Evolution of magmatic volatiles during Miocene seamount to shield stage of Gran Canaria (Canary Islands): Evidence from Ol- and Cpx-hosted melt and fluid inclusions

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Magmatic volatiles (1) play an important role for melt generation in the mantle, (2) affect physical properties of melts and, therefore, the character of volcanic eruptions, and (3) have an impact on global climate. We have studied volatile components (H_2O, CO_2, F, Cl, S) and S^{6+}/S_{tot} ratios in fluid and naturally quenched glass inclusions in Ol and Cpx phenocrysts from Miocene basaltic hyaloclastites drilled during ODP Leg 157. Our goal is to understand the behaviour of magmatic volatiles from magma generation to eruption during the seamount to shield stages of Gran Canaria - a well studied oceanic intraplate volcano.

Methods

Concentrations of major elements, F, Cl and S, and S^{6+}/S_{tot} ratios in glass inclusions were analysed with a Cameca SX50 electron microprobe (GEOMAR, Kiel, Germany), and H_2O concentrations - with ion microprobes Cameca IMS 3f (CRPG, Nancy, France) and IMS 4f (Microelectronics Inst., Yaroslavl, Russia). Microthermometry of fluid inclusions was performed using a Fluid Inc.® heating-cooling stage at GEOMAR Research Center.

Results

Microthermometry of fluid inclusions trapped in olivine Fo_{85-88} showed that fluid coexisting with melt was composed of >95 mol% CO_2 (triple point $-56.6 \pm 0.2°$ C), whereas H_2O and other volatiles (i.e. CO, H_2S, SO_2, N_2) can only be present in minor or trace concentrations. Inclusions homogenize in the vapour at +27.7° to +29.7°C (n = 14) and in the liquid phases at +29.6° to 30.4°C (n = 14) that corresponds to CO_2 densities of 0.28−0.61 g/cm^3 and yields a lithostatic pressure of 1−3 kbar calculated for the temperature range of 1100−1300°C. Based on existing CO_2 solubility models (e.g. Dixon et al.,

1995), we expect 0.04−0.1 wt.% CO_2 dissolved in the melt. A range of 0.14−1.2 wt.% H_2O was obtained for Ol- and Cpx-hosted glass inclusions by ion microprobe. H_2O does not correlate with K_2O, and only the highest H_2O concentrations (H_2O/K_2O = 0.8−1.2) correspond to those of MORB and OIB magmas (Carroll and Holloway, 1994) (Fig. 1). Both CO_2 and H_2O concentrations are in good agreement with the results of FTIR studies of glass inclusions from the same or similar samples (0.01−0.1 wt.% CO_2 and 0.06−1.4 wt.% H_2O; Wallace, 1998).

Sulphur shows considerable scatter and two groups of glass compositions can be recognized: (1) inclusions with relatively high S concentrations (~0.1 to ~0.5 wt.% S) correlating positively with FeO and likely representing S-saturated, undegassed magmas; and (2) inclusions having a spread from ~0.15 to ~0.01 wt.% S at a given FeO, suggesting progressive magma degassing (Fig. 2a). The S^{6+}/S_{tot}
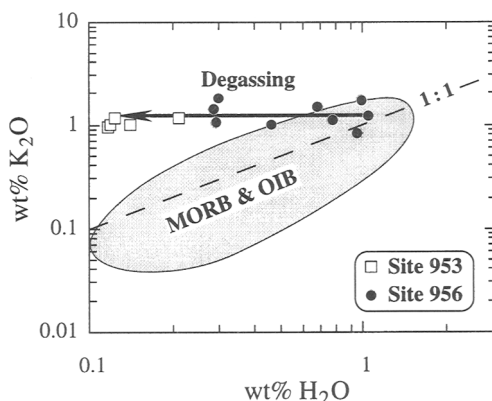

FIG. 1. H_2O vs K_2O in Ol- and Cpx-hosted glass inclusions. Here and in Fig. 2, shaded area represents submarine MORB and OIB tholeiitic and alkali glasses (Carroll and Holloway, 1994: Dixon et al., 1997 and refs. therein.
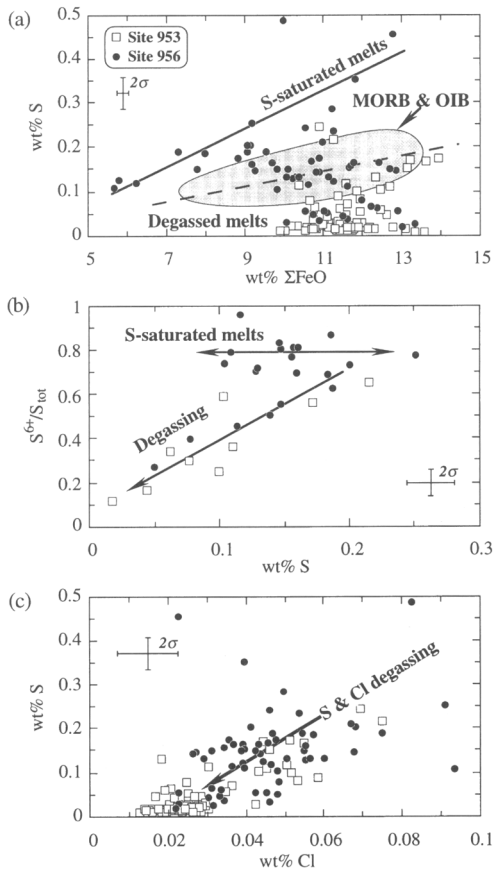
FIG. 2. S and Cl concentrations, and S^{6+}/S_{tot} ratios in Ol- and Cpx-hosted glass inclusions. Dashed line represents S saturation of basaltic melts (Mathez, 1976).

ratios positively correlate with S concentrations, and vary from 0.11 to 0.95 showing a systematic difference between Site 953 (average 0.37 ± 0.19) and 956 (average 0.68 ± 0.17) (Fig. 2b). No correlation of chlorine (0.01−0.09 wt.% Cl) with MgO, or K_2O and other incompatible elements was observed. In contrast, fluorine (0.09−0.2 wt.% F) increases with decreasing MgO and increasing K_2O in the melt, and has behaved incompatibly during magma crystallization.

Discussion

The studied inclusions are believed to represent the compositions of melt and fluid during phenocryst crystallization. Two possibilities can be suggested to explain the variations of H_2O, S and Cl: (1) inclusions with low concentrations of H_2O, S and

Cl have lost dissolved volatiles due to syn- or post-eruptive cracking of the host mineral; (2) inclusions represent partially to strongly degassed magmas. Many of the inclusions found in Ol and Cpx phenocrysts were altered to clay, probably due to seawater infiltrating along the cracks in host phenocrysts. Leakage of H_2O, S and Cl from the still fresh and glassy melt inclusions is, therefore, unlikely. The observed ranges of H_2O, S and Cl concentrations, the lack of correlation with MgO and K_2O, and the positive covariation of S with Cl (Fig. 2c) and with H_2O suggest that the magmas may have been partially to strongly degassed at varying depths in the magma plumbing system.

The oxygen fugacities estimated from S^{6+}/S_{tot} ratios range from NNO-0.5 to NNO+1 and are similar to f_{O_2} values independently obtained from Fe^{3+}/Fe^{2+} ratios in Ol- and Cpx-hosted spinel inclusions (FMQ to NNO+1). At the redox conditions more oxidized than NNO, sulphide melt becomes unstable, and the oxidation state of S dissolved in the melt is mostly controlled by the equilibrium between silicate melt and vapour phase (e.g. Nilsson and Peach, 1993). Therefore, the positive correlation between S concentrations and S^{6+}/S_{tot} ratios may suggest: (1) solubility of sulphate is greater than that of sulphide, so that up to 0.5 wt.% S can be dissolved in the basaltic melt; and (2) oxidized S preferentially partitions into coexisting fluid phase upon magma degassing.

Acknowledgements

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