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Possible Contribution of *Gallionella ferruginea* to the Formation of Liomonite Ore Deposits

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Abstract - Limonite ore deposits exist in northwestern Aso caldera, Kyusyu, Japan. *Gallionella ferruginea* inhabited in the reddish brown microbial mats at northwestern Aso caldera. SEM observation revealed the formation process of the microbial mats by *G. ferruginea*, and *G. ferruginea* contributed to forming limonite ore deposits.

I. Introduction

The limonite ore deposits are located in northwestern part of Aso caldera, Kumamoto prefecture where reddish brown microbial mats are formed with iron rich under ground water. So-called the limonite is a mixture of similar hydrated iron oxide minerals. Generally, iron oxidizing bacteria such as *Leptothrix* sp., *Toxothrix* sp., *G. ferruginea* inhabit in reddish brown microbial mats at neutral pH [1]. The microbial mats in Aso caldera are of predominantly *G. ferruginea* which is a bean-shaped bacterium that produces a twisted stalk. In short, *G. ferruginea* produces iron hydroxide by own metabolism [2].

In this study, SEM observation revealed that the formation process of reddish brown microbial mats with *G. ferruginea* in Aso caldera. The role of *G. ferruginea* in limonite ore deposits formation was descrived in this report.

II. Geological setting

Mt. Aso, which located in the central part of Kyushu, is an active composite volcano with the caldera. The caldera is stretching 18 km to the east-west and 24 km to the north-south direction and was produced by 4 times of large-scale pyroclastic flows between 90,000-300,000 years ago (Fig. 1). A central volcanic cone exists in the central part of the caldera, and the Hontuka volcano exists in a northern part. The Hontuka volcano was formed about 46,000 years ago. Whereas, the lake called "Asoyako" existed in the northern caldera during 6,000-40,000 years ago, and the limonite ore deposits was formed at this time [3, 4].

On the other hand, the water quality in the Aso caldera is classified into five types such as, Gairinzan type, Aso type, Akamizu type, Shimoda type, and lacustrine type, by water quality are distributed in this region [5, 6] (Fig. 2). Especially, Akamizu type caused by spring of the Hontuka volcano is distributed over northwestern caldera, and contains high Fe concentration. Moreover, reddish brown microbial mats are formed in the river water (flowing into Kuro-kawa) where the water flow in this region.

III. Materials and methods

Reddish brown microbial mats and river water flowing on the microbial mats were collected from northwestern of Aso caldera on the March, 2002. Microbial mats sample were fixed by adding 2.5 % glutaraldehyde solution.

The river water shows pH 5.5, Eh 113 mV, EC 0.2 mS/cm, DO 5.5 mg/l, and WT 22 ℃. That was measured by portable water quality inspection meter (pH; F-24, Eh; D-13, EC; ES-12, DO; OM-12). The measurement was carried twice in the field.

After air-drying, microbial mats was ground to fine powder for Energy dispersive X-ray fluorescence spectrometer (ED-XRF) analysis. The powder mounted on the Mylar film measured by an energy dispersive X-ray fluorescence spectrometer (JEOL JSX-3201), using Rh Kα, which operated at an accelerating voltage of 30 kV under a vacuum condition.

The mineralogical properties of microbial mats were analyzed by X-ray powder diffractometer (Rigaku RINT1200) with a CuKα radiation, generated at 40 kV and 30 mA and scanned speed of 2 °/ min. The powder material was mounted onto slide glasses to fit the diffractometer sample-holder.

The microbial mats were air-dried onto brazen stubs and imaged with a scanning electron microscope (SEM; JEOL JSM-5200LV). After air-drying, the surface of the sample was coated with carbon and observed by SEM with an accelerating voltage of 15 kV. Chemical composition of the sample was analyzed by energy dispersive X-ray spectrometer (EDX; Philips PV9800).

Samples were air-dried onto copper grids and viewed with a JEM-2000 transmission electron microscope (TEM). The electron diffraction option, SAED, was used to determine whether a sample was crystalline or amorphous. The accelerating voltage was set 160 kV with different magnifications.

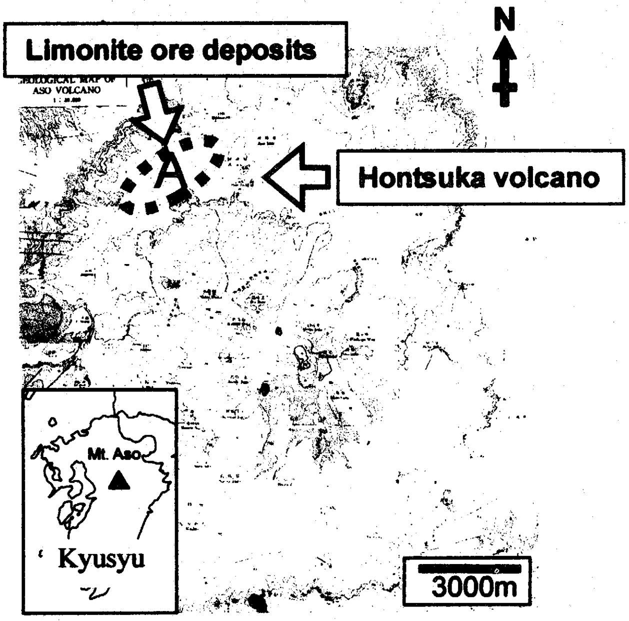

Fig. 1. Geological map of Mt. Aso located in central part of Kyusyu, Japan. Gray Parts show pyroclastic rock and lava flow. Hontsuka volcano exists in the northern part of the caldera (after Ono and Watanabe, 1985). Limonite ore deposits exist in northwestern part of the caldera (part of A).

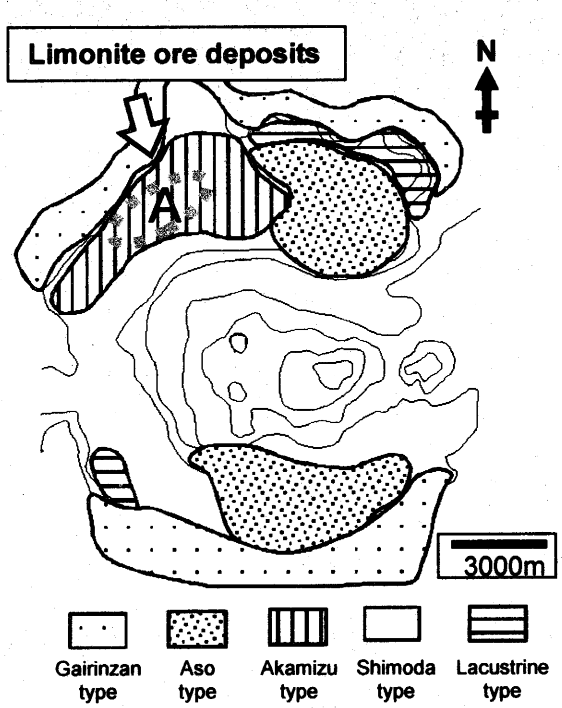

Fig. 2. Water quality distributed map. Aso caldera is classified into five types in this region. Especially, Akamizu typed water contain high Fe concentration (after Nagai *et al.*, 1986). Whereas part of A shows region of limonite ore deposit.

IV. Results and Discussions

A. Chemical and mineralogical analyses of microbial mats

The ED-XRF analysis of reddish brown microbial mats collected from Aso caldera showed the high concentration of Fe associated with the traces of Si, P, S, and Ca. Whereas, the XRD results of same microbial mats showed presence of amorphous materials. It is indicated that the microbial mats mainly composed of Fe, and formed an amorphous iron oxides.

B. Microscopic observation and EDX analysis of microbial mats

SEM observation reveals that reddish brown microbial mats showed the bacterial colony consisted of ion oxidizing bacteria, such as *G. ferruginea*. (Fig. 3A). SEM micrograph of the same microbial mats showed the stalk of *G. ferruginea* covered with spherical minerals that are less than 1.0 μm in size (Fig. 3B). Beside this, EDX spectrum indicated the high concentration of Si and Fe (Fig. 3B'). Whereas stalk of *G. ferruginea* tangle each other (C), moreover, fabricating a block of iron hydroxides (D). The results suggested that the processes of *G. ferruginea* forming reddish brown microbial mats. Furthermore, under the higher magnification of TEM showed the stalk of *G. ferruginea* have two type forms (Fig. 4). Stalks consist of spherical minerals identified as ferrihydrite showing diffraction of diffused rings at 2.68 Å and 1.50 Å (Fig. 4A' inset), whereas others consist of needle-like hematite showing diffraction of spots at 3.68 Å, 2.52 Å, 1.86 Å (Fig. 4B' inset).

C. The relation between formation of limonite ore deposits and reddish brown microbial mats

Distribution of limonite ore deposits and water quality of Akamizu type are overlapped. Hontsuka volcano has existed since the time of forming limonite ore deposits. It is concerned Fe rich springs from Hontsuka volcano formed limonite ore deposits. When limonite ore deposits were formed, water quality of northwestern part of caldera was as same as Akamizu type, and *G. ferruginea* inhabited dominantly. Soggard *et al.*, (2000) was reported that under microaerobic conditions (e.g., in freshwater pH = 7, O_2 concentrations = 60 μ mol·L^{-1}, and Fe^{2+} ~200 μ mol·L^{-1}), iron oxidation by *G. ferruginea* is >60 times faster than the abiotic reactions [7]. It is suggested that *G. ferruginea* was contributing to be a significant factor for forming of limonite ore deposits.

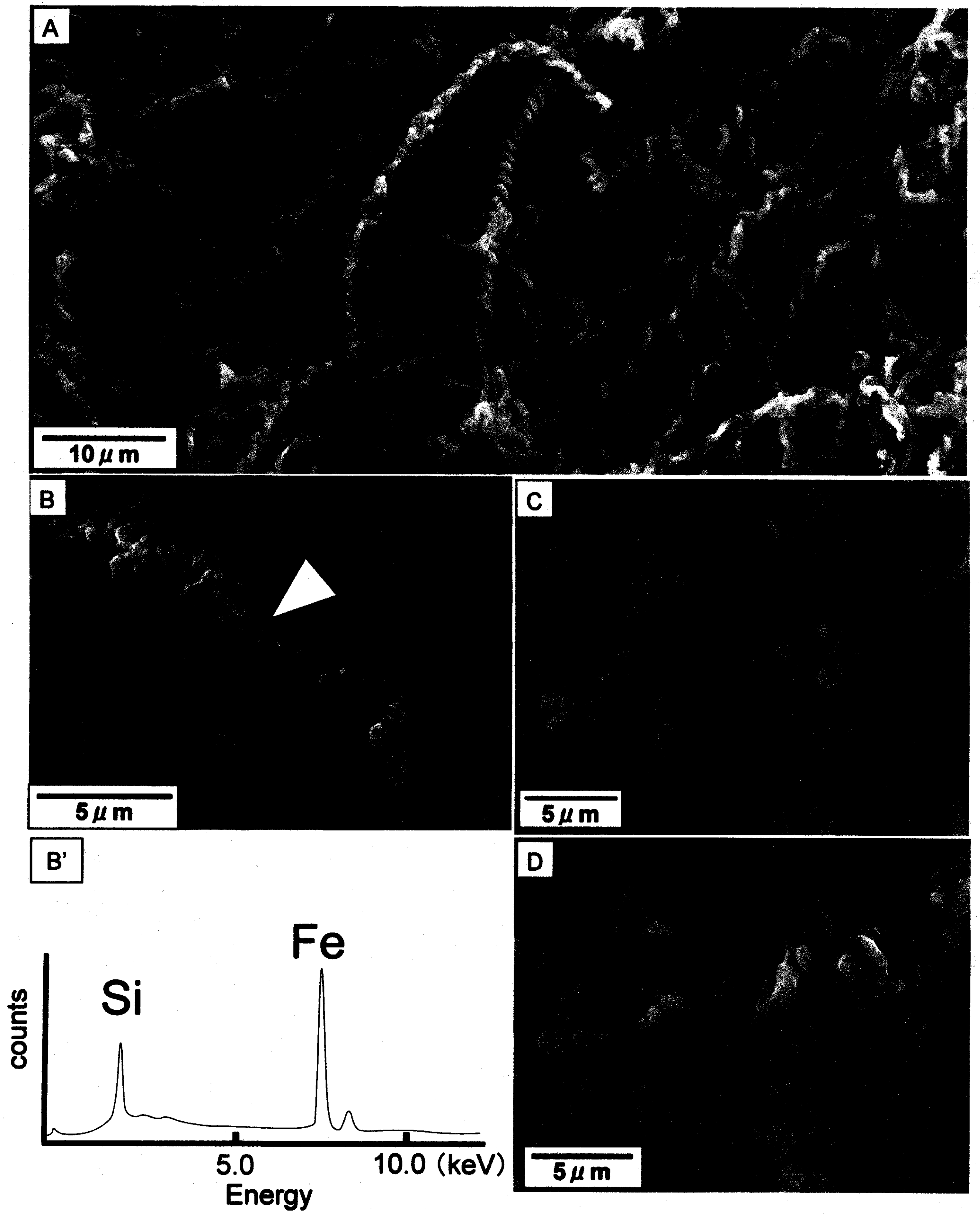

Fig. 3. SEM micrographs of reddish brown microbial mats were collected from Aso caldera, showing the bacterial colony consisted of ion oxidizing bacteria, such as *G. ferruginea* (A). Close up stalk of *G. ferruginea* coverd with spherical materials (B). The EDX spectrum of a small particle (arrow in B) indicating the presence of Fe and Si (B'). Stalk of *G. ferruginea* tangle each other (C), and fabricating a block of iron hydroxides (D).

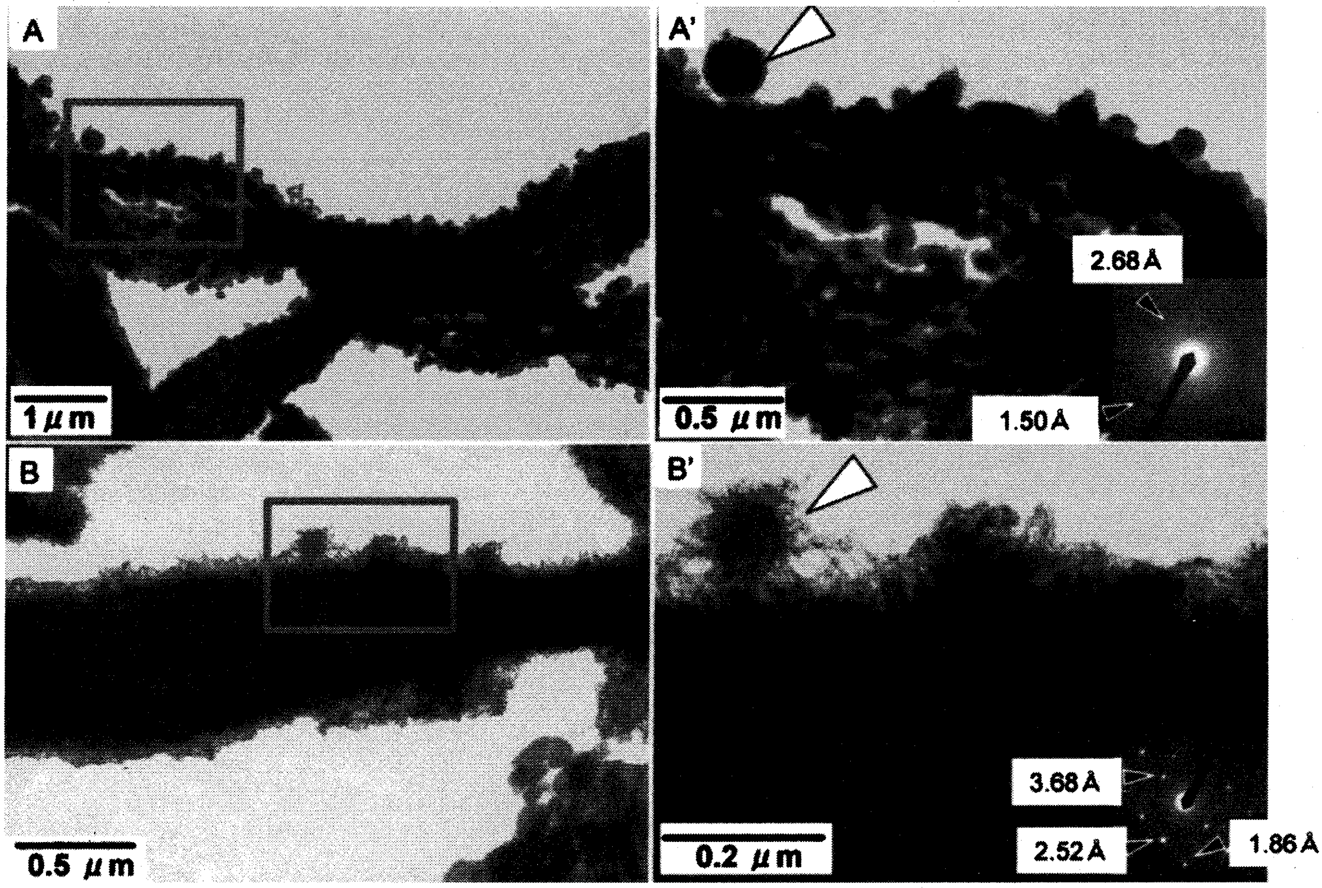

Fig. 4. TEM micrographs of stalk of *G ferruginea* were collected from Aso caldera indicating two typed stalks (A, B). Under higher magnification of A shows spherical materials identified as ferrihydrite with 2.68 Å and 1.50 Å (A' inset), whereas others consist of needle-like hematite with 3.68 Å, 2.52 Å, 1.86 Å (B' inset). Arrows show analytical points.

V. Conclusion

Reddish brown microbial mats in Aso caldera contain high concentration of Fe and composed of *G ferruginea* which inhabit dominance in colony. Stalk of *G ferruginea* have two typed formation. One is spherical ferrihydrite, the other is needle-like crystalline materials such as hematite. These microbial mats revealed that stalk of *G ferruginea* tangle each other, and fabricate a block of iron hydroxides.

The results suggested that *G ferruginea* produces ferrihydrite and hematite, and play an important role contributed to be a significant factor for forming the limonite ore deposit in Aso caldera.

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