## A new insight on the chloritization mechanism of biotite in hydrothermally altered granite

\*Takahiro Ishii<sup>1</sup>, Toshihiro Kogure<sup>1</sup>, Ryosuke Kikuchi<sup>1</sup>, Ritsuro Miyawaki<sup>2</sup>, Takashi Yuguchi<sup>3</sup>

1. University of Tokyo, 2. National Museum of Nature and Science, 3. Yamagata University

Chlorite commonly forms by hydrothermal alteration of biotite in granitic rocks. This "chloritization" mechanism of biotite has been paid attention and investigated for a long time to understand alteration history of granitic rock which is one of the most common lithofacies. However, it looks that previous studies have focused either crystallographic [1, 2] or chemical aspect [3] of the chloritization, not both. This study investigated the chloritization process of biotite, by analysing both the crystal structures and chemical compositions of the chlorite. As a result, a new insight for the chloritization, simultaneous occurrence of the two transformation mechanisms, is proposed.

The rock investigated was Toki granite, distributed in Central Japan. The sample was collected from the borehole in the Mizunami Underground Research Laboratory; in the altitude range from -274m to -314 m above sea level [3]. Observation of the petrographic thin sections revealed that the granite contains biotite with various stages of chloritization. Generally, biotite grains of various chloritization are homogeneously distributed in a thin section. X-ray diffraction (XRD) patterns obtained using a Gandolfi camera confirmed that the dominant polytype of unaltered biotite is 1*M* and the polytypic group of the emerald-like coloured chlorite grains is II*bb*. Electron microprobe analysis revealed that emerald-like coloured, completely chloritized grains contain no titanium (Ti) which is a constituent element of biotite in granite ( "Ti-free chlorite"). On the other hand, element mapping of partially chloritized biotite grains indicated that the grains contain thin regions with no potassium (namely no biotite component) but with a certain amount of Ti. Considering existence of other elements, these thin regions are also considered to be chlorite ( "Ti-bearing chlorite"). Quantitative analysis of these Ti-free and Ti-bearing chlorite showed different Al contents and Mg/Fe ratios between them, beside the amount of Ti. Investigation using TEM confirmed that both Ti-free and Ti-bearing chlorites are really "chlorite", from electron diffraction and high-resolution imaging.

This compositional difference can be ascribed to different chloritization mechanisms; Ti-bearing chlorite took over the 2:1 layer from biotite, and Ti-free chlorite was formed via dissolution-recrystallization process. In biotite, Ti is expected to locate in the octahedral sheet of the 2:1 layer. Hence, chlorite transformed from biotite must contain Ti, if the 2:1 layer was inherited from biotite without significant cation diffusion. On the contrary, chlorite can be Ti-free, if the 2:1 layer was once dissolved and new 2:1 layers formed from the hydrothermal fluid. In this case, Ti formed titanite, CaTiSiO<sub>5</sub>, which is common within chloritized grains, with calcium and silicon transported via the fluid. In TEM, Ti-bearing chlorite showed a diffraction pattern indicating a mixture of different polytypic groups, indicating structural discontinuity with completely chloritized grains which were IIbb from XRD. IIbb is considered to be the most stable polytypic group and expected to form if chlorite was formed from solution. However, if chlorite was transformed from biotite via a solid-to-solid pathway inheriting the 2:1 layer, complete IIbb stacking may not be expected owing to the difference of the interlayer structures between biotite and chlorite [2]. Finally, high-resolution imaging support that Ti-bearing chlorite inherited the 2:1 layer from biotite, because this chlorite has 2:1 layers whose orientation is uniform, which is the same characteristic as biotite-1*M*. On the other hand, Ti-free chlorite consists of 2:1 layers whose orientation is considerably disordered.

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