VOLATILE TRANSFER FROM MAGMA SOURCES IN THE TAUPO VOLCANIC ZONE: A QUARTZ-HOSTED MELT INCLUSION STUDY IN RHYOLITES

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ABSTRACT

The central Taupo Volcanic Zone (TVZ) is a rifted arc where dominantly silicic magmatism and volcanism is closely related to tectonics. Two distinct rhyolite magma types (dry-reducing and wet-oxidizing) have erupted from the central TVZ over the past ~550kyrs. We measured volatile concentrations and Boron (B) isotopes in quartz-hosted melt inclusions from rhyolitic eruptions representing these distinct types to identify spatial and temporal variation in the volatile contributions to the overlying hydrothermal systems. Dry magma in the upper crust may not be volatile saturated and, therefore, would contribute very little to the overlying hydrothermal system.

Melt inclusions from the dry Ohakuri and Mamaku eruptions (~240 ka) have high chlorine values (0.25-0.36wt%), and show a positive correlation between chlorine and incompatible elements, suggesting that no vapour phase was exsolved prior to eruption. In comparison, volatile data from the wet Kaharoa eruption (~1314AD) show Cl loss to a coexisting volatile phase, i.e. exsolution of a volatile phase occurred during crystallization.

Measured B and $\delta^{11}B$ in these two different types of systems also reveal distinct signatures. The boron content of the Kaharoa magma ranges from 20-30ppm, and the isotopic composition is homogeneous, with $\delta^{11}B$ of + 4‰. As the Kaharoa was volatile saturated prior to eruption, a much higher boron content may have existed (B preferentially partitions into the volatile phase). The Mamaku and Ohakuri melts, on the other hand, have homogeneous boron contents around 15 ppm, but isotopic ratios ranging from – 3 to + 3‰. We attribute these two different magmatic signatures to a variation in slab-derived fluid flux across the TVZ.

The spatial distribution of the two different types of rhyolite (wet vs. dry) can be mapped in the TVZ and directly linked to the input of slab-derived fluids. As such, boron could be an effective tracer for volatile transfer to overlying geothermal systems where magmas are suspected to be saturated.

1. INTRODUCTION

Volatiles play an important role in the evolution and understanding of magmatic processes and the physics of volcanic eruptions; however, they are also integral to the development of magmatic-derived hydrothermal systems. It is well documented that during crystallisation, exsolution of an immiscible volatile phase from the melt occurs [e.g. Bishop Tuff, California (Wallace et al. 1995), Bandelier Tuff, New Mexico (Dunbar and Hervig 1992)]. Consequently, this exsolved volatile phase will participate in the heat and mass transfer (advection) to geothermal systems, which is a more efficient heat transfer mechanism than conduction from the magma body alone.

In this study, we present trace element and volatile data (Cl, F and S) including boron isotopes in quartz-hosted melt inclusions from rhyolites of three volcanic centres in the Taupo Volcanic Zone (TVZ), New Zealand. The studied magmas represent the two end-member rhyolite compositions that erupt in the TVZ (Deering et al. 2010); the hot-dry-reducing Ohakuri and Mamaku, and the cold-wet-oxidizing Kaharoa eruptives (Okataina Volcanic Centre, OVC).

The objectives are to: 1) determine if the magma was volatile saturated during crystallisation, and 2) identify disparities in the volatile contributions to the overlying hydrothermal systems. We particularly focus on determining the relationship between volatile contents and the type of rhyolite erupted across the TVZ.

2. GEOLOGY

The TVZ is a rifted arc (Wilson et al. 1995) that reflects the northwest-directed subduction of the Pacific plate beneath the North Island (Fig.1) and NW-SE extension of 5-15mm/yr, from SW to NE, respectively (Wallace et al. 2004). The central segment has been dominated by explosive caldera-forming rhyolitic eruptions (more than 6,000 km^3 of magma erupted over a period of ~1.6 Ma), with only minor dacites and basalts (Wilson et al. 2009). Extension related graben structures shape this central segment, and there is a close relationship between tectonics, magmatism and volcanism (Rowland et al. 2010).

The rhyolites from the central TVZ represent a geochemical continuum between cold-wet-oxidizing and hot-dry-reducing magmas (Deering et al. 2008, Table 1), caused by changes in conditions in the lower crust dictated by slab-derived fluids from the subduction zone (Deering et al. 2010).

The Rotorua and Ohakuri calderas, separated by approximately 30 km, are located adjacent to the western border of the central TVZ (Fig.1). The caldera forming eruptions, the Mamaku and Ohakuri respectively, erupted >145 km^3 (Milner et al. 2003) and >100 km^3 (Gravley et al. 2007) of rhyolitic magma almost simultaneously (Gravley et al. 2007). The Mamaku and Ohakuri eruptions evacuated

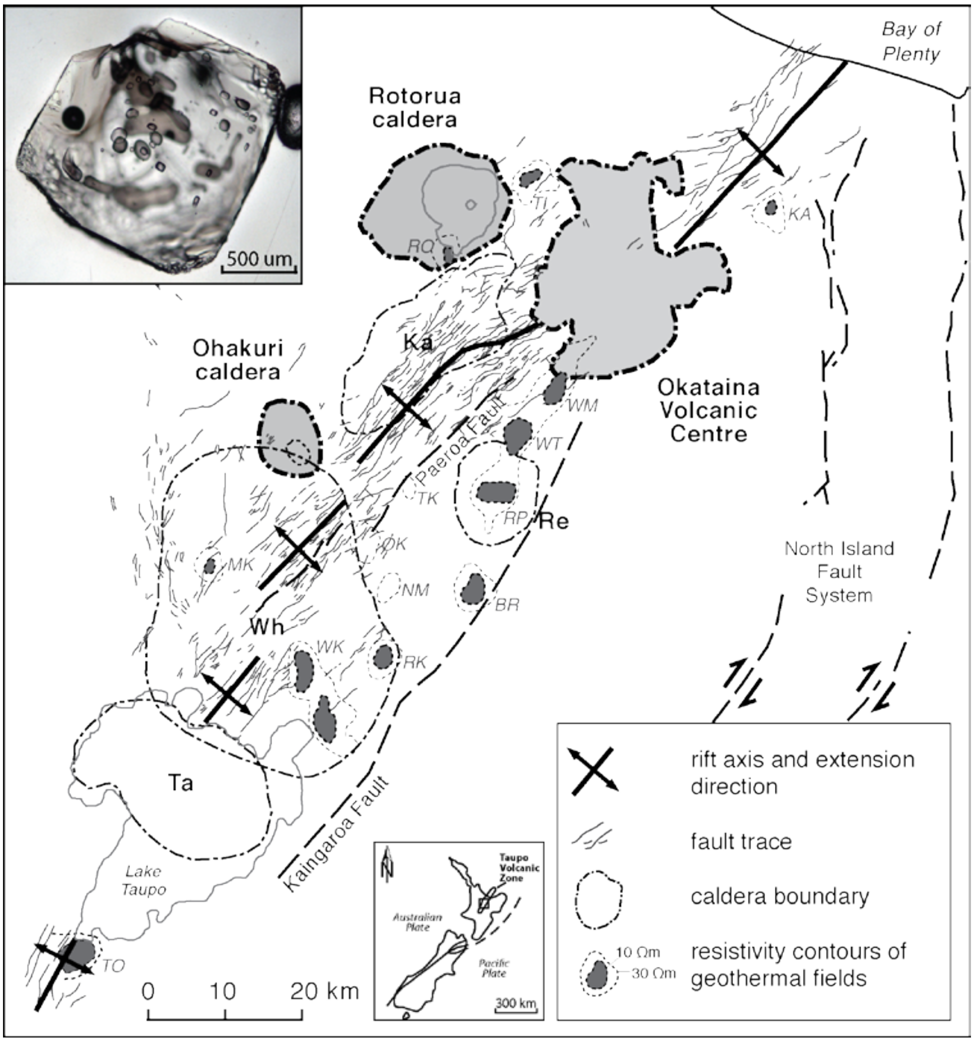

Figure 1: Map of the TVZ, New Zealand. Caldera boundaries and structures after Rowland et al. (2010), resistivity contours and geothermal fields after Bibby et al. (1995). Inset shows a photomicrograph of melt inclusions in an Ohakuri quartz crystal. Abbreviations for calderas: Wh-Whakamaru, Ta-Taupo, Ka-Kapenga; for geothermal fields: TO-Tokaanu, WK-Wairakei, RK-Rotokawa, MK-Mokai, NM-Ngatamariki, BR-Broadlands Ohaaki, OK-Orakei Korako, RP-Reporoa, TK-Te Kopia, WT-Waiotapu, WM-Waimangu, RO-Rotorua, TI-Tikitere, KA-Kawerau.

three different magma types each, from a rhyo-dacitic (type 3) to more evolved rhyolite compositions (type 2 and type 1) (Milner et al. 2003; Gravley et al. 2007), which are all hot-dry-reducing rhyolites as described in Table 1 (Deering et al. 2010). The Ohakuri eruption started with an airfall event (Gravley et al. 2007), which is included in our analysis.

The Okataina Volcanic Centre (OVC) records multiple caldera-forming eruptive events, controlled by regional tectonics (Cole et al. 2010). It lies within the rift axis on a transfer zone, which accommodates displacements and interaction between two rift segments (Cole et al. 2010 and references therein) (Fig.1). In contrast to the Ohakuri and Mamaku eruptions, the OVC has produced, nearly continuously, cold-wet-oxidizing rhyolites as described in Table 1 (Deering et al. 2010). In this study we focused on the ~AD 1314 Kaharoa eruptives, from the Tarawera volcano within the OVC (Nairn et al. 2004).

Hot –Dry – Reducing **(i.e. Mamaku and Ohakuri magmas)**	**Cold – Wet – Oxidizing** **(i.e. Kaharoa (OVC) magma)**
Crystal-poor (<10%)	Crystal-rich (10-45%)
dominantly anhydrous mineral phases (orthopyroxene ± clinopyroxene)	dominantly hydrous mineral phases (hornblende ± cummingtonite ± biotite)
low fO_2 (log $fO_{2\Delta QFM}$=0-1)	high fO_2 (log $fO_{2\Delta QFM}$=1-2)

Table 1: Differences between hot-dry-reducing (Mamaku-Ohakuri) and cold-wet-oxidizing (OVC) magma in the TVZ (after Deering et al. 2010)

3. SAMPLES AND ANALYTICAL METHODS

We cleaned, oven-dried (50°C), and crushed 35 individual pumices from the Ohakuri airfall deposit and ignimbrite, the Mamaku ignimbrite, and the Kaharoa fall deposit. We identified quartz-hosted melt inclusions with immersion oil (refractive index 1.54) and chose only fully enclosed, glassy, and >50 µm inclusions for analysis.

Major element contents of melt inclusions (some within the same quartz crystal) were determined using an electron microprobe (Jeol 733 Superprobe at the University of Washington, UW). We applied standard analytical conditions with an acceleration voltage of 15kV, a beam current of 5nA, and a defocused beam of 10 µm diameter.

We measured volatiles (Cl, F and S) using the beam blanking technique described in Witter and Kuehner (2004), with the same electron microprobe at UW. An acceleration voltage of 10kV, a beam current of ~100nA, and a defocused beam of 10 µm in diameter were used. Analytical error for Cl and F measurements are <15%. However, for a majority of the melt inclusions the measured S didn't exceed the detection limit, which varied between 35 and 50 ppm.

Trace element contents (including B) were measured with the secondary ion mass spectrometer IMS Cameca 6f at Arizona State University (ASU). The primary O^- beam intensity was set at 10nA, and we used the composition of the standard NIST 610, that was measured several times during each session, to convert the measured trace element/Si ratios into trace element concentrations (in ppm). The analytical error depends on the measured element and is always <5%.

Boron isotopes in melt inclusions were determined with the same IMS Cameca 6f at ASU, using the approach of Chaussidon et al. (1997), with a primary O^- beam intensity of ~5nA. We used NIST 612 as a standard, and corrected for observed matrix effects relative to rhyolite glass using the approach recommended by Rosner et al. (2008). The instrumental mass fractionation (IMF) during each analytical session was determined by measuring the $\delta^{11}B$ of the standard several times. Among the analytical sessions, the IMF varied largely between 30 and 85‰, however, it remained relatively constant during individual sessions.

	Mamaku	Ohakuri	Kaharoa (OVC)
$Cl_{avg.}$ (wt%)	0.3	0.29	0.19^a
$F_{avg.}$ (ppm)	610	530	n/a
$WBD_{avg.}$ (wt%)	5.4 ± 1^c	4.8 ± 1^c	4.78^a
$Ba_{avg.}$(ppm)	560	600	832^a
$B_{avg.}$(ppm)	15	17	21
$\delta^{11}B_{avg.}$ (‰)	$+1.55 \pm 1^b$	-1.15 ± 1^b	$+4.3 \pm 1^b$

[a] data from Jonhson et al. (2011), H_2O measured by FTIR
[b] analytical error
[c] minimal error on water by difference (WDB) values

Table 2: Average volatile and selected trace element contents in quartz-hosted melt inclusions of Mamaku, Ohakuri and Kaharoa eruptives.

The boron isotopic composition is expressed in per mil deviation $\delta^{11}B$ relative to the NIST 612, as calculated in the following equation:

$$\delta^{11}B\ (‰) = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{NIST\ 612} - 1] \times 10^3,$$

and then corrected for the IMF. The 2σ errors on $\delta^{11}B$ within each pumice type are very high for the Mamaku and Ohakuri samples (up to 5‰ for Ohakuri type 1). 2σ errors for the Kaharoa melt inclusions are 0.7‰.

In a planned future session, we will address the problems of the IMF variation and the large 2σ errors.

4. RESULTS AND DISCUSSION

4.1 Volatiles in the Mamaku and Ohakuri eruptives

Average results for volatiles and boron isotopes are presented in Table 2.

Melt inclusions hosted in Ohakuri quartz have high chlorine values between 0.25 and 0.36 wt%, and most individual types show a positive correlation between chlorine, fluorine and Rb/Sr ratio (Fig.2 and 3). The Mamaku type 1 melt inclusions yield more scattered results for the F content and no clear trend is visible (Fig. 2), but there is an obvious linear increase in Cl with Rb/Sr ratio (Fig. 3).

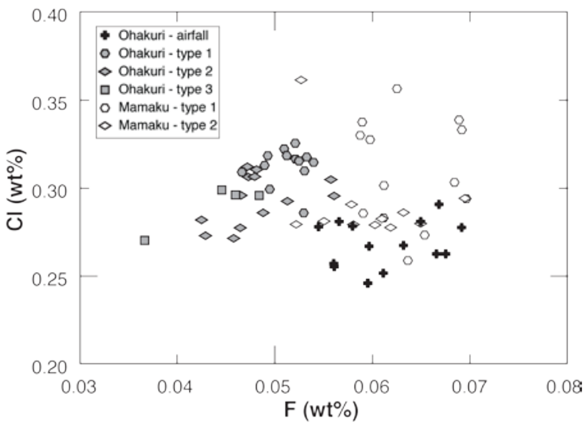

Figure 2: Plot of Cl (wt%) vs. F (wt%) for the Mamaku and Ohakuri rhyolite. Increase of Cl with F, both incompatible elements in these rhyolites, but Cl preferentially partitions into a volatile phase, F will stay in the melt.

Chlorine is an incompatible element in these rhyolite magmas, and will partition in favour of a volatile phase, if present, unlike Rb or F, which are also incompatible elements, but will preferentially stay in the melt. Its solubility is complex and is strongly dependant on pressure, temperature, water content and magma chemistry (Webster and Holloway, 1988; Webster, 1997). The increasing Cl in the Mamaku type 1 melt, the Ohakuri airfall, and most likely Ohakuri type 2 and 3 suggests Cl was not lost to another phase and therefore, might not have been volatile saturated prior to eruption. Otherwise Cl would have left the melt to partition into the coexisting volatile phase, and the Cl values would plateau (Webster, 1997). This observation remains inconclusive for the other Mamaku and Ohakuri types. However, H_2O measurements are essential for confirming volatile saturation, and we are planning to obtain this data as part of this study.

In contrast, Johnson et al. (2011) reported vapour-saturated crystallization (i.e. exsolution of a volatile phase during quartz crystallisation) in a melt inclusion study from the OVC rhyolites. The mineral assemblage of the OVC where hydrous phases are present (Table 1) also indicate that these magmas had a higher H_2O content, compared to the Mamaku and Ohakuri rhyolites.

The Cl content in the OVC rhyolites is lower than in the Mamaku and Ohakuri magmas (Fig. 4), but as previously mentioned, the Cl will preferentially partition into the coexisting volatile phase and, therefore, plateaus at 0.2wt% Cl in the melt (Johnson et al., 2011). To compare the Mamaku and Ohakuri results with the OVC, we have to consider the bulk Cl content of the OVC magma, i.e. the Cl in the melt and the volatile phase. We calculate this using a minimal partition coefficient $D_{Cl}^{vap./melt}$= 6 (Signorelli et al. 2000), however, depending on the chemistry, pressure and temperature, D_{Cl} could be higher (up to 130; Webster and Holloway 1988); and using 5, 10 and 20 vol% exsolved gas. 20 vol% exsolved gas corresponds to the percolation threshold (C. Huber, pers. commun., 2012), i.e. sufficient gas is exsolved for bubble coalescence to create permeability in the melt, allowing the volatiles to escape the magmatic system.

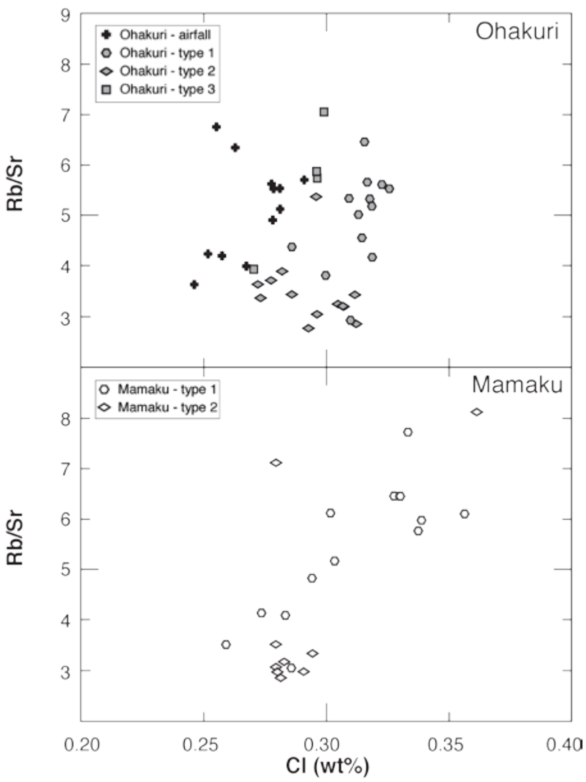

Figure 3: Plots of Cl (wt%) vs. Rb/Sr ratio for the Ohakuri (top) and Mamaku rhyolite. Like F, Rb is incompatible in these rhyolite magmas.

The calculated Cl values for the bulk OVC magmas can be up to 0.55 wt% for 20vol% bubbles (Fig. 4), and the Ba/La ratio, used as an indicator of the amount of slab-derived fluid contribution, is also higher in the OVC (Johnson et al. 2011) than in the Mamaku and Ohakuri.

These volatile data indicate that the contribution of slab-derived components were probably not as important for the Mamaku and Ohakuri as for the Okataina rhyolites.

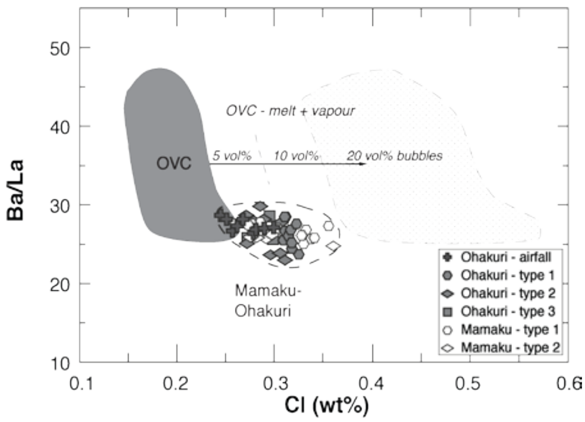

Figure 4: Plot of Cl (wt%) vs. Ba/La ratio for the dry type Mamaku-Ohakuri magmas and the wet type OVC (grey shaded field) (from Jonhson et al. 2011). Dotted field and arrow represent the bulk Cl content of the OVC (melt and volatile phase), using a minimal partition coefficient of $D_{Cl}^{vap/melt}$= 6 (Signorelli and Caroll, 2000) and for 5, 10 and 20 vol% exsolved gas.

4.2 Boron and boron isotopes

The combination of boron and boron isotopes is an effective tracer of the volatile contribution from slab-derived fluids, because: 1) boron acts conservatively and will preferentially partition into the fluid phase (Schatz et al. 2004), 2) high isotopic fractionation between the melt and the fluid ($\Delta^{11}B_{melt-fluid}$ = -6.5 ‰ at 700°C), Wunder et al. (2005), and 3) isotopes don't fractionate during magmatic processes (Ishikawa et al. 2001).

The Mamaku and Ohakuri rhyolites have an isotopic composition ranging from -3 to +3 ‰, and a homogeneous boron content around 15 ppm (Fig. 5; Table 2). In contrast, the Kaharoa rhyolite has a homogenous isotopic composition, with $\delta^{11}B$ of + 4‰, but a larger range in boron content between 20 and 30 ppm (Fig. 5; Table 2).

For comparison of the Mamaku-Ohakuri and Kaharoa signatures, we have to estimate the boron concentration and isotopic signature of the bulk magma, as boron preferentially partitions into the fluid phase (Schatz et al. 2004), and the fractionation $\Delta^{11}B_{melt-fluid}$ is large (Wunder et al. 2005).

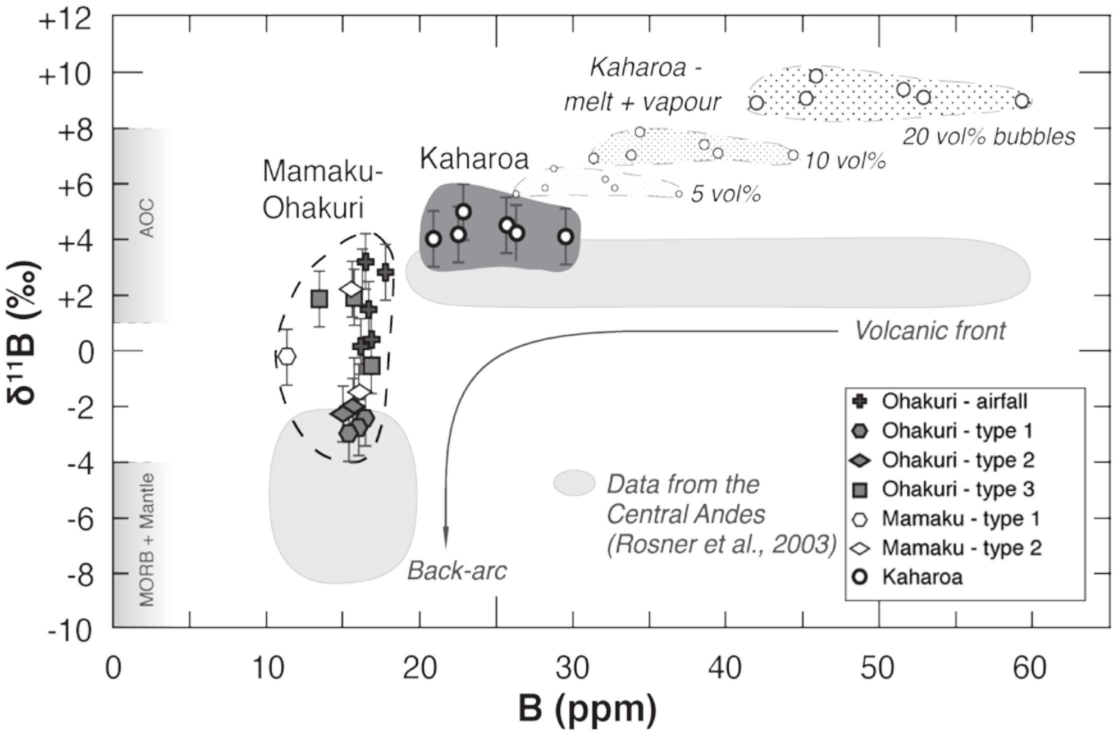

Figure 5: Plot of B (ppm) vs. $\delta^{11}B$ (‰) for the Mamaku-Ohakuri and Kaharoa (OVC) rhyolites. Compositional disparity in melt inclusion between these two these two types of rhyolite. Dotted fields represent the bulk magma B content and isotopic signature of the Kaharoa magma for 5, 10 and 20 vol% exsolved gas. $\delta^{11}B$ values for MORB, mantle and altered oceanic crust (AOC) after Chaussidon and Marty (1995) and Smith et al. (1995). Grey shaded fields and arrow represent across arc data in the Andes Central Volcanic Zone (after Rosner et al. 2006), with their interpretation of back-arc and volcanic front (text for explanations). (Error bars represent the analytical error of ±1 ‰).

We calculate the bulk boron content of the Kaharoa for 5, 10 and 20 vol% exsolved gas, using $D_B^{fluid/melt} = 4.6$ (Schatz et al. 2004). For the isotopic composition we assume a simple Rayleigh distillation model:

$$\delta^{11}B_{initial} = \left[\frac{(\delta^{11}B_{restite} + 10^3) * (B_{initial}{}^{(\alpha-1)})}{B_{restite}{}^{(\alpha-1)}} \right] - 10^3$$

where $\delta^{11}B_{restite}$ and $B_{restite}$ are the isotopic composition and concentration of the melt after exsolution of a volatile phase, i.e. the measured values in melt inclusions, and $\delta^{11}B_{initial}$ and $B_{initial}$ are the unknown bulk isotopic signature and composition. For the isotopic fractionation factor, we used the value of Wunder et al. (2005) of $\alpha = 1.0065$ at 700°C.

With 20 vol% exsolved gas, the Kaharoa boron content and isotope values shift to 60ppm and +9‰, indicating a distinct difference between Mamaku-Ohakuri and Kaharoa (Fig. 5). We compared these results to the data of the Central Andes (Rosner et al. 2003, Fig. 5). Their results show that the volcanic front has higher B content and $\delta^{11}B$ than the back-arc, which reflects a higher contribution from slab derived fluids, in contrast to a higher mantle signature in the back-arc magmas. The TVZ magmas follow a similar trend (volcanic arc vs. back-arc), which we interpret as a difference in the slab-derived fluid component that contributed to the generation of these magma types.

The boron isotopic composition of the TVZ decreases with increasing depth of the subducted slab (Fig. 6). Similar results have been observed in other subduction zones (Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Ishikawa et al. 2001; Rosner et al. 2003), and been interpreted as a decrease in fluid flux from the dehydration of the slab with an increased depth of the Wadati-Benioff Zone. For the TVZ, the Ba/La ratio and Cl results also supports this hypothesis of less slab influence for the Rotorua and Ohakuri calderas, compared to OVC. In Fig. 6, the decrease in $\delta^{11}B$ with increasing depth, considering the bulk $\delta^{11}B$ for Kaharoa (for 20 vol% exsolved gas), has a steep gradient, similar to the Eastern Kamtchatka trend. This supposedly reflects a hot and young subducting slab (Ishikawa et al. 2001, Wunder et al. 2005), but the slab of the New Zealand subduction zone is cold and old (120Ma) (Reyners et al., 2006). An alternative explanation is that subduction of the 17 km thick Hikurangi plateau beneath the North Island, which is mostly composed of heavily altered volcanic rocks (Wood and Davy 1994; Mortimer and Parkinson 1996), could have a large influence on the slab fluid flux and composition (Reyners et al. 2006) despite its age and temperature.

Another added complexity in the TVZ, which will be considered in our future work, is the influence of active rifting within the Central TVZ (and the OVC) (Fig. 1) on the slab fluid flux. Preliminary data indicates that there may be a strong relationship between slab input and vent location relative to the rift axis.

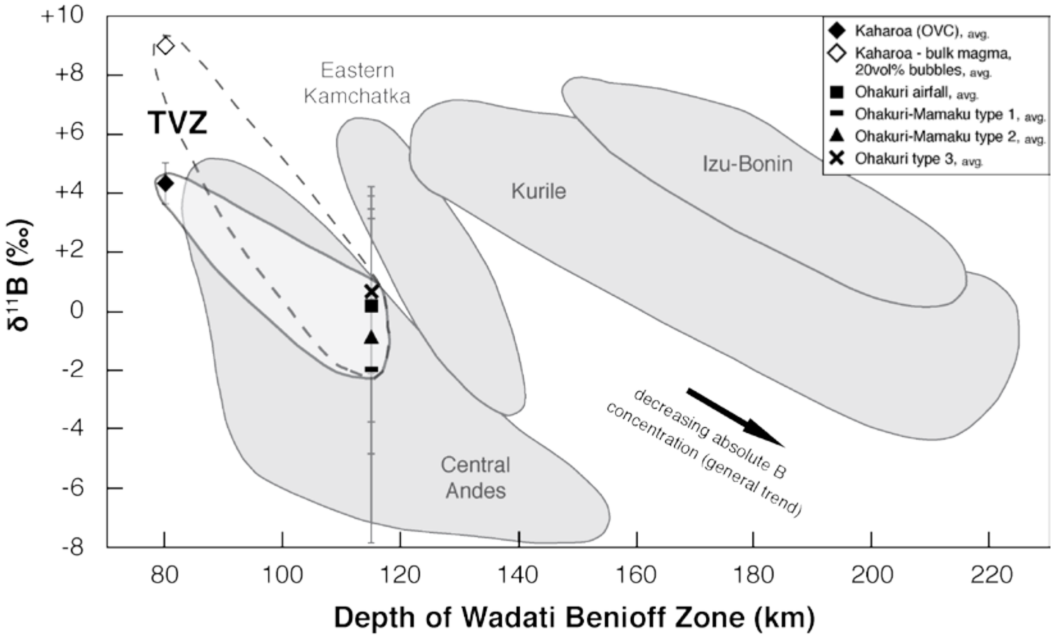

Figure 6: Plot of $\delta^{11}B$ (‰) vs. depth of Wadati Benioff Zone (WBZ), after Wunder et al. (2005). For TVZ, this study and WDB depths from Reyners et al. (2006); Central Andes, Rosner et al. (2003); Eastern Kamtchatka, Ishikawa et al. (2001); Kurile, Ishikawa and Tera (1997), Izu-Bonin, Ishikawa and Nakamura (1994). (Error bars represent 2σ errors of average values for each pumice type).

5. CONCLUSION

This volatile study on quartz-hosted melt inclusions of the 240ka Mamaku and Ohakuri rhyolites of the TVZ shows that these dry-reducing magma types were likely undersaturated in volatiles and that no immiscible phase was present during crystallization. This has important implications for assessing the heat and mass transfer from the magmatic systems to the overlying geothermal systems – as well as global volatile flux estimates. Without an exsolved volatile phase, the predominant heat transfer mechanism is conductive. In contrast, the wet and oxidizing OVC rhyolites were volatile saturated, so advection, which is a more efficient heat transfer, was more likely to be prevalent, provided that it was an open system, i.e. sufficient permeability for the gas to flux through the magmatic system and the overlying crust. As a result, our methodology can determine if a magmatic system is volatile saturated, and hence, could help identify areas in the upper crust where there is a maximum potential for heat transfer to the overlying geothermal system.

Boron and boron isotope data from these same melt inclusions reveal different signatures for the dry and Mamaku-Ohakuri and the wet and saturated Kaharoa (OVC) rhyolites. This difference is related to a decrease of the slab fluid flux with increasing distance from the trench; similar boron and boron isotope trends have been observed in other volcanic arcs around the globe.

Boron isotopes yield promising results for the TVZ; it could potentially be a very useful tracer for volatile transport processes where magmas are saturated (e.g. OVC). Future work will focus on the spatial distribution and temporal aspect of the volatiles and especially boron isotopes in the central TVZ to understand the influence of the rift structures on the slab fluid flux. Therefore, we will study the Kaingaroa eruption (Reporoa caldera) located at the eastern border of the Central TVZ, which erupted at the same time as the Mamaku and Ohakuri ignimbrites and is also a hot-dry-reducing rhyolite type (Deering et al. 2010), and the wet-oxidizing Matahina ignimbrite, that erupted 320ka ago from the OVC (Fig. 1).

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REFERENCES

Bibby, H.M.,Caldwell, T.G., Davey, F.J. and Webb, T.H., 1995. Geophysical evidence on the structure of the Taupo Volcanic Zone and its hydrothermal circulation. *Journal of Volcanology and Geothermal Research*, 68(1-3), pp.29-58.

Chaussidon, M. and Marty, B., 1995. Primitive boron isotope composition of the mantle. *Science*, 269(5222), pp.383-386.

Chaussidon, M., Robert, F., Mangin, D., Hanon, P., Rose, E.F., 1997. Analytical procedures for the measurement of boron isotope compositions by ion microprobe in meteorites and mantle rocks. *Geostandards Newsletter*, 21(1), pp.7-17.

Cole, J.W., Spinks, K.D., Deering, C.D., Nairn, I.A. and Leonard, G.S., 2010. Volcanic and structural evolution of the Okataina Volcanic Centre; dominantly silicic volcanism associated with the

Taupo Rift, New Zealand. *Journal of Volcanology and Geothermal Research*, 190(1-2), pp.123-135.

Deering, C.D., Cole, J.W. and Vogel, T. A., 2008. A Rhyolite Compositional Continuum Governed by Lower Crustal Source Conditions in the Taupo Volcanic Zone, New Zealand. *Journal of Petrology*, 49(12), pp.2245-2276.

Deering, C.D., Gravley, D.M., Vogel, T.A, Cole, J.W. and Leonard, G.S., 2010. Origins of cold-wet-oxidizing to hot-dry-reducing rhyolite magma cycles and distribution in the Taupo Volcanic Zone, New Zealand. *Contributions to Mineralogy and Petrology*, 160(4), pp.609-629.

Dunbar, N.W. and Hervig, R.L., 1992. Volatile and Trace Element Composition of Melt Inclusions from the Lower Bandelier Tuff: Implications for Magma Chamber Processes and Eruptive Style. *Journal of Geophysical Research*, 97(B11), pp.15151–15.

Gravley, D.M., Wilson, C.J.N., Leonard, G.S. and Cole, J.W., 2007. Double trouble: Paired ignimbrite eruptions and collateral subsidence in the Taupo Volcanic Zone, New Zealand. *Geological Society of America Bulletin*, 119(1-2), pp.18-30.

Ishikawa, T. and Nakamura, E., 1994. Origin of the slab component in arc lavas from across-arc variation of B and Pb isotopes. *Nature*, 370.

Ishikawa, T. and Tera, F., 1997. Source , composition and distribution of the fluid in the Kurile mantle wedge□: Constraints from across-arc variations of Br,Nb and B isotopes. *Earth and Planetary Science Letters*, 152, pp.123-138

Ishikawa, T., Tera, F. and Nakazawa, T., 2001. Boron isotope and trace element systematics of the three volcanic zones in the Kamchatka arc. *Geochimica et Cosmochimica Acta*, 65(24), pp.4523-4537.

Johnson, E.R., Kamenetsky, V.S., McPhie, J. and Wallace, P.J., 2011. Degassing of the H2O-rich rhyolites of the Okataina Volcanic Center, Taupo Volcanic Zone, New Zealand. *Geology*, 39(4), pp.311-314.

Milner, D.M., Cole, J.W. and Wood, C.P., 2003. Mamaku Ignimbrite: a caldera-forming ignimbrite erupted from a compositionally zoned magma chamber in Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research*, 122(3-4), pp.243-264.

Mortimer, N. and Parkinson, D., 1996. Hikurangi Plateau: a Cretaceous large igneous province in the southwest Pacific Ocean. *Journal of Geophysical Research*, 101(B1), pp.687-696.

Nairn, I.A., Shane, P.R., Cole, J.W., Leonard, G.J., Self, S. and Pearson, N., 2004. Rhyolite magma processes of the ~AD 1315 Kaharoa eruption episode, Tarawera volcano, New Zealand. *Journal of Volcanology and Geothermal Research*, 131(3-4), pp.265-294.

Reyners, M., Eberhart-Phillips D., Stuart G. and Nishimura Y., 2006. Imaging subduction from the trench to 300 km depth beneath the central North Island, New Zealand, with Vp and Vp/Vs. *Geophysical Journal International*, 165(2), pp.565-583.

Rosner, M., Erzinger, J., Franz, G. and Trumbull, R.B., 2003. Slab-derived boron isotope signatures in arc volcanic rocks from the Central Andes and evidence for boron isotope fractionation during progressive slab dehydration. *Geochemistry Geophysics Geosystems*, 4(8).

Rosner, M., Wiedenbeck, M. and Ludwig, T., 2008. Composition-Induced Variations in SIMS Instrumental Mass Fractionation during Boron Isotope Ratio Measurements of Silicate Glasses. *Geostandards and Geoanalytical Research*, 32(1), pp.27-38.

Rowland, J.V., Wilson, C.J.N. and Gravley, D.M., 2010. Spatial and temporal variations in magma-assisted rifting, Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research*, 190(1-2), pp.89-108.

Signorelli, S. and Carroll, M., 2000. Solubility and fluid-melt partitioning of Cl in hydrous phonolitic melts. *Geochimica et Cosmochimica Acta*, 64(16), pp.2851–2862.

Schatz, O.J., Dolejs, D., Stix, J., Williams-Jones, A.E. and Layne, G.D., 2004. Partitioning of boron among melt, brine and vapor in the system haplogranite-H2O-NaCl at 800 °C and 100 MPa. *Chemical Geology*, 210(1-4), pp.135-147.

Smith, H.J., Spivack, A.J., Staudigel, H. and Hart, S.R., 1995. The boron isotopic composition of altered oceanic crust. *Chemical Geology*, 126(2), pp.119–135.

Wallace, P.J., Anderson, A.T. and Davis, A.M., 1995. Quantification of pre-eruptive exsolved gas contents in silicic magmas. *Nature*, 377(19), pp.612–616.

Wallace, P., 2001. Volcanic SO2 emissions and the abundance and distribution of exsolved gas in magma bodies. *Journal of Volcanology and Geothermal Research*, 108(1-4), pp.85-106.

Wallace, L.M., McCaffrey, R. and Desmond, D., 2004. Subduction zone coupling and tectonic block rotations in the North Island, New Zealand. *Journal of Geophysical Research*, 109(B12), pp.1-21.

Webster, J.D. and Holloway, J.R., 1988. Experimental constraints on the partitioning of Cl between topaz rhyolite melt and H_20 and $H_20 + CO_2$ fluids□: New implications for granitic differentiation and ore deposition. *Geochimica et Cosmochimica Acta*, 52, pp.2091-2105.

Webster, J.D., 1997. Chloride Solubility in Felsic Melts and the Role of Chloride in Magmatic Degassing. *Journal of Petrology*, 38(12), pp.1793-1807.

Wilson, C.J.N., Houghton, B.F., Mcwilliams, M.O., Lanphere, M.A., Weaver, S.D. and Briggs, R.M., 1995. Volcanic and structural evolution of Taupo Volcanic Zone, New Zealand: a review. *Journal of*

Volcanology and Geothermal Research, 68(1-3), pp.1-28.

Wilson, C. J. N., Gravley, D. M., Leonard, G. S. and Rowland, J. V., 2009. Volcanism in the central Taupo Volcanic Zone, New Zealand: tempo, styles and controls. In: T. Thordarson, G. Larsen, S. K. Rowland, S. Self, A. Hoskuldsson (eds.) Studies in Volcanology: The Legacy of George Walker. Special Publications of IAVCEI 2, 225-247. Geological Society, London.

Witter, J.B. and Kuehner, S.M., 2004. A simple empirical method for high-quality electron microprobe analysis of fluorine at trace level in Fe-bearing minerals and glasses. *American Mineralogist*, 89(1), p.57.

Wood, R. and Davy, B., 1994. The Hikurangi Plateau. *Marine geology*, 118, pp.153-173.

Wunder, B., Meixner, A., Romer, R.L., Wirth, R. and Heinrich, W., 2005. The geochemical cycle of boron: Constraints from boron isotope partitioning experiments between mica and fluid. *Lithos*, 84(3-4), pp.206-216