# Copper Contents in Basalt Magma of Ishi-zumi-ga-hana Cape, Hachijo-jima Island, Tokyo

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#### Abstract

Red colored anorthite phenocrysts of basalt lava from Ishi-zumi-ga-hana Cape, Hachijo-jima Islands, are investigated, with special reference to the thermal properties of native copper in the mineral.

Metallic minerals are found in red colored anorthite. They are tiny and thin, usually less than one to several micrometers in size. They often occur as minute spotty particles scattered as platy or fringe-like aggregates, and are distributed within narrow veinlets as lace-like aggregates or frameworks, or as swarmed clusters. They also occur as round small balls in melt inclusions. Microscopic observation and EPMA reveal that these metallic minerals are native copper.

On heating, native copper grains disappear, and red color of anorthite fades out at approximately 1,200°C, suggesting that they are the products of exsolution from high temperature anorthite. Native copper in melt inclusions homogenize into silicate melt, also at about 1,200°C, suggesting high concentrations of copper and low oxygen fugacities at the magmatic stage.

A simple calculation suggests that the basalt magma at Ishi-zumi-ga-hana Cape had extremely high contents of copper, 3-5 % in weight!

Keywords; anorthite, basalt magma, Hachijo-jima, native copper, copper contents

#### 1. Introduction

Red colored anorthite has been well known as phenocrysts of basalt lava from Miyake-jima and Hachijo-jima Islands, Tokyo. Isshiki (1958) described the modes of occurrence and the feature of red colored anorthite from Hachijo-jima Island, and reported that the color originated from the presence of hematite. Murakami *et al.* (1991) reported the characteristic feature of red colored anorthite from Miyake–jima Island, and reported that the color is originated from the presence of native copper. Nishida *et al.* (1994) reported the characteristic feature of red colored anorthite from Hachijo-jima Island, and reported that the color is originated from the presence of native zinc, copper and brass alloys of Zn and Cu. Kimata *et al.* (1994) discussed the significance of metal for magmatism according to those findings and the presence of plagioclase megacrysts. Tanaka (2011), Hokayama

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(2012), and Ushigome (2012) reported the mineralogical and thermal considerations of red colored anorthite from Hachijo-jima Island. Enjoji *et al.* (2012) reported the thermal features of native copper and surrounding minerals, and discussed the significance of the metal in magmatism at Hachijo-jima Island. Thus the presence of native metal in basaltic lava suggests the close relationship with oceanic magmatism.

In this study, the feature of red colored anorthite from Ishi-zumi-ga-hana Cape, Hachio-jima Island is investigated, with special references to the thermal properties of native copper in the mineral. Native copper occurs as minute spotty particles scattered, as platy or fringe-like aggregates aligned in veinlets, and as the daughter minerals in melt inclusions. Thermal treatment reveals that native copper mostly disappears by the time temperature is raised to 1,200°C. This suggests that fairly large amount of copper dissolved in anorthite at elevated temperature, and that the magma at the time of formation of anorthite phenocrysts, had a large amount of copper, reaching 3-5 % in weight.

## 2. Geological Setting

Hachijo-jima Island is a complex volcanic

island, about 15 km in length and 8 km in width. It is situated around 300 km south of the Tokyo Metropolis (Fig. 1a). The island is formed from two stratovolcanoes, Mt. Higashi-yama and Mt. Nishi-yama. Higashi-yama (or Mihara-yama) has a height of 701 m, and was active from 100,000 BC to around 1,700 BC. Basalt lavas from Ishi-zumiga-hana Cape were formed by this volcanism, after the Aira Tn volcanic eruption (27,000-24,000 BC). Nishi-yama (or Hachijo-fuji) has a height of 854 m, and is rated as a Class C active volcano with eruptions recorded in recent history until 1606.

Most volcanic rocks of Hachijo-jima Island are basalt to basaltic andesite. Basalt lava that occurs at Ishi-zumi-ga-hana Cape (Fig. 1b), located at latitude 33° 04.8' N and longitude 139° 51.5' E, has remarkable porphyritic texture with large phenocrysts of anorthite and olivine (Fig. 2). Anorthite crystals are often 3 to 5 cm in length, and often show distinct color zoning with vivid red tint in core portion. Often several anorthite crystals gather together, accompanied with olivine crystals or include them. The presence or absence of red colored tint does not appear to be related to crystal size. From the initial evidence, formative conditions of the crystals might be various in the



Fig. 1. Location of the sampling point. (a) Hajijo-jima Is. is a complex volcanic island, situated around 300 km south of the Tokyo Metropolis. (b) Ishi-zumiga-hana Cape is located at the eastern edge of the island, which consists of basalt lava.

molten magma, and the same may be true for the material that causes the color zoning (Fig. 3).

# 3. Origin of the Red Color of Anorthite

Observing the red colored portion of anorthite crystal of the polished thin section under the microscope, a large quantity of remarkably small opaque particles are found. They are tiny and thin, usually less than several micrometers in size. They are arranged within narrow veinlets, as lacelike aggregates or frameworks (Fig. 4), or as a swarmed clusters. They also occur as round tiny balls in melt inclusions (Fig. 5). Often a part of the colored zone fades out into colorless zone, as if they were influenced by the later mineralization. In transmitted light the area shows "bluish" tint. (Tanaka, 2011)

Dense red color portions were quantitatively analyzed by EPMA with an accelerating voltage of 15 kV, a beam current of 0.4 nA, a beam diameter of 10  $\mu$ m, and a counting time of 100 sec. Several analyses reveal that red colored anorthite has copper contents from 0.35 to 0.81 in weight % of Cu in addition to the normal anorthite composition.

Observing the section under the incident light, it is clear that the opaque particles are native copper from their optical properties especially characteristic reflected color (Figs. 4 and 5). Point analyses by EPMA yielded Cu weight percent totals of 28.4, 78.9, 31.7, 60.7, and 70.8; these totals are less than 100 because of beam overlap on phases adjacent to the very fine metal inclusions. No EDS peaks other than Cu and elements such as Ca, Al, Si, which can be attributed host phases were identified (Fig. 6). These results strongly show that the mineral is native copper. Thus, the origin of the red color might be due to the presence of a large quantity of tiny opaque particles of native copper.

## 4. Change of Color

Anorthite crystals having reddish color were sliced and double-polished for heating experiments. The small fragments were heated in an electric furnace, followed by observation under the microscope after quenching. The furnace is controlled by programming and has an accuracy of about  $\pm 5^{\circ}$ C. Sample specimens were heated at a gradient of approximately 1,000°C per hour to the designated temperature, held one hour, and quenched to room temperature. Changes of color, phase, and shape were observed under the microscope (Hokayama, 2012).

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As higher designated temperatures were reached, native copper particles become smaller and less abundant, presumably dissolving into host anorthite, and probably the shape more round. As the size is very small, the shape change is not obvious. At higher temperatures, bulk color turned pale and faded from reddish tints to colorless, and mostly disappeared as temperatures approached 1,200°C (Fig. 7a and 7c; Hokayama, 2012).

# 5. Native Copper in Melt Inclusions

In some cases, melt inclusions are aligned in planes, in concordance with the euhedral shapes of host anorthite. In other cases, melt inclusions occur apparently at random in their anorthite hosts. From the modes of occurrence, they seem to be primary melt inclusions which were included during crystallization of host crystals. The general shape is spherule, round oval, and irregular, less than 5-10 micrometers in size. In each inclusion, there are one or two transparent crystals, opaque balls, and vapor bubbles, with transparent glass comprising the remainder of the inclusion, although the fine grain size and overlapping textures of these features cause some ambiguities. The volume ratios of the sum of opaque balls to each inclusion appear to be similar, suggesting that the opaque phase is a daughter mineral that crystallized from trapped melt. Under the incident light microscope, it is clear that opaque balls consist of native copper based on the characteristic reflected color when the opaque balls occur on the polished surface. Even enclosed in crystals beneath the polished surface, this phase shows a peculiar color. One or two vapor bubbles often make empty holes on the polished surface. On heating, the constituent crystals homogenized into the glass phase, at about 1,200°C (Fig. 7b; Ushigome, 2012).

The copper contents in the melt inclusions are estimated as follows. As a first step, the diameters of the opaque balls are measured. Then the volume ratio of native copper relative to the melt inclusion was calculated from:

$$\label{eq:VM} \mathbf{V}_{\mathrm{M}} = \mathbf{V}_{\mathrm{T}} - \mathbf{V}_{\mathrm{V}} - \mathbf{V}_{\mathrm{C}} - \mathbf{V}_{\mathrm{X}}$$
 where:

 $V_M$  = the volume of silicate melt, present now as a glass phase in the melt inclusion

 $V_{T}$  = total volume of the melt inclusion, as an ellipsoid or sphere

 $V_{v}$  = the volume of gas bubble, usually as sphere

 $V_{\rm C}$  = the volume of native copper, usually as sphere

 $V_x$  = the volume of transparent crystals.

We do not include a factor for the possible deposition from the included melt on the inner wall of the inclusion, and we assume that the density of silicate melt and transparent crystals is  $3.0 \text{ g/cm}^3$ , same as basalt, and that of native copper is  $8.9 \text{ g/cm}^3$ . Then, the volume ratio of native copper to total melt is simply calculated by the following formula. (See also Fig. 5)

Cu (wt %) = 
$$\frac{V_C \times 8.9}{(V_T - V_V - V_C) \times 3.0 + V_C \times 8.9}$$

Given the uncertainties in our volume estimates, these calculated concentrations should be considered preliminary and tentative. Nonetheless, these simple measurements and calculations were done for several melt inclusions. The calculations reveal that the contents of copper in silicate melt is 3.4-4.8 % ! The reasons why the anorthites show a red color instead of copper color (or reddish brown) and why some areas show "bluish" tint still remain unknown.

## 6. Conclusions

1) Metallic minerals are found in red colored anorthite phenocrysts of basalt from Ishi-zumi-gahana Cape, Hachijo-jima Island, Tokyo.

2) The metallic minerals are tiny and thin, usually ranging from less than one to several micrometers in size. They are distributed within narrow veinlets as latticeworks or frameworks, or as swarmed clusters. They also occur as tiny spherules in melt inclusions.

3) Microscopic observations and the EPMA reveal that these metallic minerals are native copper.

4) On heating, native copper grains disappeared and the red color of host anorthite fades out, suggesting the native copper of this type are the products of exsolution from high temperature anorthite.

5) On heating, native copper in melt inclusions homogenized into silicate melt at approximately 1,200°C, suggesting the high concentrations of the copper and low oxygen fugacities at the magmatic stage of these rocks.

6) A simple calculation suggests that the magma formed basalt from Ishi-zumi-ga-hana Cape had extremely high contents of copper, on the order of 3-5 % by weight.

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Fig. 3. A megacryst of anorthite with red colored portion and olivine crystals.



Fig. 2. Modes of occurrences. (a) The basalt with red colored anorthite. (b) A mineral assemblage of the basalt. an: anorthite, cpx: clinopyroxene, ol: olivine. (c) A clump of native copper in groudmass of the basalt.



Fig. 4. Inclusions of native copper in anorthite, occuring as flaky and lace-like aggregates (a). (b-left) by transmitted light, and (b-right) by reflected light.





Fig. 5. Melt inclusion in red-colored anorthite.





Fig. 7. Sequencial images from the heating experiments. (a) Reddish tint in anorthite mostly diappears into colorless phase. (b) A melt inclusion homogenize into colorless glass phase on heating at 1,200 °C. (c) Lace-like aggregates of native copper also disappeared into the host crystal at similar temperatures on heating.

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