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Sericitization of Tourmaline in a Pegmatite : a HRTEM Study

페그마타이트에서 산출하는 전기석의 운모화작용 : 고분해능 투과전자현미경(HRTEM) 연구

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ABSTRACT : Partially sericitized tourmaline from a pegmatite, Black Hills, South Dakota, U. S. A., was investigated using high-resolution transmission electron microscopy (HRTEM). Muscovite occurs as the only alteration product of tourmaline, and it is developed extensively as narrow veinlets along the {110} and {100} cleavage directions of tourmaline, indicating that a cleavage-controlled alteration mechanism was dominant. Muscovite was characterized mainly as two-layer polytypes with minor stacking disorder, but tourmaline is almost free of structural defects. HRTEM images of tourmaline-muscovite interfaces revealed that the interfaces between two minerals are composed of well-defined {110} and {100} boundaries of tourmaline. The (001) of muscovite is in general parallel to the c-axis of tourmaline, but tourmaline and replacing muscovite do not show specific crystallographic orientation relationship; muscovite consists of numerous 100-1000Å thick subparallel packets, and the angles between the (001) of muscovite and (110) of tourmaline is highly variable. Al/Si ratios of both minerals suggest that tourmaline to muscovite alteration by late magmatic fluids has been facilitated by their similar Al/Si ratio in the incipient alteration stage, in that the hydration reaction with preservation of Al and Si would require only addition of K^+ and H_2O. Aluminous minerals other than muscovite were not characterized as the alteration products of tourmaline, indicating that tourmaline reacted directly to muscovite; the tourmaline alteration apparently occurred by the presence of residual fluids in which K^+ is available and silica was not undersaturated.

요약 : 이 연구에서는 고분해능 투과전자현미경 (HRTEM) 을 이용하여 페그마타이트에서 산출되는 부분적으로 운모화된 전기석을 조사하였다. 전기석의 변질물로서는 백운모가 유일하게 관찰되는데, 백운모는 전기석내에 {110}와 {100} 벽개 방향을 따라 미세한 맥으로 잘 발달하고 있다. 이는 전기석의 변질작용이 초기에 주로 벽개를 따라 진행되었음을 지시한다. 백운모는 약간의 stacking disorder를 보이는 2-layer 다구조형(polytype)으로 주로 나타나지만, 전기석은 결함구조를 거의 보이지 않는다. 고분해능 전자현미경을 이용한 전기석과 백운모 경계면의 관찰에 의하면 두 광물의 경계면은 잘 발달된 전기석의 {110}와 {100}을 따라서 형성되었음을 알 수 있다. 백운모의 (001)은 일반적으로 전기석의 c 축과는 서로 평행하지만 두 광물들은 변질작용시 결정구조에 의한 특별한 방향성을 나타내지는 않는다. 백운모는 100-1000Å 두께의 얇은 입자들이 비교적 평행하게 배열되어 있으며, 백운모의 (001)과 전기석의 (110)는 다양한 각도를 유지하고 있다. 두 광물이 유사한 Al/Si 값을 보이며 이러한 유사한 Al/Si 값에 의하여 초기 단계에 백운모를 생성하는 변질작용이 촉진되었을 가능성을 시사하는데, 이는 Al과 Si이 보전되는 반응에서는 K^+과 H_2O의 공급만이 필요하기 때문이다. 백운모 이외의 다른 Al 광물이

변질물로서 산출되지 않는데 이는 전기석이 다른 중간과정을 거치지 않고 직접 백운모로 반응하였음을 나타내며, 또한 전기석이 백운모로 반응시 마그마 잔류용액에는 K^+이 충분히 공급되었으며 규산이 결핍되지 않았음을 지시한다.

INTRODUCTION

Various minerals in pegmatites are subject to late sericitic replacement by residual fluids that can cause a diverse array of alterations (Černý and Hawthorne, 1982). Especially, Al-rich minerals are easily altered; K^+ and H^+ metasomatism commonly results in muscovite or other mineral assemblages containing muscovite as alteration products (Černý and Burt, 1984). When aluminous minerals are altered by late fluids of pegmatites, they react either directly to muscovite as a final alteration product or through various intermediate stages as the fluids evolve and as equilibrium is attained. Such diverse alteration characteristics of aluminous minerals in pegmatites can be found in the alteration of spodumene (London and Burt, 1982) and andalusite (Burt and Stump, 1984; Ahn et al., 1988).

Tourmaline, which typically occurs as a common boron-containing mineral in granite pegmatites and some metamorphic rocks, is known to be quite resistent to weathering (Dietrich, 1985); it is frequently observed as detrital minerals in sedimentary rocks and soils (Krynine, 1946; Graham, 1957; Allen, 1972; Allen et al., 1974). However, tourmalines from pegmatites commonly show partially sericitized features; muscovite is found in tourmaline crystals along with other minerals as pseudomorphs, inclusions, and an intergrown phase (see the reviews by Dietrich, 1985), and Dietrich (1985) suggested that most natural alteration of tourmaline is apparently caused by residual magmatic fluids.

Alteration of rock-formaing minerals can be profitably investigated by using high-resolution tranmission electron microscopy (HRTEM); it can reveal the reaction interfaces as well as crystallographic relationship occurring during alteration (e. g., Eggleton, 1984; Ahn et al., 1988; Banfield and Eggleton, 1990). In the present study, HRTEM study of partially sericitized tourmaline has been carried out to investigate detailed minerlalogical and structural characteristics involved in the alteration of tourmaline and to examine if other intermediate phases are present during the alteration process.

SPECIMENS AND EXPERIMENTAL METHODS

The specimen investigated in this study is a partially sericitized tourmaline from a pegmatite, Black Hills, South Dakota, U. S. A. Polished thin sections of tourmaline crystals were prepared using Crystalbond that can be melted by gentle heating and soluble in acetone. Thin sections were cut perpendicular to the elongation direction (c-axis) of tourmaline, and the orientations of crystals on thin sections were confirmed from their optic-axis interference figures.

Specimens were analyzed using electronprobe microanalyzer (EPMA) prior to transmission electron microscope (TEM) investigation, and general features of alteration were investigated using back-scattered electron (BSE) imaging method as well as petrographic microscope. EPMA analysis (Table 1) indicates that the tourmaline investigated in this study is olenite containing significant Mn (Burt, 1989).

Selected areas for TEM observation were covered by 3-mm washer grids using epoxy glue. The washer-mounted specimens were detached from glass slides by heating and were cleaned using acetone prior to ion-milling. Specimens were investigated using a JEOL JEM-4000EX transmission electron microscope with top-entry stage having tilting angles of $\pm 15°$, spherical aberration coeffi-

Table 1. Representative EPMA analyses of tourmaline and muscovite.

Oxides	Tourmaline	Muscovite
SiO_2	35.69	47.08
Al_2O_3	43.01	38.11
MgO	0.00	0.00
FeO*	0.41	0.08
MnO	2.57	0.12
TiO_2	0.26	0.12
K_2O	0.01	8.85
Na_2O	2.26	0.52
CaO	0.31	0.00
F	0.42	0.00
Total	84.94 wt%	94.88 wt%

Ions per formula unit

Tourmaline		Muscovite**	
Si***	6.00	Si	3.08
B****	3.00	Al(Ⅳ)	0.92
Al(Z)	6.00	ΣTet.	4.00
Al(Y)	2.52	Al(Ⅳ)	2.02
Mg	0.00	Mg	0.00
Fe*	0.06	Fe*	0.00
Mn	0.37	Mn	0.01
Ti	0.03	Ti	0.01
ΣYsite	2.98	ΣOct.	2.04
K	0.00	K	0.74
Na	0.74	Na	0.07
Ca	0.05	Ca	0.00
ΣXsite	0.79	ΣInt.	0.81
F	0.22	F	0.00

* Iron reported as FeO

** Muscovite formula normalized to $O_{10}(OH)_2$

*** Tourmaline formula normalized to 6 silicon

**** Boron assumed to be stoichiometric

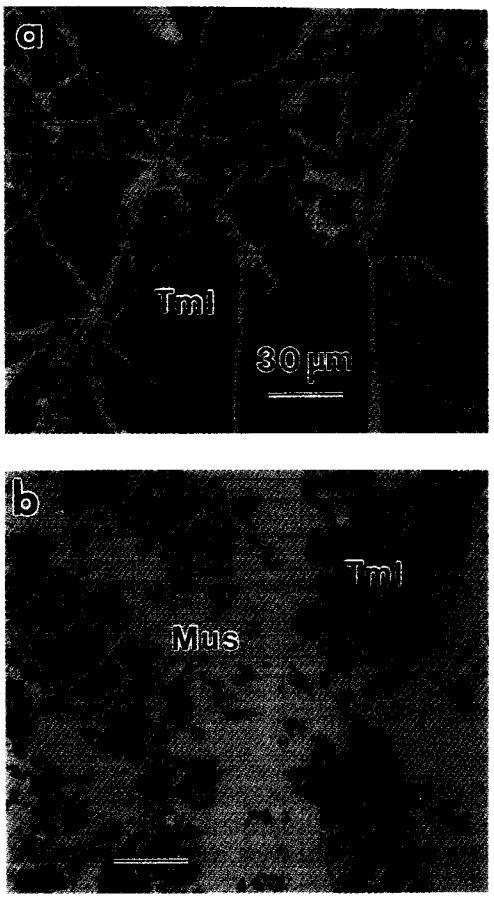

Fig. 1. BSE images of (a) partially altered and (b) highly altered tourmalines showing gerneral features of alteration. Note that tourmaline (Tml) shows darker contrast than muscovite (Mus) does as a result of different average atomic numbers of both phases. Fine muscovite veinlets are developed within tourmaline crystals generally along {110} and {100}. Both images are at the same magnification.

cient (Cs) of 1.0mm, and structure resolution of 1.7Å (Smith et al., 1986). A 40-μm objective aperture and a 150-μm condenser aperture were used for HRTEM imaging.

RESULTS

The degree of alteration of tourmaline to muscovite varies even within a crystal. In the area of partially altered tourmaline, fine-grained muscovite aggregates replace tourmaline as narrow veinlets normally thinner than 5μm (Fig. 1a); fine muscovite veinlets tend to develop, in general, along the {110} and {100} cleavage directions of tourmaline, but some of the replacing veinlets were formed along irregular directions. In highly altered areas, tourmaline crystals having irregular shape are observed as reaction remnants within

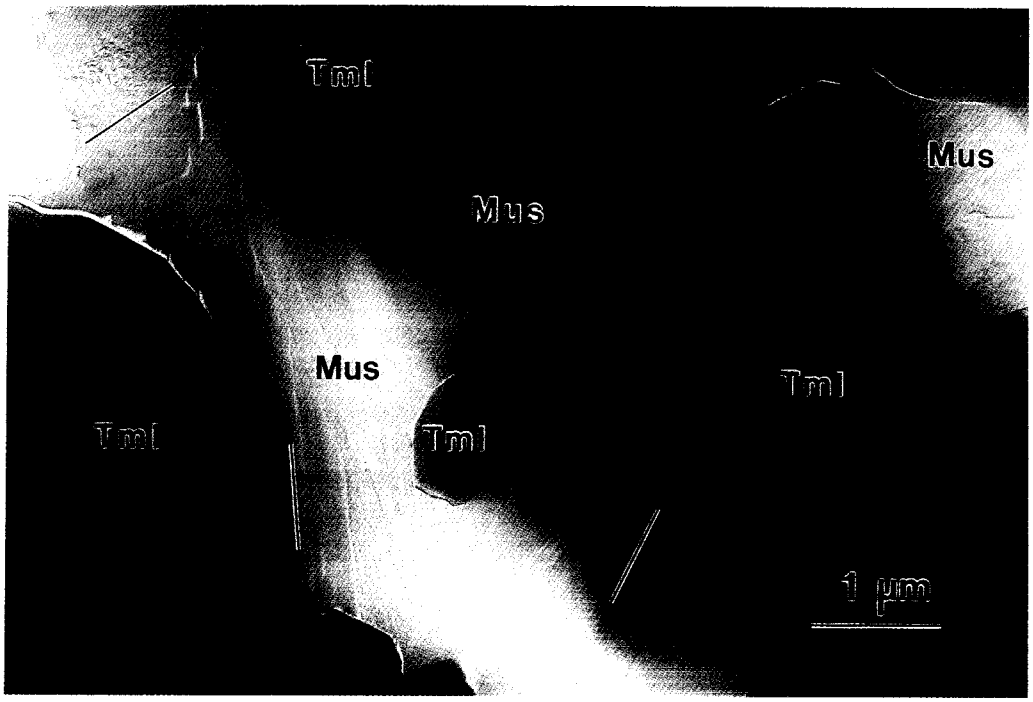

Fig. 2. Low-magnification TEM image of altered tourmaline. Subparallel packets of muscovite layers occur as an alteration product within the tourmaline crystals that show irregular outlines. The bars marked in muscovite region indicate the (001) of muscovite aggregates.

muscovite (Fig. 1b). Fine muscovite veinlets are also commonly developed within remnant tourmaline crystals. These alteration features indicate that alteration of tourmaline has progressed by producing fine muscovite veinlets along the {110} and {100} of tourmaline at the early stage of alteration.

In TEM images, muscovite tends to show brighter image contrast than tourmaline does (Fig. 2), indicating that muscovite, which composed of numerous small crystal aggregates, has been ion-milled faster and is usually thinner than tourmaline. Muscovite produced from tourmaline occurs mostly as thin packets whose thickness ranges between 100 and 1000 Å, and muscovite shows locally separated gaps at the boundaries with tourmaline (Fig. 2). In general, the muscovite packets are subparallel, resulting in low-angle grain boundaries. In some areas, muscovite packets are, however, almost perpendicular each other. Occasionally, unreacted tourmaline crystals still remain within muscovite aggregates as small isolated islands (Fig. 2), but any minerals other than muscovite were not observed as alteration products of tourmaline.

Any distinct crystallographic orientation relationship between tourmaline and muscovite at the reaction boundaries cannot be unambiguously identified in low-magnification TEM images (Fig. 2). However, HRTEM images reveal that the interfaces between muscovite and tourmaline consist of well-defined crystal faces, and muscovite layers contact tourmaline surface at various angles. Fig. 3 shows that tourmaline exhibits outlines well-defined by (110) and (100), with which (001) muscovite layers are in contact; the angle between the (001) of muscovite and (110) of tourmaline is approximately 49°. The (001) lattice fringes of muscovite do not exhibit any unusal contrasts at the interfaces with tour-

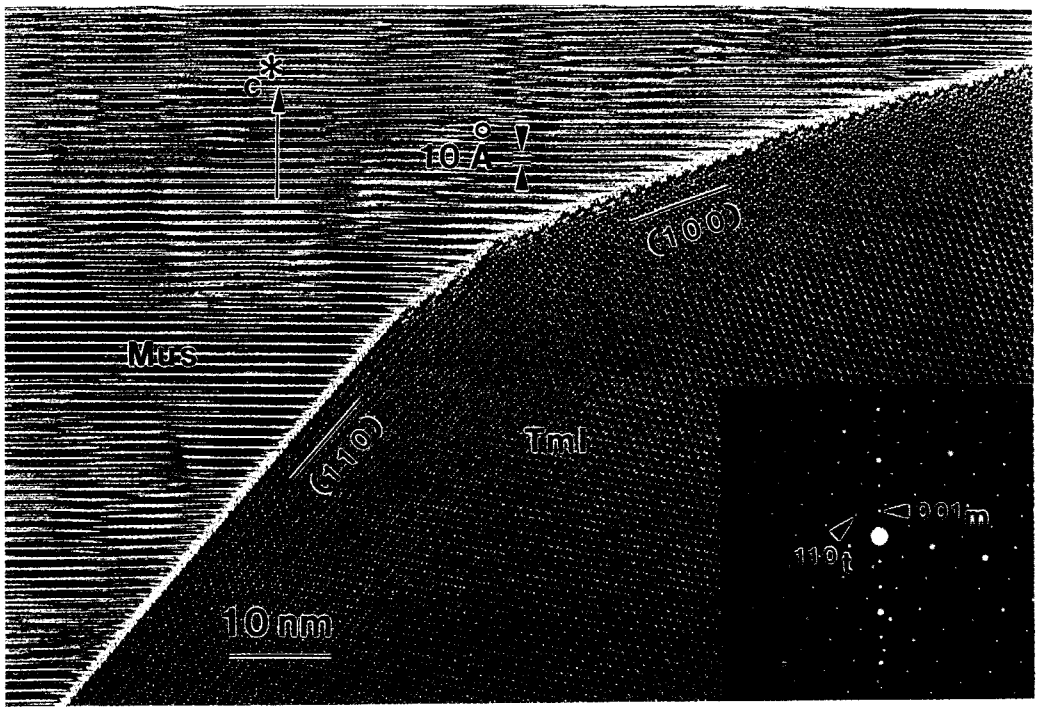

Fig. 3. HRTEM image showing the boundaries between tourmaline (Tml) and muscovite (Mus). Muscovite layers are in contact with well-defined (110) and (100) interfaces. Tourmaline image was obtained from [001] projection, and muscovite shows (001) lattice fringes. The inset shows a SAED pattern from the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

maline, suggesting that there is almost no crystal strain or distortion at the interfaces. Relatively sharp outlines of tourmaline and the (001) lattice fringes in HRTEM images collectively suggest that the interfaces between two minerals are extended parallel to the c-axis of tourmaline.

Altered tourmaline commonly show (110) boundaries, and they are at relatively high angle with respect to the (001) of muscovite (Fig. 4). The angle between the (001) of muscovite and (110) of tourmaline is variable;Fig. 4a and Fig. 4b show values 49° and 26°, respectively. Fig. 5 shows an interface at which the angle between the (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 the interfaces are partially bent and wrapping tourmaline crystal surface, and part of muscovite layers are deformed (Fig. 4), suggesting that muscovite layers apparently slipped at some part of interfaces.

The muscovite occurs mainly as two-layer polytype, and SAED pattern shows weak streaking along c* indicating the presence of minor stacking disorder (Figs. 4b and 6a). TEM images of muscovite exhibit lenticular layer separations, and muscovite layers adjacent to them are gently curved. Such lenticular gaps were apparently produced by electron-beam damages, and therefore they are artifacts produced during the TEM observation (Ahn et al., 1986). The SAED pattern of beam-damged muscovite shows diffuseness of 00l reflection spots along circular direction as a result of the presence of such fissures (Fig. 6a). Muscovite does not show any interlayering of other sheet silicates. In contrast to muscovite, the HRTEM image of tourmaline shows well-ordered periodicity, and SAED does not show any diffuse-

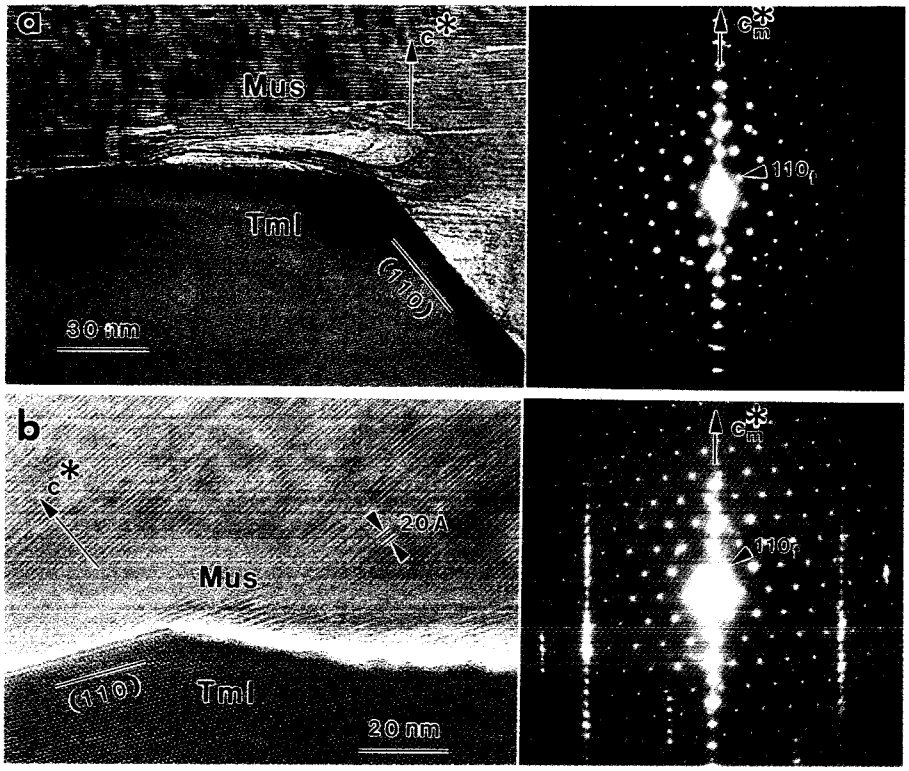

Fig. 4. HRTEM images and their SAED patterns of tourmaline-muscovite interfaces showing different crystallographic orientation relationship. The angles between the (001) of muscovite and (110) of tourmaline are approximately 49° and 26°, respectively in (a) and (b). Note that (001) muscovite layers at the interfaces are partially bent and deformed.

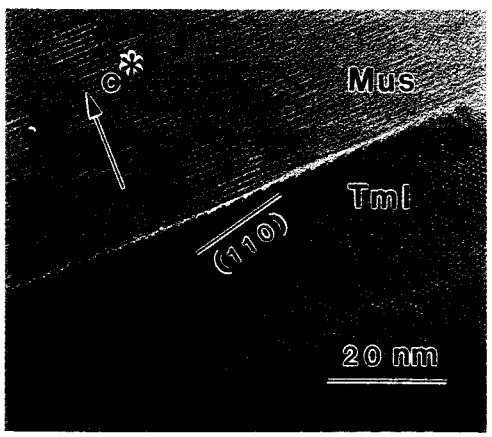

Fig. 5. HRTEM image showing the tourmaline-muscovite interfaces where the (001) of muscovite is in gnenerall parallel with the tourmaline boundary. The tourmaline shows serrated features, and the angle between the (001) of muscovite and (110) of tourmaline is approximately 15°.

ness in the [001] SAED pattern (Fig. 6b) indicating that tourmaline is almost free of structural defects. HRTEM images of tourmaline were first reported by Iijima et al. (1973), and the HRTEM image obtained from the present study is in agreement with their structural interpretation. Despite the scarcity of structural defects in tourmaline, a dislocated region along (110) was found in part of a tourmaline crystal (Fig. 7).

DISCUSSION AND CONCLUSIONS

Microstructures of Tourmaline and Muscovite

The crystallographic orientation of tourmaline with respect to other minerals associated within it is of interest to many workers (see the reviews by

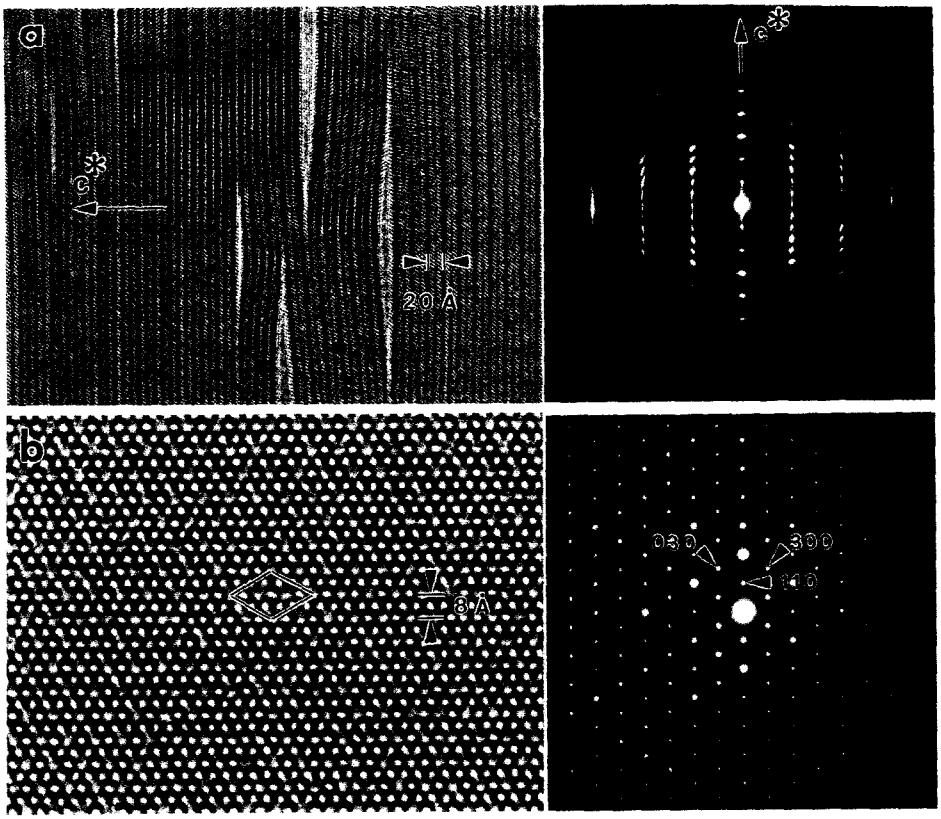

Fig. 6. HRTEM images and their SAED patterns of (a) muscovite and (b) tourmaline. (a) The (001) lattice fringes of muscovite show two-layer periodicites in part of the image, and lenticular gaps are spread within muscovite. (b) The [001] tourmaline image and SAED pattern exhibit well-ordered periodicities and sharp diffraction spots, respectively. A unit-cell of tourmaline structure is outlined on the HRTEM image of tourmaline.

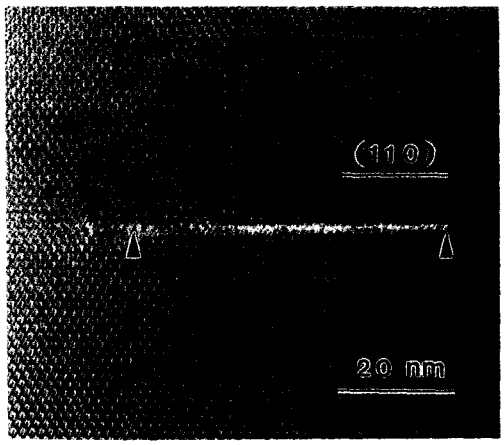

Fig. 7. HRTEM image of tourmaline showing a (110) dislocation region. The dislocated area is marked by arrows.

Dietrich, 1985). Frondel (1936) analyzed many tourmaline inclusions in muscovites using X-ray diffraction method; he found tendencies for arrangement of inclusions in preferred crystallographic orientations on statistical study, although orientation is not restricted to specific, limiting conditions of crystallographic coincidence. However, orientation relationship between tourmaline and other associated minerals produced by direct alteration reaction has not been reported.

HRTEM images show that relatively irregular tourmaline outlines observed in BSE images consist of the combined {110} and {100} boundaries (Figs. 3 and 4). Muscovite packets produced from tourmaline occur in subparallel orientation along (001) (Fig. 2), and the boundaries between musco-

vite and tourmaline show relatively sharp interfaces in the [001] tourmaline images indicating that the interface is parallel to the c-axis of tourmaline. However, the (001) of muscovite shows various angles with respect to the {110} of tourmaline (Figs. 3, 4, and 5). Although the (001) of muscovite is parallel to the c-axis of tourmaline, muscovite does not show any preferred orientation relationship with the {110} of tourmaline.

The structures of tourmaline and muscovite do not possess topotactic similarity, and therefore their interfaces are not expected to have excellent structural fit; tourmaline structure consists of distribution of six-membered silicon tetrahedra and partly edge-shared octahdra along (001), and these basic structures repeat toward the c-axis. The {110} of tourmaline does not show any specific orientation relationship with the (001) of muscovite, but the (001) of muscovite is mostly parallel to the c-axis of tourmaline. The predominance of {110} interfaces of tourmaline and occurrence of (001) muscovite layers parallel to the c-axis of tourmaine suggest that a cleavage-controlled alteration mechanism was dominant. Furthermore, the relatively sharp interfaces of tourmaline at the reaction boundaries indicate that hydration reaction has progressed much faster along the c-axis direction rather than the direction perpendicular to the c-axis.

Some muscovites in contact with tourmaline are partially bent and deformed along the interfaces (Fig. 4). This may have been caused by the strain exerted during the alteration reaction, in that the volume of replacing muscovite is apparently not the same as that of replaced tourmaline; tourmaline to muscovite reaction may accompany volume change, which can result in structural strain and eventually slip along the interfaces.

Tourmaline Alteration to Muscovite

The EPMA data (Table 1) show that the Al/Si ratio of muscovite ($\simeq$1.0) is not significantly different from that of tourmaline ($\simeq$1.4), indicating that alteration occurred through a hydration reaction in which the Al/Si ratio was in general preserved. Tourmaline to muscovite alteration has been apparently facilitated by the similar Al/Si ratio of both phases at the incipient alteration stage. The susceptibility of aluminous minerals to other sheet silicates was reported in eucryptite to muscovite alteration, where Al/Si ratio of $\simeq$1 is maintained (London and Burt, 1982). Another examples can be found in andalusite to donbassite alteration (Ahn et al., 1988; Ahn and Buseck, 1988) and margarite replacement of andalusite where Al/Si ratio of 2 is preserved (Velde, 1971; Guidotti and Cheney, 1976; Guidotti et al., 1979). Such replacements of Al-rich minerals by micas having similar Al/Si ratios are favored, in that alteration reaction with preservation of Al and Si would require only addition of alkali cations and H_2O.

Our TEM and EPMA observations revealed that tourmaline reacts directly to muscovite and no intermediate phases are involved in the alteration. When sericitization of aluminous minerals occurs by late fluid in pegmatites, sericitization occurs directly from aluminous minerals or through intermediate steps as the fluids evolve (Černý and Burt, 1984). Ahn et al. (1988) showed that andalusite from a pegmatite reacts to either muscovite + corundum or directly to donbassite, which is Al-rich di,dioctahedral chlorite, depending on the availability of K^+ in the fluids. London and Burt (1982) also showed that spodumene alters to eucryptite + albite and that eucryptite eventually reacts to muscovite. The formation of muscovite directly from tourmaline suggests that the alteration has been caused by the fluids in which K^+ was available. The alteration of tourmaline would release B^{3+}, in that the muscovite does not take B in its structure. The reaction of tourmaline to muscovite would result in alkali tetraborate melt species, addition

of which to granitic melt will increase the solubility of H_2O significantly in silicate melt (London, 1986).

The slightly lower Al/Si ratio of muscovite compared with that of tourmaline would result in silica definciency in the alteration reation, and highly aluminous phases such as corundum or diaspore could form as by-products of alteration in silica-deficient environments (Rose, 1957;Burt and Stump, 1984). However, such aluminous phases were not observed as the alteration products, suggesting that tourmaline alteration does not occur in a silica-understaturated environment.

Muscovite that occurs as alteration product consists of relatively thick packets and it shows relatively well-ordered two-layer periodicities. Furthermore, any intergrowth of other sheet silicates was not observed in the present study. Micas formed at low temperature tend to be highly disordered in stacking sequence and are susceptible to various mixed-layering with other sheet silicates (Lee et al., 1984, 1985;Peacor, 1992;Essene and Peacor, 1995;Hochella and Banfield, 1995). The two-layer periodicity and lack of imperfections in muscovite are in agreement with the alteration of tourmaline by residual magmatic fluids of relatively high temperature and exclude the possible origin of muscovite by a low-temperature process, such as weathering or low-grade metamorphism.

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