

# Generation of CO<sub>2</sub> - SO<sub>2</sub> fluxes in the lithospheric mantle beneath El Hierro (Canary Islands) on metasomatic reactions of carbonate-rich silicate melts

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At the Canary Islands, chemical heterogeneities in the lithospheric mantle are result from infiltration of a volatile-rich metasomatic agent having a debated nature (Frezzotti et al., 1994; 2002a, b; Neumann et al., 2002). Melt and fluid inclusions preserved in mantle xenoliths can reveal the nature of metasomatic agents and processes. We studied a peridotite xenolith suite from El Julan Cliff (El Hierro, Canary Islands) comprising 1 spinel Ol(olivine)-orthopyroxenite, 3 spinel lherzolites, and 5 spinel harzburgites. The Ol-orthopyroxenite consists of Ol porphyroclasts, up to 61 vol% of poikilitic Opx (orthopyroxene) grains, and minor Sp (spinel). Harzburgites and lherzolites (protogranular textures) consist of Ol and Opx porphyroclasts, and subordinate Cpx (clinopyroxene) and Sp. All rocks show evidence of modal and cryptic metasomatism, although hydrous phases are absent.

In peridotites, abundant glass microveins are present in Ol, and between Ol and Opx. Ol in contact with glass microveins is embayed, whereas Opx shows overgrowths. Microveins consist of colorless silicate glass and carbonate droplets. The silicate glass is trachytic and silica oversaturated (SiO<sub>2</sub> = 62.55-68.57, K<sub>2</sub>O + Na<sub>2</sub>O = 8.13-10.01, in wt%; Na<sub>2</sub>O/K<sub>2</sub>O = 1.0 - 1.6). Carbonate in droplets is calcite. In Ol, glass microveins are associated with melt and fluid inclusions. Melt inclusions consist of Anh, Cc, and subordinate sulphide aggregates. Two distinct types of fluid inclusions (FI) are observed associated with microveins and melt inclusions: a) FI1's (≤3-15 μm in size) contain CO<sub>2</sub>+N<sub>2</sub> (N<sub>2</sub> ≤18 mol%) and are present as intragranular trails. They have densities ≤1.19 g/cm<sup>3</sup>, corresponding to 1.8±0.02 GPa at 950°C (Oglialoro et al., 2017); b) large FI2 (20-50 μm in size), present in the same trails, which contain CO<sub>2</sub>±N<sub>2</sub> (N<sub>2</sub> ≤0.3 mol%) and more than 70 vol% daughter minerals, including Anh, Mg-Cc, Dol, hydrated Mg-sulph., Shl, Ap, Sp, Mag, and Tlc. In metasomatic Opx, FI3 (≤3-10 μm in size) present with a primary distribution and negative-crystal shapes, which contain CO<sub>2</sub>±N<sub>2</sub>±SO<sub>2</sub> (N<sub>2</sub> 0.01-0.03 mol%; SO<sub>2</sub> 0.6-1.30 mol%; d = 1.10-0.99 g/cm<sup>3</sup>). When SO<sub>2</sub> is present, S<sup>0</sup> is detected.

FI4 are late pure CO<sub>2</sub> fluids (3-40 μm in size; d = 1.11-0.65 g/cm<sup>3</sup>) along intragranular trails in all main mineral phases, originated by magma degassing on ascent (Oglialoro et al., 2017).

Data show infiltration of a volatile-rich carbonate - silicate melt, enriched in SO<sub>3</sub>, P, Cl, and N<sub>2</sub>, at the base of the oceanic lithosphere beneath the Canary Islands. Similar metasomatic melts react with Ol to form Opx (e.g., Ol-orthopyroxenite). As reactions proceed, the silicate component in the melt decreases whereas the carbonate component increases to form Cpx±Ol from Opx. At this stage, evidence for immiscibility between volatile-saturated carbonate, sulphate and silicate melts could be preserved by coeval sulphate-, carbonate-rich inclusions, and FI. CO<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O-salt fluids could be generated and unmix to form coexisting CO<sub>2</sub>±N<sub>2</sub>±SO<sub>2</sub>-rich fluids (FI1 and FI3) and high density (CO<sub>2</sub>-N<sub>2</sub>) saline melts (FI2).

The geochemical nature of the metasomatic melt (e.g., silica oversaturation, high K<sub>2</sub>O, and Na<sub>2</sub>O; high SO<sub>3</sub>, CO<sub>3</sub><sup>2-</sup>, Cl, and N<sub>2</sub>) points to a possible origin by partial melting of crustal mafic rocks (Rosenthal et al., 2014) at asthenospheric depths, as predicted to explain the HIMU signature of Canary Island magmatism (Day et al., 2011). High fluxes of CO<sub>2</sub> and SO<sub>2</sub> are generated on metasomatic reactions. These will ascend through the lithosphere feeding the magmas of El Hierro, which are known to degas significant amounts of CO<sub>2</sub> and SO<sub>2</sub> (about 1.3-2.1 Mt CO<sub>2</sub> and 1.8–2.9 Mt S, Longpré et al., 2017).

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## References

- Day J.M. et al. (2011) *EPSL* 305:226-234.
- Frezzotti M.L. et al. (1994) *EJM* 6:805-818.
- Frezzotti M.L. et al. (2002a) *EJM* 14:891-904.
- Frezzotti M.L. et al. (2002b) *Lithos* 64:77-96.
- Longpré M.-A. et al. (2017) *EPSL* 460:268-280.
- Neumann E.-R. et al. (2002) *J. Petrol.* 43:825-857.
- Oglialoro E. et al. (2017) *Bull. Volcanol.* 79:70.
- Rosenthal A. et al. (2014) *Sci. Rep.* 4:6099.