volcanic Zone, New Zealand: Chem. Geol., v. 314-317, p. 96-112. (2012).

Sonney, R. and Mountain, B.W.: Experimental simulation of greywacke-fluid interaction under geothermal conditions. Geothermics, v. 47, 27-39 (2013).