

## 山野井 勇太 (Yuta YAMANOI)

Color change processes of volcanic materials by spectro-colorimetry and *in-situ* high temperature visible spectroscopy

### ABSTRACT

Color change processes of volcanic materials are expected to provide useful information on volcanic eruptive processes. These color change processes have been quantitatively investigated by using CIE L\*a\*b\* color values from spectro-colorimetry. In this study, I developed *in-situ* high temperature visible spectroscopy for measuring color changes with time of volcanic materials, especially in a short time scale, and investigated color change pathways of some representative rock-forming minerals and volcanic rocks by this method.

I first investigated color change processes of natural volcanic materials (basaltic scoria, andesitic pumice and andesitic volcanic bomb) and some common materials in volcanic rocks [olivine, orthopyroxene (enstatite), clinopyroxene (diopside), hornblende, rhyolitic glass (obsidian) and Fe-Ti oxides]. Powdered materials having grain sizes of about ten micrometers were heated in an electric furnace at 500 to 1000°C for 50 minutes to 168 hours. The a\* (red) and b\* (yellow) values of basaltic scoria, andesitic pumice and andesitic volcanic bomb powders increase with heating time at all the temperatures. Ferrous iron contents determined by phenanthroline method and absorbance around 10000 cm<sup>-1</sup> (1000 nm) in VIS-NIR spectra of heated materials decrease by heating. Therefore, the color changes upon heating of volcanic materials reflect mainly oxidation from ferrous to ferric iron.

The a\* (red) and b\* (yellow) values of olivine and enstatite first increase with heating time, and then decrease at relatively high temperature for longer heating periods. Those of diopside and Fe-Ti oxide increase at all the temperatures. Their a\* (red) value increase rates at 700°C show the following order: olivine > hornblende > enstatite > diopside > rhyolitic glass.

However, these color changes of volcanic materials are too fast to be monitored by this batch type of heating experiments in an electric furnace, especially at the initial stage (b\* increase) at higher temperatures. In order to study detailed kinetics of color change in a short time scale, I developed here *in-situ* high temperature visible microspectroscopy for volcanic materials.

I first developed *in-situ* high temperature visible microspectroscopy for transmittance spectral change with time for thin section samples. The spectrometer consists of the visible - Raman microspectrometer and a commercial heating stage. The

high temperature visible spectra of olivine thin sections can be obtained by using this instrument, and they show a gradual increase with time in absorbance in the shorter wavelength region (400 – 600 nm). The 430 nm absorbance (ligand field transition of  $\text{Fe}^{3+}$ ) increased more with time at higher temperatures. This increase kinetics can be fitted by a diffusion model, suggesting a diffusion process as a rate-limiting process of the color change of olivine.

Secondly, I developed dark field reflection *in-situ* high temperature visible microspectroscopy (above *in-situ* high temperature visible microspectroscopy with a dark field optics) in order to obtain diffuse reflectance spectra and color values at high temperatures. Hematite is employed here as a representative material and its color change with temperature is investigated *in-situ*. The reflectance of hematite powders in the longer visible wavelength region than 550 nm decrease gradually with increasing temperature. The shoulder centered around 570 nm and the reflectance maximum near 750 nm also become unclear. The calculated  $L^*$  (white),  $a^*$  (red) and  $b^*$  (blue-yellow) values decrease with increasing temperature ( $[L^*, a^*, b^*]=[40.3, 26.2, 12.0]$  at room temperature  $\rightarrow [28.5, 1.3, -1.5]$  at 800°C for 100 wt% hematite). This means that red color of hematite becomes black with the temperature increase. The calculated absorption intensities (Kubelka – Munk functions) suggest that this temperature dependence of the hematite powder reflectance spectra can be mainly explained by change in absorption edges by band gap for semiconductors (Urbach rule).

Thirdly, I conducted time-resolved *in-situ* high temperature visible spectroscopy of olivine powders for studying their color changes with time at high temperature. By adding an original program (Seki Technotron Corp., UniTMGCtrl1) into the above *in-situ* high temperature visible reflection microspectroscopy, the alternate measurements of reflectance spectra and thermal radiation spectra at every minute could be performed to obtain dark field spectral change with time without effects of thermal radiation. The  $L^*a^*b^*$  color value changes of olivine powders were measured at high temperatures for studying color change pathways especially for the rapid initial changes. These are found to be explained by the mixing of the following three components: 1) unheated olivine including mainly ferrous iron ( $a^*, b^* = -2, 7$ ), 2)  $\text{Fe}^{3+}$ -bearing olivine (relatively large  $b^*$  value), and 3) hematite ( $a^*, b^* = 27, 17$ ).

*In-situ* high temperature reflection visible microspectro-colorimetry of olivine at isothermal conditions (600 – 800°C) shows that  $a^*$  and  $b^*$  values first increase and then decrease with time. By considering the temperature dependences of colors of the two components [(1) initial olivine:  $b^*$  values increase with almost constant  $a^*$  values under inert conditions, and 2) formed hematite:  $a^*$  and  $b^*$  values decrease significantly

with temperature], the color change trends by the *in-situ* method can be explained by the same three component mixing model as above (unheated olivine including mainly ferrous iron, Fe<sup>3+</sup>-bearing olivine, and hematite). In particular, the *in-situ* method can detect the formation of Fe<sup>3+</sup>-bearing olivine or hematite in a short time scale.

Color change processes of other rock-forming minerals and volcanic rocks heated at 600 – 800°C for several tens of hours in the electric furnace can also be explained by the same mechanisms as those for olivine and summarized as follows:

1. Color change process of a silicate mineral due to the oxidation of ferrous iron in the mineral structure has a color change trend with high b\*/a\* ratios of 2 – 4, becoming yellowish.
2. Color change process of a silicate mineral due to the formation of hematite-like ferric-ferric pairs has a color change trend with low b\*/a\* ratio of ~0.5, becoming reddish.
3. Color change process of a Fe-Ti oxide producing hematite has a color change trend with a b\*/a\* ratio of ~0.5 similar to the hematite trend.
4. In silicate minerals, the following two color change trends are observed [(1) b\*/a\* is 2 – 4 and (2) b\*/a\* is negative with decrease in b\* values]. The second trend may not be recognized if the formation of hematite is not easy in the mineral structures. Orders in both color value change degree and a\* change rates by heating at 600 – 800°C for several tens of hours are roughly consistent with the order in silicate polymerization degree. These results suggest that color change processes of silicate minerals are constrained by their mineral structures.

Based on these above color change processes of rock-forming minerals, color changes of volcanic rocks including multiple components can be explained by those of their constituent materials.

Although further studies on color changes of multiple component samples and further systematic experiments of volcanic materials and rock-forming minerals based on the simulation heating experiments under controlled fO<sub>2</sub> conditions are needed, color change processes of volcanic materials by easy and rapid spectro-colorimetry even on-site and by newly developed *in-situ* high temperature visible spectroscopy, investigated in this doctoral thesis, are expected to become common useful methods for studying volcanic eruption processes and their time and temperature scales.