

## **Barian titanian phlogopite from potassic lavas in northeast China: Chemistry, substitutions, and paragenesis**

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### **ABSTRACT**

Magmatic barian titanian phlogopite ( $\text{BaO} = 4.2\text{--}11.2$  wt% and  $\text{TiO}_2 = 10.1\text{--}13.1$  wt%) occurs in the groundmass and in a magmatic inclusion of olivine leucitites from northeast China. In addition, titanian phlogopite ( $\text{BaO} < 0.3$  wt% and  $\text{TiO}_2 \leq 6.4$  wt%) formed by reaction between olivine phenocrysts and late fluids also occurs as coronas rimming olivine phenocrysts in associated leucite basanites. Compositions of the barian titanian phlogopite vary systematically;  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  increase and  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{FeO}$ , and  $\text{K}_2\text{O}$  decrease with increasing  $\text{BaO}$ . Substitutions deduced from such variations include  $\text{Ba} + (\text{Al}, \text{Fe}^{3+}) = \text{K} + \text{Si}$  and  $2(\text{Mg}, \text{Fe}^{2+}) = \text{Ti} + \square$ . Ti-O and Ti-Tschermak's substitutions may also be present in subordinate amounts. The  $\text{Ba} + \text{Al} = \text{K} + \text{Si}$  substitution is common to most magmatic barian micas, except for some lamproitic micas. In contrast, no general Ti substitution scheme is applicable, as Ti substitutions vary with melt compositions and intensive variables.

These phlogopite samples crystallized as a late phase at low pressures and temperatures. Differences in mineral assemblages between olivine leucitites and leucite basanites contribute significantly to the observed disparities in chemical composition between the barian titanian phlogopite and the corona phlogopite and, in general, among phlogopite from other alkalic magmatic rocks.

### **INTRODUCTION**

Titanian phlogopite occurs in lamproites and other potassic rocks (e.g., Mitchell, 1985; Wagner and Velde, 1986; Mitchell and Bergman, 1991), as well as in some alkalic basaltic rocks (e.g., Ryabchikov et al., 1981; Qi and Xiao, 1985), and varies widely in composition. Magmatic phlogopite enriched in both Ba and Ti is rare. The occurrences of barian titanian phlogopite have been reported in some potassic rocks (e.g., Thompson, 1977; Wendlandt, 1977; Birch, 1978, 1980; Holm, 1982; O'Brien et al., 1988) and in a few alkalic rocks such as nephelinites, olivine melilitites, and aillikites (e.g., Mansker et al., 1979; Velde, 1979; Mitchell and Platt, 1984; Barnett et al., 1984; Boctor and Yoder, 1986; Cao and Zhu, 1987; Rock, 1991). There is no general agreement regarding the substitution schemes in barian titanian phlogopite (e.g., Mansker et

al., 1979; Bol et al., 1989; Guo and Green, 1990). Little attention has been paid to their chemical variations and paragenetic implications. In this paper, we report chemical data for barian titanian phlogopite samples in potassic lavas and a magmatic inclusion from northeast China, compare them with other magmatic phlogopite samples, and discuss their substitution schemes and parageneses.

### **GEOLOGICAL SETTING AND PETROLOGY**

Three adjacent volcanic fields of potassic volcanic rocks, Wudalianchi, Erkeshan, and Keluo (WEK), in northeast China ( $125^{\circ}30'\text{--}126^{\circ}45'\text{E}$ ,  $48^{\circ}00'\text{--}49^{\circ}30'\text{N}$ ), are located between the Songliao Basin (a late Mesozoic basin) and the Xing'an Mountains (a Paleozoic fold belt) (Hsü, 1989). These lavas, which cover an area of  $>1400$  km<sup>2</sup>, were erupted during three main episodes: late Miocene (9.6–7.0 Ma), late Pleistocene (0.56–0.13 Ma), and Recent (AD 1719–1721) (Zhang et al., 1991).

The WEK potassic rocks are porphyritic, with groundmass textures varying from vitric to holocrystalline. They

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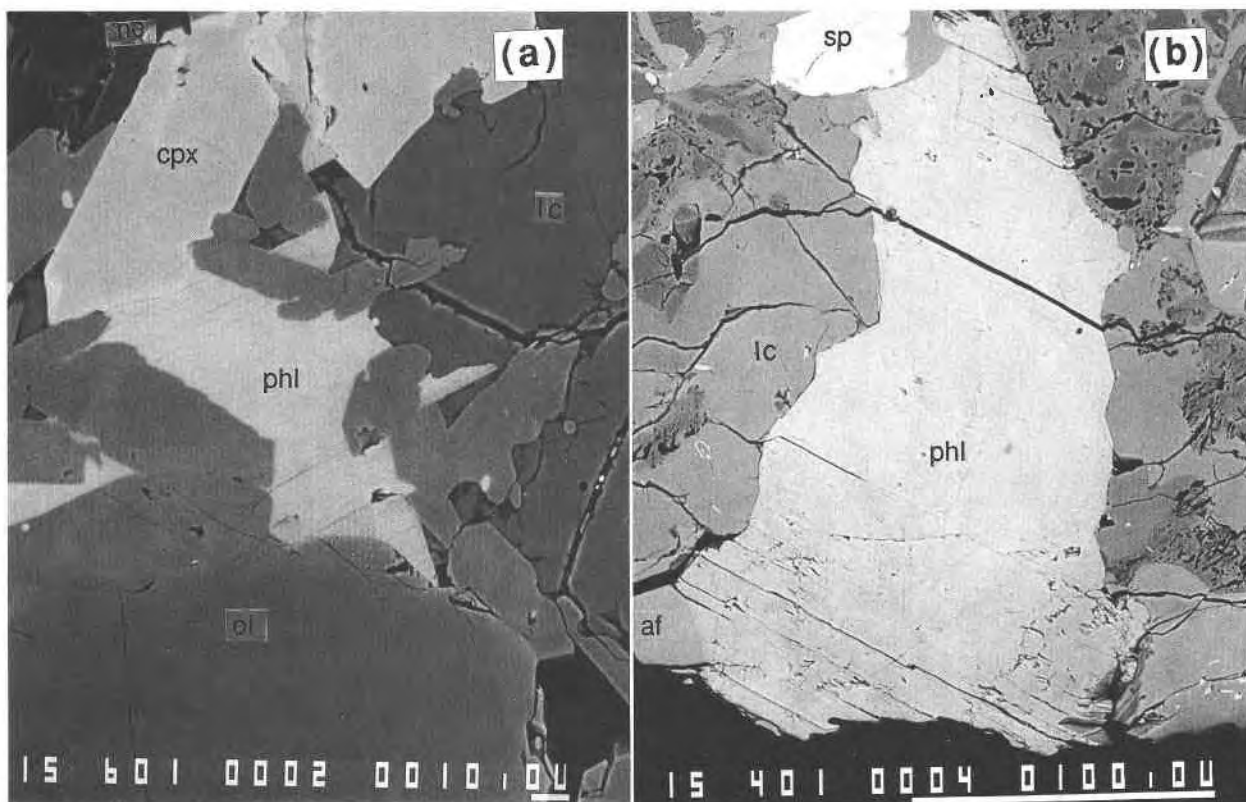


Fig. 1. Backscattered electron images of the WEK barian titanian phlogopite (a) in an olivine leucitite sample and (b) in DZ2n. Abbreviations: phl = phlogopite; ol = olivine; cpx = clinopyroxene; af = hyalophane; ne = nepheline; lc = leucite; sp = Fe-Ti oxides.

are divided into three types; olivine leucitite, leucite basanite, and trachybasalt. Both olivine leucitite and leucite basanite contain phlogopite. Olivine (8–13%), clinopyroxene (2–4%), and leucite (14–20%) phenocrysts in olivine leucitites are dispersed in a matrix of olivine, clinopyroxene, leucite, Fe-Ti oxides, nepheline, phlogopite, and rare sodalite. Leucite basanites have a phenocryst assemblage of olivine (4–9%), leucite (1–7%), and clinopyroxene (0–11%). Matrix phases are potassium feldspar (up to 50%) and clinopyroxene (up to 35%), plus minor leucite, olivine, and Fe-Ti oxides.

Olivine leucitites have lower  $\text{SiO}_2$  but higher MgO and  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  ratios (43–45 wt%, 14–10 wt%, and 0.78–0.71) than leucite basanites (47–55 wt%, 3.8–8.0 wt%, and 0.68–0.52). Most olivine leucitites and some leucite basanites are primary or nearly primary, formed by partial melting of the mantle sources at different pressures (Zhang et al., 1991).  $\text{K}_2\text{O}$  content is high and variable (3.6–7.1 wt%), and most samples have  $\text{K}_2\text{O}/\text{Na}_2\text{O} > 1$ .  $\text{TiO}_2$  and Ba concentrations are 2.0–3.1 wt% and 1300–2200 ppm, respectively. Olivine leucitites and leucite basanites are not systematically different in Ba, whereas the former generally contain lower  $\text{TiO}_2$  and  $\text{K}_2\text{O}$  than the latter. For additional details, see Zhang et al. (1991, 1993).

### OCCURRENCES OF PHLOGOPITE

Phlogopite occurs in the WEK potassic lavas as (1) a matrix phase in olivine leucitites, (2) a constituent of a magmatic inclusion (DZ2n), and (3) coronas rimming olivine phenocrysts in a leucite basanite (WZK16). Phlogopite samples found in the first two occurrences are Barich ( $\text{BaO} > 4.2$  wt%), whereas the phlogopite coronas contain much lower BaO ( $< 0.3$  wt%).

Interstitial phlogopite platelets (0.01–0.1 mm, Fig. 1a) constitute up to 3 modal% of olivine leucitites. A few larger anhedral grains, up to 0.2 mm, enclose early groundmass phases such as clinopyroxene and Fe-Ti oxides. They show very strong, distinctive red-brown to pinkish yellow pleochroism, which may be attributed to high  $\text{TiO}_2$  contents (Mitchell, 1985).

DZ2n is a small inclusion (1 cm) composed of barian titanian phlogopite, hyalophane (9–20 mol% celsian), leucite, and sodalite. Subhedral phlogopite grains (0.2–0.3 mm, Fig. 1b) exhibit the same distinctive pleochroism as those from olivine leucitites.

Phlogopite coronas rimming olivine phenocrysts are found in a holocrystalline leucite basanite (WZK16) sampled from the central portion of a thick lava flow ( $> 20$  m thick). These mica flakes are  $< 0.05$  mm in the direc-

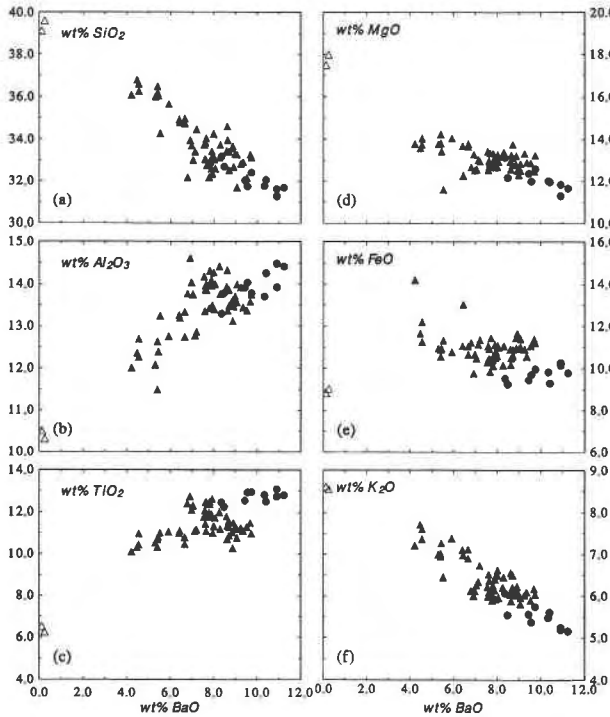


Fig. 2. (a–f) BaO vs. other elements for the WEK phlogopite. Solid triangles = olivine leucitite; solid circles = DZ2n; open triangles = corona.

tion perpendicular to (001) and show pale red to light yellow pleochroism.

**ANALYTICAL TECHNIQUE**

Analyses of mica chemistry were mainly performed at Imperial College (IC), University of London, using a Cambridge Instruments Microscan 5 electron microscope fitted with a Link energy-dispersive detector. Analytical conditions were accelerating voltage = 15 kV, fixed specimen current on a Co standard = 4.0 nA, and counting time = 100 s. ZAF corrections were used, and synthetic BaTiO<sub>3</sub> was analyzed to monitor interference between BaL $\alpha_1$  and TiK $\alpha_1$  lines, which proved to be negligible.

A subset of barian titanian phlogopite samples has also been analyzed using a Jeol 733 Superprobe equipped with wavelength-dispersive detectors at Southern Methodist University (SMU), in order to analyze F and Cl contents and to crosscheck the Ba-Ti interference. Analytical conditions were accelerating voltage = 15 kV, current = 20 nA, and beam spot diameter = 10  $\mu$ m. The X-ray counting rates were corrected using the  $\alpha$  matrix correction (Bence and Albee, 1968). Synthetic fluor-phlogopite and natural scapolite were used as standards for F and Cl. Benitoite (BaTiSi<sub>3</sub>O<sub>9</sub>) analyses gave BaO 37.15–38.38 wt%, TiO<sub>2</sub> 18.35–18.86 wt%, and SiO<sub>2</sub> 43.41–43.51 wt%, in good agreement with the theoretical values of 37.08, 19.32, and 43.58, respectively. The two sets of analyses are generally comparable.

**TABLE 1.** Representative phlogopite analyses

No. Host	65 DZ4	62 DZ4	2a DZ4	82 DZ6	94 DZ6	2d DZ2n	25 DZ2n	2 WZK16
SiO <sub>2</sub>	34.94	32.87	34.16	36.75	33.24	31.52	31.60	39.59
Al <sub>2</sub> O <sub>3</sub>	12.73	13.43	12.56	12.35	13.57	13.86	14.47	10.31
TiO <sub>2</sub>	10.44	11.09	10.54	10.28	11.47	12.48	13.06	6.25
FeO	10.64	10.54	10.57	11.64	11.36	10.09	10.24	9.03
MnO	n.a.	n.a.	0.12	n.a.	0.01	0.11	0.09	0.09
MgO	13.76	12.87	14.57	13.56	12.46	12.47	11.82	17.99
CaO	0.55	0.15	0.23	0.35	0.34	0.12	0.13	0.04
BaO	6.67	9.36	7.70	4.48	9.69	9.49	10.91	0.24
Na <sub>2</sub> O	0.93	0.63	0.83	0.90	0.48	0.87	1.01	0.90
K <sub>2</sub> O	6.89	6.08	6.55	7.70	6.16	5.20	5.18	8.55
F	n.a.	n.a.	1.34	n.a.	n.a.	0.93	n.a.	n.a.
Total*	97.54	97.03	98.61	98.01	98.78	96.36	98.51	92.99
Mg'	0.698	0.685	0.711	0.675	0.662	0.688	0.673	0.78
<b>O = 22</b>								
Si	5.259	5.075	5.181	5.439	5.066	4.905	4.849	5.896
Al	2.258	2.444	2.245	2.154	2.437	2.542	2.617	1.810
Ti	1.182	1.288	1.203	1.144	1.314	1.461	1.507	0.700
Fe	1.340	1.361	1.341	1.441	1.448	1.313	1.314	1.125
Mn	n.a.	n.a.	0.015	n.a.	0.001	0.014	0.012	0.011
Mg	3.088	2.962	3.294	2.992	2.831	2.893	2.704	3.994
Total	12.982	13.130	13.279	13.169	13.097	13.128	13.002	13.530
Ca	0.089	0.025	0.037	0.055	0.056	0.020	0.021	0.006
Ba	0.393	0.566	0.458	0.260	0.579	0.579	0.656	0.014
Na	0.272	0.190	0.244	0.258	0.142	0.262	0.300	0.260
K	1.322	1.198	1.267	1.454	1.198	1.032	1.014	1.624
Total	2.077	1.979	2.006	2.027	1.974	1.893	1.991	1.905
F	n.a.	n.a.	0.643	n.a.	n.a.	0.458	n.a.	n.a.
Charge**	46.871	46.916	46.411	46.777	47.033	46.934	47.377	45.507

Note: numbers 2a and 2d analyzed at SMU; others at IC. Fe<sub>tot</sub> as FeO; n.a. = not analyzed.

\* Less O = F.

\*\* Calculated with tetrahedral + octahedral = 14.

### MICA CHEMISTRY

This study is based on about 80 phlogopite analyses. Representative results are given in Table 1. Figure 2 illustrates chemical variations of the phlogopite samples in a series of variation diagrams that show BaO vs. other compositional variables.

#### Barian titanian phlogopite

Barian titanian mica samples found in WEK olivine leucitites and in DZ2n contain 4.2–11.2 wt% BaO and 10.1–13.1 wt% TiO<sub>2</sub>. Mg' [= atomic ratio Mg/(Mg + Fe<sub>tot</sub>)] values are 0.627–0.711. Thus, most of them are phlogopite (Deer et al., 1962). These phlogopite samples have moderate but variable SiO<sub>2</sub> (31.7–36.8 wt%) and Al<sub>2</sub>O<sub>3</sub> (11.5–14.6 wt%), whereas MgO and FeO (Fe<sub>tot</sub>) are 11.3–14.2 and 9.2–14.2 wt%, respectively. K<sub>2</sub>O is low and variable (5.2–7.7 wt%). Na<sub>2</sub>O and CaO are below 1.1 and 0.4 wt%, respectively, and do not correlate with BaO. They contain <0.06 wt% Cl, but moderate amounts of F (0.50–1.39, av. 0.90 wt%). Although many of the analyzed phlogopite grains are heterogeneous, no systematic zoning patterns have been detected.

SiO<sub>2</sub>, MgO, FeO, and K<sub>2</sub>O decrease whereas Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> increase with increasing BaO in the barian titanian phlogopite (Fig. 2). Phlogopite samples in DZ2n are generally more enriched in BaO than those in olivine leucitites; thus they have higher Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> but lower SiO<sub>2</sub>, MgO, FeO, and K<sub>2</sub>O. However, the coherent element trends and overlapping Mg' values demonstrate similar substitution schemes and suggest a genetic affinity between the two groups of phlogopite, despite their different occurrences.

Si and Al cations (O = 22) are <8.00 (7.38–7.73; av. 7.5 ± 0.06) pfu, implying that Al is confined exclusively to the tetrahedral occupancy. The sums of octahedral cations are <6.0 (5.29–5.93, av. 5.6 ± 0.09), lower than those for an ideal trioctahedral mica. In contrast, the occupancy in the 12-fold-coordinated interlayer site is almost stoichiometric (av. 1.99 ± 0.006).

#### Phlogopite coronas

Phlogopite coronas in WEK16 are chemically distinct from the barian titanian phlogopite. They have very low BaO (<0.24 wt%) and moderate TiO<sub>2</sub> (6.38 wt%), but high Mg' value (0.78), similar to the olivine phenocrysts (Fo<sub>81–79</sub>, Zhang, unpublished data). The phlogopite coronas contain higher SiO<sub>2</sub> (39.5 wt%) and K<sub>2</sub>O (8.6 wt%) but lower Al<sub>2</sub>O<sub>3</sub> (10.4 wt%) than the barian titanian phlogopite. They have fewer vacancies in the tetrahedral and octahedral sites (<sup>14</sup>R = 7.72, <sup>16</sup>R = 5.79) but do not have sufficient interlayer ions (A site = 1.90).

#### Comparison with other barian phlogopite

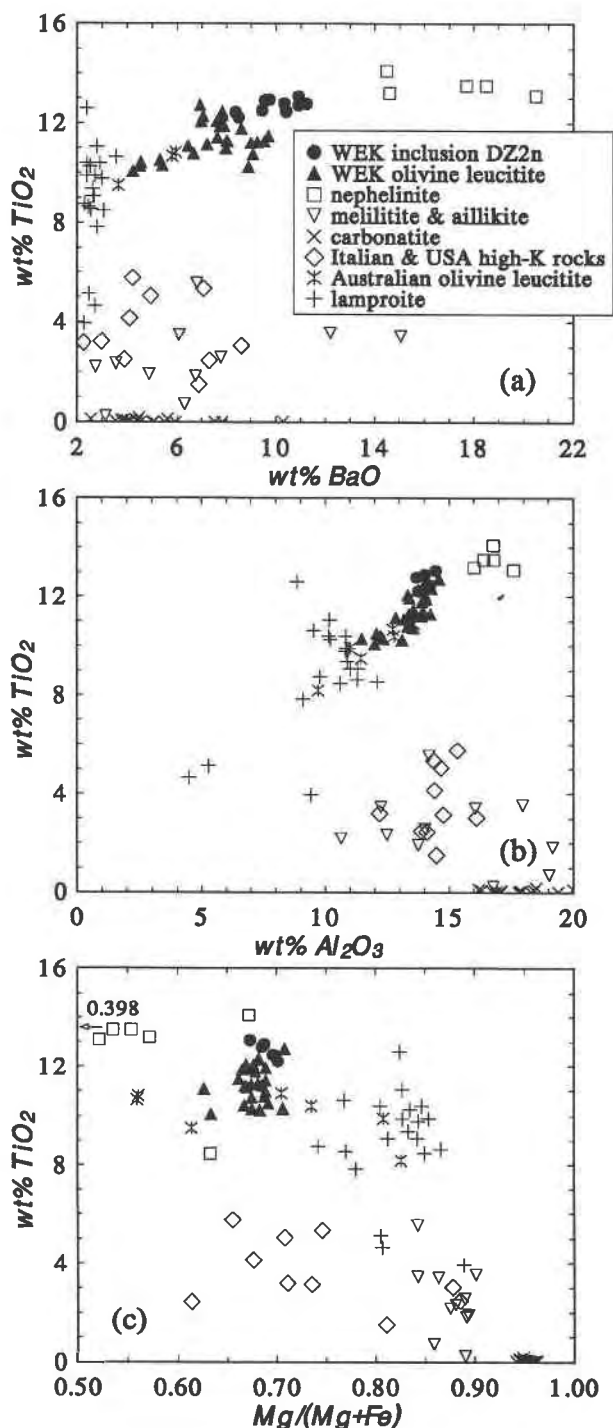
The compositions of barian phlogopite (arbitrarily set as BaO > 2 wt%) differ significantly among three categories of host alkalic rocks: (1) nephelinites, (2) aillikites, melilitites, and carbonatites, and (3) mafic potassic rocks. Figure 3 shows variations of BaO, Al<sub>2</sub>O<sub>3</sub>, and Mg' vs.

TiO<sub>2</sub> for the WEK phlogopite samples and the other samples from the literature.

Mica samples in Hawaiian nephelinites are the most enriched in BaO (14.3–20.4 wt%), TiO<sub>2</sub> (13.0–14.5 wt%), and Al<sub>2</sub>O<sub>3</sub> (15.8–17.6 wt%) but have the lowest Mg' (as low as 0.40) among all the samples concerned. This is in agreement with their reported occurrence as a late groundmass phase. On the other hand, those in aillikites and melilitites show wide variation in BaO (3–15 wt%) but relatively low TiO<sub>2</sub> (<4.0 wt%). Their Al<sub>2</sub>O<sub>3</sub> contents are variable, but generally high (up to 19.3 wt%). High Mg' values (>0.84) reflect the ultramafic nature of the hosts (Rock, 1991). The composition of barian phlogopite in the silicate bands of Jacupiranga carbonatites (Brazil) is characterized by extremely high Mg' (0.94–0.96) and low TiO<sub>2</sub> (<0.2 wt%). The high Mg' values are consistent with the dolomite-dominant host carbonatites (Gaspar and Wyllie, 1987). Al<sub>2</sub>O<sub>3</sub> is high (16–20 wt%), but BaO is variable (<1.0–10.2 wt%). Chemical characteristics of barian titanian phlogopite in potassic rocks are apparently related to tectonic settings (e.g., Barton, 1979). The phlogopite from potassic rocks associated with subduction (e.g., Roman Province, Italy, and Montana) shows a wide range in BaO contents (2–9 wt%) and Mg' (0.61–0.89) but, as expected from the host magmas, contains lower TiO<sub>2</sub> (<6.0 wt%) than the phlogopite from potassic rocks of intraplate settings (e.g., WEK and East Australian leucitites, >8.0 wt%). The Australian phlogopite samples are similar to the WEK ones in terms of TiO<sub>2</sub>, BaO, and Al<sub>2</sub>O<sub>3</sub> contents but are lower in Mg' (0.56–0.61) than the latter (Fig. 3). Mica samples in lamproites rarely have BaO > 3.0 wt%, despite strong enrichment of Ba in the hosts.

#### Comparison with phlogopite from other potassic rocks

TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and FeO contents of the WEK phlogopite samples are plotted in Figure 4 for comparison with those from other potassic rocks, including lamproites, minettes, Italian and Ugandan potassic rocks, and Mongolian leucite basanites. The WEK phlogopite samples can be readily distinguished by their generally higher Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents from those hosted by lamproites and the Ugandan kamafugites. The latter generally evolve toward very low Al<sub>2</sub>O<sub>3</sub> at various TiO<sub>2</sub> and FeO contents, forming a late-stage tetraferri phlogopite. This chemical signature is apparently imparted by the peralkaline nature of host magmas. Although most of the WEK samples plot in the field distinguished by micas from minettes and the Italian potassic rocks in the Al<sub>2</sub>O<sub>3</sub> vs. FeO diagram (Fig. 4a), they have much higher TiO<sub>2</sub> contents (Fig. 4b). The combination of a negative correlation between Al<sub>2</sub>O<sub>3</sub> and FeO and a positive correlation between Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> for the WEK samples (Fig. 4) is distinctive and has not been observed elsewhere. The WEK phlogopite samples are similar to the Mongolian mica megacrysts in terms of TiO<sub>2</sub> content (Fig. 4b) and Mg' (0.63–0.71 and 0.59–0.67, respectively), but WEK phlogopite samples lower in Al<sub>2</sub>O<sub>3</sub> and FeO than the mica megacrysts (Fig. 4a).



#### SUBSTITUTION SCHEMES

Assigning a unique set of substitutions to the WEK barian titanian phlogopite is hindered by (1) the complexity of substitution schemes in micas, which can be represented in terms of various linear combinations of end-members (Hewitt and Abrecht, 1986), (2) the unconstrained Fe and Ti valencies and H<sub>2</sub>O contents, and (3)

Fig. 3. TiO<sub>2</sub> vs. (a) BaO, (b) Al<sub>2</sub>O<sub>3</sub>, and (c) Mg/ for magmatic barian micas. For the sake of clarity, one-half to two-thirds of the WEK data points have been omitted from Fig. 3, 4, 6, and 7. Data sources: nephelinite—Hawaii, Mansker et al. (1979); southeast China, Cao and Zhu (1987); aillikite and melilitite—South Africa, Velde (1979), Boctor and Yoder (1986); Greenland, Rock (1991); carbonatite—Brazil, Gaspar and Wyllie (1987); potassic rocks—East Australia, Birch (1978; 1980); Roman Province, Thompson (1977), Holm (1982); Montana, Wendlandt (1977), O'Brien et al. (1988); lamproite—Mitchell and Bergman (1991).

the possibility that Ti, Fe, and even Mg (Foley, 1990) may occur in tetrahedral coordination. However, as the WEK phlogopite samples have genetic affinities, the substitution schemes can be evaluated by their coherent chemical departures from end-member phlogopite (Hewitt and Abrecht, 1986) in light of relevant experimental data.

#### Ba substitutions

There are two alternative substitutions involving Ba and the interlayer sites. One, suggested by Shmakin (1984) and Wagner and Velde (1986) and implied from coupled substitutions proposed by Mitchell (1981) and Guo and Green (1990), is



Another, proposed by Wendlandt (1977), Mansker et al. (1979), and Bol et al. (1989), is



The WEK phlogopite samples have almost stoichiometric interlayer occupancy and plot along the line of 1:1 substitution of Ba for K + Na + Ca (Fig. 5a), which favors Substitution 2 over 1. As Ba cations per formula unit (0.25–0.70) are  $>^{141}\text{Al} - 2.0$  (0.15–0.62), Al is insufficient to compensate for the charge imbalance. Thus, even if Substitution 2 describes the general form of coupled Ba substitution, another cation, probably Fe<sup>3+</sup>, must also be present in tetrahedral coordination to compensate for both the tetrahedral site deficiency and the charge imbalance.

Chemical data for the other barian trioctahedral micas from the literature also define a similar negative correlation between Ba and K + Na + Ca, as shown by the WEK samples. The sums of the interlayer cations are nearly 2.0 pfu for all but a few samples from the Leucite Hills and Smoky Butte lamproites, whose interlayer cations are as low as 1.8 pfu and whose BaO contents are  $<3$  wt% (Ba  $\leq 0.2$  pfu) (Mitchell and Bergman, 1991). Therefore, Substitution 2 may be applicable to the majority of magmatic barian micas, except for those from lamproites.

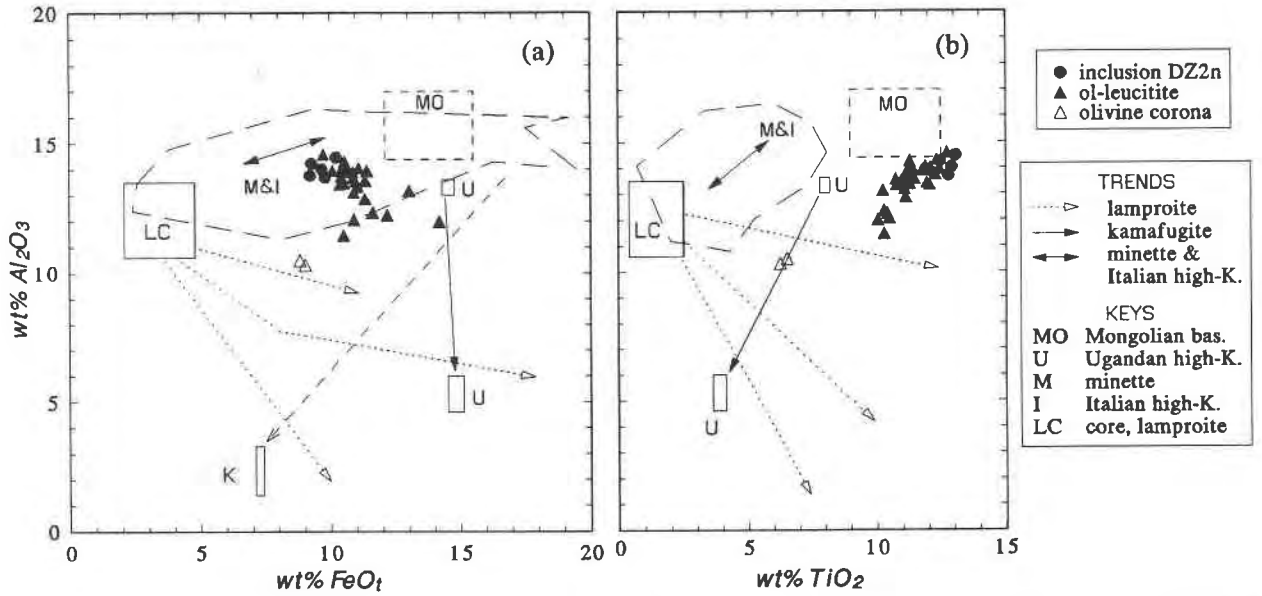


Fig. 4. Al<sub>2</sub>O<sub>3</sub> vs. (a) FeO and (b) TiO<sub>2</sub> for phlogopite from potassic rocks. Data sources: lamproite, Mitchell (1981), Mitchell and Bergman (1991); kamafugites, Edgar (1979); Italian potassic rocks, Thompson (1977), Holm (1982); minettes, Bachinski and Simpson (1984); Mongolian leucite basanites, Ryabchikov et al. (1981).

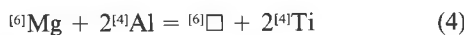
**Ti substitutions**

The role of Ti in barian titanian phlogopite depends upon Ti valence and occupancy. The relationship between Ti cations and excess positive charge (Fig. 6a) on the basis of 14 tetrahedral + octahedral cations (e.g., Bol et al., 1989) lends strong support for Ti<sup>4+</sup>, as most of the WEK samples plot close to or above the line defined by Σ ionic charge - 44 = 2Ti. Values of *f*<sub>O<sub>2</sub></sub> calculated from Fe-Ti oxides in the WEK olivine leucites are 0.5 log units above the FMQ buffer (Zhang, unpublished data), further suggesting that all Ti in the potassic magma could be quadravalent.

Another controversy concerns Ti occupancy in micas. In light of the tetrahedral deficiencies in all WEK samples, Substitutions



and



are theoretically possible.

Optical absorption and Mössbauer spectral results fail to provide conclusive evidence in favor of <sup>[4]</sup>Ti in micas (see summaries of Edgar and Arima, 1983; Dymek, 1983; Abrecht and Hewitt, 1988; Brigatti et al., 1991). In particular, the presence of <sup>[4]</sup>Ti in barian titanian phlogopite would increase lattice energy by electrostatic repulsion between <sup>[4]</sup>Ti and <sup>[12]</sup>Ba, and hence decrease phlogopite stability (Bol et al., 1989). With regard to the WEK micas, Substitution 3 cannot explain observed variations in the sum of tetrahedral + octahedral cations (about 0.5 pfu), nor does the positive correlation between Al and Ti (Fig. 4b) support Substitution 4. For these reasons, oc-

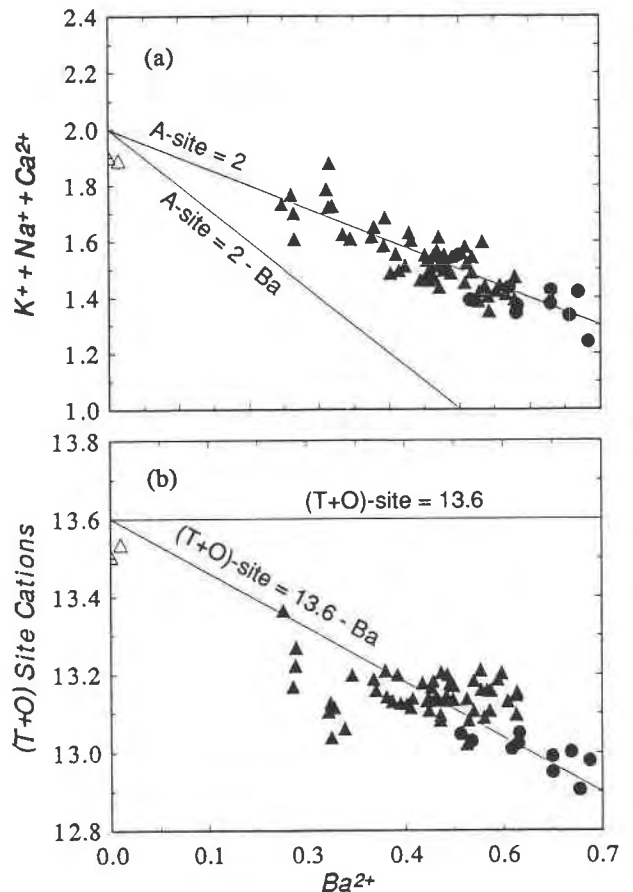


Fig. 5. Ba vs. (a) K + Na + Ca and (b) tetrahedral + octahedral site cations for the WEK phlogopite. Calculated with O = 22. Symbols as in Fig. 2.

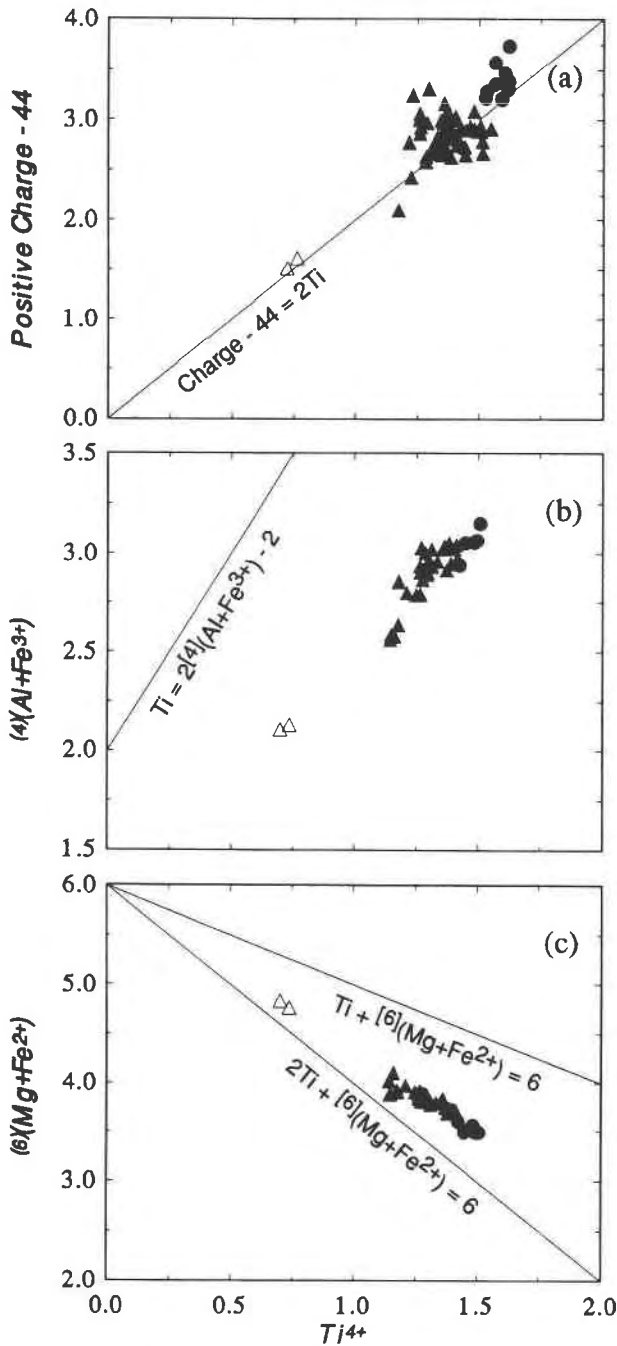


Fig. 6. Ti vs. (a) excess positive charge, (b)  $4(\text{Al} + \text{Fe}^{3+})$ , and (c)  $6(\text{Mg} + \text{Fe}^{2+})$  for the WEK phlogopite; a, calculated with tetrahedral + octahedral = 14; b and c, with O = 22. Sufficient  $\text{Fe}^{3+}$  is calculated from  $\text{Fe}_{\text{tot}}$  and added to Si + Al to fill the T sites and is subtracted from  $\text{Fe}_{\text{tot}}$  on the O sites. Symbols as in Fig. 2.

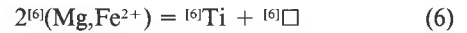
tetrahedral occupancy of Ti, and thus tetrahedral occupancy of  $\text{Fe}^{3+}$ , is strongly preferred.

Assuming that Ti occurs as  ${}^{6}\text{Ti}^{4+}$ , three basic substitutions involving Ti are frequently proposed (e.g., Dymek, 1983). They are

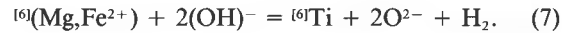
Ti-Tschermak's:



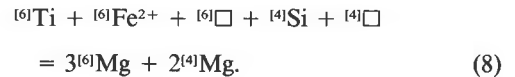
Ti vacancy:



Ti-O:



In addition, Foley (1990) suggests another substitution for lamproitic micas formed under reducing conditions,



This substitution is, however, inapplicable to the WEK micas because of the antipathetic correlation between Si and Ti (ref. Fig. 2a, 2c).

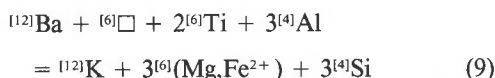
Although the data for the WEK barian titanian phlogopite define a slope broadly parallel to the line representing Ti-Tschermak's substitution [ $\text{Ti} = 2(\text{Al} + \text{Fe}^{3+}) - 2$ ], the amount of Ti is much too high for this to be the only or even dominant substitution (Fig. 6b). Distinction between Ti vacancy (Tronnes et al., 1985) and Ti-O (Bol et al., 1989) is equivocal because the correlation shown in Figure 6a is consistent with both interpretations, and because the importance of an oxy substitution cannot be evaluated without independent  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}$  determinations (Dymek, 1983; Abrecht and Hewitt, 1988). A well-defined negative correlation between Ti and  $\text{Mg} + \text{Fe}^{2+}$  for the WEK samples (Fig. 6c), which plot parallel and close to the line at  $2\text{Ti} + (\text{Mg} + \text{Fe}^{2+}) = 6$ , is strong evidence for the Ti-vacancy to be a dominant substitution. The tetrahedral + octahedral site deficiency (Fig. 5b) also points to the same conclusion. An alternative explanation is that the deficiency is an artifact of normalizing to O = 22. The Ti-O substitution could produce a positive correlation between O and Ti and, as O > 22, higher calculated tetrahedral + octahedral cations. If this were the case, and a fixed-cation normalization tetrahedral + octahedral = 14 were used instead, the calculated interlayer cations per formula unit would be on average >2.13 (up to 2.35), rather than being stoichiometric. The extra interlayer cations, however, must be used with great caution, as evidence against Ti-O substitution because it may result from an effect of substitution of F for OH upon the normalization procedure. This substitution results in O < 22 and thus increases the sum of the interlayer occupancy calculated from fixed cations. Since the maximum F content in the WEK phlogopite is 1.4 wt%, corresponding to  $[(\text{OH})_{3.29}\text{F}_{0.71}]_{4.00}$ , the calculated interlayer cations can only be increased by 0.04 pfu relative to an F-free stoichiometric phlogopite, far less than necessary to compensate for the apparent excess in interlayer cations. In other words, if the calculated excess of the A-site occupancy were to solely reflect the presence of F, the WEK barian titanian phlogopite should contain

at least 4 wt% F. Therefore, although no conclusive choice from the alternatives can be made, the data favor a Ti vacancy substitution.

The above arguments are based on coherent chemical variations of the WEK phlogopite using simple parameters such as the amounts of cation(s) or site occupancy. Some plots with complex parameters representing linear combinations of various substitutions have been employed (e.g., Mansker et al., 1979; Wendlandt, 1977; Guo and Green, 1990) in an attempt to identify specific combinations of the basic substitutions for barian titanian phlogopite. Nevertheless, the results fail to provide better discrimination and sometimes could be misleading because the apparently linear relationships might be an artifact derived from correlations among simple parameters (Foley, 1990). Three cases will be considered below to elucidate the problems associated with this approach.

1. In Figure 7  $2(\text{Al} + \text{Fe}^{3+}) + \text{Ti}$  is plotted vs.  $2\text{Si} + (\text{Mg} + \text{Fe}^{2+})$  for the WEK phlogopite. Wendlandt (1977) interpreted a relationship similar to that shown in Figure 7 as evidence for the Ti-Tschermak's substitution in barian phlogopite from the Montana potassic rocks. In fact, compositions that are parallel to the join defined by phlogopite and Ti-Tschermak's end-member can be derived from a linear combination of Substitutions 2 and 7. Moreover, the offset of data points below the join requires some type of vacancy substitution. Even Substitution 6 cannot significantly change the slope of the trend because Si and Al, which assume greater weight than Ti and Mg in the plot, apparently control the trend. Thus, the slope of the trend in Figure 7 is not a sensitive indicator for particular substitutions.

2. From a near ideal linear trend with a slope of  $-1$  between  $\text{Ba} + 2\text{Ti} + 3\text{Al}$  and  $\text{K} + 3(\text{Mg,Fe}) + 3\text{Si}$ , Mansker et al. (1979) argued for a combined substitution of



for the Hawaiian barian titanian biotite. As Substitution 9 involves an O-site vacancy, the 1:1 replacement should indicate a deviation from the proposed substitution rather than an accordance with it. This trend does not parallel the join linking phlogopite and an end-member created by Substitution 9,  $\text{KBaMg}_3\text{Ti}_2\text{Si}_3\text{Al}_5\text{O}_{20}(\text{OH})_4$ , which is a linear combination of Substitutions 2, 5, and 6 in the proportions 1:1:1. Whereas a constant Ba:Ti ratio of 0.5 is specified by Substitution 9, the Hawaiian biotite samples have variable Ba:Ti ratios (0.54–0.81, Mansker et al., 1979). Therefore, the data indicate that all the three substitutions operate in the Hawaiian biotite samples at variable ratios.

3. Recently, Guo and Green (1990) proposed another substitution,

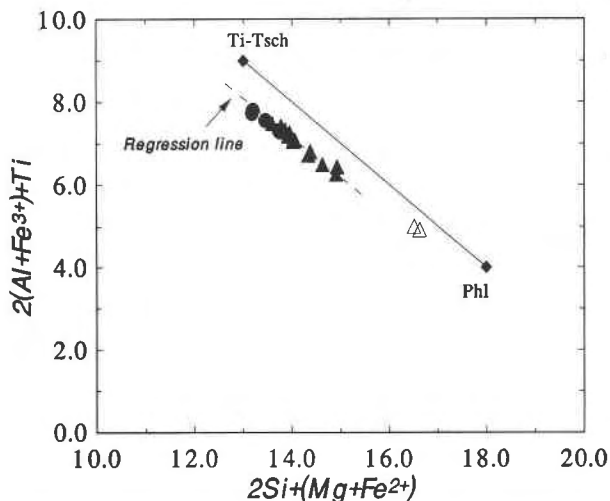
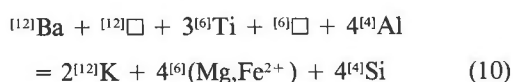


Fig. 7. A plot of  $2\text{Si} + (\text{Mg} + \text{Fe}^{2+})$  vs.  $2(\text{Al} + \text{Fe}^{3+}) + \text{Ti}$  for the WEK phlogopite. Calculated with  $\text{O} = 22$ . Symbols as in Fig. 2.

as a best fit for natural and synthetic phlogopite from potassic rocks (mainly lamproites). It is a linear combination of Substitutions 1, 6, and 5 in the proportions of 1:1:2. Therefore, it cannot be verified for the same reason the Hawaiian biotite cannot be. As Substitution 10 involves a significant proportion of the Ti-Tschermak's end-members, it is very unlikely to be applied to phlogopite samples in lamproites because of their Al-deficient character (e.g., Mitchell, 1981) and a negative correlation between  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  (Fig. 4b). The Hawaiian data (Mansker et al., 1979) fit both Substitutions 9 and 10 well, further illustrating that complex parameters cannot discriminate sensitively among alternative substitutions.

Ti substitution schemes vary among micas crystallized from diverse magma compositions and under different physical conditions (Edgar and Arima, 1983). Therefore, no general applicability of a particular scheme can be assumed. For instance, Ti vacancy and  $^{4}\text{Fe}^{3+} = ^{4}\text{Al}$  substitutions (Mitchell, 1981), but not Ti-Tschermak's, may be predominant in lamproitic micas for the reasons discussed above. In contrast, Tschermak's substitution is likely to prevail, accompanied by minor Ti-Tschermak's, in phlogopite in potassic rocks related to subduction (e.g., Roman Province).

#### PARAGENESIS AND MICA COMPOSITION

Textural relations indicate that the phlogopite in the WEK lavas is a late phase crystallized from residual potassic melts at near-surface pressures and low temperatures, e.g.,  $<960^\circ\text{C}$  in olivine leucitites (Fe-Ti oxide temperature, Zhang, unpublished data). The presence of leucite in inclusion DZ2n also suggests that it formed at low pressures (probably  $<4$  kbar, Taylor and Mackenzie, 1975). As  $\text{Mg}'$  values for the phlogopite in DZ2n (62.7–



70.1) are slightly lower than for the phlogopite in the groundmass of olivine leucitites (66.5–71.1), DZ2n may have crystallized from a more evolved potassic magma.

Differences in composition between the barian titanian phlogopite in olivine leucitite and the corona phlogopite in leucite basanite cannot be attributed to the different host magma compositions. The corona phlogopite shows lower BaO, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> but higher Mg' than the barian titanian phlogopite, whereas the host for the former (leucite basanite WZK16) is higher in Ba, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> but lower in Mg' than for the latter (olivine leucitites). Differences in paragenesis between WEK olivine leucitites and leucite basanites may provide an explanation for the contrast. Neither leucite nor nepheline, both of which are present in the olivine leucitites, is the repository for Ba. Ba is hardly above 0.06 wt% in leucite and even lower in nepheline (Zhang, unpublished data). Therefore after crystallizing >85% Ba-free phases, the residual olivine leucitic melts are so enriched in Ba that barian titanian phlogopite can crystallize (Zhang et al., 1993). In contrast, potassium feldspar, a major groundmass phase in the leucite basanites, incorporates a moderate amount of BaO (0.2–1.8 wt%, av. 0.5 wt%; Zhang, unpublished data). Thus, the residual liquids in WZK16, with which olivine phenocrysts interacted to form phlogopite, must have undergone Ba depletion. Higher Mg' in the phlogopite coronas is attributed to the forsteritic olivine phenocrysts that dominate the MgO budget of the reaction, whereas low Al<sub>2</sub>O<sub>3</sub> content reflects the combined effects of Al<sub>2</sub>O<sub>3</sub>-absent olivine phenocrysts plus Al<sub>2</sub>O<sub>3</sub>-depleted residual liquids caused by potassium feldspar crystallization. Therefore, the chemistry of magmatic phlogopite depends on not only the composition of host magmas and intensive variables but also mineral assemblages (Foley, 1990) and crystallization sequences. The latter factors can be employed to explain the lack of barian phlogopite in extremely Ba-rich lamproites because Ba-rich accessory phases, such as priderite, jeppeite, and shcherbakovite, compete for Ba.

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