

Comparison of biotite dissolution in the laboratory and in the field by high-resolution transmission electron microscopy

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The dissolution of minerals are generally explained by protonation, deprotonation and the subsequent detachment of metal species (e.g. Stumm, 1992) based on laboratory experiments under 'far from equilibrium' conditions. The process is considered to be applicable to the dissolution of sheet silicates in which Si and Al ions dissolve from the edges of the 2:1 layers (e.g. Wieland and Stumm, 1992; Nagy, 1995). However, weathering in the field seems to be different from laboratory dissolution in terms of the saturation state with respect to primary minerals and the formation of secondary minerals. In particular, biotite weathering is usually accompanied by vermiculite overgrowth within a biotite grain (Banfield and Eggleton, 1988) partly because there is no significant differences between biotite and vermiculite except for the small differences in the interlayer cations and occupancies, and the compositions of the 2:1 layers. Thus, the process observed in the laboratory is not consistent with that in the field. Recently, Kogure and Murakami (1996) successfully identified biotite and vermiculite layers in hydrobiotite by high-resolution transmission microscopy (HRTEM) in the atomic scale. Using their technique, we compare the process of biotite dissolution in the laboratory with that in the field in the early stage of dissolution.

Experimental

We used biotite crystals of coarse-grained granite from Inada, central Japan. The granite mainly consists of quartz, plagioclase, K-feldspar, and biotite. We collected different types of granite rocks in terms of the extent of weathering. Biotite crystals with brown stains by naked eye, which indicates the oxidation of ferrous ions, were chosen as biotite in the early stage of weathering (sample B-3'). Some of fresh biotite crystals (sample B-1) were used for the following dissolution experiment. Fresh biotite crystals of 50 mg were reacted with deionized, pure water of 10 mL in a Teflon vessel at 150°C for 1, 4, and 10 days. After the dissolution experiments, pHs were measured at room temperature, and the

solutions were analysed by inductively coupled plasma atomic emission spectrometry. The reacted biotite crystals for 10 days (sample 150-10) were subjected to HRTEM. Samples B-1, B-3', and 150-10 were examined by X-ray diffraction (XRD) analysis.

For HRTEM image observation, samples B-1, B-3', and 150-10 were examined in a JEOL JEM 2010 microscope with a point resolution of 0.2 nm ($C_s = 0.5$ mm). TEM negatives were digitized and processed to remove noise and the image of amorphous material by rotational filtering (NCEM package of Kilaas and Siddnei implemented within Digital Micrograph V. 2.5, Gatan Ltd.). Simulated images calculated using MacTempas software (Total Resolution Co.) were compared to the filtered images to provide atomic information of the biotite and vermiculite structures. The crystal structure of 1M biotite for the simulation

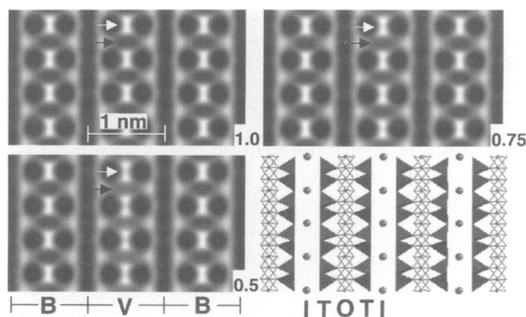


FIG. 1. [100] simulated images of vermiculite-like layers (V) in biotite layers (B) along with a schematic representation of the corresponding biotite structure. The conditions of the simulations are: defocus, -42 nm; thickness, 4.8 nm. The numbers in the right bottom of the simulated images represent K occupancies at the K sites of the vermiculite-like layers. White and black arrows correspond to vacant and K sites, respectively. The basal spacing of the vermiculite-like layers collapse to 1 nm under a high vacuum of TEM. The contrast of the K sites becomes lighter with decreasing the K occupancy. I represents an interlayer; T, a tetrahedral sheet; and O, an octahedral sheet.

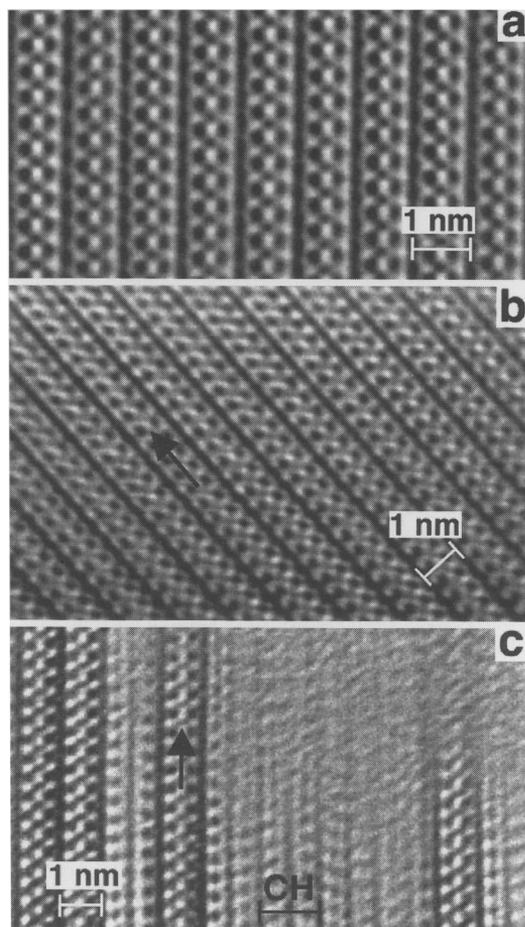


FIG. 2. HRTEM images of (a) fresh biotite (sample B-1), (b) slightly weathered biotite (sample B-3'), and (c) experimentally reacted biotite (sample 150-10). The contrast in the interlayers shown by the arrows indicates the formation of vermiculite. CH represents one chlorite layer.

was based on that by Brigatti and Davoli (1990); the vermiculite structure in biotite was made removing a certain amount of K ions from the interlayers.

Results and discussion

The solution analysis for the dissolution experiments reveals that biotite dissolves incongruently with releasing K ions preferentially (Table 1). The increase in Si concentration in solution with increasing time indicates the obvious breakdown of the biotite structure and the detachment of Si ions

TABLE 1. Cation concentrations in solutions after the dissolution experiment (mol/L)

Cation	1 day	4 day	10 day
Si	2.6×10^{-5}	4.5×10^{-5}	5.6×10^{-5}
Al	n.d.	9.5×10^{-7}	1.3×10^{-5}
K	8.9×10^{-5}	1.4×10^{-4}	1.1×10^{-4}

into solution as predicted by the above process (e.g. Stumm, 1992). The XRD analyses show that biotite is the only mineral species present in samples B-1, B-3', and 150-10; the XRD cannot detect vermiculite.

Figure 1 shows [100] simulated images of vermiculite-like layers (V) in biotite layers (B) along with a schematic representation of the corresponding biotite structure. The contrast of the K sites (black arrows in Fig. 1) becomes lighter and that of the vacant sites (white arrows in Fig. 1) darker with decreasing the K occupancy, i.e. with vermiculitization of biotite. The change in contrast was used to identify vermiculite-like layers in biotite layers of the weathered and reacted samples. The interlayers of the fresh biotite (sample B-1) (Fig. 2a) have the same contrast as that simulated (Fig. 1). Most of the slightly weathered and experimentally reacted biotite (samples B-1 and 150-10, respectively) have the same structure images as that of the fresh biotite, i.e. they are not altered. This is consistent with the XRD results. However, the contrasts in the interlayers of some of samples B-1 and 150-10 indicate K deficiency (Fig. 2b,c, respectively). This strongly suggests vermiculitization has started in biotite. The formation of vermiculite, at least partly, accounts for the preferential dissolution of K in the dissolution experiments.

Our data suggest that in the early stage of dissolution or weathering of biotite, dissolution (or the breakdown of the structure) and vermiculitization occur at the same time both in the laboratory and in the field. Biotite is dissolved on one hand, and vermiculite grows in biotite on the other hand. Thus, the dissolution rates of biotite are obscured by the presence of vermiculite.

References

- Banfield, J.F. and Eggleton, R.A. (1988) *Clay. Clay Mineral.*, **36**, 47–60.
- Brigatti, M.F. and Davoli, P. (1990) *Amer. Mineral.*, **75**, 305–13.
- Kogure, T. and Murakami, T. (1996) *Mineral. J.*, **18**, 131–7.