Na/K ratios of sulfate-bearing saline fluid inclusions in harzburgite xenoliths from Pinatubo: Comparison with H_2O-rich components in arc and back-arc basin basalts

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Sulfate ion and sulfate minerals were found in the H_2O-CO_2-Cl fluid inclusions in the harzburgite xenoliths from Pinatubo volcano located at the volcanic front of the Luzon arc, the Philippines (Kawamoto et al. PNAS 2013). Thanks to a newly installed Raman mapping system, SO_4^{2-} ion, gypsum ($CaSO_4 \cdot 2H_2O$) and/or anhydrite ($CaSO_4$) were found in one fourth of the analyzed fluid inclusions. Mg-sulfate hydrite was reported in CO_2-H_2O-Cl fluid inclusions in the Ichinomegata lherzolite xenoliths from northeastern Japan (Kumagai et al. 2014, CMP); however, we did not find sulfur in the Pinatubo in our previous work. Sulfur contents in the Pinatubo fluid inclusions can be <0.5wt% S/H_2O. This range is consistent with those in serpentinites (Alt et al. 2012 EPSL). Origin of the fluids in the Pinatubo harzburgite is supposed to be from serpentinites whose water was originally brought via sedimentary pore fluids on the basis of halogen systematics (Kobayashi et al., 2017 EPSL). High Pb contents in the amphiboles from the Pinatubo harzburgite can be explained by such sulfate bearing fluids in addition to the effects of salinity (Yoshikawa et al. 2016 Lithos).

Olivine-hosted melt inclusions show a positive correlation between water contents and Fe^{3+}/Fe^{2+} ratios (Kelley and Cottrell 2009 Science). Presence of sulfate ions in the fluid inclsuions, which can be slab-derived fluids, can explain such sulfate-bearing fluids can provide H2O and oxidize the wedge mantle. This also provides insights into the genesis of calc-alkaline rock series characterized by a high oxygen fugacity (Miyashiro 1974 Am J Sci). Our observation solves the missing link between high-S in arc magmas (Le Voyer 2010 J Petrol) and presence of sulfate in the slab serpentinites (Alt et al. 2012) and high-pressure metamorphic rocks (Frezzotti and Ferrando 2007 Per Mineral). Current estimate of S content in the aqueous fluids in forearc (<0.5wt% S/H_2O) is more than an order of magnitude lower than that in melt inclusions in arc basalts (6-60wt% S/H_2O; Le Voyer 2010, J Petrol). This indicates that sulfur can be enriched during partial melting of the mantle with larger S/H_2O than that of slab-derived fluids. Alternatively fluids released beneath sub-arc contain larger amount of S by increasing solubility in supercritical fluids.

The Na/K ratio was determined in the fluid inclusions (>0.02 mm) in olivine crystals using a quadrupole inductively coupled plasma-mass spectrometry equipped with a 193 nm excimer laser ablation system. The obtained Na/K ratios ($Na_{0.73}K_{0.27}$) are a little more K-rich than those of aqueous fluids in the generation of the Mariana trough back-arc magmas ($Na_{0.82}K_{0.18,}$ Stolper and Newman 1995, EPSL), H_2O-rich components in Mt. Shasta ($Na_{0.77}K_{0.23,}$ Grove et al. 2002, CMP), and similar to those between two H_2O-rich components in Mt. Shasta ($Na_{0.70}K_{0.30}$ of melt or supercritical fluids components and $Na_{0.87}K_{0.13}$ of aqueous fluids components, Le Voyer et al. 2010, J Petrol).

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