

## Transmission electron microscopy of muscovite alteration of tourmaline

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### ABSTRACT

Partially sericitized tourmaline from a pegmatite was investigated using high-resolution transmission electron microscopy (HRTEM). Fine-grained muscovite crystals form extensive narrow veinlets preferentially developed along the {110} and {100} cleavages of tourmaline, indicating that a cleavage-controlled alteration mechanism was dominant. HRTEM images show that tourmaline-muscovite interfaces parallel well-defined {110} and {100} of tourmaline. In general, (001) of muscovite parallels the *c* axis of tourmaline, but otherwise tourmaline and replacing muscovite lack crystallographically oriented relationships. The muscovite consists of numerous 100 to 1000 Å thick subparallel packets, and the angles between (001) of muscovite and (110) of tourmaline are highly variable. Aluminous minerals other than muscovite were not observed as alteration products of tourmaline, suggesting that the tourmaline reacted directly to form muscovite; the alteration apparently involved residual fluids in which K<sup>+</sup> was available and silica was not deficient.

### INTRODUCTION

Tourmaline is a common boron-rich mineral in granitic pegmatites and some metamorphic rocks (Henry and Dutton 1996; London et al. 1996). It is quite resistant to weathering and typically occurs as a detrital mineral in sedimentary rocks and soils (Krynine 1946; Graham 1957; Allen et al. 1974). However, tourmaline in pegmatites may be partially sericitized or altered to various aluminous minerals; most alteration of such tourmaline is apparently caused by late magmatic fluids (Dietrich 1985). In addition to the alterations in pegmatites (cf. Dietrich 1985), recent studies report tourmaline breakdown by hydrothermal fluids in ore deposits (Shaw et al. 1993; Slack 1996) and retrograde shear zones (Slack et al. 1990).

Various minerals in pegmatites, especially Al-rich minerals, are subject to late sericitic replacement by residual fluids (Černý and Hawthorne 1982); K<sup>+</sup> and H<sup>+</sup> metasomatism commonly results in assemblages containing muscovite as an alteration product (Černý and Burt 1984). Aluminous minerals either react directly to form muscovite as a final alteration product or indirectly through various intermediate stages as the fluids evolve and equilibrium is attained. Such alteration of aluminous minerals in pegmatites can be found in spodumene (London and Burt 1982) and andalusite (Burt and Stump 1984; Ahn et al. 1988).

Alteration of rock-forming minerals can be investigated in detail by use of high-resolution transmission electron microscopy (HRTEM), which can reveal reaction interfaces as well as crystallographic relationships occurring as a

result of alteration (e.g., Eggleton 1984; Ahn et al. 1988; Banfield and Eggleton 1990; Hochella and Banfield 1995). In the present study, HRTEM of partially sericitized tourmaline was used to investigate the detailed mineralogical and structural aspects of the alteration and to determine if intermediate phases developed during the alteration.

### SPECIMENS AND EXPERIMENTAL METHODS

The partially sericitized tourmaline comes from a pegmatite associated with the Harney Peak Granite at the

TABLE 1. Representative electron microprobe analyses of tourmaline and muscovite

Oxides (wt%)				Ions per formula unit			
Tourmaline		Muscovite		Tourmaline		Muscovite	
SiO <sub>2</sub>	35.69	SiO <sub>2</sub>	47.08	Si†	6.00	Si	3.08
Al <sub>2</sub> O <sub>3</sub>	43.01	Al <sub>2</sub> O <sub>3</sub>	38.11	B‡	3.00	Al(Tet)	0.92
MgO	0.00	MgO	0.00	Al(Z)	6.00	ΣTet.	4.00
FeO§	0.41	FeO§	0.08				
MnO	2.57	MnO	0.12	Al(Y)	2.52	Al(Oct)	2.02
TiO <sub>2</sub>	0.26	TiO <sub>2</sub>	0.12	Mg	0.00	Mg	0.00
K <sub>2</sub> O	0.01	K <sub>2</sub> O	8.85	Fe	0.06	Fe	0.00
Na <sub>2</sub> O	2.26	Na <sub>2</sub> O	0.52	Mn	0.37	Mn	0.01
CaO	0.31	CaO	0.00	Ti	0.03	Ti	0.01
F	0.42	F	0.00	ΣY site	2.98	ΣOct.	2.04
Total	84.94	Total	94.88				
				K	0.00	K	0.74
				Na	0.74	Na	0.07
				Ca	0.05	Ca	0.00
				ΣX site	0.79	ΣInterlayer	0.81
				F	0.22	F	0.00

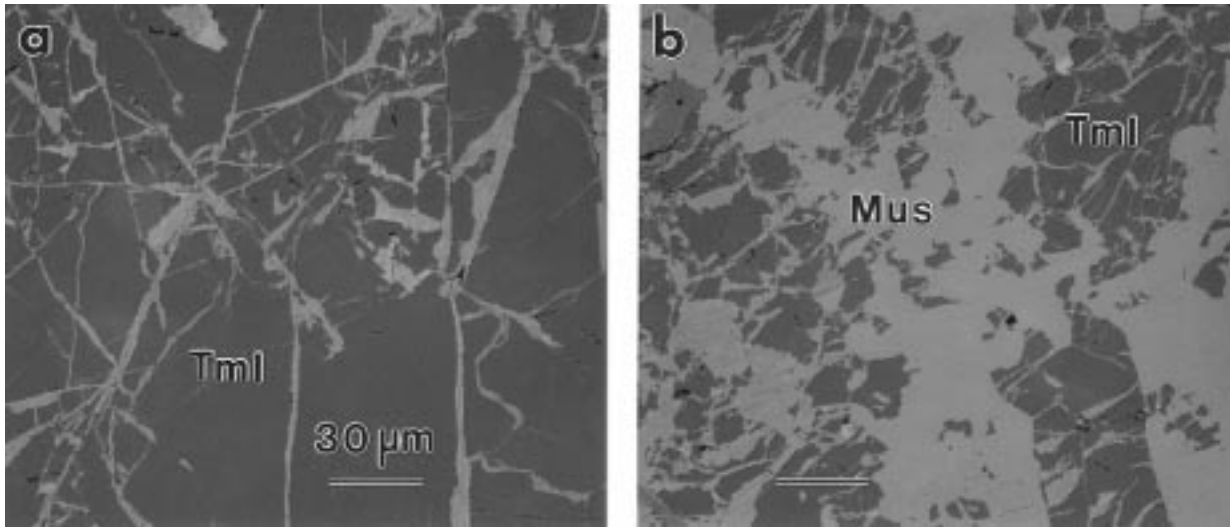
\* Muscovite formula normalized to O<sub>10</sub>(OH)<sub>2</sub>.

† Tourmaline formula normalized to 6 Si atoms.

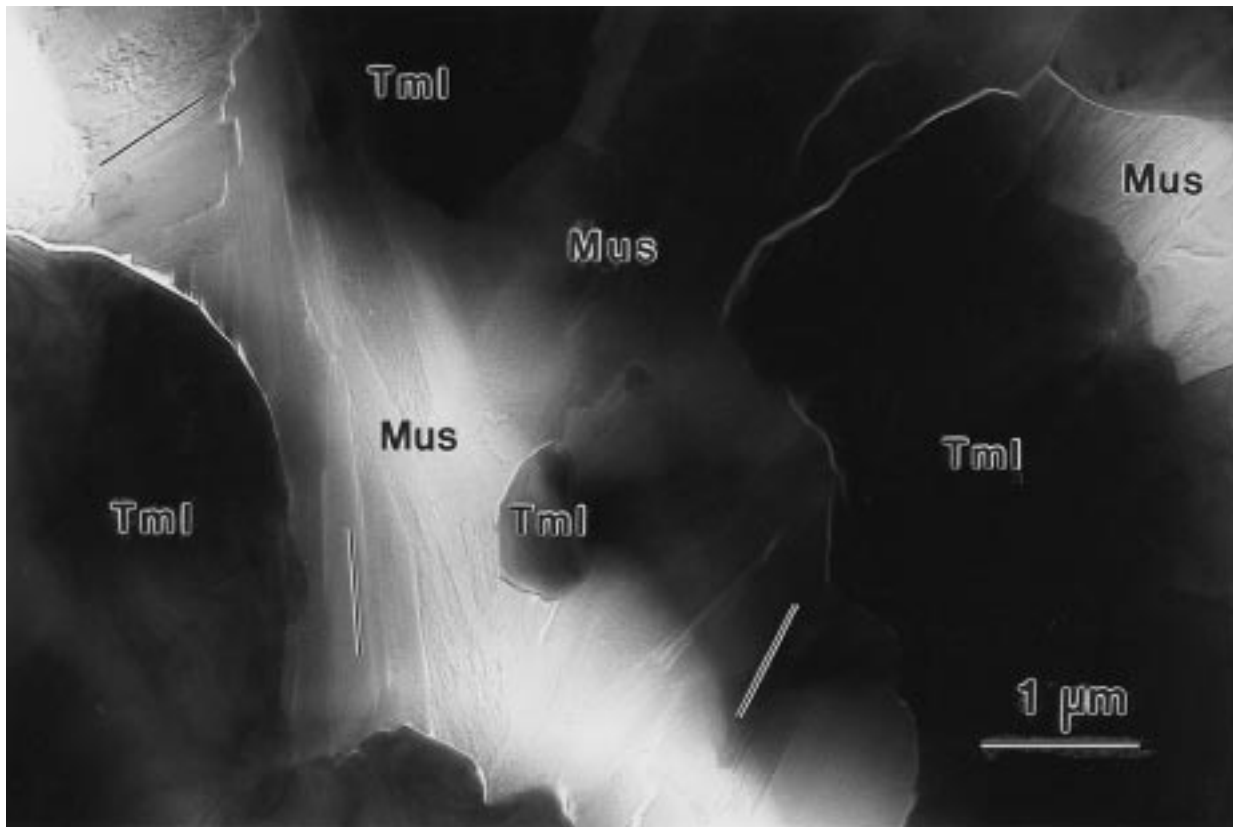
‡ Boron assumed to be 3 ions per formula unit.

§ Total Fe reported as FeO.

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**FIGURE 1.** BSE images of (a) partially altered and (b) highly altered tourmalines showing general alteration features. Note that tourmaline (Tml) shows darker contrast than muscovite (Mus), which reflects the different average atomic numbers of the two minerals. Fine muscovite veinlets are developed, in general, along  $\{110\}$  and  $\{100\}$  of tourmaline. Both images are at the same magnification.



**FIGURE 2.** Low-magnification TEM image of altered tourmaline. Subparallel packets of muscovite layers occur as alteration products inside the tourmaline crystal. White bars marked in the muscovite region indicate (001) of the muscovite aggregates.

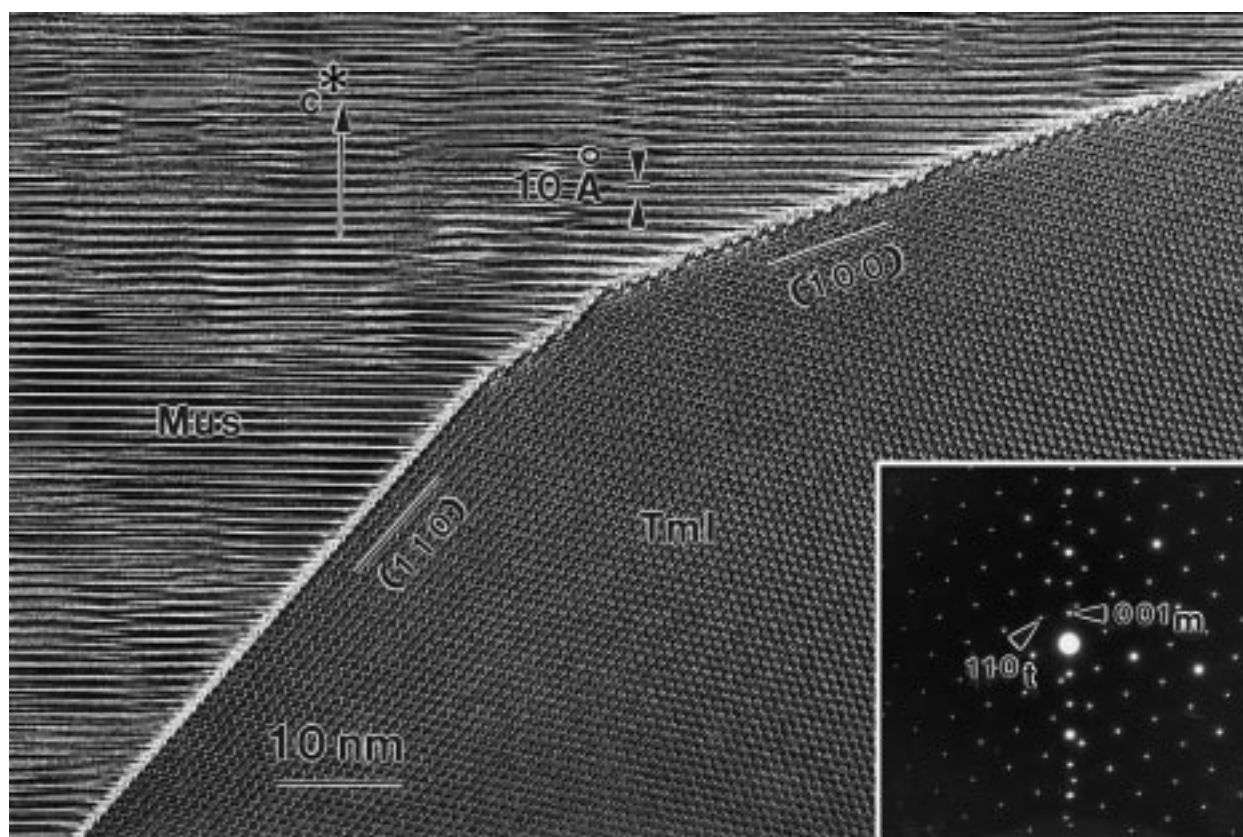


FIGURE 3. HRTEM image showing boundaries between tourmaline (Tml) and muscovite (Mus). The muscovite layers are in contact with well-defined (110) and (100) interfaces. The tourmaline image is a [001] projection, and muscovite shows (001) lattice fringes. The inset shows an SAED pattern from the image.

core of the Precambrian terrane of the Black Hills, South Dakota (Page et al. 1953; Redden 1963; Norton et al. 1964; Jolliff et al. 1986). The tourmaline crystal is dark gray and 5 cm in diameter; white mica flakes developed inside the crystal are macroscopically visible. Polished thin sections were cut perpendicular to the *c* axis of tourmaline and mounted using Crystalbond, which melts near 120 °C and is soluble in acetone. Specimens were analyzed using an electron microprobe before electron microscopy. The general features of alteration were studied using a petrographic microscope as well as by backscattered electron (BSE) imaging with an electron microprobe. Electron microprobe analyses indicate that the tourmaline is an olenite with significant Mn (Table 1). The low total for tourmaline is consistent with the presence of hydrogen and boron.

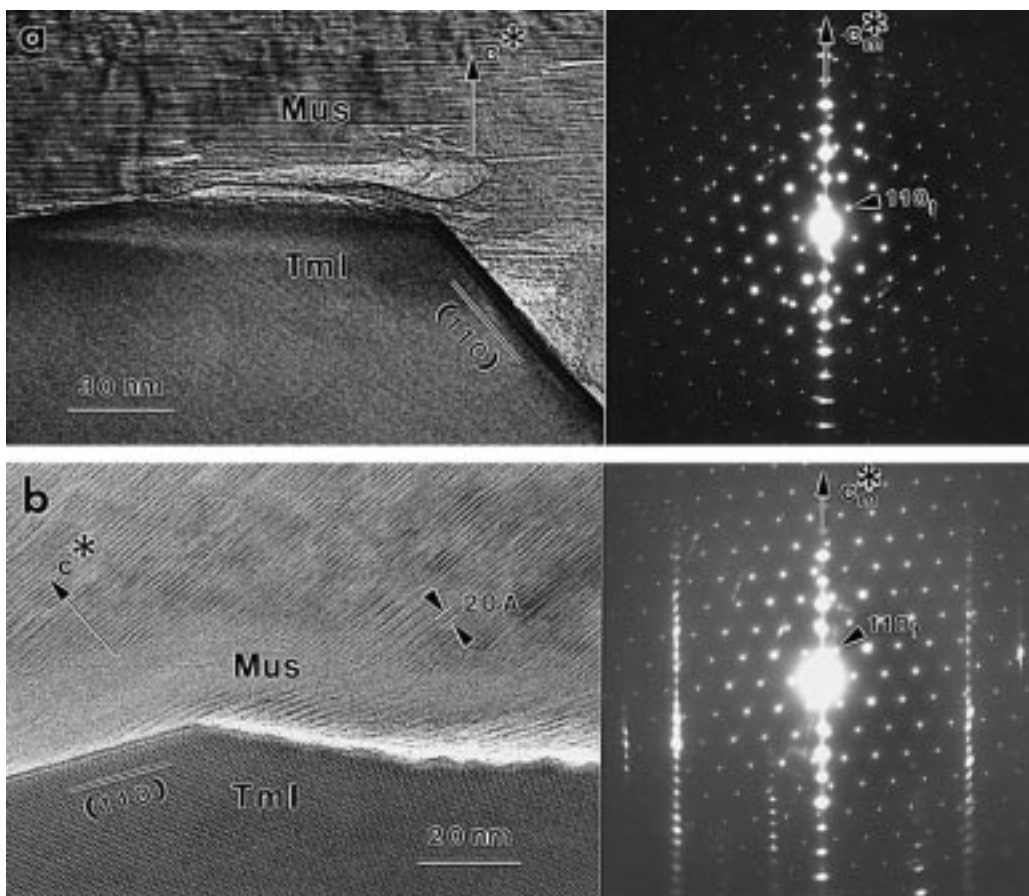
Areas selected for TEM observation were covered by 3 mm washer grids using epoxy. The washer-mounted specimens were detached from the glass slides by heating and were cleaned using acetone prior to ion-milling. Specimens were studied using a JEOL JEM-4000EX transmission electron microscope equipped with a top-entry stage having tilting angles of  $\pm 15^\circ$ , a spherical ab-

erration coefficient ( $C_s$ ) of 1.0 mm, and a structure resolution of 1.7 Å (Smith et al. 1986). A 40  $\mu\text{m}$  objective aperture and a 150  $\mu\text{m}$  condenser aperture were used for HRTEM imaging.

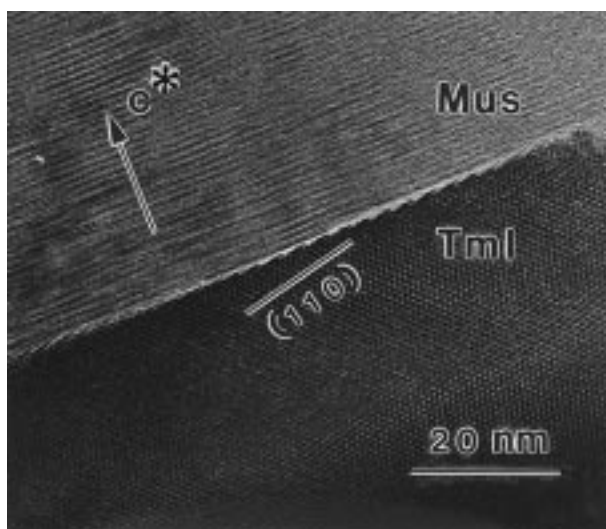
## RESULTS

The degree of alteration of tourmaline to muscovite varies even within a given crystal. Fine-grained muscovite aggregates replace tourmaline as narrow veinlets, many of which are thinner than 5  $\mu\text{m}$  (Fig. 1a); fine muscovite veinlets are developed, in general, along the {110} and {100} cleavages of tourmaline, but some veinlets extend along irregular directions. In highly altered areas, tourmaline crystals having irregular shapes form remnants within muscovite (Fig. 1b). Thin muscovite veinlets also occur within remnant tourmaline crystals. These features indicate that the tourmaline-to-muscovite reaction progressed along {110} and {100} of tourmaline at an early stage of alteration.

In TEM images, muscovite tends to show brighter image contrast than does tourmaline (Fig. 2), indicating that the muscovite, which consists of numerous small crystal aggregates, was ion-milled faster and is commonly thin-



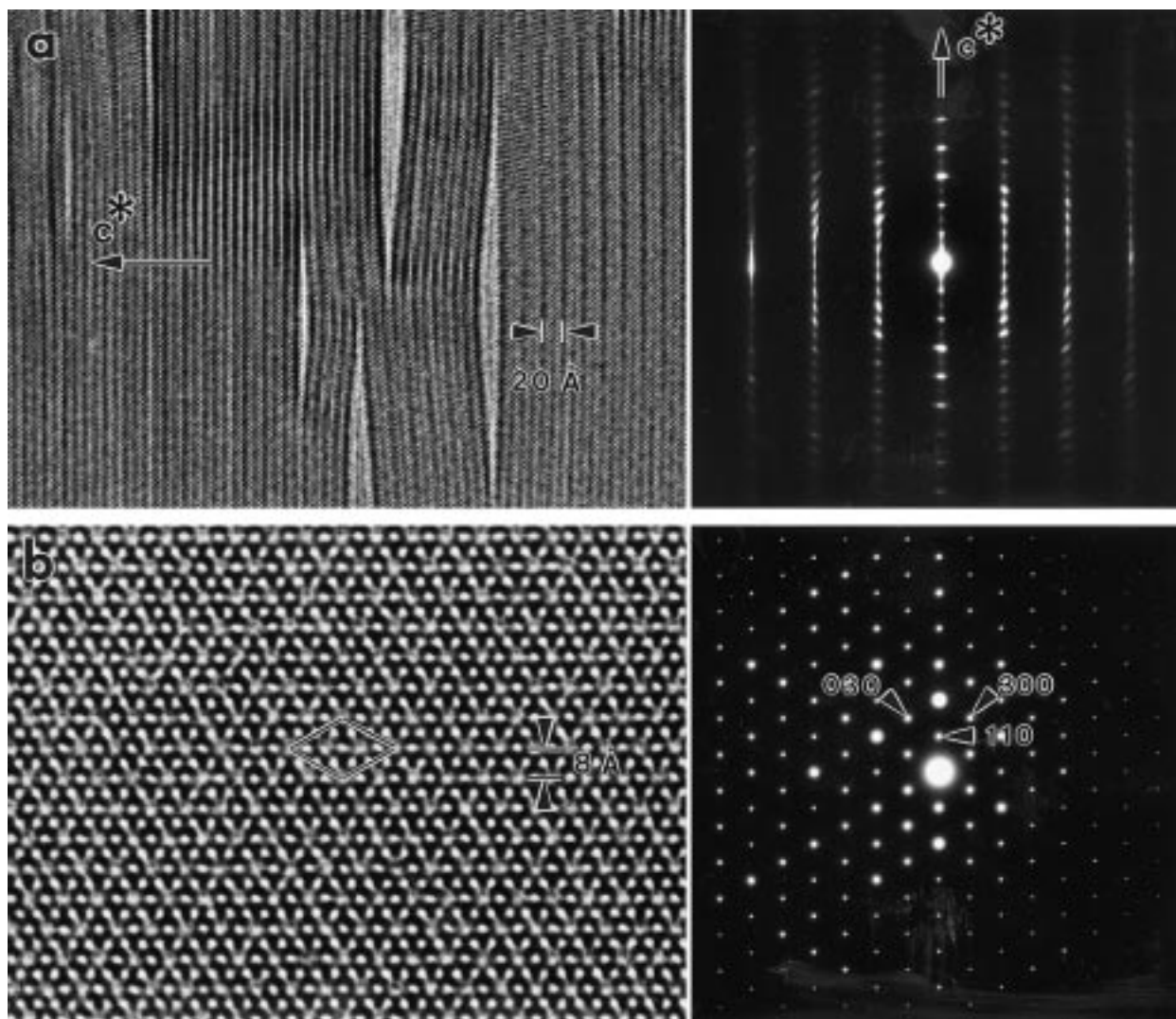
**FIGURE 4.** HRTEM images and SAED patterns of tourmaline-muscovite interfaces showing different orientation relationships. Angles between (001) of muscovite and (110) of tourmaline are approximately 49° and 26°, respectively, in (a) and (b). Note that the (001) muscovite layers at the interfaces are partially bent and deformed.



**FIGURE 5.** HRTEM image showing an interface where (001) of muscovite is roughly parallel to the tourmaline boundary. The tourmaline shows serrated features, and the angle between (001) of muscovite and (110) of tourmaline is approximately 15°.

ner than the tourmaline. The muscovite mostly occurs as packets whose thicknesses range between 100 and 1000 Å; locally it shows separated gaps at the boundaries with tourmaline (Fig. 2). In general, the muscovite packets are subparallel, resulting in low-angle grain boundaries. However, in some areas muscovite packets are nearly perpendicular to each other. Unreacted tourmaline crystals remain within muscovite aggregates as small islands (Fig. 2), but minerals other than muscovite were not observed in TEM images and selected-area diffraction (SAED) patterns.

No distinct orientation relationship between tourmaline and muscovite at the reaction boundaries can be unambiguously documented in low-magnification TEM images (Fig. 2). However, HRTEM images reveal that the interfaces consist of sharply defined tourmaline crystal faces. Figure 3 shows that well-defined (110) and (100) faces of tourmaline are in contact with (001) muscovite layers; the angle between (001) of muscovite and (110) of tourmaline is approximately 49°. The (001) lattice fringes of muscovite lack unusual contrast at the interfaces with tourmaline, suggesting that little or no strain or distortion exist at the interfaces.



**FIGURE 6.** HRTEM images and corresponding SAED patterns of (a) muscovite and (b) tourmaline. (a) The (001) lattice fringes of muscovite show two-layer periodicities (20 Å) in part of the image as well as lenticular gaps. (b) The [001] tourmaline image and SAED pattern exhibit well-ordered periodicities and sharp diffraction spots, respectively. A unit cell of tourmaline structure is outlined on the image.

Altered tourmaline commonly shows (110) boundaries, and the angle between (001) of muscovite and (110) of tourmaline is variable; Figures 4a and 4b display values of 49° and 26°, respectively. Figure 5 shows an interface for which the angle between (001) of muscovite and (110) of tourmaline is 15°, and the (001) of muscovite layers are almost parallel to the tourmaline boundary. Muscovite layers at some interfaces are partly bent, wrapping around tourmaline crystal surfaces, and some muscovite layers are deformed (Figs. 4a and 4b).

The muscovite mainly occurs as a two-layer polytype without any interlayering of other sheet silicates, and SAED patterns show weak streaking along  $c^*$  indicating the presence of minor stacking disorder (Figs. 4b and 6a). TEM images display lenticular layer separations; such gaps were apparently produced by electron-beam damage

(cf. Ahn et al. 1986). The SAED pattern of beam-damaged muscovite shows diffuse  $00l$  reflection spots in a roughly circular pattern as a result of such fissures (Fig. 6a). Tourmaline has a well-ordered periodicity and lacks any diffuseness in its [001] SAED pattern (Fig. 6b), indicating that the tourmaline is almost free of structural defects.

#### DISCUSSION AND CONCLUSIONS

HRTEM images show that the irregular tourmaline outlines observed in BSE images consist of combined {110} and {100} boundaries (Figs. 3 and 4). The predominance of {110} interfaces of tourmaline with respect to muscovite and the occurrence of (001) muscovite layers parallel to the  $c$  axis of tourmaline suggest that a cleavage-controlled alteration mechanism was dominant. Further-

more, the relatively sharp interfaces of tourmaline at the reaction boundaries indicate that the hydration reaction progressed faster along the *c* axis direction than perpendicular to it.

Muscovite packets produced from tourmaline occur in subparallel orientations along (001) (Fig. 2), and the boundaries between them show relatively sharp interfaces in the [001] tourmaline images, indicating that the interfaces are extended parallel to the *c* axis of tourmaline. The structures of tourmaline and muscovite do not possess topotactic similarity, and therefore their interfaces are not expected to have excellent structural fits at the reaction boundaries. Although (001) of muscovite is parallel to the *c* axis of tourmaline, muscovite lacks a preferred orientation relative to {110} of tourmaline.

The electron microprobe data (Table 1) show that both tourmaline and muscovite are highly aluminous and that alteration occurred mainly through a hydration reaction. The susceptibility of aluminous minerals to alter to form sheet silicates was reported in the eucryptite-to-muscovite alteration, where an Al/Si ratio of  $\cong 1$  is maintained (London and Burt 1982). Additional examples can be found in the andalusite-to-donbassite alteration (Ahn et al. 1988; Ahn and Buseck 1988), and the margarite replacement of andalusite in which an Al/Si ratio of  $\cong 2$  is preserved (Velde 1971; Guidotti and Cheney 1976; Guidotti et al. 1979). Such replacements of Al-rich minerals by micas are favored because the alteration reaction mainly requires addition of alkali cations and H<sub>2</sub>O.

Our TEM and BSE imaging observations reveal that tourmaline reacts directly to form muscovite without the involvement of intermediate phases. When sericitization occurs by late magmatic fluids in pegmatites, muscovite forms directly from aluminous minerals or through intermediate steps (Černý and Burt 1984). Ahn et al. (1988) showed that andalusite from a pegmatite reacts to either muscovite + corundum or directly to donbassite (an Al-rich di, dioctahedral chlorite) depending on the availability of K<sup>+</sup> in the fluids. If the alteration reaction is balanced assuming constant Al, the analyzed data (Table 1) could result from an approximate reaction of tourmaline + 2.1K<sup>+</sup> + 2.9SiO<sub>2</sub> + 2.5H<sub>2</sub>O = 2.9muscovite + 3.0B<sup>3+</sup> + 2.2O<sub>2</sub> + 0.5Na<sup>+</sup> with the involvement of minor elements such as Mn, Fe, and Ca. The formation of muscovite directly from tourmaline suggests that the alteration was caused by fluids in which K<sup>+</sup> was available. Although B can be incorporated in the muscovite structure (Foord et al. 1991), the analyzed muscovite apparently does not contain significant B, judging from its oxide total and cation occupancies (Table 1). Therefore, tourmaline alteration would release B<sup>3+</sup>, and the late-magmatic reaction of tourmaline to muscovite would result in alkali tetraborate melt species, addition of which to granitic melt significantly increases the solubility of H<sub>2</sub>O (London 1986).

The slightly lower Al/Si ratio of muscovite relative to tourmaline results in a silica deficiency in the alteration reaction; aluminous phases such as corundum or diaspor

could form as by-products of aluminous-mineral alteration as long as the supply of silica is limited (Rose 1957; Burt and Stump 1984). However, such aluminous phases were not observed as alteration products in our study, suggesting that alteration of the tourmaline did not occur in a silica-deficient environment.

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