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Link Between Magmatic Degassing and Geothermal Systems; Taupo Volcanic Zone, New Zealand

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ABSTRACT

The central segment of the Taupo Volcanic Zone (TVZ) is one of the world's most productive areas of silicic volcanism and geothermal activity. Rhyolites and their pyroclastic equivalents largely predominate the eruptive output in the central TVZ, with only minor basalts, andesites and dacites. Identifying the magmatic input into the hydrothermal systems is not straightforward due to the diluted nature of the hydrothermal fluids. The high temperature geothermal systems have previously been subdivided into two groups; 1) low-gas (i.e. CO_2), high Cl, low B and Li/Cs ratio systems suggested to have chemical affinities with basaltic (and rhyolitic) magmas related to back-arc fluids, or hereafter 'rift fluids', on the western side of the central TVZ, and 2) high-gas, low Cl, high B and Li/Cs ratio systems having chemical affinities with andesitic magmas, related to 'arc fluids' along the eastern border.

Here, we investigate the relationship between the chemistry of the geothermal fields and the volatiles dissolved in the magmas erupted nearby. We present magmatic volatile and fluid-mobile element compositions (i.e. H_2O, Cl, F, Li, B, Cs) from rhyolitic melt inclusions of the central TVZ. Rhyolitic magma compositions are subdivided into two types (R1 and R2) showing significant differences in their volatile concentrations in melt inclusions. The R1 melt inclusions have a Cl/H_2O ratio of ~ 0.04 indicating exsolution dominated by a vapour phase, and R2 melts have a ratio of ~ 0.075 indicating exsolution dominated by a hydrosaline phase. We calculate degassing trends for R1 and R2 melt compositions and estimate Cl concentrations of the magmatic volatile phase (vapour and hydrosaline phase). These results indicate that there should be a considerable effect on the magmatic fluid composition contributing to the hydrothermal systems depending on the type of rhyolite residing in the subsurface. Andesitic melt inclusions from the southern TVZ (Mt. Ruapehu) have a significantly lower Cl concentration and are not likely to exsolve a hydrosaline fluid phase (at the time of melt inclusion entrapment).

Hydrothermal fluids in the central TVZ have maximum Cl concentrations of ~2500 ppm (in geothermal wells), considering their diluted nature (>90 % meteoric water), these fluids must have interacted with another Cl-rich fluid of magmatic origin. Considering the likely exsolution of a highly concentrated hydrosaline fluid from R2 magmas, there is a possibility that the 'arc' and 'rift' hydrothermal systems have a significant rhyolitic fluid component (even the systems on the eastern border of the central TVZ). A comparison of B among greywacke samples, melt inclusions, and hydrothermal fluids indicates that there is a B enrichment likely related to fluid-rock interaction with greywacke basement. In particular, the southern TVZ melt inclusions from Mt. Ruapehu have two to four times more B than the central TVZ melt inclusions.

Boron and Cl concentrations in the hydrothermal system for the central and southern TVZ plot along distinct trends suggesting mixing between meteoric water and at least four end-member fluid compositions. Among these end-members are: three distinct magmatic fluids compositions, with R1, R2 and andesitic fluids, and chemical constituents leached from the greywacke basement and/or other host-rocks in the geothermal fields.

1. INTRODUCTION

Magmatic degassing in volcanic hosted hydrothermal systems plays a key role in terms of hydrothermal alteration and mineralisation, and heat and mass transfer. Degassing may occur during several stages, from the initial establishment of a magmatic system (e.g. Anderson et al., 1989; Wallace and Gerlach, 1994; Wallace, 2005 for a review) to eruption and/or through the transition to pluton formation and intrusion-related ore-deposition (e.g. Hedenquist and Lowenstern, 1994; Lowenstern, 1994; Candela, 1997; Seedorf et al., 2005; Williams-Jones and Heinrich, 2005; Tosdal et al., 2009; Sillitoe, 2010). The exsolved volatiles associated with these different stages in the life of a magmatic system have variable compositions and phase relations, depending on pressure-temperature conditions, the solubility of the volatile species present and the composition of the magma. Consequently, the magmatic component of the hydrothermal systems can be difficult to decipher in the fluid and gas compositions of geothermal wells; in particular, in continental hosted geothermal systems (Henley and Ellis, 1983). Further complexity in characterising the magmatic component in hydrothermal fluids is related to processes that significantly change the composition of the fluid after the magmatic contribution, such as: dilution, boiling, mixing, pressure-temperature variations and fluid-rock interaction.

The rhyolite-dominated central Taupo Volcanic Zone (TVZ), New Zealand, is a good example of an active volcanic-hosted hydrothermal system where the contribution from magmatic degassing is difficult to detect and quantify. The TVZ has one of the highest heat fluxes measured globally, with a natural heat output of 4200±500 MW (Bibby et al., 1995). Large-scale fluid convective systems in the upper crust, dominated by meteoric water, are driven by an underlying magmatic heat source (e.g. Bibby et al., 1995; Hochstein, 1995). A small magmatic fluid contribution (~15% volume) has been suggested to be present in the hydrothermal fluids (e.g. Henley and McNabb, 1978; Giggenbach, 1995; Christenson et al., 2002; Simmons and Brown, 2007; Bernal et al., 2014). Several studies have focused on the chemistry of discharge water including the pioneering study by Giggenbach (1995) who proposed two types of deep supply fluids: (1) a high gas and CO_2 content and geochemical affinities similar to andesitic fluids (high B/Cl, Li/Cs, CO_2/He and N_2/Ar ratios) related to arc magmatism, and (2) a low gas and CO_2, but a higher Cl content, which has chemical affinities with rhyolitic fluids related to back-arc magmatism. A spatial distribution of these two types of hydrothermal systems has been suggested, with the first type being mostly present along the eastern side of the TVZ, which is also where the heat flux appears to be more concentrated (Fig. 1; Bibby et al., 1995), and the second type focused around the western side of the central TVZ (Giggenbach, 1995). A simplified drawing of this model is presented in Figure 2 (modified after Giggenbach, 1995; Bernal et al., 2014). Hereafter, we use the terminology of 'arc systems' vs. 'rift systems', as in Reyes and Trompetter (2012), to describe the high-gas, low Cl, and low-gas, high Cl hydrothermal systems, respectively. Importantly, this terminology should not be confused with the recognition that there is no magmatic-tectonic-volcanic distinction between arc and rift systems in the TVZ as discussed in the next section.

In this study, we test the Giggenbach (1995) model (Fig. 2) focusing on the magmatic composition and contribution to the hydrothermal systems. We use the volatile concentration from melt inclusions of the rhyolites in the central TVZ (data from Bégué et al., in press), which represent more than 90% of the eruptive deposits (Wilson et al., 1995; 2009) and andesites from the southern TVZ (data from Kilgour et al., 2013). These concentrations are used as an analogue for the present day magmatic systems.

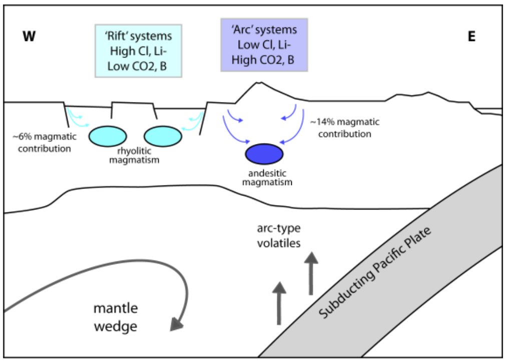

Figure 1 (left): Map of the TVZ, New Zealand. Caldera boundaries and structures after Rowland et al., (2010), resistivity contours and geothermal fields after Bibby et al., (1995). Abbreviations of geothermal fields: TO-Tokaanu, WK-Wairakei, RK-Rotokawa, MK-Mokai, NM-Ngatamariki, BR-Broadlands Ohaaki, OK-Orakei Korako, RP-Reporoa, TK-Te Kopia, WT-Waiotapu, WM-Waimangu, RO-Rotorua, TI-Tikitere, KA-Kawerau, Kt-Ketatahi, Rp-Ruapehu Crater Lake.

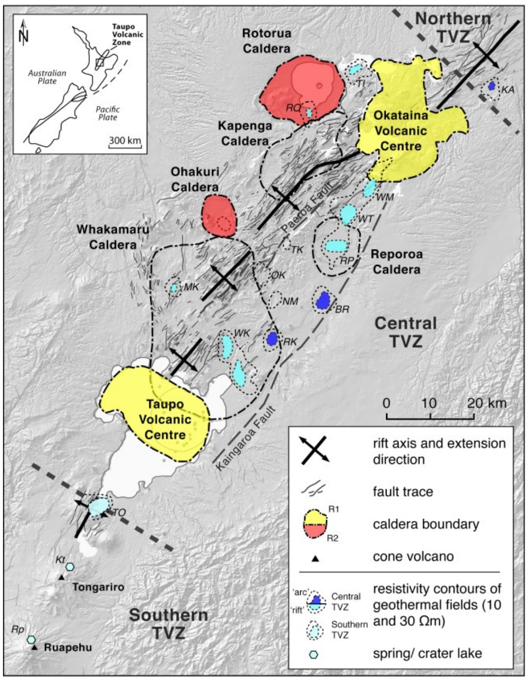

Figure 1 (top): Schematic representation of the current model of the hydrothermal fluid distribution in the central TVZ (modified after Giggenbach, 1995; Bernal et al., 2014). Arc vs. back-arc (or 'rift') distribution is suggested to be related to andesitic and rhyolitic magmatic systems.

2. TAUPO VOLCANIC ZONE

The Taupo Volcanic Zone (TVZ) is a rifted volcanic arc, which means that active rifting coexists in geographic space with arc volcanism and thus the tectonic setting is not the same as more 'classic' arc to back-arc subduction settings (Wilson et al., 1995).

The TVZ is currently subject to a NW-SE extensional regime reflecting the subduction of the Pacific plate beneath the Australian plate (e.g. Wallace et al., 2004; Reyners et al., 2006). It is magmatically and structurally segmented, with its northern and southern segments being dominated by andesitic cone-building volcanoes (Fig. 1; e.g. Wilson et al., 1995). Caldera-forming eruptions and dome complexes of rhyolitic composition largely dominate the central segment of the TVZ (> 6,000 km^3 bulk volume of rhyolites over a period of ~1.8 Ma), with only minor dacites, andesites and basalts (e.g. Houghton et al., 1995; Wilson et al., 2009). Andesitic volcanism in the southern TVZ is persistent from ~0.34 Ma (Wilson et al., 1995), and represents less than 10% in volume of the total erupted magma in the entire TVZ.

Extensive rifting in the central TVZ leads to thinning of the crust, which allows for a heavily intruded lower crustal region (from ~16 to 30 km depth; e.g. Harrison and White, 2006), and for accommodation of significant volumes of silicic magma at shallow crustal levels (~4 km; Allan et al., 2012; Shane and Smith, 2013; Bégué et al., in review). Regional tectonics related to the extensional regime are closely linked to magmatism and volcanism in the central TVZ (e.g. Wilson et al., 2009; Rowland et al., 2010), and play a significant role in reservoir depth of the magmatic systems, magma transport, and eruptive processes (Gravley et al., 2007; Allan et al., 2012). These regional faults also form essential pathways for fluids circulating in the upper crust (e.g. Rowland and Sibson, 2004; Rowland and Simmons, 2012).

2.1 TVZ Magmatism

Current models for the petrogenesis of voluminous rhyolites in the central TVZ involve multiple stages of crustal assimilation and fractional crystallisation processes (AFC) from a basaltic parent (e.g. McCulloch et al., 1994; Graham et al., 1995; Price et al., 2005; Deering et al., 2008; 2011). A significant mantle component in the silicic magmas has been suggested, with <25 % assimilation in the lower crustal region (e.g. McCulloch et al., 1994), based on Pb, Nd, Sr, and O isotopes. From recent bulk-rock data on the erupted basalts, Rooney and Deering (2014) established a strong genetic connection between two distinct types of basalt with two types of rhyolites.

The two types of rhyolites represent two end-member compositions based on their relative bulk-rock and mineral chemistry and petrography (Deering et al., 2008; 2010). Hereafter the terminology R1 and R2 is used to distinguish between the two end-member rhyolite types; the main characteristics between R1 and R2 are summarized in Table 1 and a simplified spatial distribution of the main caldera centres producing these two rhyolite types is shown in Figure 1. The compositional variability present in the rhyolites has been suggested to reflect differences in melting and magma generation. Consequently, changes in fH_2O, fO_2, and P-T conditions in the lower- to mid-crust (15-30 km), where the evolved magmas are generated through fractionation and melt extraction from crystal-rich residues from repeated basalt intrusions are present (Deering et al., 2008; 2011).

Table 1. Summary of the main characteristics of R1 and R2 rhyolites and recent southern TVZ andesites.

	Central TVZ rhyolites				Southern TVZ andesites	
	R1	***Std. Dev.***	**R2**	***Std. Dev.***	**Ruapehu**	***Std. Dev.***
Mineral assemblage	qtz + plg + opx ± bt ± hbl ± cum		qtz + plg + opx ± hbl		plg + cpx + opx	
Crystallinity (%)	~15-30		<10		25 - 40 %	
Melt inclusions (avg. in ppm)						
H_2O (wt.%)	4.8	1	4.2	0.6	1.4	0.4
Cl	2000	130	2900	500	715	210
F	255	130	550	110	1040	260
B	25	3	15	2	55	9
Li	68	14	58	16	42	9
Cs	3	1	5	1	-	-

bt-biotite; cum-cumingtonite; hbl-hornblende; opx-orthopyroxene; cpx-clinopyroxene; plg-plagioclase; qtz-quartz

Compilation from the following sources: Liu et al. (2006); Deering et al. (2008); Johnson et al. (2011); Kilgour et al. (2013); Bégué et al. (in press).

2.2 Magmatic volatile compositions in the TVZ

Bégué et al. (in press) show significant variation in the volatile composition between that R1 and R2, based on quartz-hosted melt inclusion data. The volatile content (i.e. H_2O, Cl, F, CO_2, S) are summarised in Table 1. R2 has high Cl and F concentrations (~2900 ppm and ~550 ppm respectively) and slightly lower H_2O concentration (~4 wt%) compared to R1 (~2000 ppm Cl, ~255 ppm F, and ~5 wt.% H_2O; Fig. 3; Table 1). CO_2 concentrations are low and share a similar range for R1 and R2, and S is below detection limit (Liu et al., 2006; Johnson et al., 2011; Bégué et al. in press). The distinct volatile concentrations in both rhyolite types are suggested to originate from multiple igneous processes from a more primitive melt and subsequent degassing histories (Bégué et al. in press). Furthermore, prior to melt inclusion entrapment, R1 rhyolites were saturated in Cl and H_2O, and R2 rhyolites were likely under-saturated or close to saturation (Bégué et al., in press). These degassing histories/differentiation is developed and discussed more below, but an important initial conclusion is that not all rhyolites (even within the same volcanic area) have the same bulk volatile concentration or degassing histories. From this conclusion, diverse compositions of magmatic volatile phases can be expected, which potentially can contribute differently to the magmatic signature in the hydrothermal systems.

Kilgour et al. (2013) present the first volatile data from pyroxene- and plagioclase-hosted melt inclusions from andesites in the southern TVZ. This study focuses on the more recent, small eruptions occurring between 1945 and 1996 from Ruapehu (Fig. 1). Volatile and fluid-mobile element concentrations are summarised in Table 1; overall, the analysed eruptives seem to represent relatively dry melts (low average H_2O of ~1.5 wt.%, Fig. 3a) in comparison to other arc andesites (Kilgour et al., 2013). Larger Ruapehu eruptions are shown to have higher H_2O concentrations (~4.5 wt.%, Pardo Villaveces, 2012). However, other volatile and trace element concentrations are to date not available for these eruptions. In comparison to the central TVZ rhyolites, the andesites have lower Cl concentrations (Fig. 3), and a much higher B and F concentration (Fig. 3). The high B concentrations in the melt inclusions are likely the result of assimilation of the B-rich greywacke basement (Reyes and Trompetter, 2012), suggested to be an important contributor to the petrogenesis of these andesites, shown with isotopic and trace element studies (e.g. Graham and Hackett, 1987; Price et al. 2012).

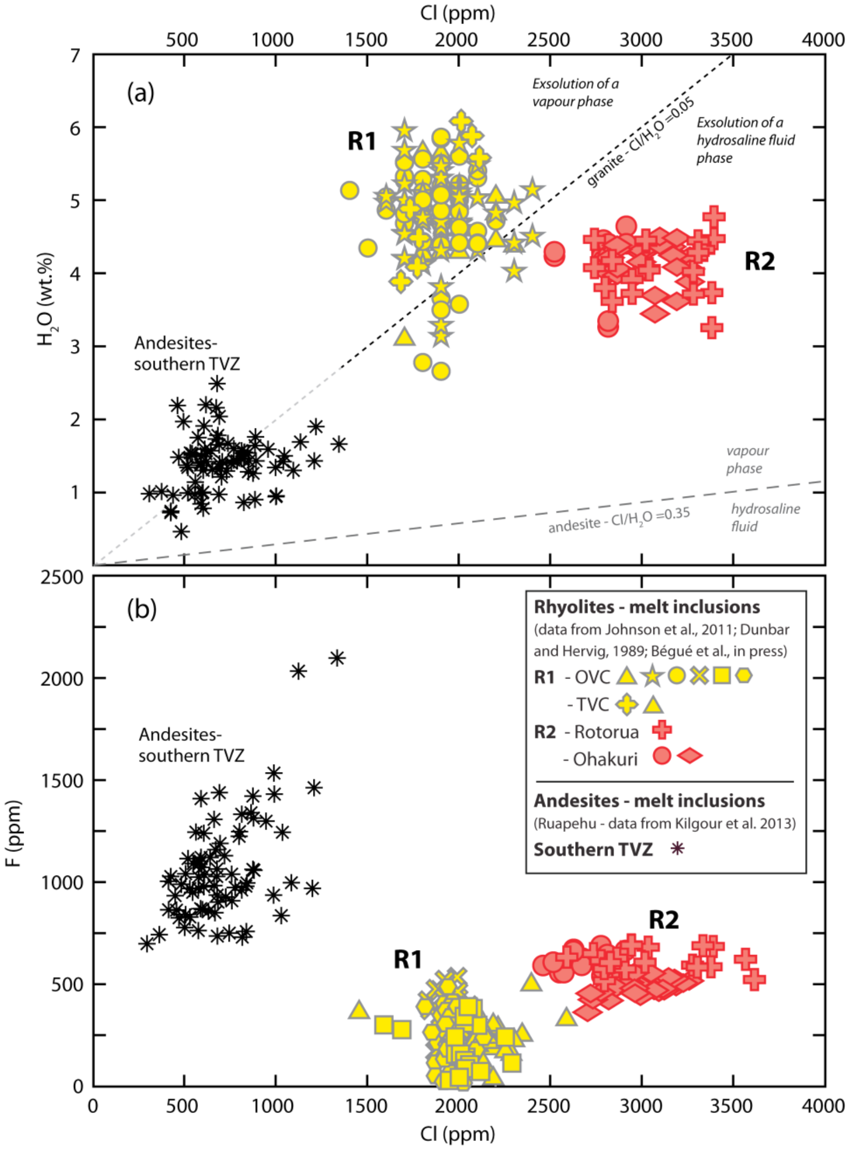

Figure 2: Summary of volatile disparities between R1 and R2 rhyolitic melt inclusions (data from Bégué et al., in press; H_2O data for R1 from Dunbar and Hervig, 1989; Liu et al. 2006; Johnson et al., 2011) and andesitic melt inclusions (southern TVZ; Kilgour et al., 2013) – (A) H_2O vs. Cl, and (B) F vs. Cl. The black dashed line in (A) represents a Cl/H_2O ratio of 0.05 (from experimental studies on granitic compositions at 200 MPa; Webster, 2004), and the grey dashed line is a Cl/H_2O ratio of 0.35 (andesitic melt compositions at 200 MPa); for compositions above the line, exsolution of a vapour phase only is suggested, and below the line a hydrosaline fluid phase (e.g. Webster, 2004).

3. MAGMATIC VOLATILE DIFFERENTIATION

Volatile degassing is an important process in magmatic systems, and influences the style of volcanic eruptions and contributions of chemical species to the atmosphere. Degassing is also a major control on hydrothermal alteration and mineralisation. In magmatic systems, volatile saturation can occur at different stages of the magmatic history, depending on pressure, temperature and composition of the system, either through decompression-driven or crystallisation-driven degassing. Exsolution of a volatile phase occurs when a volatile species (i.e. H_2O, CO_2, Cl, F, S) reaches saturation, which is strongly dependent on the solubility of each volatile element. Volatile saturation can occur at considerable depth, especially for insoluble species such as CO_2 (Lowenstern, 2001; Wallace, 2005), and it is also possible for magmas to become volatile saturated (e.g. in CO_2) before and independently of

H_2O-rich volatile saturation (Witham et al., 2012). Exsolution of a volatile phase(s) in natural systems has been recognised through fluid and melt inclusion studies in intrusive and extrusive rocks, intrusion related fossil hydrothermal systems, as well as surface gas flux surveys in volcanic areas. Direct evidence of magmatic volatile exsolution is represented by greisens (i.e. autogenic alteration of plutonic rock as a result of interaction with magmatic fluids), and other intrusion related ore deposits. Pegmatites may also be related to crystallisation in the presence of magmatic volatile phases (e.g. Cerni et al., 2012; London and Morgan, 2012).

In parts of a silicic magma system, subsolidus conditions play an important role in allowing magma to remain in the upper crust to form plutons (e.g. Bachmann et al., 2007; Lipman 2007, and references therein). In the TVZ, evidence for this is recorded in plutonic lithics present in many ignimbrites (Brown et al., 1998; Burt et al., 1998; Shane et al., 2012). Further, the 0.71-0.65 Ma Ngatamariki intrusive complex (microdiorite, diorite, tonalite and mafic dykes) which was intercepted by three wells at ~2 km depth represents the only known occurrence of in-situ plutonic rocks in the TVZ (Browne et al., 1992; Chambefort et al., 2014), and is further evidence for emplacement of shallow plutons. The intrusive-extrusive ratio (i.e. non erupted vs. erupted melt) is poorly constrained for the central TVZ (Deering et al., 2011); commonly this ratio is suggested to be between 3:1 and 5:1 for most magmatic systems associated with subduction zones (Crisp, 1984; White et al., 2006; Deering et al., 2011). Regardless of the correct ratio, we can assume that large portions of un-erupted magma likely reside in the upper crust, and their degassing is part of the global volatile flux and contributes (mass and heat) to overlying hydrothermal systems.

Evidence for magmatic volatile exsolution in the central TVZ has been shown or invoked in many studies, with: (1) pre-eruptive degassing from melt inclusion studies in the Okataina Volcanic Centre and Oruanui rhyolites (Taupo Volcanic Centre; Fig. 1) (R1 rhyolites; Liu et al., 2006; Johnson et al., 2011); (2) hypersaline multiphase fluid inclusions in the Ngatamariki plutonic complex and related hydrothermal system (e.g. Christenson et al., 1998); (3) high CO_2 soil gas flux (e.g. Rotorua area, Werner and Cardellini, 2006) with a significant magmatic $\delta^{13}C$ component (e.g. Rotokawa geothermal field, Bloomberg et al., in review) and calcite deposition with a $\delta^{13}C$ magmatic signature (e.g. Ngatamariki geothermal field; Horton et al., 2012); (4) an anomalously high Au and Ag flux in the central TVZ hydrothermal systems linked to degassing of magma at depth (Simmons and Brown, 2007); and (5) high temperature acid alteration, fluorine mineralisation (topaz and fluorite) and metal and rare-earth elements enrichment (greisen type) of the hydrothermal alteration halo above the Ngatamariki intrusive complex, indicating late-stage exsolution of the more soluble species (Lewis et al., in review).

R1 and R2 rhyolites have distinct bulk volatile concentrations, and the melt inclusions represent distinct degassing histories. Pressure conditions for these two types (~100 MPa; e.g. Allan et al., 2012; Shane and Smith, 2013; Bégué et al., in review) suggest that, instead of exsolving one single aqueous phase, fluid immiscibility occurs (e.g. Metrich and Rutherford, 1992; Shinohara, 1994; Webster, 2004). The relative concentrations of Cl and H_2O in the melt and coexisting volatile phase will be a determining factor for the phase(s) exsolving from the melt (e.g. Shinohara, 1994). The TVZ rhyolites show distinct Cl/H_2O ratios with R1 being ~0.04 (Johnson et al., 2013) and R2 being ~0.075 (Bégué et al., in press; Fig. 3a). Experimental studies on granitic melts (at 200 MPa) demonstrate that exsolution of a vapour phase only occurs if the Cl/H_2O is less than 0.05, whereas exsolution of a vapour and co-existing hydrosaline fluid is more likely with Cl/H_2O higher than 0.05 (Webster, 2004). This ratio likely increases at lower pressure conditions and for andesitic melt compositions (0.35; Fig. 3a; Metrich and Rutherford, 1992; Webster, 2004). As already suggested by Johnson et al. (2013) for the OVC rhyolites, these results show that volatile saturated R1 rhyolites would more likely just exsolve a vapour phase before eruption. Whereas, R2 rhyolites, with their higher Cl/H_2O ratio, are more likely to exsolve an immiscible low-density vapour and a high-density hydrosaline fluid phase (Fig. 3a). Many studies on the genesis of magmatic-hydrothermal ore deposits focus on the phase relations of the exsolved magmatic phase(s), as it plays an essential role in the partitioning of metals and other fluid-mobile elements (e.g. Hedenquist and Lowenstern, 1994; Harris et al., 2003; William-Jones and Heinrich, 2005; Audétat et al., 2008; Zajacz et al., 2008, 2012). Hence, the results presented here may have significant implications for metal transport and deposition in silicic environments.

4. LINK BETWEEN MAGMATIC DEGASSING AND HYDROTHERMAL SYSTEMS

The hydrothermal systems in the central TVZ have been previously subdivided into two distinct groups; the ‘arc’ (andesite) and ‘rift’ (rhyolite) systems, based on differences in composition and stable isotopes of fumaroles, hot springs and pools (e.g. Giggenbach 1995; Bernal et al., 2014); here we focus on Cl and B concentrations (Fig. 4-5). Data on hydrothermal fluids used in this study come from the following sources: Christenson and Wood (1993), Giggenbach (1995), Christenson (2000), Christenson et al. (2002), REGEMP II (2013) and Bernal et al. (2014). In a bivariate plot illustrating Cl vs. B (Fig. 4), hydrothermal fluids plot along linear trends radiating from the origin (i.e. the meteoric water composition). Four groups are discernible from the difference in slope of the trend line (Fig. 4): (1) the Ketatahi springs (southern TVZ) have almost no Cl and follow the y-axis, (2) the ‘arc systems’ of the central TVZ and the Tokaanu geothermal field, which is at the boundary between central and southern TVZ (Fig. 1), (3) the ‘rift systems’ from the central TVZ, and (4) the Ruapehu hydrothermal system (southern TVZ), with very low B and high Cl concentrations. These trends indicate mixing between meteoric water and other end-member compositions having diverse B and Cl concentrations. From the current knowledge on the TVZ, the other potential end-member compositions for these hydrothermal systems are magmatic fluids and chemical constituents leached from greywacke basement and other host-rocks in the geothermal fields.

The volatile compositions of melt inclusions represent a starting point in inferring the composition of primary magmatic fluids exsolving from the most evolved magmas; however, as mentioned earlier, the compositions may reflect already degassed melt (e.g. R1; Fig. 4a). We can predict the composition of the volatile phase based on calculations of degassing trends assuming exsolution of a vapour phase and/or a hydrosaline fluid (Fig. 4b). In our calculations, we use a simple approach that assumes constant partition coefficients, 100% incompatibility in crystallising minerals, and isobaric, isothermal and isocompositional conditions. The partition coefficients are from Webster et al. (1989), Schatz et al. (2004) and Zajacz et al. (2008). Importantly, closed-system degassing is also considered until the exsolved gas reaches ~20-30 vol.%, representing the percolation threshold (i.e. sufficient gas is exsolved for bubble coalescence to create permeability in the melt, allowing the volatiles to escape the magmatic system; Candela, 1991; Huber et al., 2012). In the case of exsolution of a hydrosaline fluid (as suggested for R2 rhyolites, Fig. 3a), Cl concentrations of that fluid will be high (up to 30 wt.% Cl from fluid inclusion data from the Ngatamariki geothermal field; Chambefort et al., Pers.

Comm., in prep) and will plot off the diagram in Figure 4. The results from the degassing trends support the premise that melt inclusion data and accounting for volatile degassing histories cannot be underestimated when characterising and quantifying the magmatic component in hydrothermal fluids.

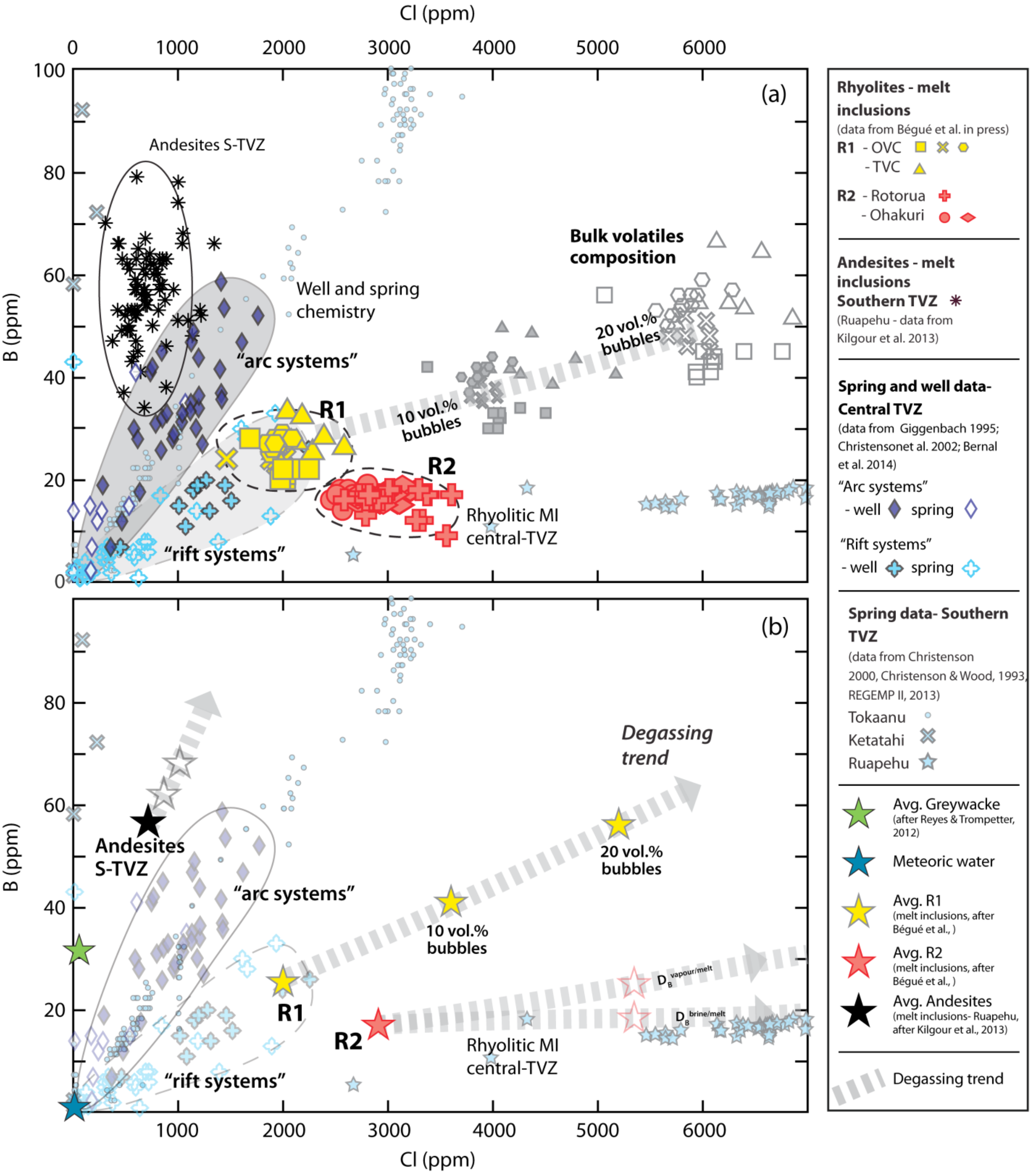

Figure 4: Variations of Cl vs B (in ppm) for hydrothermal fluids and rhyolitic and andesitic melt inclusions (Kilgour et al., 2013; Bégué et al., in press); average greywacke composition after Reyes and Trompetter (2012). Bulk volatile concentration of R1 magma are calculated using a simplified degassing trend for 20 vol.% exsolved volatile phase; partitioning coefficients after Webster et al. (1989), Schatz et al. (2004) and Zajacz et al. (2008; 2012) (rhyolites: $D_{Cl}^{volatile/melt}$ ~ 8; $D_B^{volatile/melt}$ ~ 6; $D_B^{brine/melt}$ ~ 1.4; andesites $D_{Cl}^{volatile/melt}$ ~2.1; $D_B^{volatile/melt}$ ~ 1.2). Chlorine concentrations for R2 melts and 20 vol.% bubbles are off the chart.

Hydrothermal fluids from the southern TVZ show a very large diversity in B and Cl (Fig. 4 and 5). The Ruapehu hydrothermal system has an anomalously high Cl and very low B concentrations (Christenson and Wood, 1993; Christenson, 2000), which contrasts to the relatively low Cl content in the andesitic melt inclusions (Fig. 4-5; Kilgour et al., 2013). The high H_2O/Cl ratio of the andesitic magmas requires that the Cl will more likely be partitioned into the vapour phase (Fig. 3a; e.g. Webster, 2004; Zajacz et al., 2012), however, there is not sufficient Cl in the melt to explain a contribution of ~7000 ppm to the Ruapehu crater lake. These results are likely to indicate hydrothermal processes (e.g. shallow boiling) concentrating Cl in the lake, as suggested by

Christenson et al. (2000). In contrast to the Ruapehu hydrothermal system, Ketatahi springs (Tongariro) follow a very different trend, with very low Cl and high B concentrations, which exemplifies the effect of fluid-rock interaction. Fluid-rock interaction is an important contributor to hydrothermal fluid chemistry in the TVZ (see Ellis and Mahon, 1964, 1967, 1977; Henley and Ellis, 1983; Giggenbach, 1989; Reyes and Trompetter, 2012), and, in particular, dissolution and leaching from volcanic host rocks significantly affects boron (Fig. 5; Reyes and Trompetter, 2012). Additionally, greywacke, which has been encountered in deep wells in almost every high-enthalpy geothermal field explored in the central TVZ (i.e. Kawerau, Broadlands-Ohaaki, Rotokawa, Ngatamariki, Tauhara; e.g. Alcaraz et al., 2012) can have considerable B concentrations (e.g. Reyes and Trompetter, 2012).

In the central TVZ, the 'arc' and 'rift' systems plot along two distinct linear trends, representing different B/Cl ratios (Fig. 4); the 'arc' systems have up to ~1800 ppm, and the 'rift' systems up to ~2500 ppm Cl concentrations. These concentrations are high considering that these fluids are strongly diluted with meteoric waters, with the magmatic contribution suggested to be only ~14 % for the 'arc' and ~6 % for the 'rift' systems (Giggenbach, 1995). Hence, these results suggest mixing with a fluid of high Cl concentration. Considering the Cl content in the melt inclusions (Fig. 3-5), such high-Cl fluids would less likely be produced from an andesitic magma, with similar composition to the melt erupted from Ruapehu the past ~50 years, compared to a rhyolitic magma, as Cl is less soluble and has a higher partition coefficient between the vapour phase and the melt in rhyolites (e.g Metrich and Rutherford, 1992; Shinohara, 1994; Webster, 1997; Zajacz et al., 2012). Additionally, exsolution of hydrosaline fluids are likely to be associated with rhyolitic magmatism, particularly with R2 magmas (Fig. 3a), or during late-stage sub-solidus crystallisation of plutons.

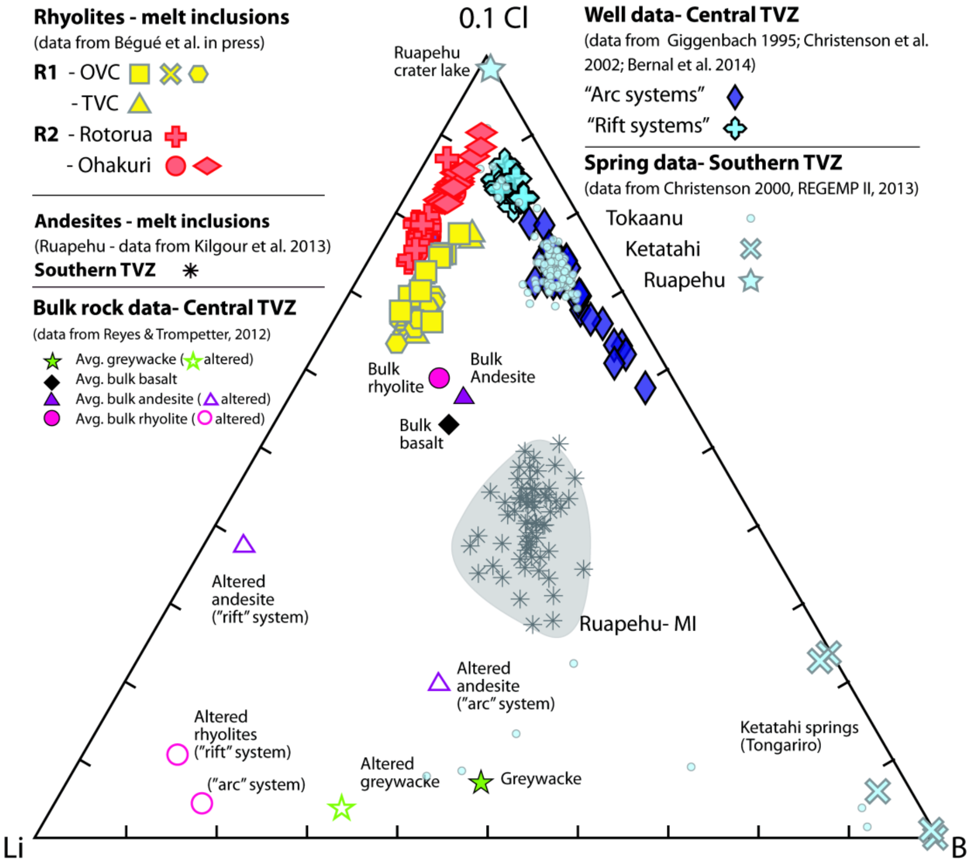

Figure 5: Summary of concentrations of Cl, Li, and B for well and spring data; rhyolitic and andesitic melt inclusions, and bulk-rock chemistry (fresh and altered) of rhyolites, andesites, basalts and greywacke (modified after Reyes and Trompetter, 2012).

Differentiation between the two groups of hydrothermal systems in the central TVZ has also been based on the CO_2 concentrations, with the high-gas 'arc' systems suggested to be andesite related, and low-gas rhyolite-related 'rift' systems (Giggenbach, 1995). CO_2 concentrations in the rhyolitic melt inclusions are low to absent in both R1 and R2 melts (Liu et al., 2006; Johnson et al., 2011; Bégué et al., in press). This can be explained by low CO_2 solubility at the shallow depths associated with the rhyolitic magmas and it has been shown in numerous studies that CO_2 exsolution and degassing occurs in deeper crustal mafic systems (e.g. Lowenstern 2001; Wallace, 2005). In the central TVZ, CO_2 degassing may occur in the deeper-seated magmas, but to date there are no published data on the volatile concentration of the TVZ basalts. Similar conclusions have been drawn for Yellowstone, where the high CO_2 likely derives from large volumes of mafic magma intruding the lower crust (Lowenstern and Hurwitz, 2008). This also suggests that Cl and CO_2 are decoupled during degassing, and are very likely related to distinct magma compositions or distinct degassing paths (e.g. Wallace 2005). Therefore, their degassing will likely reflect distinct stages in the life of the magmatic systems.

From the spatial distribution of the hydrothermal systems in the central TVZ (Fig. 1, same colour coding is used in the map as in the figures 3 to 5), the 'arc' systems are concentrated along the eastern boundary of the TVZ, as suggested by Giggenbach (1995).

However, the ‘rift’ systems are not strictly limited to the western boundary, as shown in figure 1. The magmatic fluids do not seem to follow a simple distribution pattern as may be expected in other subduction zones, where the arc and the back-arc are clearly spatially separated (e.g. Fischer and Marty, 2005, Fischer, 2008), and which has been suggested in the original models (Fig. 2, Giggenbach, 1995). In the rifted-arc setting of the TVZ (i.e. no delineated difference in an arc and back-arc) the magmatic and subduction zone-related fluid/melt distribution may be controlled by different processes. From geophysical studies of the TVZ subduction system, Reyners et al. (2006) suggest that fluid/melt is focused along the actively rifting portion of the central TVZ, where rhyolitic magmatism predominates. This interpretation contrasts with conventional models on fluid/melt distribution in subduction zones, where the slab-derived fluids/melts are more concentrated along the volcanic arcs (e.g. Fig. 2). Additionally, the subducting slab in the New Zealand subduction system is twice as thick as a normal oceanic crust (subduction of the Hikurangi Plateau, 17km; e.g. Davy and Wood, 1994), which is suggested to cause more dehydration and releasing of fluids into the mantle wedge, and eventually at up to greater depth in the mantle (Reyners et al., 2006). The location of the hydrothermal systems, which has not changed in the past 0.3 Ma at least (Browne, 1979; Arehart et al., 2002), and has not been significantly disrupted by volcanic eruptions, is, therefore, more likely controlled by regional tectonics and fault permeability (e.g. Rowland and Sibson, 2004; Rowland and Simmons, 2012). The east-west distribution representing arc back-arc fluids (Fig. 1 and 2) is, thus, not an appropriate model for the central TVZ.

5. CONCLUSION

Identifying the magmatic input into the hydrothermal systems in the central TVZ is not straightforward due to: 1) the strong dilution from meteoric water, 2) multiple types of magmatic compositions, 3) the complex tectonic environment, 4) boiling of hydrothermal fluids, and 5) the potential contribution from leached continental crust. Over the past few decades several studies have focused on interpreting the type of magmatic contribution to the hydrothermal system by measuring chemical species in surface fluids. The results of these studies, summarized by Giggenbach (1995), led to the suggestion that there are two distinct contributions to the hydrothermal systems in the central TVZ. One represented the typical ‘arc’ system, had a geochemical affinity with andesitic fluids and was located along the eastern margin of the TVZ, and the second represented the typical ‘rift’ system, had a geochemical affinity with rhyolitic fluids and was located along the central and/or western region of the TVZ (Fig. 2). By utilizing melt inclusion compositions from the central TVZ rhyolites and southern TVZ andesites we re-evaluate the magmatic contribution into the hydrothermal systems, with a particular focus on B and Cl. The results of this study indicate a more diverse variety of contributions to the meteoric water in the TVZ hydrothermal systems.

Boron and Cl concentrations in the hydrothermal system plot along distinct trends suggesting mixing between meteoric water and four end-member fluid compositions having diverse B and Cl concentrations. From the volatile concentration measured in the melt inclusions, at least three distinct magmatic fluids compositions are recognised: R1, R2 and andesitic fluids. Chemical constituents leached from the greywacke basement and/or other host-rocks in the geothermal fields also represent an end-member fluid composition.

In the central TVZ, Cl concentrations in the hydrothermal systems can be up to 2500 ppm, and considering the degree of dilution with meteoric water (~90 vol.%), we suggest that this can be explained by mixing with a Cl-rich hydrosaline fluid, such as a hydrosaline fluid phase for instance. Volatile compositions of R2 melt inclusions reveal a likelihood for exsolution of such a hydrosaline volatile phase. These results also show that the current model with an east-west distribution of ‘arc’ and ‘rift’ fluids is not viable for the central TVZ. An important outcome is that melt inclusion data and their volatile degassing history have been underutilised (both in the TVZ and globally) when characterising and quantifying the magmatic component in hydrothermal fluids. For the assessment of a robust mixing model, the end-member fluid compositions contributing to the hydrothermal systems need to be better constrained.

REFERENCES

Alcaraz, S.A., Rattenbury, M.S., Soengkono, S., Bignall, G. and Lane, R. (2012) A 3D multi-disciplinary interpretation of the basement of the Taupo Volcanic Zone, New Zealand. In Proceedings, 37th workshop on geothermal reservoir engineering, Stanford, CA.

Allan, A.S.R., Wilson, C.J.N., Millet, M.-A. and Wysoczanski, R.J. (2012) The invisible hand: Tectonic triggering and modulation of a rhyolitic supereruption. Geology 40, 563–566.

Anderson, Jr. A.T., Newman, S., Williams, S.N., Druitt, T.H., Skirius, C. and Stolper, E. (1989) H2O, CO2, Cl, and gas in Plinian and ash-flow Bishop rhyolite. Geology, 17, 221–225.

Arehart, G.B., Christenson, B.W., Wood, C.P., Foland, K.A. and Browne, P.R.L. (2002) Timing of volcanic, plutonic and geothermal activity at Ngatamariki, New Zealand. Journal of Volcanology and Geothermal Research 116, 201–214.

Audetat, A., Pettke, T., Heinrich, C.A. and Bodnar, R.J. (2008) The Composition of Magmatic-Hydrothermal Fluids in Barren and Mineralized Intrusions. Economic Geology, 103, 877.

Bachmann O., Miller, C.F. and de Silva, S.L. (2007) The volcanic–plutonic connection as a stage for understanding crustal magmatism. Journal of Volcanology and Geothermal Research 167, 1–23.

Bégué, F., Gravley, D.M., Chambefort, I., Deering, C.D. and Kennedy, B.M. (in press) Magmatic volatile distribution as recorded by rhyolitic melt inclusions in the Taupo Volcanic Zone, New Zealand. In: The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas, Special Publication, Geological Society of London.

Bégué, F., Gualda, G.A.R., Ghiorso, M.S., Pamukcu, A.S., Kennedy, B.M., Gravley, D.M., Deering, C.D. and Chambefort, I. (in review) Phase-equilibrium geobarometers for silicic rocks based on rhyolite-MELTS. Part 2: Application to Taupo Volcanic Zone rhyolites. Contributions to Mineralogy and Petrology.

Bernal, N.F., Gleeson, S.A., Dean, A.S., Liu, X. and Hoskin, P. (2014) The source of halogens in geothermal fluids from the Taupo Volcanic Zone, North Island, New Zealand. Geochimica et Cosmochimica Acta 126, 265–283.

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, 29–58.

Bloomberg, S., Werner, C., Rissmann, C., Mazot, A., Horton, T., Gravley, D., Kennedy, B., and Oze, C. (in review) Soil CO_2 emissions as a proxy for heat and mass flow assessment, Taupo Volcanic Zone, New Zealand. Geochemistry, Geophysics, Geosystems (Gcubed).

Brown, S.J.A., Burt, R.M., Cole, J.W., Krippner, S.J.P., Price, R.C. and Cartwright, I. (1998) Plutonic lithics in ignimbrites of Taupo Volcanic Zone, New Zealand; sources and conditions of crystallisation. Chemical Geology 148, 21–41.

Browne, P.R.L. (1979) Minimum age of the Kawerau geothermal field, North Island, New Zealand. Journal of Volcanology and Geothermal Research, 6, 213-215.

Browne, P.R.L., Graham, I.J., Parker, R.J. and Wood, C.P. (1992) Subsurface andesite lavas and plutonic rocks in the Rotokawa and Ngatamariki geothermal systems, Taupo Volcanic Zone, New Zealand. Journal of Volcanology and Geothermal Research 51, 199–215.

Burt R.M., Brown, S.J.A., Cole, J.W., Shelley, D. and Waight, T.E. (1998) Glass-bearing plutonic fragments from ignimbrites of the Okataina caldera complex, Taupo Volcanic Zone, New Zealand: remnants of a partially molten intrusion associated with preceding eruptions. Journal of Volcanology and Geothermal Research 84, 209–237.

Candela, P. (1991) Physics of aqueous phase evolution in plutonic environments. American Mineralogist, 76, 1081–1091.

Candela, P. (1997) A Review of Shallow, Ore-related Granites: Textures, Volatiles, and Ore Metals. Journal of Petrology, 38,1619–1633.

Chambefort, I., Lewis, B., Wilson, C.J.N., Rae, A.J., Bignall, G., Coutts, C. and Ireland, T.R. (2014) Stratigraphy and structure of the Ngatamariki geothermal system: New U-Pb geochronology and its implications for Taupo Volcanic Zone evolution. Journal of Volcanology and Geothermal Research 274, 51-70.

Chambefort, I., Heinrich, C., Dilles, J.H. and Walle, M. (In preparation) From magma to mudpool: Geochemical evolution of geothermal fluids.

Christenson, B.W. (2000). Geochemistry of fluids associated with the 1995–1996 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic-hydrothermal system. Journal of Volcanology and Geothermal Research 97, 1–30

Christenson, B.W., Mroczek, E.K., Kennedy, B.M., van Soest, M.C., Stewart, M.K. and Lyon, G. (2002) Ohaaki reservoir chemistry: characteristics of an arc-type hydrothermal system in the Taupo Volcanic Zone, New Zealand. Journal of Volcanology and Geothermal Research 115, 53–82.

Christenson, B.W., Wood, C.P. and Arehart, G.B. (1998) Shallow magmatig degassing: Processes and PTX constraints for paleo-fluids associated with the Ngatamariki diorite intrusion, New Zealand. Water-Rock Interaction.

Christenson, B. and Wood, C. (1993) Evolution of a vent-hosted hydrothermal system beneath Ruapehu Crater Lake, New Zealand. Bulletin in Volcanology 55, 547–565.

Cerny, P., London, D. and Novak, M. (2012) Granitic Pegmatites as Reflections of Their Sources. Elements 8, 289–294

Crisp, J.A. (1984) Rates of magma emplacement and volcanic output. Journal of Volcanology and Geothermal Research 20, 177–211.

Davy, B. and Wood, R. (1994) Gravity and magnetic modelling of the Hikurangi Plateau. Marine Geology 118, 139–151

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, 609–629.

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, 2245–2276.

Deering, C.D., Bachmann, O., Dufek, J. and Gravley, D.M. (2011) Rift-Related Transition From Andesite to Rhyolite Volcanism in the Taupo Volcanic Zone (New Zealand) controlled by Crystal-Melt Dynamics in Mush Zones With Variable Mineral Assemblages. Journal of Petrology 52, 2243-2263.

Dunbar, N.W., Hervig, R.L. and Kyle, P.R. (1989) Determination of pre-eruptive H2O, F and Cl contents of silicic magmas using melt inclusions: Examples from Taupo Volcanic Center, New Zealand. Bulletin of Volcanology, 51, 177–184.

Ellis, A.J. and Mahon, W.A.J. (1967) Natural hydrothermal systems and experimental hot water/rock interactions (Part II). Geochimica et Cosmochimica Acta 31, 519–538.

Ellis, A.J. and Mahon, W.A.J. (1977) Chemistry and Geothermal Systems. Academic Press, New York. 392 pp.

Ellis, A.J. and Mahon, W.A.J. (1964). Natural hydrothermal systems and experimental hot-water/rock interactions. Geochimica et Cosmochimica Acta 28, 1323–1357.

Fischer, T.P. and Marty, B. (2005) Volatile abundances in the sub-arc mantle: insights from volcanic and hydrothermal gas discharges. Journal of Volcanology and Geothermal Research 140, 205-216.

Fischer, T. (2008) Fluxes of volatiles (H2O, CO2, N2, Cl, F) from arc volcanoes. Geochemical Journal, 42, 21–38.

Giggenbach, W.F. (1989) Processes cotrolling CO2-and Cl-contents of thermal discharges from the Taupo-Rotorua volcanic-magmatic-hydrothermal system, New Zealand. Proc. Int. Symp. Water-Rock Interaction 6, 259-262.

Giggenbach, W.F. (1995) Variations in the chemical and isotopic composition of fluids discharged from the Taupo Volcanic Zone, New Zealand. Journal of Volcanology and Geothermal Research, 68, 89–116.

Graham I.J, Hackett, W.R. (1987) Petrology of calc-alkaline lavas from Ruapehu volcano and related vents, Taupo volcanic zone, New Zealand. Journal of Petrology 28, 531-657.

Graham, I., Cole, J., Briggs, R., Gamble, J. and Smith, I. (1995) Petrology and petrogenesis of volcanic rocks from the Taupo Volcanic Zone: a review. Journal of Volcanology and Geothermal Research 68, 59–87.

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, 18–30.

Harris, A.C., Kamenetsky, V.S., White, N.C., van Achterbergh, E. and Ryan, C.G. (2003) Melt inclusions in veins: linking magmas and porphyry Cu deposits. Science 302, 2109–2111.

Harrison, A. and White, R.S. (2006) Lithospheric structure of an active backarc basin: the Taupo Volcanic Zone, New Zealand. Geophysical Journal International 167, 968–990.

Hedenquist, J.W. and Lowenstern, J.B. (1994) The role of magmas in the formation of hydrothermal ore deposits. Nature 370, 519–527.

Henley, R. and Ellis, A.J. (1983) Geothermal systems ancient and modern: a geochemical review. Earth-science Review 19, 1–50.

Henley, R.W. and McNabb, A. (1978) Magmatic vapor plumes and ground- water interaction in porphyry copper emplacement, Economic Geology, 73, 1-20.

Hochstein M (1995) Crustal heat transfer in the Taupo Volcanic Zone (New Zealand): comparison with other volcanic arcs and explanatory heat source models. Journal of Volcanology and Geothermal Research 68, 117–151.

Horton, T.W., Atkinson, L. and Oze, C. (2012) Hydrothermal carbonate geochemistry of the Ngatamariki subsurface reservoir, New Zealand. 37th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California.

Houghton, B.F., Wilson, C.J.N., McWilliams, M.O., Lanphere, M.A., Weaver, S.D., Briggs, R.M., Pringle, M.S. (1995) Chronology and dynamics of a large silicic magmatic system: Central Taupo Volcanic Zone, New Zealand. Geology 23, 13.

Huber, C., Bachmann, O., Vigneresse, J.L., Dufek, J. and Parmigiani, A. (2012) A physical model for metal extraction and transport in shallow magmatic systems. Geochemistry, Geophysics, Geosystems (Gcubed)13.

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, 311–314.

Johnson, E.R., Kamenetsky, V.S. and McPhie, J. (2013) The Behavior of Metals (Pb, Zn, As, Mo, Cu) During Crystallization and Degassing of Rhyolites from the Okataina Volcanic Center, Taupo Volcanic Zone, New Zealand. Journal of Petrology, 1641–1659.

Kilgour, G., Blundy, J., Cashman, K. and Mader, H.M. (2013) Small volume andesite magmas and melt–mush interactions at Ruapehu, New Zealand: evidence from melt inclusions. Contributions to Mineralogy and Petrology 166, 371–392.

Lewis, B., Chambefort, I., Rae A., Bignall, G., and Ganefianto, N. (in review) Ngatamariki: the Porphyry-Epithermal Transition in the Taupo Volcanic Zone, New Zealand. Economic Geology.

Lipman, P.W. (2007) Incremental assembly and prolonged consolidation of Cordilleran magma chambers: Evidence from the Southern Rocky Mountain volcanic field. Geosphere 3, 1-29.

Liu, Y., Anderson, A.T., Wilson, C.J.N., Davis, A.M. and Steele, I.M. (2006) Mixing and differentiation in the Oruanui rhyolitic magma, Taupo, New Zealand: evidence from volatiles and trace elements in melt inclusions. Contributions to Mineralogy and Petrology 151, 71–87.

London, D. and Morgan, G.B. (2012) The Pegmatite Puzzle. Elements 8, 263–268.

Lowenstern, J.B. (1994) Dissolved volatile concentrations in an ore-forming magma. Geology, 22, 893–896.

Lowenstern, J.B. (2001) Carbon dioxide in magmas and implications for hydrothermal systems. Mineralium Deposita, 36, 490–502.

Lowenstern, J. and Hurwitz, S. (2008) Monitoring a supervolcano in repose: Heat and volatile flux at the Yellowstone Caldera. Elements 4, 35–40.

McCulloch, M.T., Kyser, T.K., Woodhead, J.D. and Kinsley, L. (1994) Pb-Sr-Nd-O isotopic constraints on the origin of rhyolites from the Taupo Volcanic Zone of New Zealand: evidence for assimilation followed by fractionation from basalt. Contributions to Mineralogy and Petrology, 115, 303–312.

Métrich, N. and Rutherford, M.J. (1992). Experimental study of chlorine behavior in hydrous silicic melts. Geochimica et Cosmochimica Acta, 56, 607–616.

Price, R.C., Gamble, J.A., Smith, I.E.M., Stewart, R.B., Eggins, S. and Wright, I.C. (2005). An integrated model for the temporal evolution of andesites and rhyolites and crustal development in New Zealand's North Island. Journal of Volcanology and Geothermal Research, 140, 1–24.

Price, R.C., Gamble, J.A., Smith, I.E.M., Maas, R., Waight, T., Stewart, R.B. and Woodhead, J. (2012). The Anatomy of an Andesite Volcano: a Time-Stratigraphic Study of Andesite Petrogenesis and Crustal Evolution at Ruapehu Volcano, New Zealand. Journal of Petrology.

Pardo Villaveces, N. (2012). Andesitic Plinian Eruptions at Mt. Ruapehu (New Zealand): From Lithofacies to Eruption Dynamics. PhD thesis, Massey University, Palmerston North, p. 296.

REGEMP II Regional Geothermal Geochemistry Monitoring Programme (2013) Interpretation of geochemical data. Waikato Regional Council, Report: TR 2013/30; Author: Golder Associates.

Reyes, a.G. and Trompetter, W.J. (2012) Hydrothermal water–rock interaction and the redistribution of Li, B and Cl in the Taupo Volcanic Zone, New Zealand. Chemical Geology 314-317, 96–112.

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, 565–583.

Rooney, T.O. and Deering, C.D. (2014) Conditions of melt generation beneath the Taupo Volcanic Zone: The influence of heterogeneous mantle inputs on large-volume silicic systems. Geology 42, 3–6.

Rowland, J.V. and Sibson, R.H. (2004) Structural controls on hydrothermal flow in a segmented rift system, Taupo Volcanic Zone, New Zealand. Geofluids 4, 259–283.

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, 89–108.

Rowland, J.V. and Simmons, S.F. (2012) Hydrologic, Magmatic, and Tectonic Controls on Hydrothermal Flow, Taupo Volcanic Zone, New Zealand: Implications for the Formation of Epithermal Vein Deposits. Economic Geology 107, 427–457.

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, 35-147.

Seedorff, E., Dilles, J., Proffet, J., Einaudi, M., Zurcher, L., Stavast, W., Johnson, D., and Barton, M., (2005) Porphyry deposits: Characteristics and origin of hypogene features, Economic Geology 100th Anniversary Volume, p. 251-298.

Shane, P., Storm, S., Schmitt, A. and Lindsay, J. (2012) Timing and conditions of formation of granitoid clasts erupted in recent pyroclastic deposits from Tarawera Volcano (New Zealand). Lithos 140-141, 1–10.

Shane, P., Smith, V.C. (2013) Using amphibole crystals to reconstruct magma storage temperatures and pressures for the post-caldera collapse volcanism at Okataina volcano. Lithos 156-159,159–170.

Shinohara, H. (1994) Exsolution of immiscible vapor and liquid phases from a crystallizing silicate melt: Implications for chlorine and metal transport. Geochimica et Cosmochimica Acta 58,5215–5221.

Sillitoe, R. (2010) Porphyry Copper Systems, Economic Geology 105, 3-41.

Simmons, S.F. and Brown, K.L. (2007) The flux of gold and related metals through a volcanic arc, Taupo Volcanic Zone, New Zealand. Geology 35, 1099.

Stern, A.T. (1987) Asymmetric back-arc spreading, heat flux and structure associated with the central volcanic region of New Zealand. Earth and Planetary Science Letters 85, 265–276.

Tosdal, R.M., Dilles, J.H. and Cooke, D.R. (2009) From Source to Sinks in Auriferous Magmatic-Hydrothermal Porphyry and Epithermal Deposits. Elements 5, 289–295.

Wallace, P.J. (2005) Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. Journal of Volcanology and Geothermal Research 140, 217–240.

Wallace, P.J. and Gerlach, T.M. (1994) Magmatic vapor source for sulfur dioxide released during volcanic eruptions: evidence from Mount Pinatubo. Science 265, 497–9.

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, 1–21.

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

Webster, J.D. (2004) The exsolution of magmatic hydrosaline chloride liquids. Chemical Geology 210, 33–48.

Webster J.D., Holloway J.R. and Hervig R.L. (1989) Partitioning of lithophile trace-elements between H2O and H2O+CO2 fluids and topaz rhyolite melt. Economic Geology 84, 116–134.

Werner, C. and Cardellini, C. (2006) Comparison of carbon dioxide emissions with fluid upflow, chemistry, and geologic structures at the Rotorua geothermal system, New Zealand. Geothermics 35, 221–238.

White, S.M., Crisp, J.a. and Spera, F.J. (2006) Long-term volumetric eruption rates and magma budgets. Geochemistry, Geophysics, Geosystems (Gcubed) 7.

Williams-Jones, A.E. and Heinrich, C.A. (2005) Vapor transport of metals and the formation of magmatic-hydrothermal ore deposits. Economic Geology 100, 1287-1312.

Wilson, C.J.N., Houghton, B.F., Mcwilliams, M.O., Lanphere, M.A., Weaver, S.D. Briggs, R.M. (1995) Volcanic and structural evolution of Taupo Volcanic Zone, New Zealand: a review. Journal of Volcanology and Geothermal Research 68, 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: Thordarson, T., Larsen, G., Rowland, S. K., Self, S. and Hoskuldsson (eds.), Studies in Volcanology: The Legacy of George Walker, Special publications of IAVCEI 2, 225–247. Geological Society, London.

Witham, F., Blundy, J., Kohn, S.C., Lesne, P., Dixon, J., Churakov, S.V. and Botcharnikov, R. (2012). SolEx: A model for mixed COHSCl-volatile solubilities and exsolved gas compositions in basalt. Computer Geoscience 45, 87–97.

Zajacz, Z., Halter, W.E., Pettke, T. and Guillong, M. (2008) Determination of fluid/melt partition coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions: Controls on element partitioning. Geochimica et Cosmochimica Acta 72, 2169–2197.

Zajacz, Z., Candela, P.a., Piccoli, P.M. and Sanchez-Valle, C. (2012) The partitioning of sulfur and chlorine between andesite melts and magmatic volatiles and the exchange coefficients of major cations. Geochimica et Cosmochimica Acta 89, 81–101.