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Effect of high temperature oxidation on ferric iron and precipitates in olivine from andesitic scoria of Kasayama volcano, Japan

T. Ejima (1), M. Akasaka (2), T. Nagao (3), and H. Ohfuji (4)

(1) Shimane, Matue, Japan (olivinefe3@yahoo.co.jp), (2) Shimane, Matue, Japan (akasaka@rico.shimane-u.ac.jp), (3) Yamaguchi, Yamaguchi, Japan (tnagao@yamaguchi-u.ac.jp), (4) Ehime, Matsuyama, Japan(Ohfujih@yahoo.co.jp)

Occurrence of ferric iron and precipitates within olivine phenocrysts in orthopyroxene-olivine andesitic scoria from Kasayama volcano, Hagi, Yamaguchi Prefecture, Japan, were investigated to evaluate an effect of high temperature oxidation. The scorias in the interior of the Kasayama scoria cone are red and weakly welded, whereas black scoria and black scoria with reddish-brown tint (red-brownish black scoria) occurs on the outer surface of the cone. Olivine phenocrysts within black scoria lack precipitate minerals, but those in the red-brownish black scoria contain small amounts of precipitates at their rims. Olivine phenocrysts in the red scoria contain abundant precipitate minerals including hematite, enstatite and magnesioferrite. The precipitates form symplectite zones on the rims of the olivine phenocrysts, symplectite domains in the cores, and fill fractures.

Forsterite contents of olivine are correlated with the volume of precipitates present. Olivines in the black and red-brownish black scoria contain 79-81 and 82-85 mol% Fo, respectively, whereas those in the red scoria reach 99 mol% Fo. To determine oxidation state of Fe in olivine in the red-brownish black scoria using Mössbauer spectroscopy, olivine phenocrysts lacking such precipitates and inclusions were separated using an isodynamic separator and handpicking under a binocular microscope. Purity of the olivine separate was examined by optical microscopy, electron microprobe analysis, X-ray powder diffraction analysis, Raman spectroscopy, and high-resolution transmission electron microscopic observation. Since precipitates were not detected in the separated olivine phenocrysts, oxidation state of iron within olivine phenocryst in the andesitic red-brownish black scoria was determined using ^{57}Fe Mössbauer spectroscopy. The ^{57}Fe Mössbauer spectrum of the separate consisted of three doublets assigned to ferrous iron at M1, ferrous iron at M2 and ferric iron at the octahedral site. The Fe^{2+}:Fe^{3+}-ratio is 95(3):5(1). By applying this value to the average iron content, 0.37(4), ferrous iron and ferric iron are calculated to be 0.35(1) and 0.019(4) apfu, respectively. Since ferric iron within olivine in this study is not due to any ferric iron-bearing impurity, ferric iron should be located at any site in olivine structure. A quadrupole splitting value of the ferric iron-Mössbauer doublet (0.53(5) mm/s) in Kasayama olivine significantly lower than published data for ferric iron at M2 in olivine and in laihunite suggests possible distribution of ferric iron at the less-distorted M1 site. Ferric iron within olivine in the red-brownish black scoria is considered to have been generated at high temperatures (perhaps above 800 ºC).