Syn-eruptive breakdown of pyrrhotite: a marker of pyroclasts oxidation and air entrainment into eruption columns

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Air entrainment in fragmented magmas controls the dynamics of explosive volcanic eruptions. Oxidation process of pyroclast can be used for measuring the duration of magma-air interaction in past eruption events. Breakdown of pyrrhotite (Po) is a potential proxy as the mechanisms are well constrained for metallurgical use. To test utilizing Po breakdown as a quantitative marker, we examined its mechanisms using erupted materials from the Sakurajima 1914-1915 Plinian eruption.

Most of the Po grains in pumices from the Plinian eruption partly or entirely breakdown into Fe oxides. The Fe oxides are composite of magnetite (Mt) and hematite (Hm), forming a columnar structure with pores along certain Po crystallographic planes. The Mt in the Fe oxides is Ti-free, indicating that the Fe oxides were quenched immediately after their formation. The Hm stable fO_2 is at least ~4 log units higher than the magma chamber fO_2 estimated from the (Fe+Cu)/S ratio of Po. This large increase of fO_2 within a rapid quenching is attributed to interaction with air during the Plinian eruption. In a clastogenic lava from the same eruption, columnar Fe oxides are almost completely oxidized to Hm. The dominance of Hm is consistent with the formation processes of a clastogenic lava in which high fO_2 and high temperature are maintained during welding. Compared with oxidation product of Po reproduced by previous experiments in oxidized gases, the columnar Fe oxides are estimated to have formed as follows: the oxidation reaction produced Mt with outgassing of SO_2 ($3Fe_{1-x}S + (5-2x)O_2 = (1-x)Fe_3O_4 + 3SO_2$). Porous reaction zone formed during this outgassing stage allowed the SO_2 gas to escape and the oxygen to access to the reaction front easily, leading to the rapid formation of Mt column. Then formation of Hm without outgassing followed ($2Fe_3O_4 + 1/2O_2 = 3Fe_2O_3$).

To constrain the timing of columnar Fe oxides formation, we compared the Hm width with reaction distance calculated from the experimentally determined growth rate of Hm assuming a conductive cooling of pumice. The average Hm width of grains located near the surface of pumices from the Sakurajima ranges 0.86–1.22 μm. On the other hand, even in the center of the pumice with 1 cm radius, the calculated Hm width is 0.35 μm. The thicker Hm width of the natural sample indicates that the pumice surfaces were maintained at a high temperature for a long time in the eruption column. From these results, we propose that Po can be a quantitative marker of magma–air interaction applicable to the dynamic processes of volcanic eruptions.

Keywords: pyrrhotite, oxidation, air entrainment, Sakurajima, eruption column

