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Insights into the behaviour of S, F, and Cl at Santiaguito Volcano, Guatemala, from apatite and glass

Jeannie A.J. Scott [a], Madeleine C.S. Humphreys [a,b,*], Tamsin A. Mather [a], David M. Pyle [a], Michael J. Stock [a]

[a] Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK
[b] Department of Earth Sciences, Durham University, Science Labs, Durham, DH1 3LE, UK

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ABSTRACT

The mineral apatite can incorporate all of the major magmatic volatile species into its structure. Where melt inclusions are not available, magmatic apatite may therefore represent an opportunity to quantify volatile concentrations in the pre-eruptive melt. We analysed apatites and matrix glasses from andesites and dacites erupted from Santiaguito Volcano, Guatemala, between the 1920s and 2002. X-ray mapping shows complex zoning of sulphur in the apatite grains, but typically with sulphur-rich cores and sulphur-poor rims. Apatite microphenocrysts are enriched in F and depleted in Cl relative to inclusions. Matrix glasses are dacite to rhyolite and contain low F but up to 2400 ppm Cl. Overall, the data are consistent with progressive depletion of Cl in the most evolved melts due to crystallisation and degassing. In the absence of pristine melt inclusions, we used apatite, together with published partitioning data, to reconstruct the likely volatile contents of the pre-eruptive melt, and hence estimate long-term average gas emissions of SO_2, HF and HCl for the ongoing eruption. The data indicate time-averaged SO_2 emissions of up to 157 tonnes/day, HCl of 74–1382 tonnes/day and up to 196 tonnes/day HF. Apatite may provide a useful measure of long-term volatile emissions at volcanoes where direct emissions measurements are unavailable, or for comparison with intermittent gas sampling methods. However, significant uncertainty remains regarding volatile distribution coefficients for apatite, and their variations with temperature and pressure.

1. Introduction

The exsolution of dissolved magmatic volatiles into bubbles during magma ascent and eruption is one of the most important processes affecting the physical properties of any volcanic system. Whereas H_2O and CO_2 are the most important volatiles by volume, S, F and Cl can have significant environmental consequences on a local to global scale, with relevance to atmospheric chemistry, human health, and ecology (e.g. Allen et al., 2000; Martin et al., 2009; Robock, 2000). Constraining the fluxes of these volatiles is an important means to assess the current and past impact of volcanic activity on the Earth's surface environment. In the absence of direct measurements of gas emissions, the volatile contents of melt inclusions, trapped in phenocrysts and isolated at depth, are routinely used to infer pre-eruptive melt volatile concentrations (e.g. Bouvier et al., 2008; Edmonds et al., 2001; Humphreys et al., 2008; Wallace, 2005). Comparison of these pre-eruptive volatile concentrations with those preserved in the matrix glass gives a petrologic estimate of volatiles degassed during volcanic eruptions (Devine et al., 1984; Thordarson et al., 1996).

However, in some magmas, melt inclusions may only be present in phases that are liable to leak or degas, or they may be present but too small for analysis, or have undergone devitrification or significant post-entrapment modification. In such cases, an alternative method for assessment of pre-eruptive volatile contents is required. Here we explore and evaluate the potential use of apatite in place of melt inclusions, to infer pre-eruptive concentrations of S, F and Cl in the magmatic liquid at Santiaguito volcano, Guatemala, commenting on the advantages and limitations of the method. This work builds on previous studies, for example at Huaynaputina, Peru (Dietterich and de Silva, 2010) and Irazú volcano, Costa Rica (Boyce and Hervig, 2009). We use the data to infer pre-eruptive volatile concentrations in magmas erupted from Santiaguito volcano, and hence estimate the time-averaged gas emissions of this long-lived, but poorly monitored, volcanic dome complex.

2. Geological background and petrology

Activity at the silicic lava dome complex of Santiaguito, Guatemala, began in 1922 and continues at the time of writing (2015). The dome sits on the shoulder of the much older Santa María volcanic edifice, which in 1902 was the site of a major bimodal explosive eruption, dominated by dacite pumice. Activity at the Santiaguito edifice is

* Corresponding author at: Department of Earth Sciences, Durham University, Science Labs, Durham, DH1 3LE, UK.
E-mail address: madeleine.humphreys@durham.ac.uk (M.C.S. Humphreys).

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characterized by extrusion of lava domes and flows, with regular explosive release of gas and ash (Bluth and Rose, 2004; Escobar Wolf et al., 2010; Rose, 1972, 1987), and substantial passive degassing between explosions (Holland et al., 2011). Persistent cloud cover, challenging terrain, and the explosive nature of the volcanic activity have limited the measurement of volatile emissions using satellite- or ground-based remote sensing methods or direct techniques (Santa María Volcano Observatory written records; Holland et al., 2011; Rodriguez et al., 2004). However, previous work indicates that the effusive eruption of Santiaguito should result in significant halogen output in the volcanic plume as a result of open-system degassing (Balcone-Boissard et al., 2010; Villemant et al., 2003).

2.1. Petrology of Santa María – Santiaguito

The chemical and petrological features of the Santa María – Santiaguito magmas have previously been described (Jicha et al., 2010; Rose, 1972, 1987; Scott et al., 2012, 2013; Singer et al., 2011, 2014), and we summarize the main points below. The Santa María magmas are typically basaltic andesite, but span a wide range of compositions from 51 wt% to 69 wt% SiO_2 (e.g. Rose, 1987). The earliest magmas erupted from Santiaguito itself were similar in composition to the 1902 pumice from Santa María (Rose 1972; Singer et al., 2011). Santiaguito eruptive products are typically porphyritic andesites to dacites (62–66 wt% SiO_2) with ~20–30 vol% plagioclase phenocrysts and ~5 vol% orthopyroxene + Fe-Ti oxides + augite ± olivine ± amphibole. The plagioclase phenocrysts commonly display one or more resorption surfaces with clear, euhedral rims; in many of the more recent samples the majority of the plagioclase crystals show severe resorption textures and a network of large, irregular, devitrified melt inclusions in the core. Accessory minerals include apatite, cristobalite, and pyrrhotite, the latter as inclusions in titanomagnetite phenocrysts. The groundmass consists of matrix glass, euhedral plagioclase, and equant to feathery microlites of orthopyroxene and titanomagnetite.

Glomerocrysts of plagioclase ± orthopyroxene ± olivine are common and contain large pools of interstitial glass (Fig. 1). These glomerocrysts preserve asymmetry at plagioclase-plagioclase-melt boundaries (Fig. 1d), due to the development of curved plagioclase-melt interfaces, rather than simple impingement textures with planar crystal surfaces. This suggests changes in the differential growth rates between different plagioclase crystallographic axes. These textures are similar to those observed in slowly cooling gabbroic cumulates (Holness et al., 2012) and, by analogy, suggests very slow growth. We therefore infer that these glomerocrysts may represent fragments of disrupted mush that would have gone on to form solid plutonic rocks at depth. Matrix and glomerocryst glass compositions range from ~66 to ~76 wt% SiO_2 and are similar to the compositions of melt inclusions (64.5–73.5 wt% SiO_2, Singer et al., 2014).

Thermobarometry based on amphibole phenocryst compositions suggests magma crystallisation temperatures of ~940–980 °C (±22 °C) at moderately oxidising conditions in the region of NNO + 0.5 to NNO + 2 (Scott et al., 2012; Singer et al., 2014), and this agrees with observed maximum surface eruption temperatures (850–950 °C, Sahetapy-Engel et al., 2004). Fe-Ti oxide compositions from the 1902 eruption give temperatures of 860–885 °C for the dacite and 925–1040 °C for the andesite (Singer et al., 2014). Petrological and geochemical studies of Santiaguito show that the lavas have become more mafic with time since the eruption recommenced in 1922 (Escobar Wolf et al., 2010; Scott et al., 2013).

Apatite is present in all samples as microphenocrysts and/or as inclusions within phenocryst phases (typically clinopyroxene), indicating early apatite saturation in the melt (Fig. 2). Some crystals are fully included within the host mineral while others are partly open to the matrix (Fig. 2), permitting variable degrees of equilibration with the host melt. The common occurrence of apatites included in pyroxene may be related to synneusis. The inclusions are equant and thus clearly distinct from the acicular quench crystals commonly observed in plagioclase phenocrysts elsewhere (e.g. Bacon, 1986; Wyllie et al., 1962), which are thought to form as a result of growth from a melt boundary

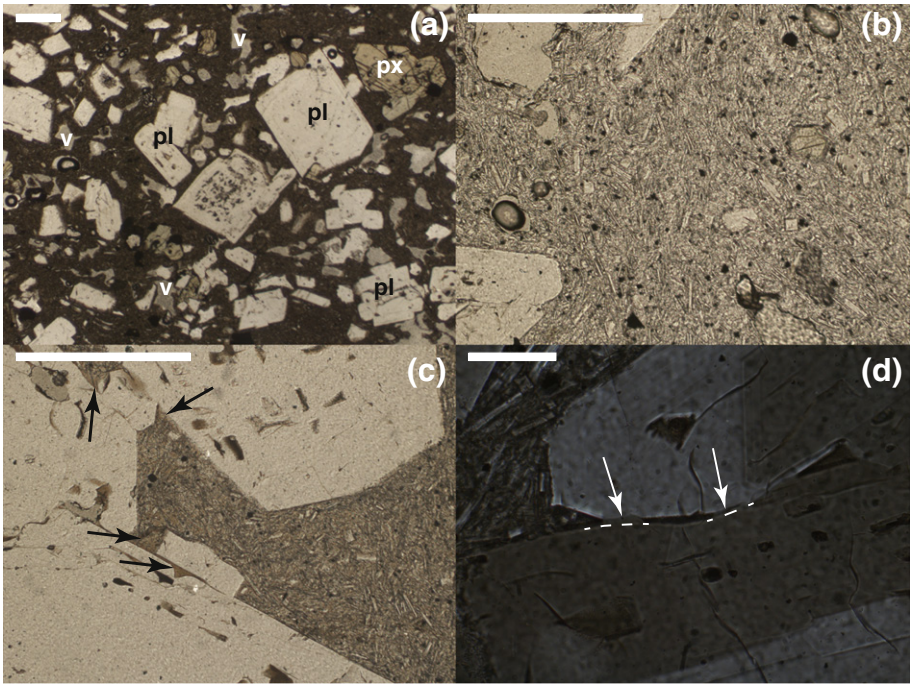

Fig. 1. Photomicrographs of typical dome rocks from Santiaguito Volcano. (a) Porphyritic texture with abundant plagioclase phenocrysts (pl), pyroxene (px) and vesicles (v). (b) Typical groundmass texture with abundant euhedral microlites of plagioclase, pyroxenes and oxides. (c) Matrix glass (arrowed) can be found as small patches and embayments near the margins of glomerocrysts. (d) Cumulate-type grain boundary textures are found in some plagioclase glomerocrysts. This is manifest as marked asymmetry of plagioclase-plagioclase junctions, resulting in small filaments of feldspar (arrowed; expected grain boundary marked with dashed line) joining adjacent grains of the glomerocryst. This is similar to that observed in gabbros (Holness et al., 2012) and suggests very slow cooling. Dark blebs are partially devitrified melt inclusions. Scale bar is 1 mm in all images except d (100 μm).