A fluid and melt inclusion study of Fogo volcano, Cape Verde archipelago

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INTRODUCTION AND STATE OF THE ART: OIB VOLCANISM

Volcanic degassing is one of the key geological processes that permit the exchange of volatiles (e.g., H_2O, CO_2, H_2S, SO_2, CH_4, Cl, F) between the Earth's interior and its surface (Oppenheimer et al., 2014; Aiuppa et al., 2017, 2019; Plank & Manning, 2019). The release of volcanogenic volatile species can drive change in the atmosphere over timescales of millions of years (Oppenheimer et al., 2014; Plank & Manning, 2019). A comprehensive understanding of the pre-eruptive volatile contents in magmas is also critical for volcano motoring, hazard assessment, and risk mitigation. Gas exsolution has been acknowledged as a critical driver of rapid magma ascent and eruptions (Edmonds & Wallace, 2017). A proper understanding of initial dissolved volatile contents in mantle-sourced magmas is challenged by degassing and differentiation experienced by magmas during their ascent to the surface (Lowenstern et al., 2003). Since erupted lavas/pyroclastic materials are then extremely volatile-depleted upon eruption, one way to indirectly study the initial volatile content in magmas is via the characterisation of fluid inclusions (FI), small volumes of fluid trapped within crystals during their growth from the fluid (Rodder, 1979), and silicate melt inclusions (MI), droplets of melt trapped during phenocrysts growth in the magma (Esposito, 2021), both the inclusions FI and MI, are entrapped in crystals from mafic volcanic rocks. Microthermometric analysis of CO_2-dominated FI provides valuable insights into the pressure, and hence depth, of pre-eruptive magma storage across multiple magma ponding levels (e.g., Hansteen et al., 1998). Furthermore, noble gas and carbon isotope compositions of FI provide insights into the geodynamic evolution and composition of the mantle source, including the presence of mantle plumes (e.g., Gurenko et al., 2006; Day & Hilton, 2011; 2021; Rizzo et al., 2018; Sandoval-Velasquez et al., 2021). On the other hand, MI are studied to quantify the dissolved volatile contents at the *P-T-X* conditions of entrapment. Additionally, they enable the determination of volatile contents in the parental melt if entrapment has occurred at or near the source (and before reaching volatile saturation) (e.g., Métrich & Wallace, 2008; Edmonds & Wallace, 2017). MI studies have been critical to estimating the abundance and distribution of volatiles in the Earth's upper mantle. Recent studies have revealed a C-rich signature of the mantle source of Oceanic Island Basalt (OIB) volcanoes (e.g., Longprè et al., 2017; Taracsák et al., 2019; Aiuppa et al., 2021). If the hypothesis suggesting the prevalence of carbon-rich OIBs globally holds true (e.g., El Hierro, Longpré et al., 2017; Taracsák et al., 2019; Piton de la Fournaise, Boudoire et al., 2018; Fogo, De Vitre et al., 2023), then OIB volcanism is expected to disproportionately contribute to the deep carbon flux into the atmosphere compared to volcanism in other settings, including Middle Oceanic Ridges (Dasgupta & Hirschmann, 2010; Hauri et al., 2019) and volcanic arcs (Plank & Manning, 2019). OIB volcanism opens a window into some of the more deeply explorable portions of the Earth's upper mantle (Hoffmann, 2003). Hence, quantifying the initial contents of volatile elements transported by such OIB magmas is crucial to understanding the cycling of volatiles from the deep planet interior (Hirschmann, 2006, 2018; Dasgupta and Hirschmann, 2010), and brings important clues on the roles of volatiles in mantle partial melting and magma generation and rise (Foley, 2011; Dasgupta, 2018). Unfortunately, however, the MI and FI dataset existing for OIB volcanoes is sparse and incomplete and biased toward a few better-studied volcanic systems such as Kilauea, Hawaii (e.g., Moore et al., 2015; Tuohy et al., 2016), Iceland (e.g., Hartley et al., 2014; Bali et al., 2018), and the Canary Islands (Longpré et al., 2017; Taracsák et al., 2019).

Cape Verde and Fogo volcano

One of the most active OIB volcanoes on the Earth is Fogo, in the Cape Verde Archipelago (West Africa) (Fig. 1). Previous studies on this volcano have provided insights into *i)* the architecture of the magma plumbing

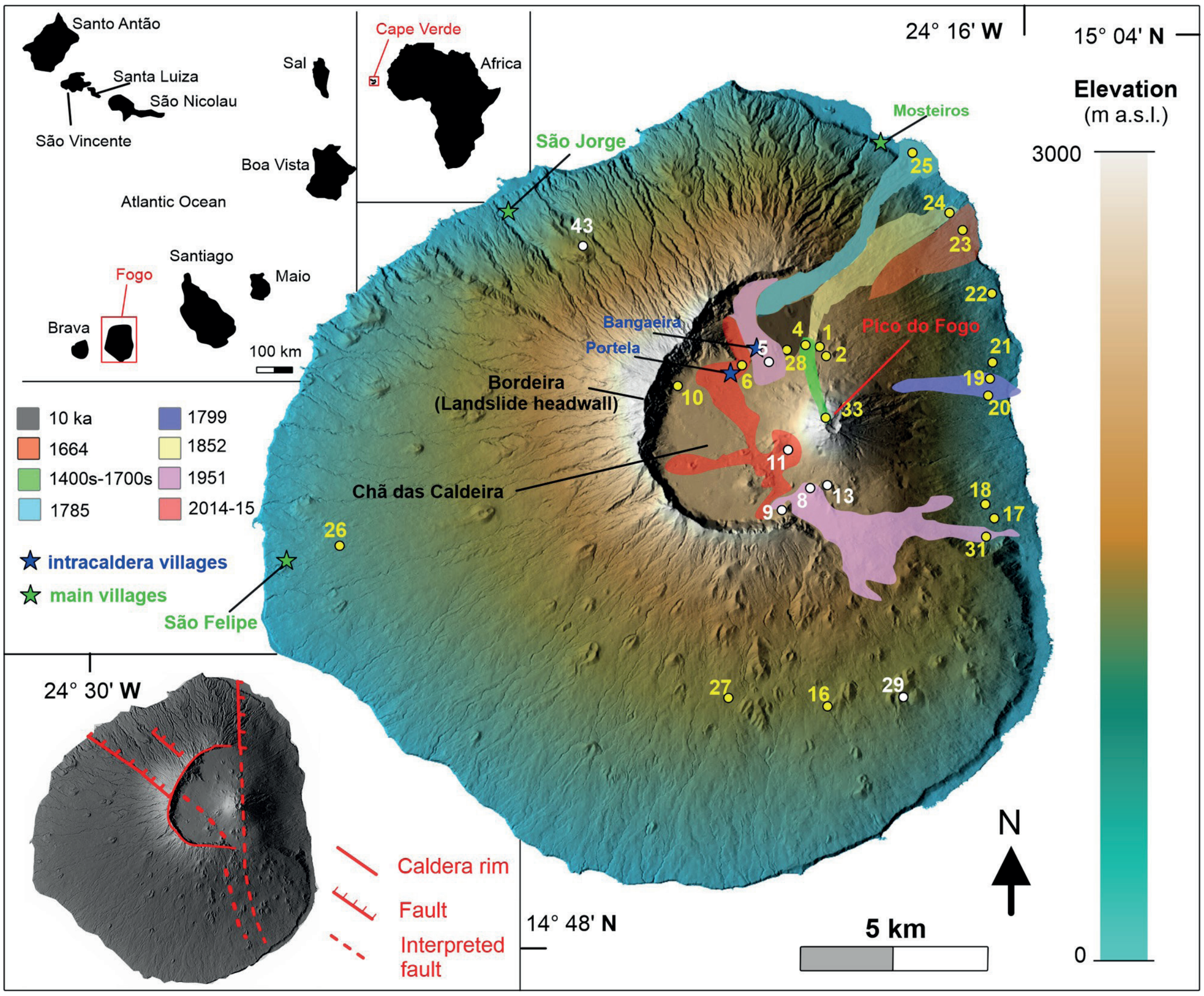

Figure 1 Digital elevation map of Fogo Island (modified from: Sketchfab website, managed by the Volcanology and Petrology lab's 3D models, Department of Geology and Geography, West Virginia University), showing sampling sites of lavas (yellow numbers) and pyroclastic deposits (white numbers). The studied eruptions are mapped from satellite images available from Google Earth and existing geological maps (Torres et al., 1997; Carracedo et al., 2015). Insets show the position of the Cape Verde archipelago (top, right), Fogo Island (top, left) and the main fault systems (bottom, left) (Day et al., 1999; Martínez-Moreno et al., 2018).

system (Klügel et al., 2020 and references therein); *ii)* the isotopic (Sr-Nd-Pb-He) composition of the mantle source (e.g., Christensen et al., 2001; Doucelance et al., 2003); and *iii)* the geochemistry of volcanic gases (Dionis et al., 2014; Aiuppa et al., 2020; Melián et al., 2021). In contrast, little information exists on the long-term stability or evolution of magma storage conditions (e.g., Hildner et al., 2011; 2012; Klügel et al., 2020) and on parental melt volatile contents and volatile evolution along the different regions of the magma plumbing system (DeVitre et al., 2023). Moreover, little is known about the factors that primarily control the isotopic diversity of the OIB mantle source, as well as the rates/modes of magma ascent prior to and during eruption.

RESULTS AND DISCUSSION

This study arises from the need to *i)* increase the actual limited knowledge on Fogo volcano and, more broadly, on the Cape Verde Archipelago and *ii)* provide new constraints useful for future assessment of volcanic risk at Fogo, where the latest eruptions (1951, 1995 and 2014/15) have proven catastrophic for local communities. Our novel data provide new constraints on the *i)* vertical arrangement of the magma plumbing system beneath Fogo Volcano, from the deep crust/upper mantle to the surface, and its evolution over the last 120 ka of activity; *ii)* initial (parental melt) volatile contents, in the attempt to test the C-enriched source hypothesis and provide additional evidence for the C-enriched nature of alkali rich, OIB magmatism; *iii)* evolution of the lithospheric mantle source beneath Cape Verde archipelago, as well as, the occurrence of mantle metasomatism and/or refertilization events, and the recycling into the mantle of noble gases due to recent or fossil subduction.

The key findings of the FI microthermometry study are: *i)* a new conceptual model of the Fogo Volcano magma system, spanning the last 120 ka of activity; *ii)* the identification of two stable magma accumulation zones at ~25 km and ~13–21 km depth; *iii)* the identification of a transient, pre-eruptive magma stagnation zone at 9–12 km depth for magmas involved in the recent (last century) eruptions; *iv)* the rapid ascent, from 25 km depth, of magmas erupted in the early post-collapse phase (~60 ka), following a general reconfiguration of the plumbing system.

The main highlights of the MI study, carried out by combining Raman Spectroscopy, Nano-SIMS, Electron micro-

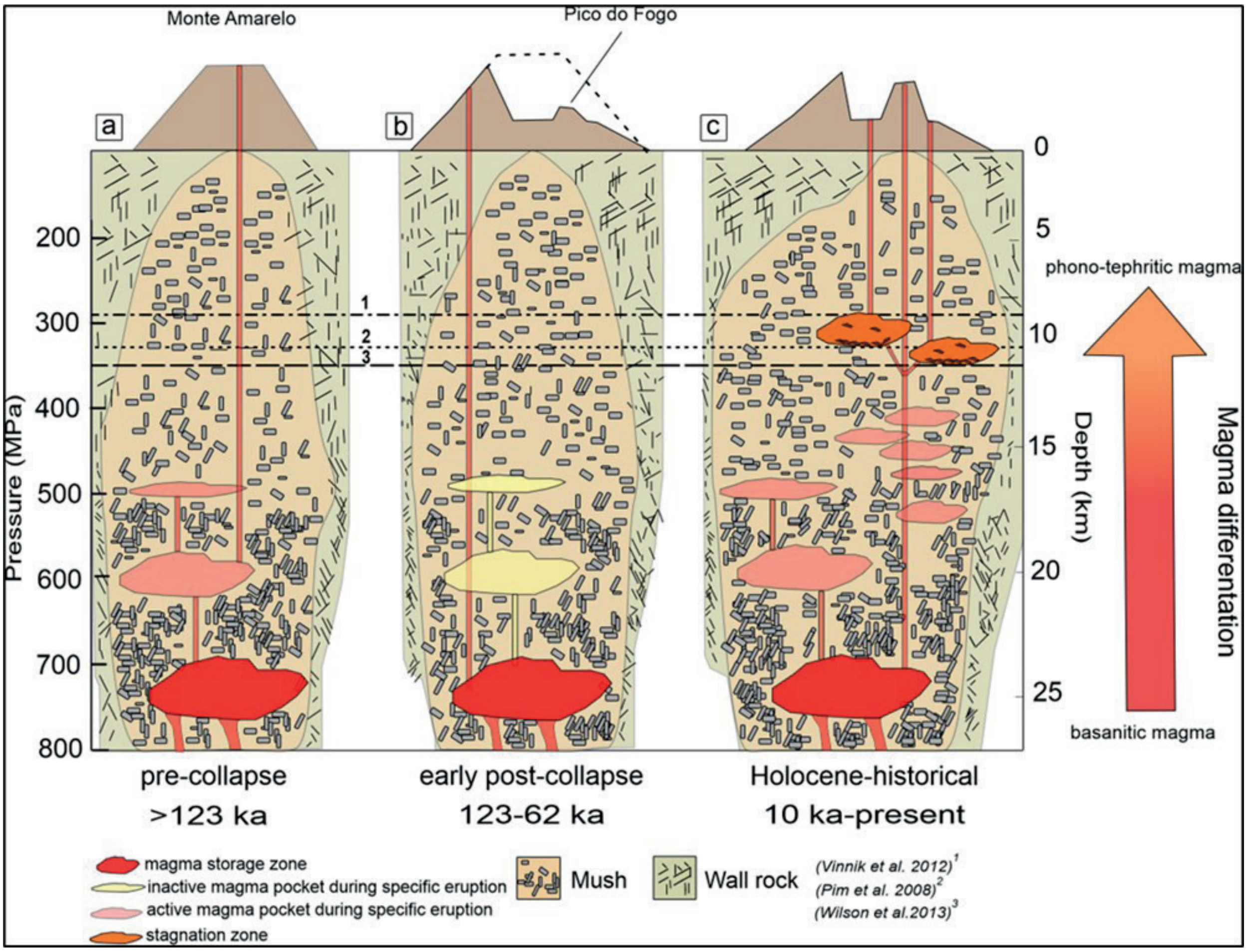

Figure 2 *Schematic cross-sections of Fogo Island (not to scale), showing the temporal evolution of the magma feeding system during (a) pre-collapse, (b) early post-collapse and (c) Holocene/historical activity. FI in Holocene-historical eruptions suggest longer residence in a shallower magma ponding zone prior to eruption at the inferred fossil Moho (1) and/or at the upper mantle-crust transition (2,3). More evolved melts (e.g., phono-tephrites) may form in this region by fractional crystallization. The ~19 km and ~ 15–17 km regions are interpreted as parts of a vertically extended magma system, in which several interconnected ponding zones exist that are periodically refilled during specific eruptions. The main region of magma storage is at ~23.7 ± 0.9 km.*

probe, and LA-ICPMS (chapter 6), are: *i)* mafic magmas feeding Fogo volcano are carbon-rich (2.1 wt. %); *ii)* a degassing model can reproduce the behaviour of volatiles (H_2O, CO_2, S, Cl, and F) during magma ascent/storage in the different magma plumbing system levels, and *iii)* the mantle source beneath Fogo exhibit extremely high carbon contents (up to 400 ppm). The characterization of the isotopic signature of carbon and noble gases in FI is discussed. The first carbon isotopic measurements in FI in the Cape Verde archipelago are illustrated and used to model the carbon isotopic evolution during degassing, from the mantle source to the surface. From this model, I predict a crustal signature for carbon in primary melts formed by upper mantle melting which is suggestive of mantle metasomatism by melts/fluids enriched in a crustal carbon component.

Temporal evolution of the Fogo volcano magma plumbing system, insights on fluid inclusion microthermometry

The architecture of the magma storage system underneath Fogo Volcano (Cape Verde Archipelago) is characterised using novel fluid inclusion results from fifteen basanites, spanning the last 120 thousand years of volcanic activity, and encompassing a major flank collapse event at ~73 ka. Fluid inclusions, hosted in olivine and clinopyroxene, are made of pure CO_2 and, based on their textural characteristics, are distinguished in an early (Type I) and a late (Type II) stage. Inclusions homogenize to a liquid phase in the 2.8 to 30.8°C temperature range. Densities values, recalculated assuming an original 10% H_2O content at the time of trapping, range from 543 to 952 kg·m^3, and correspond to entrapment or re-equilibration pressure ranges of 500–595 MPa, 700–740 MPa, and 245–610 MPa respectively for pre-collapse, early post-collapse, and Holocene/historical eruptions. These entrapment pressures are interpreted as reflecting the existence of two main magma accumulation zones at ~25 km and ~ 13–21 km depth, and a zone of fluid inclusion re-equilibration at 9–12 km depth. There is evidence of a complex temporal evolution of the magma system. Historical eruptions, and especially the three most recent ones (occurred in 1951, 1995 and 2014–25), bring fluid inclusion evidence for transient, pre-eruptive shallow (9–17 km depth) magma ponding. Early post-collapse (60 ka) volcanics, in contrast, document fast magma trans-

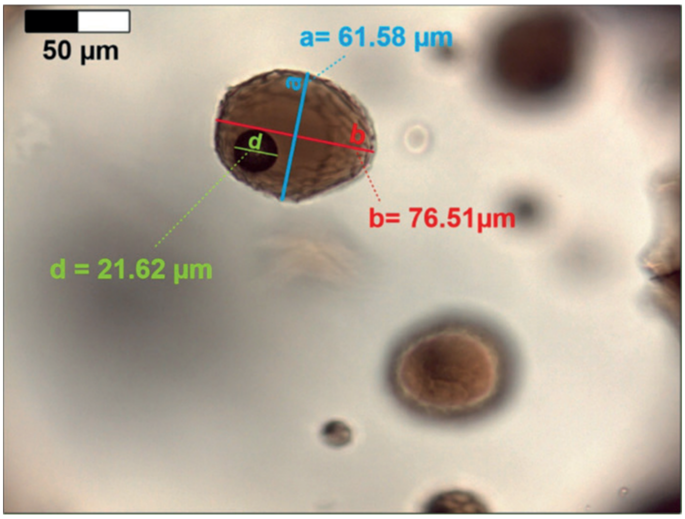

Figure 3 Measurements of the major (a) and minor (b) axes of the MI for the determination of the melt volume and measurement of the diameter (d) of the shrinkage bubble for the calculation of its volume.

port from ~25 km, and suggest a reconfiguration of the magma system after the Monte Amarelo collapse event (Fig. 2).

High CO_2 in the Cape Verde mantle source

Some of the most CO_2-rich magmas on Earth are erupted by intraplate ocean island volcanoes. Here, we characterise olivine-hosted melt inclusions (Fig. 3) from recent (< 10 ky) basanitic tephra erupted by Fogo, the only active volcano of the Cape Verde Archipelago in the eastern Atlantic Ocean. We determine H_2O, S, Cl, and F in glassy melt inclusions and recalculate the total (glass + shrinkage bubbles) CO_2 budget by three independent methodologies.

We find that the Fogo parental basanite, entrapped as melt inclusion in forsterite-rich (Fo_{80-85}) olivines, contains up to ~2.1 wt.% CO_2, 3–47% of which is partitioned in the shrinkage bubbles. This CO_2 content is among the highest ever measured in melt inclusions in OIBs. In combination with ~2 wt.% H_2O content, our data constrain an entrapment pressure range for the most CO_2-rich melt inclusion of 648–1430 MPa, with a most conservative estimate at 773–1020 MPa. Our results, therefore, suggest the parental Fogo melt is stored in the lithospheric mantle at minimum depths of ~27 to ~36 km, and then injected into a vertically stacked magma ponding system. Overall, our results corroborate previous indications for a CO_2-rich nature of alkaline ocean island volcanism. We propose that the Fogo basanitic melt forms by low degrees of melting (F = 0.06–0.07) of a carbon-rich mantle source, containing up to 355–414 ppm C. If global OIB melts are dominantly as carbon-rich as our Fogo results suggest, then OIB volcanism may cumulatively outgas as high as ~16–21 Tg of carbon yearly, hence substantially contributing to the global deep carbon cycle.

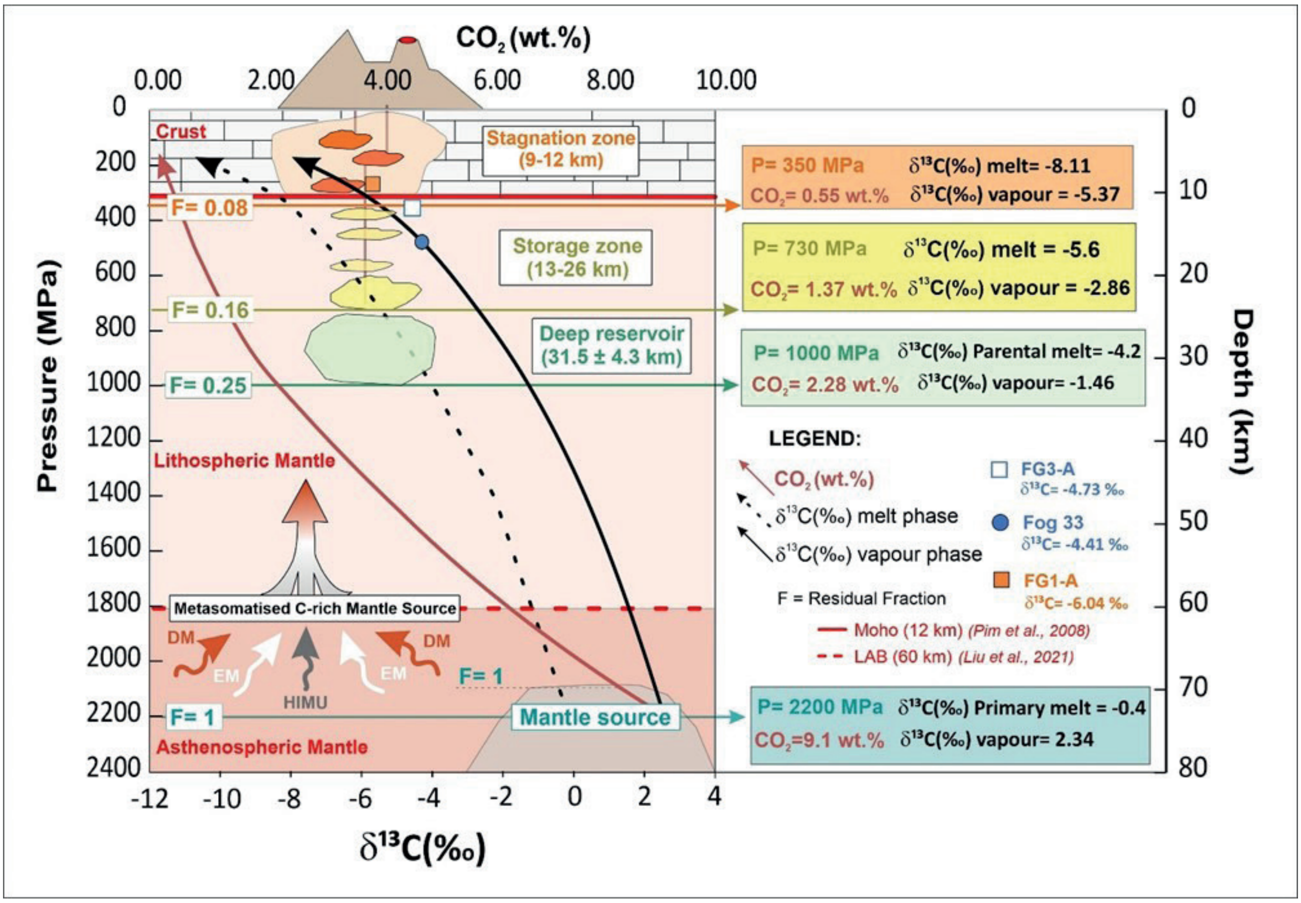

Figure 4 Conceptual model for CO_2 degassing in the Fogo storage system, illustrating the pressure-dependent evolution of (i) dissolved CO_2 in the melt (red line), (ii) $\delta^{13}C$ in the melt phase (dash black line), and (iii) $\delta^{13}C$ in the vapour phase (solid black line).

THE HELIUM AND CARBON ISOTOPIC SIGNATURE OF OCEAN ISLAND BASALTS: CLUES FROM FOGO VOLCANO, CAPE VERDE ARCHIPELAGO

Fluid inclusions (FI) entrapped in phenocrysts carried by Ocean Island Basalts (OIB) contain key information on volatiles' abundance and origin in their mantle sources. Here, we add a new piece of knowledge to our understanding of volatile geochemistry in global OIB magmas, by presenting new noble gas (He-Ne-Ar) and carbon (C) isotope results for olivine- and clinopyroxene-hosted FI from enclaves, lavas, tephra and volcanic gas samples from Fogo, the only frequently active volcano at the Cape Verde archipelago (eastern Atlantic Ocean). FI, together with crater fumaroles, constrain the Fogo $^3He/^4He$ signature at 7.14-8.44 Rc/Ra (where RC is the air-corrected $^3He/^4He$ isotope ratio, and Ra is the same ratio in air), which is within the typical MORB (Mid-Ocean Ridge Basalt) mantle. The carbon isotopic ratio ($\delta^{13}C$ vs. Pee Dee Belemnite) of CO_2 in FI and fumaroles ranges from -6.04 to -4.41‰. We identify systematic variations of $\delta^{13}C$ and He/Ar* with FI entrapment pressure (estimated from a combination of host mineral barometry and FI microthermometry), from which we develop a model for volatile degassing (Fig. 4) in the mantle-to-crustal magma storage system. The model predicts a crustal-like signature for carbon ($\delta^{13}C$ of -0.4±1.0‰) in primary melts formed by mantle melting at ~2200 MPa (~77 km) and a source He/Ar* ratio of 0.90-0.24, which are indicative of variably depleted mantle metasomatized by carbon enriched melts/fluids from a crustal component. We also use our results to characterise regional (in the Cape Verde and Canary archipelagos) and global trends in C and He isotope composition from OIB. From a comparison with the few other OIB localities for which $\delta^{13}C$ are available, we propose that a carbon-enriched crustal component could be recurrent at a global scale in OIB magmatism, although often masked by isotope fractionation during magmatic degassing. We additionally find that, at the regional scale, He isotopes in the OIB scale inversely correlate with the degree of partial melting of the mantle beneath individual islands' (inferred from the La/Yb ratio of erupted basalts). More widely, our results corroborate previously established global relationships between OIB He isotopic signature, plume buoyancy flux and overlying plate velocity. In this interpretation, the MORB-like $^3He/^4He$ (8±1 Ra) at Fogo reflects a combination of (i) low to medium magma productivity, (ii) relatively low plume buoyancy flux (~1.1 Mg/s), and (iii) slow average velocity (~3 cm/yr) of the overlying plate.

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