Direct identification of biotite/vermiculite layers in hydrobiotite using high-resolution TEM

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Abstract

The microstructure of hydrobiotite, interstratified biotite/vermiculite, was examined to demonstrate an atomic scale investigation of weathering of minerals by high-resolution transmission electron microscopy (HRTEM). Vermiculite basal spacing was collapsed to about 0.95 nm, compared to the unchanged biotite 1.0 nm spacing, by dehydration probably during the ion-milling sample preparation. Atom-resolving structure images with 0.2 nm point resolution show a distinct difference between K-containing and K-depleted interlayers, corresponding to biotite and vermiculite respectively. Thus, the difference in image enables us to identify vermiculite layer positions in hydrobiotite unambiguously. Although the vermiculite layers are randomly formed in the original biotite, there is a tendency to form 1:1 regular biotite/vermiculite interstratification locally. In some interlayers the contrast of potassium columns changed gradually, which suggests that biotite is directly transformed to vermiculite in the weathering process. These observations demonstrate atom-resolving HRTEM is a useful method for structure analyses of such water containing secondary minerals as vermiculite in spite of spacing changes caused during sample preparation or observation in TEM.

Introduction

Alteration of phyllosilicates often results in the formation of interstratified structures with two or more kinds of minerals. Hydrobiotite, interstratified biotite and vermiculite (Gruner, 1934), is often formed in the weathering process of biotite (e.g., Banfield and Eggleton, 1988; Vali *et al.*, 1992). This mineral is characterized by a K deficient (not completely lost), and ferric iron and water containing chemical composition compared to fresh biotite, and a very broad 1.1 - 1.2 nm peak in X-ray diffraction pattern (Gruner, 1934). To understand the weathering mechanism of biotite, it must be useful to examine the structure (the stacking order of interstratification of biotite/vermiculite, etc.) of hydrobiotite with TEM. Water molecules and hydrated cations in the interlayers of vermiculite are, however, removed in vacuum and the interlayers collapse easily, which leads to vermiculite having almost the same basal spacing as that of biotite. Therefore, it is difficult to distinguish these two kinds of layers (for example, Vali *et al.*, 1992). However, Banfield and Eggleton (1988) reported non-collapsed vermiculite layers in the sample prepared using conventional ion-

milling, which is probably due to the different nature of the vermiculite interlayers they have investigated. In order to overcome this problem, not only for hydrobiotite but also for other water-containing interstratified minerals, several methods have been proposed, including intercalation of organic materials (Yoshida, 1973; Lee and Peacor, 1986; Bell, 1986; Vali *et al.*, 1992), considerably overfocused imaging (Ahn and Peacor, 1989; Guthrie and Veblen, 1989; Veblen *et al.*, 1990), sample freezing (Murakami *et al.*, 1993) and fixation using LR White resin (Kim *et al.*, 1995).

Recent improvement of the resolution of TEM makes it possible to identify relatively heavy atoms in a crystal structure routinely. Our recent investigations reveal that 200 kV TEM observations with 0.2 nm point resolution can clearly identify potassium ions in the interlayers of biotite, which suggests the possibility to distinguish K-depleted vermiculite layers from biotite layers in hydrobiotite in spite of the similar basal spacing. The present paper reports unambiguous identification of biotite/vermiculite layers in hydrobiotite using atom-resolving HRTEM.

Experimental

The samples used were pseudo-hexagonal crystals (about 2 mm in lateral and 1 to 2 mm thick) picked up from highly weathered biotite granite at Hatsugano in Yamanashi Prefecture, Japan. The color of (001) cleaved surface was yellow-brown or gold and the crystals can be easily cut with knife. The powder X-ray diffraction pattern showed broad peaks at about 1.2 nm and 0.35 nm indicating the presence of hydrobiotite. Ethylene glycolation did not change the diffraction pattern. Cleaved fragments of the crystal were mounted in resin and sliced perpendicularly to the basal plane. The mechanically thinned specimen was further thinned by argon ion milling, and carbon coating was made for TEM observation. Electron microscopy was performed at 200 kV using a JEOL JEM-2010 microscope (Cs = 0.5 mm) with a LaB₆ filament. All observations were made setting the crystal into its [100], [110] or [110] parallel to the electron beam. Practically these three directions are almost indistinguishable due to the stacking disorder in biotite/vermiculite. Thin wedged areas were selected and the images were recorded at near Scherzer focus to obtain the structure images which distinguish one cation sheet from another. The multi-slice image simulation was performed using MacTempas program on a Macintosh computer and the atomic parameters of phlogopite reported by Hazen and Burnham (1973).

Results and Discussion

Fig. 1 shows a typical high-resolution image and the corresponding selected area diffraction pattern of hydrobiotite. The specimen consists of crystalline and amorphous regions. The amorphous regions were probably not generated during the sample preparation, but were intrinsic to the material because well crystalline phyllosilicate samples (biotite, mus-

FIG. 1. (a) High resolution image and (b) related SAED pattern of hydrobiotite. The positions indicated by arrows are K-depleted interlayers. The SAED pattern indicates the basal spacing of about 1.0 nm and considerable stacking disorder.

covite, chlorite etc.) prepared by the similar method do not contain such amorphous regions. The amorphous regions are considered to be formed by the dissolution of the original biotite (Banfield and Eggleton, 1988). Although all unit layers in Fig. 1 have a basal spacing of about 1.0 nm, our careful observation indicates that there are two kinds of contrasts of unit layers, one of which (attributed to collapsed vermiculite as described below) is indicated by arrows in the figure. The higher magnification image of another region shows the detailed difference in the contrast (Fig. 2). Compared with simulated images (Fig. 3), it is clearly indicated that the difference in the contrast is generated at the interlayer positions. Although the simulated images in Fig. 3 were calculated normal to the $[100]$ beam direction, the images with the other two directions ($[110]$ and $[1\bar{1}0]$) have the identical features around the interlayer positions due to the pseudo-hexagonal arrangement of atoms. The continuous white contrast at the interlayers as indicated by "V"s in Fig. 2 corresponds to the simulated image of K-depleted biotite (K occupancy is 0.0) with the specimen thickness less than 10 nm in Fig. 3, whereas the normal biotite has the dot-like contrast of K ions at the interlayers in both the observed and simulated images (K occupancy is 1.0). Moreover, image shift by 1.0 nm of the upper part of photograph against the bottom one perpendicular to the basal plane in Fig. 2 reveals a basal spacing of the layers containing the K-depleted interlayers

FIG. 2. Magnified structure image of hydrobiotite. The interlayers indicated by "V"s have a continuous white line contrast compared to adjacent biotite interlayers, suggesting K-depletion in these interlayers (see the simulation results in Fig. 3). The K-depleted interlayers are considered to be formed by the collapse of vermiculite layers. The upper portion of the photograph is shifted by 1.0 nm to the right against the bottom one, so that a slightly smaller basal spacing (about 0.95 nm) of the "vermiculite" layer than that of biotite (1.0 nm) as indicated by arrows can be easily recognized.

slightly smaller than that of normal biotite as indicated by arrows in the figure. These layers have about a 0.95 nm basal spacing, which is very close to the reported value, 0.92-0.94 nm (Gruner, 1934), of completely dehydrated vermiculite heated to 750°C in air. From these results, the 0.95 nm, K-depleted layers are considered as the collapsed vermiculite layers which originally possessed about a 1.5 nm spacing. As shown in Fig. 2, these dehydrated vermiculite layers are unambiguously identified using atomic resolution images. Although the distribution of vermiculite layers (Figs. 1 and 2) indicates that the vermiculite layers are randomly formed in original biotite, there is a tendency to form 1:1 regular biotite/vermiculite interstratification locally. More statistical evaluation is under progress.

In some vermiculite layers we observed the interlayers which have a gradual change of the contrast of potassium as shown in Fig. 4. In the figure, the interlayer marked A has the contrast of K gradually diminishing from the top to the bottom, whereas interlayer B has the contrast of a continuous white line around the center of the image, which changes to discontinuous white spots at the bottom. These changes of the contrasts are not due to the difference in the specimen thickness or orientation, because the contrast of the adjacent biotite

FIG. 3. Multi-slice simulated images of biotite as functions of the specimen thickness and K occupancy in the interlayer. The beam direction is [100] and defocus value is -42 nm (Scherzer focus). The right figure is the corresponding crystal structure of biotite (only cations are shown). The arrows at the top indicate the interlayer positions. Note that K-depleted interlayer (K occupancy is 0.0) in the left side image has a continuous white contrast whereas that of normal biotite (K occupancy is 1.0) has spots formed by K columns.

layers is not changed. This observation suggests that the formation of vermiculite layers is progressed by direct transformation from the original biotite, and that the transition zone, where the interlayers have the intermediate contrast, is very short, several nanometers in distance (Fig. 4)(Banfield and Eggleton, 1988). However, if vermiculite with the white interlayers has originally a 1.5 nm spacing, the original biotite/vermiculite interstratified structure in Fig. 4 must be considerably bent by the transitional interlayers. It should be mentioned that the relatively straight stratification of biotite/vermiculite in Fig. 4 may be formed by the removal of water molecules.

Finally this work has demonstrated that atom-resolving HRTEM, beyond the previous HRTEM works which generally observe only lattice fringes of basal planes of layer silicates, is a powerful tool to investigate the alteration of layer silicates. Such images as shown in Figs. 2 and 4 can be used not only for vermiculite identification but also for the analysis of stacking relation of cation sheets which form mica polytype. Biotite areas which do not

FIG. 4. Structure image showing interlayers changing their contrast locally. The interlayer marked "A" has a similar contrast as that of adjacent biotite in the upper portion which gradually changes into a continuous white contrast downward. The interlayer B has the normal biotite contrast at the bottom that changes into a white contrast upward. C is another K-depleted interlayer with a continuous white contrast in the image.

include vermiculite in Fig. 2 and 4 indicate that the original biotite has a 1M polytype structure, whereas some areas of biotite in Fig. 1 indicate a random stacking sequence. Further investigations may give some insights into the relationships between polytype structures of the original mica and locations of vermiculization in the crystal structures.

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