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Mantle to surface degassing of carbon- and sulphur-rich alkaline magma at El Hierro, Canary Islands

Marc-Antoine Longpré [a,b,*], John Stix [c], Andreas Klügel [d], Nobumichi Shimizu [e]

[a] School of Earth and Environmental Sciences, Queens College, City University of New York, Queens, NY 11367, USA
[b] The Graduate Center, City University of New York, New York, NY 10016, USA
[c] Earth and Planetary Sciences, McGill University, Montréal, Québec, H3A 0E8, Canada
[d] Fachbereich Geowissenschaften, Universität Bremen, 28334 Bremen, Germany
[e] Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

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ABSTRACT

Basaltic volcanoes transfer volatiles from the mantle to the surface of the Earth. The quantification of deep volatile fluxes relies heavily on estimates of the volatile content of primitive magmas, the best archive of which is provided by melt inclusions. Available data from volcanoes producing mafic alkaline lavas in a range of tectonic settings suggest high volatile fluxes, but information remains sparse, particularly for intraplate ocean islands. Here we present measurements of volatile and trace element concentrations, as well as sulphur speciation, in olivine-hosted melt inclusions and matrix glasses from quenched basanite lava balloon samples from the 2011–2012 submarine eruption at El Hierro, Canary Islands. The results reveal remarkably high concentrations of dissolved volatiles and incompatible trace elements in this magma, with ~80 ppm Nb and up to 3420 ppm CO_2, 3.0 wt.% H_2O and 5080 ppm S. Reconstructed primitive CO_2 contents, considering CO_2/Nb systematics and possible CO_2 sequestration in shrinkage bubbles, reach weight percent levels, indicating that carbon is a major constituent of Canary Island magmas at depth and that exsolution of a CO_2-rich fluid begins in the mantle at pressures in excess of 1 GPa. Correlations between sulphur concentration, sulphur speciation and water content suggest strong reduction of an initially oxidised mantle magma, likely controlled by coupled H_2O and S degassing. This late-stage redox change may have triggered sulphide saturation, recorded by globular sulphide inclusions in clinopyroxene and ulvöspinel. The El Hierro basanite thus had a particularly high volatile-carrying capacity and released a minimum of 1.3–2.1 Tg CO_2 and 1.8–2.9 Tg S to the environment, causing substantial stress on the local submarine ecosystem. These results highlight the important contribution of alkaline ocean island volcanoes, such as the Canary Islands, to volatile fluxes from the mantle.

1. Introduction

Magma degassing of volatile compounds (CO_2, H_2O, S, F, Cl) is central to numerous Earth science problems, ranging from explosive volcanic eruptions, to ore-forming processes, and atmospheric chemistry and climate change. Deep CO_2 emissions from volcanoes, for example, are a poorly constrained, yet crucial input for modelling the long-term carbon cycle (Kelemen and Manning, 2015). Sulphur, in turn, with its multiple valences in silicate melts and volcanic gases, participates in key redox reactions in the mantle and atmosphere (Wallace and Edmonds, 2011). Quantifying fluxes of deep volatiles towards the surface requires estimates of their primary concentrations in basaltic magmas (including alkaline varieties) erupted at mid-ocean ridges, subduction zones and intraplate hotspots. During partial melting of the mantle, volatiles behave like other incompatible elements and are strongly concentrated in the melt phase (Saal et al., 2002). However, because the solubility of volatiles in silicate melts is primarily a function of pressure, erupted magmas typically do not preserve primary melt volatile contents — especially CO_2, H_2O and S — due to strong degassing upon ascent-driven decompression. To circumvent this problem, researchers turn to melt inclusions, which represent droplets of silicate melt trapped during crystal growth at depth. Protected by their mineral host acting as a pressure vessel, melt inclusions can retain volatiles during decompression and, assum-

* Corresponding author.
E-mail address: mlongpre@qc.cuny.edu (M.-A. Longpré).

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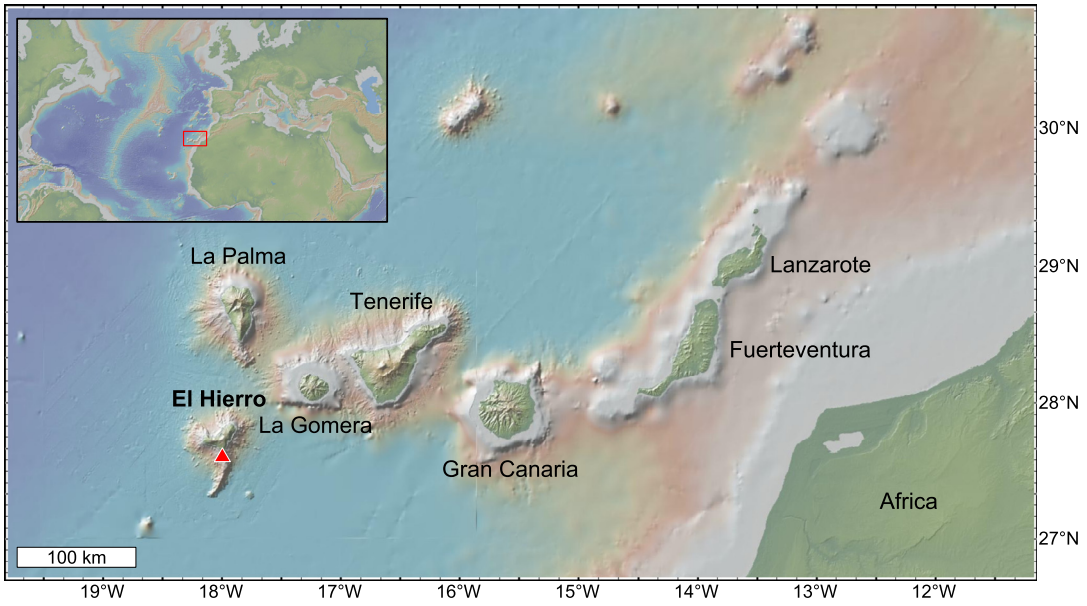

Fig. 1. The Canary Islands. The triangle indicates the site of the 2011–2012 submarine eruption just south of El Hierro. The inset shows the location of the archipelago in the eastern Atlantic Ocean. Map constructed with GeoMapApp (www.geomapapp.org).

ing that any post-entrapment modification of their composition can be assessed, provide unique information on the degassing histories and original concentrations of volatiles in magmas (Métrich and Wallace, 2008).

Alkaline volcanism, in a range of tectonic settings, produces SiO_2-undersaturated magmas typically enriched in incompatible trace elements, reflecting low degrees of partial melting of possibly enriched mantle sources (e.g., McKenzie and O'Nions, 1991). Available melt inclusion data indicate that mafic alkaline magmas are volatile-rich (Hudgins et al., 2015; Oppenheimer et al., 2011; Spilliaert et al., 2006) and oxidised (Jugo et al., 2010; Métrich et al., 2009; Métrich and Clocchiatti, 1996; Moussallam et al., 2014), consistent with experimental evidence (e.g., Dixon, 1997; Lesne et al., 2011; Shishkina et al., 2014). This suggests that alkaline volcanoes, despite relatively modest magma output rates, may contribute significantly to deep volatile fluxes (e.g., Oppenheimer et al., 2011), but data remain sparse, particularly in intraplate oceanic settings.

The Canary Islands are a voluminous group of intraplate ocean island volcanoes that dominantly erupt alkaline magmas derived from a heterogeneous, deep (≥60–100 km) mantle source (e.g., Day et al., 2010; Gurenko et al., 2006; Sigmarsson et al., 1998). Information pertaining to the volatile budget of Canary Island magmas is scarce. Wallace (1998) reported CO_2 and H_2O concentrations reaching 1430 ppm and 1.4 wt.%, respectively, in melt inclusions from basaltic hyaloclastites from the submarine flanks of Gran Canaria. Gurenko and Schmincke (2000) studied similar samples and observed high S concentrations reaching 5800 ppm, of which up to 95% was found to be dissolved as sulphate. Abundant data on fluid inclusions exist, however, and attest to the presence of pervasive CO_2-rich fluids in the mantle beneath the Canaries (e.g., Hansteen et al., 1991, 1998).

From October 2011 to March 2012, a submarine eruption occurred about 2 km south of El Hierro, the westernmost and youngest island of the archipelago (Fig. 1) (see Carracedo et al., 2015 for a review). The eruption produced peculiar lava balloons (e.g., Kelly et al., 2014) that were collected while floating and degassing at the sea surface above the vent. Petrological and geophysical data indicate that mantle-derived basanite magma intruded the lower crust, where it migrated subhorizontally for ~15 km, and then rapidly transited to the surface, all within a few months (Longpré et al., 2014; Martí et al., 2013; Meletlidis et al., 2015).

In this paper, we present volatile and trace element concentrations, as well as sulphur speciation measurements, in olivine-hosted melt inclusions and their host matrix glasses from the El Hierro lava balloons. This represents the first comprehensive effort to constrain the degassing behaviour and volatile fluxes at Canary Island volcanoes. The results reveal the strong degassing and associated redox change of the initially volatile-rich and oxidised 2011–2012 magma as it ascended from the mantle to produce a Strombolian-type submarine eruption. Our findings also add to a growing body of evidence of high volatile outputs at alkaline volcanoes.

2. Samples and methods

The quenched lava balloon fragments studied here were erupted at 100–300 m water depth and collected on 31 October, 27 November, and 6 December 2011, as well as 28 January 2012. We also analysed the matrix glass composition of the essentially aphyric basanitic crust of a bicoloured sample erupted on 15 October 2011, representing the minor, earliest eruptive products (e.g., Troll et al., 2012). Detailed petrologic investigations of the lava balloon samples were previously presented by Martí et al. (2013), Longpré et al. (2014), and Meletlidis et al. (2015). In brief, the lava contains phenocrysts of olivine, clinopyroxene, ulvöspinel and rare ilmenite that are set in a glassy matrix containing microlites of the same minerals, in addition to minor plagioclase. Phenocrysts host inclusions of Fe–Ti oxides, glass (melt inclusions) and CO_2-rich fluid. Notably, large (up to 200 μm across) globular sulphides also frequently occur as inclusions in clinopyroxene and ulvöspinel, often near or on the rims of crystals (Fig. 2c), but not in olivine nor as a free phase in matrix glass. This work focuses on melt inclusions (20–150 μm) in olivine, virtually all of which feature vapour bubbles occupying 5 ± 2% of the inclusion volume (Fig. 2). Some melt inclusions also contain microlites, most commonly Fe–Ti oxide, tiny (0.1 ± 0.1 vol%, i.e. ≤5 μm) sulphide spheres and clinopyroxene (Fig. 2). We generally targeted glassy melt inclusions lacking evidence of possible leakage and microlites larger than the vapour bubbles. However, in some cases we could not avoid inclusions with smaller microlites.

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