



Volatile behavior and trace metal transport in the magmatic–geothermal system at Pūtauaki (Mt. Edgecumbe), New Zealand



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ARTICLE INFO

Article history:

Received 19 June 2015

Received in revised form 16 February 2016

Accepted 17 February 2016

Available online 26 February 2016

Keywords:

Melt inclusion

Volatile exsolution

Andesite

Trace elements

Partition coefficient

ABSTRACT

The present-day hydrothermal system beneath the Kawerau Geothermal Field, in the Taupo Volcanic Zone, New Zealand, is likely heated from the Pūtauaki (Mt. Edgecumbe) magma system. The aim of this work, as an analog for present day processes, is to identify whether or not earlier erupted Pūtauaki magmas show evidence for volatile exsolution. This may have led to the transfer of volatile components from the magmatic to hydrothermal systems. To accomplish this, minerals and melt inclusions from volcanic products were analyzed for abundances of volatile and ore-forming elements (S, Cl, Li, Cu, Sn, Mo, W, Sb, As, and Tl). The variations in abundance of these elements were used to assess magma evolution and volatile exsolution or fluxing in the magma system. Melt inclusions suggest the evolution of Pūtauaki andesite–dacite magmas is predominantly driven by crystallization processes resulting in rhyodacite–rhyolite glass compositions (although textural and geochemical evidence still indicate a role for magma mixing). Measured mineral–melt partition coefficients for trace metals of interest indicates that, with the exception of Tl in biotite, analyzed metals are all incompatible in Pūtauaki crystallization products. Excluding Li and Cu, other volatile and ore metals recorded in melt inclusions behave incompatibly, with concentrations increasing during evolution from rhyodacitic to rhyolitic melt compositions. Li and Cu appear to have increased mobility likely resulting from diffusive exchange post-crystallization, and may be related to late volatile fluxing. Although S and Cl concentrations decrease with melt evolution, no mineralogical evidence exists to indicate the exsolution and mobility of ore-forming metals from the magma at the time of crystallization. This observation cannot rule out the potential for post-crystallization volatile exsolution and ore-forming metal mobilization, which may only be recorded as diffusive re-equilibration of more rapidly diffusing elements (e.g., Li and Cu).

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1. Introduction

The influence of magmatism on hydrothermal systems, evidenced by isotopic and trace element analyses in hydrothermal fluids and gases in volcanically active regions, is widely recognized (e.g., Hedenquist and Lowenstern, 1994; Giggenbach, 1995; Williams-Jones and Heinrich, 2005; Tosdal et al., 2009; Reyes and Trompeter, 2012; Bernal et al., 2014). Similarly, petrologic studies of porphyry systems have identified a link between intrusions and the transport of ore-forming metals in hydrothermal fluids (e.g., Kamenetsky et al., 2004; Halter et al., 2005; Chambefort et al., 2013; Mercer et al., 2015). However, fewer petrologic studies of young erupted volcanics have attempted to quantify magmatic fluid exsolution linked to active, young hydrothermal systems (e.g., Rapien et al., 2003; Rowe et al., 2008; Johnson et al., 2013; Bégué et al., 2015). This study attempts to identify volatile exsolution in the

shallow magma plumbing system that may contribute chemical components to an active geothermal system.

Volatiles are a crucial component of magmatic systems that control the transportation of metals within magmatic and hydrothermal systems (e.g., Hedenquist and Lowenstern, 1994; Johnson et al., 1994; Barnes, 1997). As magma moves through the crust, the total volatile content changes as a function of solubility of elements (decreasing upon decompression) and crystallization of the magma (increasing concentration of incompatible elements). The volatiles exsolve once saturation in the magma is reached (from ascending and cooling magmas), separating a fluid and/or a gas from the system (Burnham, 1967; Shinohara, 2008).

During volatile exsolution, ore-forming metals are likely to be incorporated into these magmatic–hydrothermal fluids most commonly as chloride (Cl^-), fluoride (F^-), various oxidized or reduced sulfur species (SO_4^{2-} , HS^- , SO_2), and hydroxyacid (OH^-) complexes during their ascent (Seward, 1981; Candela, 1989; Keppler and Wyllie, 1991; Hemley and Hunt, 1992; Johnson et al., 1994;

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Arculus, 2004; Candela and Piccoli, 2005; Seedorff et al., 2005; Nadeau et al., 2010; Sillitoe, 2010; Marques et al., 2011). Many experimental and in situ studies (Keppler and Wyllie, 1991; Simon et al., 2006; Zajacz et al., 2008, Richards, 2011; Zajacz et al., 2012) show that chalcophile (Cu, Zn, As, Ag, Sn, Sb, Pb) and siderophile (Mo, PGE, Au) elements partition strongly into the aqueous phase exsolving from silicate melts, forming porphyry and epithermal deposits in arc settings (e.g., Richards, 2011). However, exsolution and transport of metals is highly dependent on available ligands, and variables such as pressure, water saturation, sulfur oxidation state, salinity, and composition of the magma, which vary in every magmatic system (Johnson et al., 1994).

Although the measurement of volatiles (H_2O , CO_2 , S, Cl) in melt inclusions (e.g., Wallace, 2005), or fluid inclusion analyses (e.g., Rainer et al., 2005) is the preferred technique for assessing volatile saturation and exsolution, often these inclusions are unavailable, or due to conditions necessary for melt inclusion formation, may preserve only a partial magmatic record (Kent, 2008). Additionally, post-entrapment modification of melt inclusions, including diffusive exchange, may alter the volatile contents of trapped melt inclusions, obscuring original magmatic variations (e.g., Mann et al., 2013). As a proxy for volatile elements, metals, which complex into exsolving fluid phases may instead be used to understand the history of magmatic volatiles (e.g., Rowe et al., 2008). Therefore, by combining variations in trace metal abundances in minerals and melt inclusions, limited magmatic volatile data, and an understanding of the magmatic evolution, we can assess whether shallow magmatic fluids (and metals) were exsolving from the magmatic system.

This research focuses on the Pūtauaki (Mt. Edgecumbe) magma system in the northern Taupo Volcanic Zone (TVZ), New Zealand (Fig. 1).

Prior studies have identified the deep roots of the Pūtauaki magma system as the likely heat source for the Kawerau geothermal system (Christenson, 1987; Bignall and Milicich, 2012; Milicich et al., 2013, 2014). However, the degree of influence the magmatic system exerts over the volatile and trace metal chemistry of the geothermal field is relatively unknown. This study's primary objective is to determine if magmatic volatile exsolution may contribute to the composition of geothermal fluids at Pūtauaki, using previously erupted intermediate magmas as an analog for those thought to be heating the present-day geothermal system. To accomplish this, a general understanding of the evolution of the magma system is also required to put melt and crystal compositions in context.

2. Regional setting

Pūtauaki (Mt. Edgecumbe) is an andesite–dacite composite cone located at the boundary between the rhyolite-dominated central TVZ and the northern andesite-dominated region of the young TVZ (e.g., Graham et al., 1995; Wilson et al., 1995; Fig. 1a). Pūtauaki is composed of andesite, high- SiO_2 andesites, and dacite erupted from at least 10 vents (Duncan, 1970) between 8350 and 2400 year BP (Duncan, 1970; Nairn, 1995; Carroll et al., 1997). Experimental ages are constrained by tephrochronology, radiocarbon dating (Carroll et al., 1997), and stratigraphic relative ages of lava flows (Duncan, 1970; Nairn, 1995). The complex is composed of a series of base flows, lahars, and lava domes (Fig. 1b; Duncan, 1970). As a result of several dome growth-and-collapse style eruptions, the total volcanic edifice stretches nearly 3 km long and stands 821 m.a.s.l. at its highest point, with successive dome growth trending $085^\circ N$ (Duncan, 1970) (Fig. 1b).

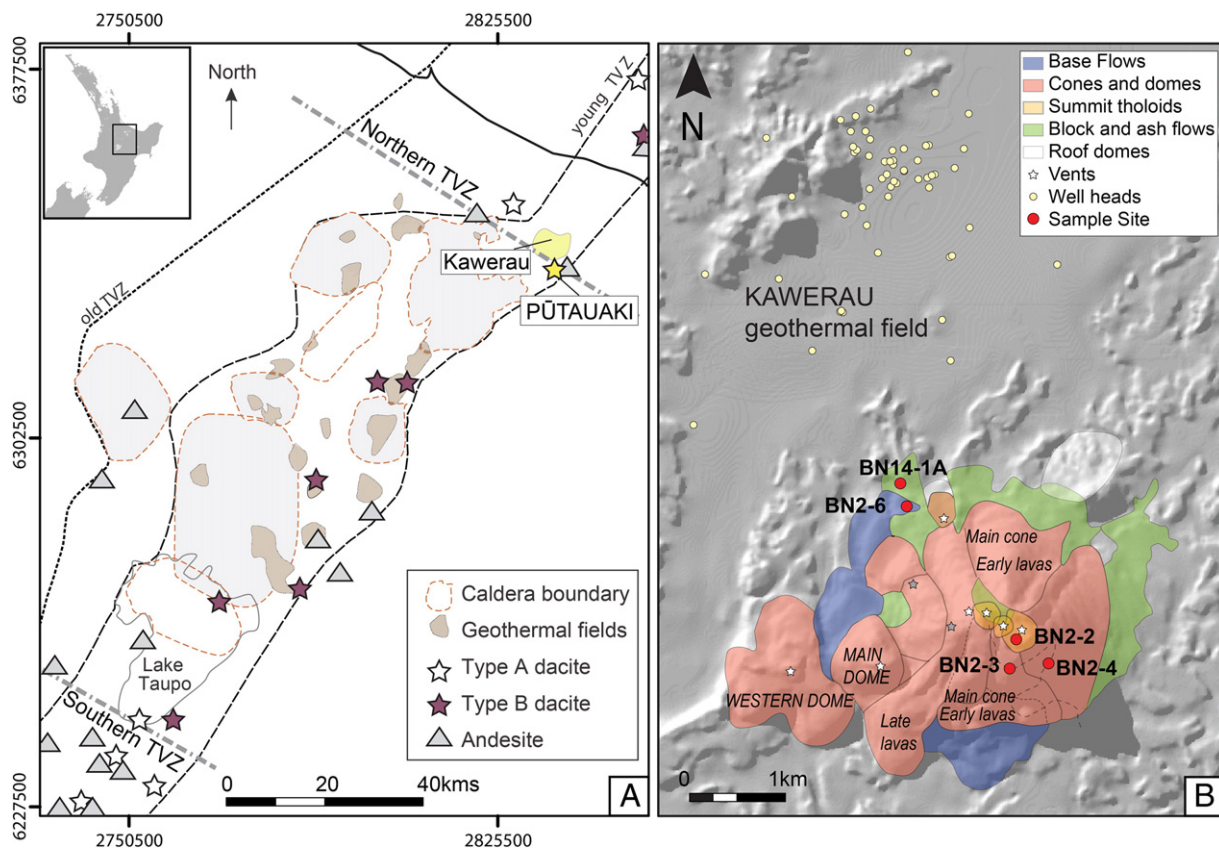


Fig. 1. (A) Location map of intermediate volcanic centers within the Taupo Volcanic Zone and the transition from southern to central to northern segments (after Wilson et al., 1995). Pūtauaki (Mt. Edgecumbe) sits at the transition between the northern and central segments in close proximity to the Kawerau geothermal field. Type "A" and "B" dacites after Graham et al. (1995). (B) Basic geologic map of Pūtauaki showing the various deposit types and sample locations (labeled circles). Also indicated are well heads associated with the Kawerau geothermal field.

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