

In-situ spectroscopy of color change processes of olivine by high temperature oxidation

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Olivine has been found to be one of the origins of red coloring of volcanic eruptive materials such as Takatsukayama scoria (Yamanoi et al., 2004). Therefore, we investigated color change processes of olivine in high temperature oxidation by means of spectro-colorimetry and in-situ visible spectroscopy. The heating experiments of olivine powders showed that the Kubelka & Munk functions (similar to absorbance) of olivine increased first in the 350 & 480 nm region, then they increased around 480 & 580 nm. The high temperature spectra for the olivine thin section at 650 & 800 C showed similar spectral changes. These results indicated that the oxidation process of olivine was composed of two stages: first mainly production of Fe³⁺ associated with vacancy in olivine (ferriolivine; absorption band around 430nm), second mainly hematite (absorption band around 550nm) formation. These oxidation processes were supported by Raman spectroscopy and electron micro probe analyses of olivine thin sections.

On the other hand, in spectro-colorimetry, first, both the x and y values of olivine increased during the heating. Then the x values of olivine increased, while the y values of olivine decreased. These color values of all the heated products were in a triangle formed by color values of ferriolivine, unoxidized olivine and hematite in the x-y color space and could be reproduced by color mixing of these 3 components. The difference in color values of heated products was considered to be due to the difference of production ratios between ferriolivine and hematite.

Moreover, the temporal changes of 430 nm absorbance (ligand field transition of Fe³⁺) obtained by in-situ high temperature visible microspectroscopy increased more at higher temperatures. Assuming diffusional transport in plane sheets, apparent diffusion coefficients were determined at temperatures of 600 - 800 C. The activation energy for this diffusion in olivine is 210 (20) kJ/mol. Obtained diffusion coefficient and activation energy values are similar to those of the metal vacancy diffusion in olivine (e.g. Kohlstedt and Mackwell, 1988). Therefore, the visible spectral change kinetics of olivine at 600 & 800 C studied here can be considered to be controlled by metal vacancy diffusion of Fe³⁺, which is oxidized from Fe²⁺ at the olivine surface.