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Kaolinitization of biotite: TEM data and implications for an alteration mechanism[1]

JUNG HO AHN,[2] DONALD R. PEACOR
Department of Geological Sciences, The University of Michigan, 1006 C. C. Little Building,
Ann Arbor, Michigan 48109, U.S.A.

ABSTRACT

Partially kaolinitized biotite from Brighton, New Zealand, was studied by using transmission and analytical electron microscopy (TEM and AEM). Kaolinite occurs in two distinct modes: (1) as 50–300-Å-thick packets of layers interstratified within biotite and (2) as two-layer units (14 Å) irregularly interlayered within biotite. Some two-layer kaolinite units terminate at single biotite layers (10 Å), implying a reaction of one biotite layer to two kaolinite layers. Structural and chemical considerations suggest an alteration mechanism consisting of complete dissolution of biotite and crystallization of kaolinite at linear boundaries. Tunnel-like structures inferred at reaction boundaries may serve as conduits for diffusion of reactant and product ions. Such linear imperfections may be significant in mass transport during the alteration of large rock volumes.

INTRODUCTION

Biotite can react to form a variety of different phases, depending on alteration and weathering environments, including vermiculite (Walker, 1949), montmorillonite (MacEwan, 1954), chlorite (Veblen and Ferry, 1983; Yau et al., 1984; Eggleton and Banfield, 1985), gibbsite (Wilson, 1966), or kaolinite (Wilson, 1966; Stoch and Sikora, 1976; Muenier and Velde, 1979; Craw et al., 1982). Although kaolinitization is a common biotite alteration phenomenon that has been investigated by optical microscopy and powder X-ray diffraction (XRD) (e.g., Wilson, 1966; Stoch and Sikora, 1976; Craw et al., 1982), little is known about the textures, chemistries, and structures involved in the alteration process. We therefore have carried out a TEM and AEM study at high resolution in order to directly characterize the mechanism of alteration of biotite to kaolinite.

The samples used in this study are partially kaolinitized biotites from the lower limit of the biotite zone of the Otago schist at Brighton, approximately 16 km south of Dunedin, New Zealand. Craw et al. (1982) described similar samples from the same locality as containing biotite having a curious greenish color and low K_2O contents (4.4–8.5 wt%). Using XRD and electron-microprobe data, Craw et al. (1982) showed that the "green biotite" actually consists of an intimate intergrowth of metamorphic biotite and secondary kaolinite that is not fully resolvable optically or with the electron microprobe. Their data implied that TEM-AEM studies of such intergrowths might yield direct images of the interfaces where biotite alters to kaolinite. Craw et al. (1982) indicated that kaolinization in these samples appears to have been accompanied by high activity of CO_2, resulting in partial loss of epidote and producing rutile and/or anatase at the expense of sphene, without oxidation of siderite. Alteration was therefore not a simple weathering process.

EXPERIMENTAL METHODS

Samples were first prepared as thin sections oriented approximately perpendicular to (001) of the partially altered biotites. Following optical examination, selected areas were ion-milled and then carbon-coated. Samples were observed at 100 kV in a JEOL JEM-100CX scanning-transmission electron microscope (STEM) fitted with a solid-state detector for X-ray energy-dispersive analysis. One-dimensional lattice fringe images were obtained in TEM observations by using only $00l$ reflections following Iijima and Buseck (1978).

TEM OBSERVATIONS

Kaolinite occurs in two modes. The first consists of packets of kaolinite layers interstratified with biotite (Fig. 1). The thickness of the packets varies from 50 to 300 Å and is therefore less than the spatial resolution of AEM analysis (≃300 Å). AEM analyses of interstratified packets of 7-Å layers yield high Al and Si contents characteristic of kaolinite, and low K, Fe, and Mg contents due to contamination by biotite in the analyzed area (Fig. 2a). This is consistent with the electron-microprobe data of Craw et al. (1982) and excludes the possibility that the specific 7-Å layers imaged by TEM are trioctahedral minerals such as serpentine or berthierine. Interfaces between biotite and kaolinite along (001) are parallel, and they display no strain contrast. Parallel intergrowth features of kaolinite and wonesite were previously reported in a TEM study of altered Na-rich biotite by Veblen (1983).

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[1] Contribution no. 428, Mineralogical Laboratory, Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

[2] Present address: Department of Geology, Arizona State University, Tempe, Arizona 85287, U.S.A.

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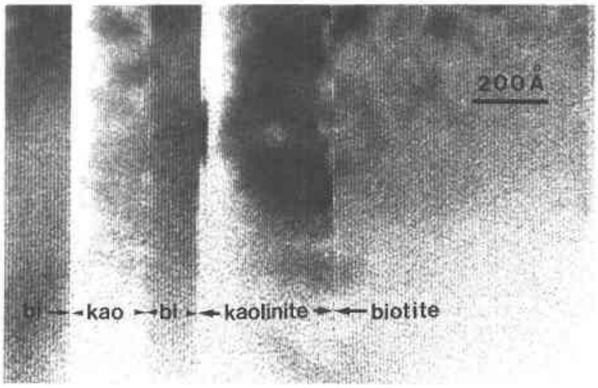

Fig. 1. Lattice fringe image of biotite and interstratified packets of kaolinite layers. (001) interfaces between biotite and kaolinite are parallel.

A second mode of kaolinite occurrence that provides direct insight into the alteration processes was also observed (Figs. 3, 4). This mode invariably occurs as pairs of kaolinite layers that are randomly interlayered within biotite. Electron-diffraction patterns from such areas exhibit intense streaking along **c*** due to random mixed layering (e.g., Fig. 3). However, several repeats of ordered sequences consisting of two-layer kaolinite units and single biotite layers occur locally (Fig. 3). AEM analyses of biotite containing such pairs of layers show a significant decrease in K, Fe, and Mg, and increase in Al and Si content compared to biotite that is free of interlayering, indicating that the interlayered 7-Å layers are kaolinite (Figs. 2a, 2b).

In addition, two-layer kaolinite units frequently are observed to terminate at a single biotite layer (Fig. 4), where the termination is inferred to extend as a linear feature at some angle to the lattice fringe images. As shown in Figure 4, there is some image contrast associated with these terminations, apparently reflecting strain in response to the replacement of a single biotite layer (10 Å) by two kaolinite layers (14 Å).

DISCUSSION

The layer transition boundaries between a single biotite layer and two kaolinite layers represent a reaction front and imply that one T–O–T unit of biotite must change to two T–O units of kaolinite, with the addition of a gibbsite-like octahedral sheet and the reversal in orientation of one tetrahedral sheet of a T–O–T unit. Concomitant chemical changes include replacement of the single Fe- and Mg-rich trioctahedral sheet by two aluminous dioctahedral sheets. Furthermore, all Al in the tetrahedral sheets must be replaced by Si, assuming that the kaolinite layers are compositionally ideal. If the biotite has approximately equal fractions of Fe and Mg, as shown by the electron-microprobe data of Craw et al. (1982), the reaction of one biotite layer to two kaolinite layers can be approximated by $K(Fe_{1.5}Mg_{1.5})Si_3AlO_{10}(OH)_2 + 3Al^{+3} + Si^{+4} + 6H_2O = 2Al_2Si_2O_5(OH)_4 + K^+ + 1.5Fe^{+2} + 1.5Mg^{+2} + 6H^+$, implying a net gain of H_2O, Al, and Si and loss of K, Mg, and Fe (if other biotite/kaolinite ratios are involved in the reaction, specific elements can be eliminated from the reaction).

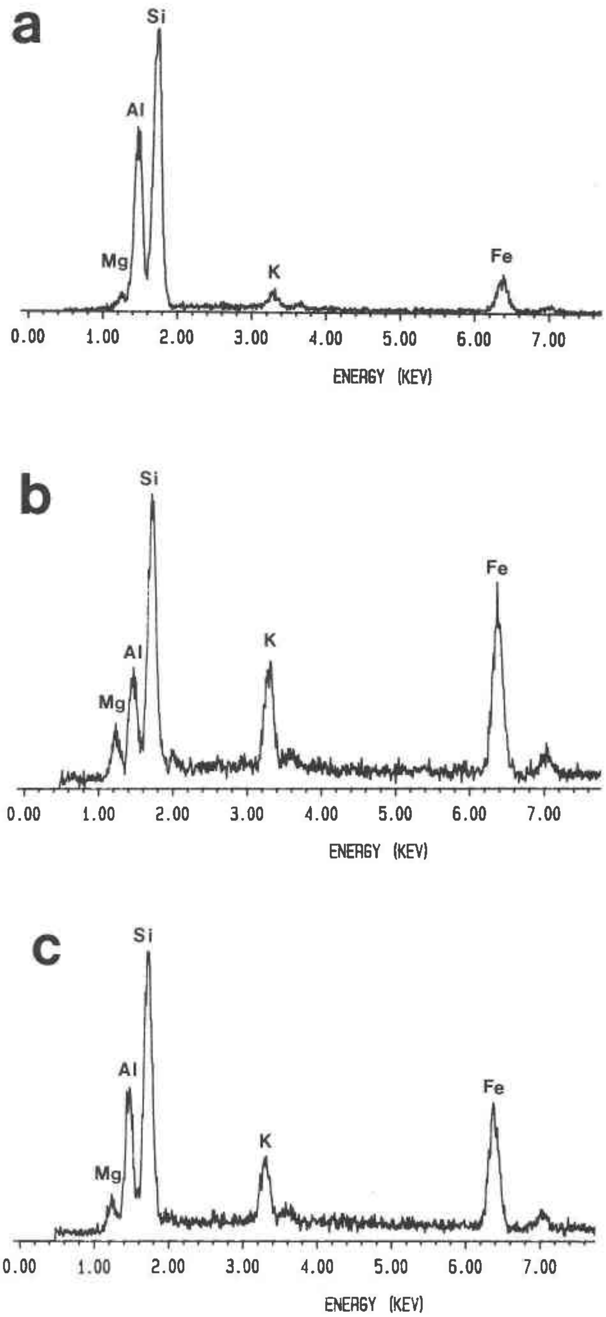

Fig. 2. Energy-dispersive X-ray spectra of (a) interstratified packet of kaolinite layers, (b) biotite free of interlayering of kaolinite layers, and (c) biotite containing interlayered kaolinite layers. Small Mg, K, and Fe peaks in spectrum (a) are due to contamination by biotite in the analyzed area. Low intensities of peaks of K, Mg, and Fe in spectrum (c) relative to spectrum (b) indicate that the interlayered 7-Å layers are kaolinite.

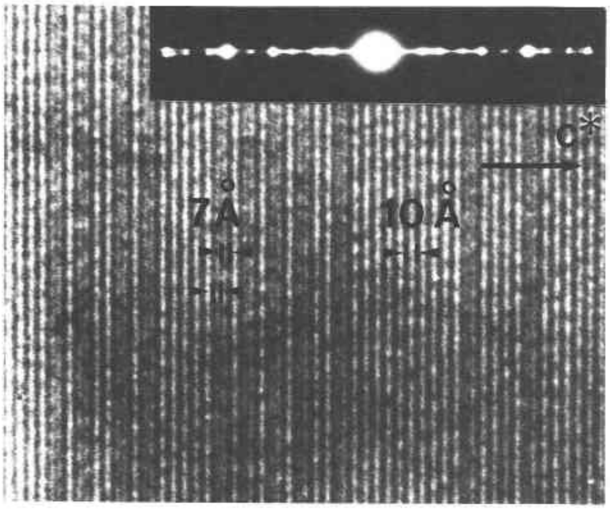

Fig. 3. Lattice fringe image of biotite and interlayered kaolinite layers (inset diffraction pattern). Kaolinite invariably occurs as pairs of layers.

Such drastic structural and chemical changes suggest that the biotite structure may be completely disarticulated; i.e., kaolinitization of biotite in these samples may involve dissolution of biotite layers and crystallization of pairs of kaolinite layers. The discontinuity in structure along the linear reaction boundaries, coupled with the large difference in layer thickness (10 vs. 14 Å), implies the existence of extended defects similar to tunnel structures at the reaction interfaces. The necessary addition of H_2O, Al, and Si and loss of H, K, Fe, and Mg require a pathway for transport. The linear boundary is inferred to serve as such a conduit especially insofar as there is an apparent absence of any other structural defects. Similar pathways for transport of ions and fluids were postulated at chain-silicate reaction interfaces (Veblen and Buseck, 1980) and at chlorite-phlogopite interfaces (Yau et al., 1984). Veblen (1985) has discussed the importance of such extended defects in mineralogical processes. Once initiated at a crystal surface, such a linear reaction boundary would be self-perpetuating and would cause alteration of a single layer of biotite within an otherwise unaffected sequence of biotite layers. Because biotite is altered pervasively over several tens of meters at Brighton, such defect-controlled transport is inferred to be an important mechanism of ion and fluid transport within individual crystals and to pervasively involve at least tens of meters of rock.

If the reaction mechanism for pairs of kaolinite layers also occurs for interstratified packets of kaolinite layers, the number of kaolinite layers in the packets should be multiples of two. However, the number of layers in kaolinite packets cannot be accurately counted because large portions of lattice fringe images of kaolinite are indistinct owing to the rapid beam damage that inevitably occurs. It is therefore not clear if the same reaction mechanism is applicable to all kaolinite. However, the observation of increased volume of kaolinite pseudomorphs after biotite (Stoch and Sikora, 1976; Parachoniak and Środoń,

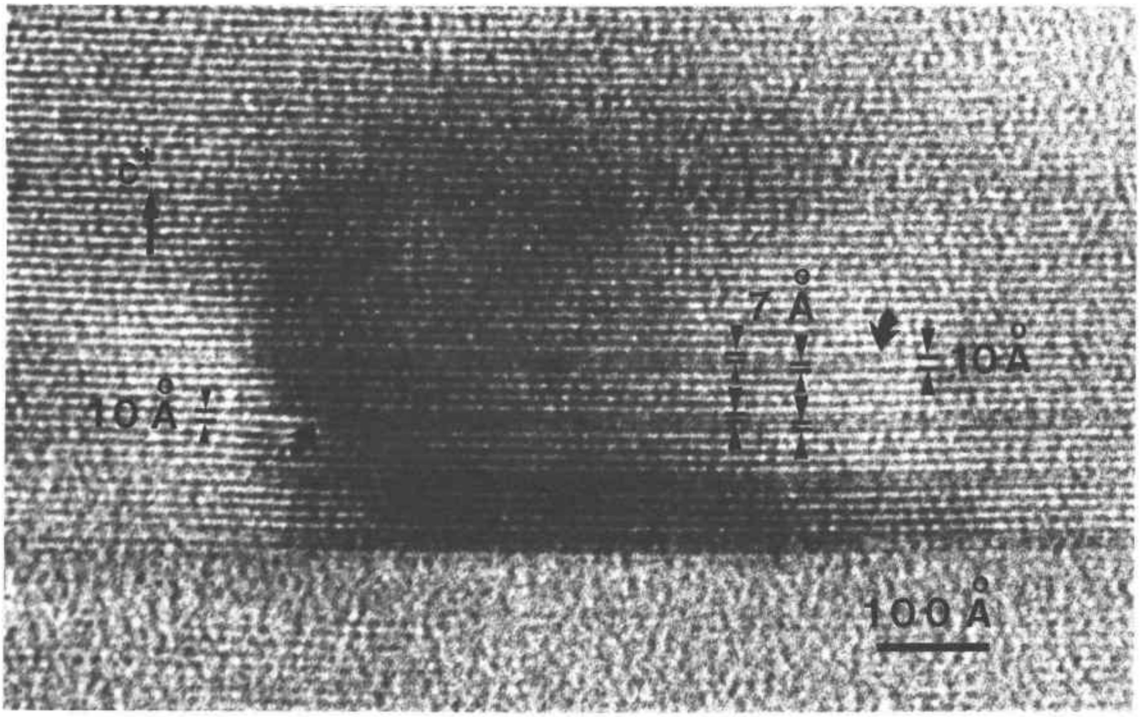

Fig. 4. Lattice fringe image of kaolinite layers interlayered in biotite. Two-layer units of kaolinite occasionally terminate at single biotite layers (see arrows).

1973) is consistent with this alteration mechanism, in that the alteration of one biotite layer (10 Å) to two kaolinite layers (14 Å) results in a significant increase in volume.

The occurrence of four repeats of 2:1 ordered sequences of kaolinite and biotite layers within a mixed-layered crystal (Fig. 3) is interesting, although the significance of such short-range sequences is questionable according to the statistical test of Veblen and Buseck (1979). Although the occurrence of various ordered mixed-layer silicates is well known (see Bailey, 1982), the genesis of such structures is not well understood. They may originate either through simultaneous primary crystallization or alteration after crystallization. There are many documented cases of 1:1 ordered mixed-layered minerals other than phyllosilicates (e.g., members of the bastnaesite family, Van Landuyt and Amelinckx, 1975), where an origin due to primary growth has been suggested. Although it may seem inherently unlikely that the alteration of one layer could affect initiation of subsequent alteration in regularly spaced, adjacent layers, this appears to be the case in this instance, albeit over short repeats. Support for such an interpretation is given by Olives Baños and Amouric (1984) and Olives Baños (1985) who observed repeats of tens of units of ordered sequences of layers of biotite and chlorite that were interpreted to be replacing the biotite. Ordered mixed layering of phyllosilicates may therefore apparently be derived either through primary growth or replacement.

Interlayers between adjacent biotite and kaolinite layers may be occupied by K in order to provide charge balance for the biotite layer. On the other hand, the presence of such interlayer cations is not compatible with the neutral charge of a kaolinite layer of ideal composition. Loss of at least some interlayer K as required by the presence of the kaolinite layer may therefore be accompanied by a charge-balancing process in biotite, such as oxidation of Fe^{+2} to Fe^{+3} or substitution of Si^{IV} for Al^{IV}. Alternatively, the interlayer K may be retained if there is a charge-balancing substitution in kaolinite, such as (Fe^{+2},Mg^{+2}) substitution for Al^{+3}. However, such details are beyond the resolution of the present study.

Finally, strain contrast was not observed in TEM images of the (001) interfaces except where layer terminations occur, although structural misfit between the dioctahedral and trioctahedral layers is expected as pointed out for mixed-layer illite-chlorite (Lee and Peacor, 1985). The systems of H bonding at the interface between biotite and kaolinite may therefore be flexible in order to accommodate the misfit at the interface.

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