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Pyrrhotite oxidation as an indicator of air entrainment into eruption columns and lava flows

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Air entrainment into eruption columns plays an important role for volcanic eruption dynamics as it causes buoyancy and temperature decrease for erupted materials. In this study, we develop a new method for quantifying the degree of air entrainment on the basis of Pyrrhotite (Po) oxidation reaction.

Since fO_2 of air is ca. 10 log units higher than that of the typical arc pre-eruptive magmas, oxidation of magmas may sensitively reflect the air entrainment. The oxidation reaction of Po proceeds quickly at high temperature within a several tens of seconds to a several tens of hours. Because this timescale corresponds to the typical eruption duration, the reaction may record the eruption dynamics. Matsumoto and Nakamura (2012) found Po crystals and their oxidized texture in the Sakurajima 1914-15 (Taisho) Plinian pumice clasts. In this study, we have additionally examined clastogenic lava (CL) (Yasui et al., 2007) and effusive lava (EL) samples of the Taisho eruption and estimated the Po oxidation conditions.

The oxidation products were identified as magnetite (Mt) and hematite (Hm) with reflective microscope and Raman spectroscopy. The Mt and Hm crystals were found to be Ti-free by using X-ray mapping except for the phenocrysts in the EL samples. The representative occurrence of Po and its oxidation texture were summarized as follows: In the pumice samples, unreacted Po was observed as well as relict Po with Mt-Hm composite reaction rims. In the CL, unreacted Po grains scarcely found and almost all the oxidation products were Hm. In the EL sample, unreacted Po, relict Po with Mt rim, Po pseudomorphs replaced entirely by Mt and Hm, and those by Hm existed. In contrast to the pumice clasts, no three-phase coexistence in a grain was found.

This occurrence of Po and oxides can be explained in terms of the 'achieved fO_2' and 'high-T and high- fO_2 duration'. The 'achieved fO_2' will be scaled by (A) pre-eruptive magma: $10^{-7.5}$?$10^{-9.0}$ bar, (B) equilibrium of Po and Mt: $10^{-6.9}$?$10^{-8.3}$ bar, (C) equilibrium of Mt and Hm: $10^{-4.7}$?$10^{-6.2}$ bar according to Matsumoto and Nakamura (2012), Huebner and Sato (1970) and Eugster and Wones (1962), and (D) the partial pressure of O_2 in air: $10^{-0.7}$ bar. Time scales of 'high-T and high- fO_2 duration' can be calculated by using (i) reaction duration for Mt rim of Po, (ii) reaction duration for Hm rim of Mt, and (iii) Ti diffusion time in Mt. Using these scales, occurrences of oxidation textures in each sample can be explained as follows: In the Plinian pumices, about half of the grains were not accompanied by oxides rim, showing that their achieved fO_2 were below (B); the rest of the grains having Hm rims experienced the fO_2 above (C). The grains between (B) and (C) rarely existed. The reaction duration of the pumices were estimated to be $<$3.5 hours (iii). The variation in the degree of oxidation reaction in the pumices can be interpreted to reflect the variation in the degree of contact with air and cooling process. The oxidation reaction of Po in CL occurred at fO_2 above (C) and was ceased in 6.3 to 22 hours (ii). The high fO_2 and relatively long reaction duration of CL is consistent with its origin; the CL magma was once fragmented, reacted with air and then welded and kept at high temperature. In EL, about half of the grains were unreacted at fO_2 below (B) and the rest grains were oxidized at fO_2 of (B) to (D). The estimated reaction duration for EL was 3.6 to 33 hours (iii). This fO_2 variation may be caused by partial fragmentation and welding with open system degassing or mixing with oxidized lava crusts. The systematic correlation between the Po oxidation reaction and the eruption processes suggests a possibility that Po oxidation can be an indicator of air entrainment into eruption columns and lava flows.

Keywords: oxidation, air entrainment, pyrrhotite, fO_2, Sakurajima