

論文の内容の要旨

**Nanoscopic structures and properties of mixed-layer biotite-vermiculite revealed by integrated mineralogical analysis**

(統合的な鉱物学的分析による黒雲母-バーミキュライト混合層鉱物の微細構造と性質の解明)

氏名： 菊池 亮佑

This thesis is dedicated for the investigation on “weathered biotite”, which is considered as a major material fixing radioactive cesium in granitic soils mainly covering contaminated areas formed by the Fukushima nuclear accident in 2011. Biotite in granitic rocks commonly transforms by weathering to vermiculite and other secondary minerals via various alteration stages. Although tremendous works on the mechanism of biotite alteration have been conducted in the past, the characteristics of the mixed-layer structures of biotite-vermiculite and heterogenous chemical features of weathered biotite are still unclear. In this thesis, complex structures and chemical compositions of the weathered biotite have been examined by means of several nanoscopic methods combining with bulk analyses. The major part of this thesis is composed of four chapters as follows.

In chapter 2, mineralogical and chemical characteristics of fresh biotite and its weathered products in a weathering profile of granodiorite rock in Fukushima Prefecture, Japan, were comprehensively investigated. Both bulk analyses such as X-ray diffraction (XRD), thermal analysis and Mössbauer spectroscopy, and microanalysis such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), electron microprobe analysis (EPMA), and transmission electron microscopy (TEM) were used in order to examine various and often heterogeneous structures of weathered biotites. Based on mineralogical and chemical analyses, three stages of biotite alteration

within the weathering profile were deduced as follows: (1) Biotite altered to lamination of almost unweathered biotite packets (~ several micrometers thick) and those with biotite-vermiculite interstratification, showing a significant release of K from biotite and incorporation of Ca into biotite from the external solution. Unlike interlayer cations (K, Na, Ca), contents of the 2:1 layer of biotite such as Si, Al, Fe, Mg, Ti were almost the same as those in the fresh biotite. Secondary minerals were hardly found. (2) A partly ordered interstratified structures gradually increased instead of segregated one, and Fe-bearing kaolinite formed around cleavages. The contents of kaolinite and iron hydroxide gradually increased as the progress of weathering. Chemical analysis showed non-stoichiometric decrease of Mg, Fe and K, and increase of Al and Si. The former change was derived from cation ejection from biotite structure, while the latter was probably due to the formation of fine packets of kaolinite within micro-cleavages. Ca-vermiculite gradually disappeared as the progress of weathering, instead Mg-vermiculite gradually became dominant. (3) Vermiculite-layers increased in the mixed-layer structures of biotite-vermiculite. The significant increase in volume of Fe-bearing kaolinite around the edge of the grain caused “fanned out” texture from the edge. The decrease of Ti was observed as well as Mg, Fe and K, and the released Ti formed TiO<sub>2</sub> particles around the cleavages.

The valence of octahedral iron in biotite structures and the effects of oxidation on vermiculitization have been a controversial issue. The previous studies on biotite weathering have well demonstrated bulk analyses of iron oxidation states of altered biotites, however, iron oxidation state at micro-scale inside mica grains during vermiculitization process has not been elucidated, yet. The microscopic methods used in chapter 2 demonstrated that vermiculitization proceeds heterogeneously inside biotite grains. In chapter 3, the weathered biotite at the 1<sup>st</sup> alteration stage as described in the chapter 2, was examined more detail, focusing its iron oxidation state at micro-meter scale in order to clarify the spatial relationship between iron oxidation state and vermiculitization. The weathered biotite studied was consist of the lamination of almost unweathered biotite packets (~ several micrometers thick) and those with biotite-vermiculite interstratification. Two types of packet were continuous from the edge to the center of the grain, parallel to cleavages. Based on the chemical composition obtained from EPMA, octahedral iron in interstratified packets were expected to be more oxidized than that in biotite packets. Micro X-ray absorption near edge structure ( $\mu$ -XANES) using synchrotron radiation, however, indicated that iron oxidation state was the same between adjacent biotite- and interstratified-packets. Fe valence exhibited the increase of Fe<sup>3+</sup> near the edge of the grains, compared to the inner regions. The charge unbalance due to iron oxidation may be compensated not

only by release of interlayer  $K^+$  but also by incorporation of  $H_3O^+$  at vermiculite interlayer and/or deprotonation of  $OH^-$  of the 2:1 layer.

In chapter 4, the Cs sorption experiments into single-crystals of the weathered biotite characterized in the previous chapters was conducted. In order to understand how Cs-sorption phenomenon proceeds at micro - nanoscopic scale, the distribution of sorbed Cs inside crystals were examined by using XRD, SEM-EDS and high-angular annular dark field imaging of scanning transmission electron microscopy (HAADF-STEM). Cs was incorporated preferentially into particular interlayers at a low Cs concentration in the solution or in a short duration. At a higher Cs concentration or with a longer duration of immersion, the remaining vermiculite interlayers interstratified in biotite were substituted by Cs. Furthermore, even at higher Cs concentration condition, vermiculite-interlayers without Cs-incorporation remained adjacent Cs-incorporated interlayers. This that heterogenous ion-exchange phenomena among interlayers may be resulted from heterogeneity in chemical compositions of the 2:1 layers. Another possibility is that chemical compositions of the vermiculite layers are uniform, and it is an intrinsic characteristic of cation exchange at the interlayer sites of 2:1 phyllosilicates that ion-exchange proceeds in an “interlayer by interlayer” manner: Once the ion exchange starts at a particular interlayer, the successive ion exchange at the same interlayer proceeds rather than the exchange starting at a new interlayer.

In chapter 5, a “vermiculite” sample from Palabora, which is equivalent to the new reference-clay-sample ‘hydrobiotite’ of the Clay Science Society of Japan, was examined. Although the “vermiculite” sample from Palabora has been often used as standard vermiculite samples for laboratory experiments in previous literatures, its mineralogical characteristics was not well described, yet. First of all, the observed XRD profile and SEM observation in the present study indicated that this sample was not uniform but complex mixture of grains with various chemical compositions and structures of mixed-layer biotite-vermiculite. Therefore, the structural and chemical compositional variances of the sample were examined by means of SEM-EDS, bulk analyses (XRD, TG-DTA and Mössbauer spectroscopy) and one-dimensional XRD profile simulation. The XRD profile indicated that the sample was predominantly composed of 1:1 regular interstratification of biotite- and vermiculite-layers, although its interstratified stacking sequence is not so regular as the ideal hydrobiotite structure. Diopside ( $Di_{75}Hd_{25}-Di_{80}Hd_{20}$ ), wollastonite, apatite and titanite, were identified as impurity minerals. One-dimensional XRD profile simulation for mixed-layer structure suggested that, at least, four different stacking sequences of mixed layers, the vermiculite- and biotite-layers

were necessary to explain the major diffraction peaks of observed XRD profile. Approximate 70% of the total mass had the hydrobiotite-like sequence of the mixed layers, which was divided into two types, whereas the other mass had the sequence rich in the biotite-layer stacking sequence. Chemical compositions, especially the amount of K, were significantly varied among individual grains, while the compositional variance inside each grain was relatively small. The contents of Fe and Mg showed negative correlation indicating the various substitutions of octahedral site in biotite-vermiculite structures. My data demonstrates that some attention should be paid for the interpretation of the experimental results obtained using this sample, due to its large heterogeneity in chemical compositions and structures at grain-to-grain scale and impurity minerals such as diopside and apatite.