Barium-titanium–rich phlogopites in marbles from Rogaland, southwest Norway

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Abstract

Phlogopites in forsterite-bearing marbles of the metasedimentary Faurefjell Formation in the high-grade Precambrian rocks of Rogaland, southwest Norway, contain up to 24.6 wt% BaO and up to 13.9 wt% TiO_2. The very high TiO_2 content and the low cation sums (Σcations < 16 and Si + Al < 8 per 22 oxygens) could be taken to indicate incorporation of tetrahedral Ti and/or Ti-vacancy substitutions. However, combinations of Ti-oxy and Ti-vacancy substitution schemes explain the analytical data better. Structural formulae of the solid-solution trend have been expressed as approximately linear combinations of pure phlogopite and a Ba-Ti component $BaMg_2TiSi_2Al_2O_{12}$, with small contributions of "eastonite" and Ti-vacancy end-member. The structural formula of the most Ba-rich mica is $(K_{0.14}Na_{0.05}Ba_{0.81})(Mg_{1.61}Fe_{0.45}Ti_{0.84}Al_{0.06}\square_{0.03})Si_{2.13}Al_{1.88}O_{12}((OH)_{0.38}O_{1.62})$, indicating that the unnamed anhydrous Ba-Ti end-member composition constitutes about 81 mol% of the solid solution.

Introduction

The Precambrian basement of southwest Norway (Fig. 1) consists of massif-type anorthosites, the layered anorthositic to mangeritic lopolith of Bjerkreim-Sokndal (Duchesne et al., 1985) and surrounding high-grade metamorphic migmatites containing intercalations of garnetiferous migmatites, augen gneisses, and rocks of the supracrustal Faurefjell Formation (Hermans et al., 1975; Maijer and Padget, 1988).

On the basis of mineral assemblages in the garnetiferous migmatites, four main stages of metamorphism (M1 to M4) have been recognized (Kars et al., 1980; Jansen and Maijer, 1980; Maijer et al., 1981; Tobi et al., 1985). The M1 phase is assigned ages of around 1200 Ma (Wielens et al., 1981). This phase is overprinted by the M2 phase, which essentially was developed in a thermal aureole associated with intrusion of the magmatic complex. The M2 phase is dated at about 1050 to 1000 Ma (Verschure, 1985). Peak metamorphic temperatures were reached during the M2 stage of metamorphism and are calculated to have been 800 °C near Oltedal, increasing to 1000 °C near the lopolith at maximum pressures of 4 to 5 kbar (Jansen et al., 1985). Th M3 phase of metamorphism is correlated with granitic injections during the post-M2 cooling history. M3 minerals reveal ages between 970 and 870 Ma (Maijer et al., 1981; Maijer and Padget, 1988). The M4 phase resulted from incipient burial metamorphism of early Paleozoic age and of very low grade metamorphism assigned to Caledonian overthrusting (Verschure et al., 1980; Sauter et al., 1983).

The Faurefjell Formation consists of metasedimentary rocks, most notably marbles and calc-silicate rocks with intercalations of metavolcanics. The major outcrops, denoted A, B, C, and D, are indicated in Figure 1. Details of the locations and related rock types are given by Sauter (1983).

Analyses of phlogopites in siliceous dolomites of the Faurefjell Formation revealed high to very high BaO contents. The BaO contents of phlogopites in sample C480 are the highest described to date for natural phlogopite (cf. Wendlandt, 1977; Mansker et al., 1979; Gaspar and Wyllie, 1982; Solie and Su, 1987). The TiO_2 contents are also high and show a strong positive correlation with BaO contents. The purpose of this paper is to discuss the mineral chemistry of the Rogaland phlogopites and to evaluate appropriate substitution schemes that involve Ba and Ti.

Petrology and petrography

Phlogopite is a common constituent in the forsterite- and diopside-bearing marbles. The phlogopites can be subdivided into two groups on the basis of their BaO content and paragenesis. One group is relatively low in BaO (0 to 4.8 wt%) and occurs in diopside-bearing rocks and forsterite-bearing marbles. In the diopside-bearing marbles, the phlogopite is associated with diopside + calcite ± dolomite, and in the diopside-bearing calc-silicate rocks, it is associated with diopside ± calcite ± spinel. In the forsterite-bearing marbles, it is accompanied by forsterite, calcite, and dolomite ± diopside ± spinel and occasionally by barite. The other group, with high BaO contents (around 20 wt%), occurs exclusively in forsterite-bearing marbles.

Commonly, the low-Ba phlogopites are developed as subhedral platelets with a maximum grain size of about

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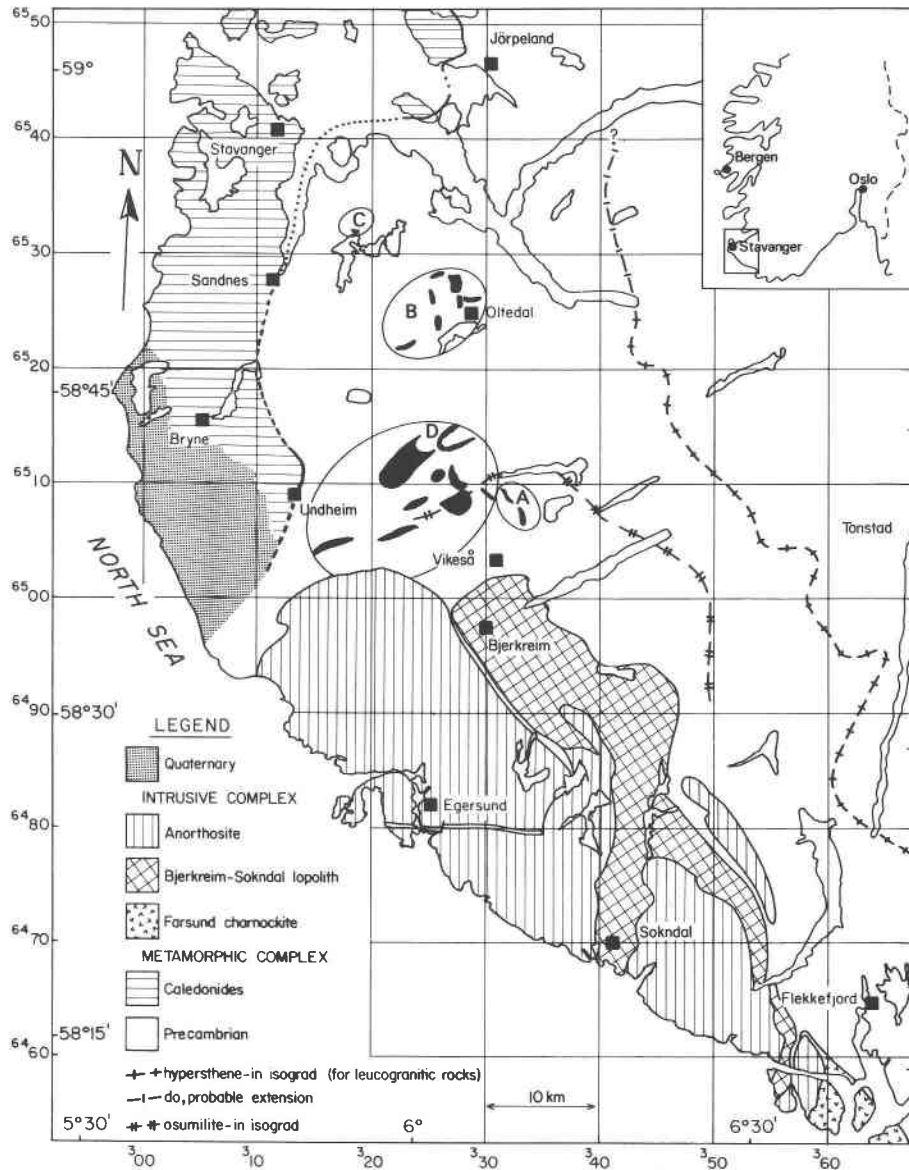* Present address: 12 Belmont Avenue, Kalgoorlie WA 6430, Australia.

Fig. 1.   Geologic sketch-map of southwest Norway. Outcrops of the Faurefjell Formation, at locations A, B, C, and D, are indicated in black (after Bol and Jansen, 1989).

2 mm (Fig. 2), and they exhibit no preferred orientation. In spinel- and forsterite-bearing marbles, the low-Ba phlogopites are entirely enclosed by forsterite crystals, and some high-Ba phlogopites are also present as large discrete grains (Fig. 3). In forsterite + spinel marble C480, the high-Ba phlogopites have a dark brown pleochroic color (O = red-brown, E = light brown), in contrast to the very pale brown pleochroic colors regularly observed in phlogopites of siliceous dolomites. Especially in samples from retrograde metamorphic exposures in location B, chloritization of the phlogopites is evident and occurred during the Caledonian low-grade metamorphic overprint (Sauter et al., 1983).

ANALYTICAL METHODS

Electron-microprobe analyses of the phlogopites are given in Table 1. Most analyses were performed with a Cambridge Scientific Instruments Geoscan and a Microscan M-9 at the Free University of Amsterdam using wavelength-dispersive techniques. Operating conditions were 20-kV accelerating voltage and 25-nA beam current. Various natural and synthetic oxide and silicate minerals were used as standards. Data were corrected with the M-9 correction program (ZAF). Some analyses were done on a TPD electron microprobe at the Institute for Earth Sciences of the University of Utrecht also using wavelength-dispersive techniques. Operating conditions were 15-kV
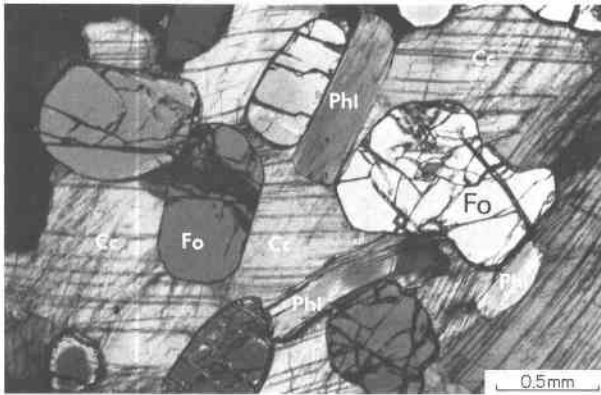
Fig. 2. Forsterite-phlogopite marble. Photomicrograph, A122, crossed nicols. Fo = forsterite, Phl = phlogopite, Cc = calcite, and Sp = spinel.

accelerating voltage and 40-nA sample current for a periclase standard. Data were corrected with the Springer correction program (ZAF). Interference of Ba and Ti peaks during the measurements proved to be negligible.

MINERAL CHEMISTRY

The X_{Mg} of the phlogopites varies between 0.95 and 0.91 in diopside-bearing rocks, from 0.97 to 0.93 in forsterite-bearing marbles, and between 0.83 and 0.76 for the high-Ba phlogopites in sample C480 (Fig. 4). The X_{Mg} is not corrected for trivalent Fe. Wet-chemical analyses for Fe^{2+} of separated fractions of phlogopites yield Fe^{2+}/ Fe^{3+} ratios of approximately 4, use of which would increase the X_{Mg} ratio to only slightly higher values.

The most remarkable feature of the phlogopites is the variation in BaO content. Phlogopites in barite-bearing marbles contain several percent BaO. The BaO content of the low-Ba phlogopites varies from 0 to 4.8 wt%. In the discrete coarse phlogopites, which are not enclosed in forsterite, the BaO contents range from 17.8 to 24.6 wt%. These phlogopites also have significantly low K_2O and SiO_2 contents, 1.2 and 23.3 wt% respectively. The TiO_2 content of the phlogopites generally is low in diopside-bearing rocks (0.4 to 0.8 wt%), but low-Ba phlogopites enclosed in forsterite crystals in the spinel- and forsterite-bearing marbles contain up to 2.7 wt% TiO_2 (e.g., sample C480, spot B021). The high-Ba phlogopites have extremely high TiO_2 contents, up to 13.9 wt%. Low-Ba phlogopites contain up to 18.6 wt% Al_2O_3, whereas high-Ba phlogopites are uniformly high in Al_2O_3, the contents of which range from 17.7 to 18.9 wt%. In all micas, Na_2O and MnO are minor components and CaO was not detected.

F concentrations range up to 3.3 wt% in low-Ba phlogopites of the forsterite-bearing marbles, corresponding to a F/(F + OH) ratio (X_F) of 0.37 assuming that the rest of the hydroxyl sites are occupied by OH. This can be compared with an X_F of 0.42 to 0.56 for coexisting clinohumite. The F contents in the high-Ba phlogopites are below the detection limit, and Cl was not detected in any mica.
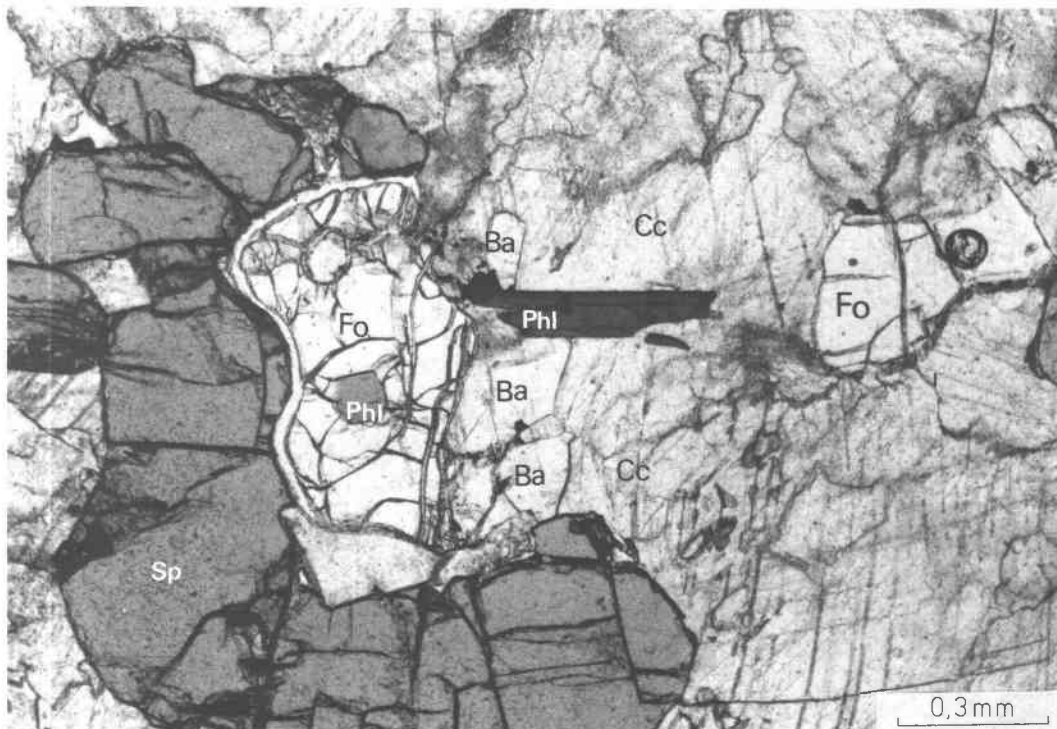

Fig. 3. Phlogopite as small inclusion in forsterite and as large grain of Ba-rich phlogopite (center). The Ba-rich phlogopite is in contact with barite (= Ba). Photomicrograph, C480, plane-polarized light.
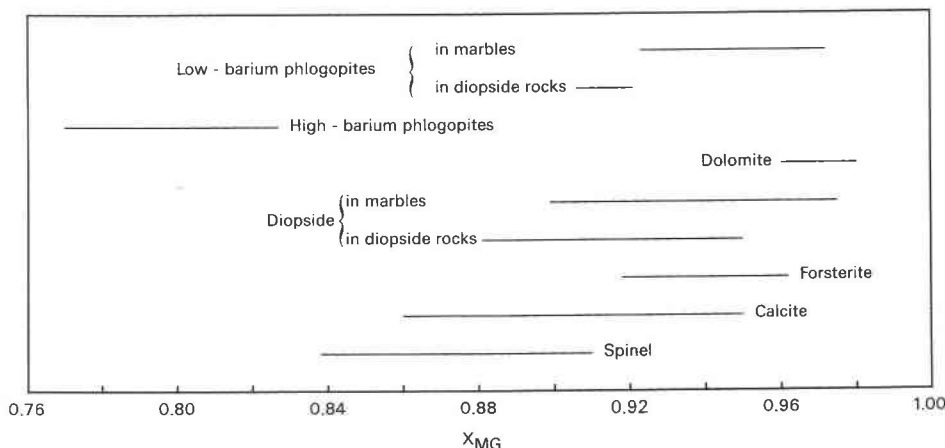
Fig. 4. Range of X_{Mg} of minerals in marbles and in diopside-bearing rocks. X_{Mg} calculated with total Fe as Fe^{2+}, except for spinel, which was corrected for magnetite.

The oxide totals of the high-Ba phlogopites generally are very high. In combination with the low F content, the high oxide totals are believed to reflect a low OH, and therefore presumably a high oxygen, occupancy of the hydroxyl sites. A detailed description of the accompanying main mineral phases is available upon request.[1]

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[1] A copy of the mineral descriptions may be ordered as Document AM-89-399 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $10.00 in advance for the microfiche.

PETROGENESIS

The formation of phlogopite in impure siliceous dolomite usually takes place by the reaction of dolomite with alkali feldspar (Rice, 1977). The equilibrium reaction commences at relatively low grade metamorphic conditions. Unfortunately, in the marbles of Rogaland, no specific reaction can be described for the phlogopite production. The rocks contain the assemblage Phlog + Cc ± Fo ± Dol, which is stable above 700 °C at P_{total} of about 5 kbar (Sauter, 1983). The coexistence of Fo + Cc + Sp is an additional indication of high-temperature metamorphism and is consistent with the inferred regional meta-


TABLE 1. Representative microprobe analyses of the Rogaland phlogopites

Sample: No.:	C165 B032		BE24 B111		C480 B021		Q75 B043		A164 B135	
SiO₂	40.31		37.25		36.37		40.74		38.21	
Al₂O₃	14.05		18.57		17.06		13.92		16.87	
TiO₂	0.41		0.64		2.70		0.49		0.50	
FeO_T	2.61		1.36		3.18		1.32		2.46	
MnO	bd		0.06		bd		bd		0.05	
MgO	26.67		24.87		22.40		26.31		24.69	
BaO	0.05		3.83		1.44		0.13		1.68	
Na₂O	0.16		0.12		0.12		0.24		0.06	
K₂O	10.50		9.43		10.25		10.84		9.98	
F	0.9		0.5		na		3.1		0.5	
Total*	95.28		96.42		93.52		95.78		94.79	
Formula proportions**										
Si	5.726	5.694	5.315	5.328	5.326	5.385	5.807	5.830	5.495	5.497
[4]Al	2.274	2.306	2.685	2.672	2.674	2.615	2.193	2.170	2.505	2.503
[6]Al	0.079	0.034	0.439	0.459	0.271	0.363	0.146	0.178	0.355	0.357
Ti	0.044	0.044	0.069	0.069	0.297	0.301	0.053	0.053	0.054	0.054
Fe	0.310	0.308	0.162	0.163	0.389	0.394	0.157	0.158	0.296	0.269
Mn			0.007	0.007			0.006	0.006		
Mg	5.646	5.614	5.289	5.302	4.889	4.943	5.589	5.611	5.292	5.291
Σ	14.079	14.000	13.966	14.000	13.846	14.000	13.951	14.000	13.997	14.000
Ba	0.003	0.003	0.214	0.215	0.083	0.084	0.007	0.007	0.095	0.095
Na	0.044	0.044	0.033	0.033	0.034	0.034	0.066	0.067	0.017	0.017
K	1.903	1.892	1.717	1.721	1.915	1.936	1.971	1.979	1.831	1.831
Σ	1.950	1.937	1.964	1.969	2.032	2.054	1.055	2.053	1.943	1.942
+Charge†		43.756		44.109		44.487		44.174		43.992

Note: Samples: Low-Ba phlogopites—C165, diopside- and phlogopite-bearing rock (location C); BE24, forsterite- and spinel-bearing marble (location A); C480, forsterite- and spinel-bearing marble (location A); Q75, forsterite-bearing marble (location B); A164, forsterite-bearing marble (location A). High-Ba phlogopites—C480, Forsterite- and spinel-bearing marble (location A). bd = below detection limit. na = not analyzed.

morphic gradient of the M2 phase. In the forsterite- and spinel-bearing marble C480, the low-Ba phlogopites are enclosed in forsterite, whereas the high-Ba phlogopites are developed as large separate grains, pointing to a later growth stage. The low-Ba phlogopites are apparently relics that survived the prograde spinel-forming reaction at high temperature, as proposed by Glassley (1975) for analogous environments:

$$6\text{Phlog} + 7\text{Cc} \rightleftharpoons 7\text{Di} + 4\text{Fo} + 3\text{Sp} \\ + 7CO_2 + 6H_2O + 3K_2O. \quad (1)$$
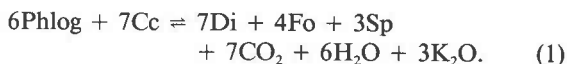
The BaO content of the Rogaland marbles is fairly constant at all investigated locations and varies between 0.2 and 0.8 wt% as it is reflected by the occurrence of accessory barite. Ba mobility is traditionally considered to be negligible during regional metamorphism (Barbey and Cuney, 1982), and an authigenic provenance for most of the barite is favored. M2 pegmatites at location B contain BaO up to 6.4 wt%. Preliminary results of a chemical study along profiles across a pegmatite-marble contact reveal that local enrichment of Ba in the pegmatite margin is related to progressive desilification. On the other hand, Ti seems to have been introduced to the marbles, as indicated by volume-composition relations in the vicinity of the marble-pegmatite contact.

The high-Ba phlogopites have, to date, been observed only in the southernmost part of area A, which is the closest occurrence of marble to the lopolith (Fig. 1). Peak metamorphic temperatures may have approached 900 °C,

suggesting that relatively high temperature may be an important factor in the formation of these micas.

DISCUSSION

The chemical composition of 33 selected phlogopites from Rogaland, southwest Norway, is plotted in Figure 5. Chemical compositions of Ba-bearing phlogopites reported by Wendlandt (1977), Mansker et al. (1979), and Gaspar and Wyllie (1982) are shown for comparison. Comparing the high-Ba phlogopites to the low-Ba phlogopites described in this study, K_2O, SiO_2, and MgO decrease with increasing BaO, whereas TiO_2 and FeO increase. Compositions of the high-Ba phlogopites show minor scatter about definite trends. The data for the low-Ba phlogopites show much more scatter than those for the high-Ba phlogopites and seem to define different trends (Fig. 5) for FeO and for MgO.

The composition of the low-Ba phlogopites is similar to that in other high-grade impure siliceous dolomite occurrences investigated by Glassley (1975), Rice (1977), Kretz (1980), and Bucher-Nurminen (1982). Ba-bearing phlogopites from peridotite and turjaite (Wendlandt, 1977) have compositions close to those of the low-Ba phlogopites from Rogaland with respect to K_2O, SiO_2, and MgO, although the Al_2O_3 contents are somewhat higher, and the FeO and TiO_2 contents are lower. The Ba-bearing phlogopite from the Jacupiranga carbonatite (Gaspar and Wyllie, 1982) has a slightly lower TiO_2 content. Brown Ba-rich micas from the Alaska Range (not

TABLE 1.—*Continued*

C480 B502		C480 B512		C480 B036		C480 B046		C480 B056	
27.88		27.55		24.31		24.34		24.31	
17.74		18.33		18.05		18.87		18.85	
10.32		11.89		13.94		13.16		13.00	
5.44		5.96		6.33		6.07		6.21	
bd		bd		bd		bd		bd	
14.60		14.17		12.47		11.98		12.35	
17.79		19.61		21.25		24.67		23.94	
0.37		0.37		0.34		0.58		0.39	
3.65		3.06		1.24		1.34		1.57	
bd		bd		bd		bd		bd	
97.79		100.94		97.93		100.96		100.62	
				Formula proportions					
4.425	4.710	4.284	4.581	3.967	4.257	3.942	4.291	3.936	4.259
3.319	3.290	3.360	3.419	3.472	3.743	3.603	3.709	3.598	3.741
	0.243		0.179		0.017		0.213		0.152
1.232	1.311	1.390	1.487	1.711	1.836	1.603	1.745	1.583	1.713
0.722	0.769	0.775	0.829	0.864	0.927	0.822	0.895	0.841	0.910
3.453	3.676	3.283	3.511	3.032	3.254	2.892	3.148	2.980	3.225
13.151	14.000	13.092	14.000	13.046	14.000	12.899	14.000	12.938	14.000
1.106	1.178	1.195	1.278	1.359	1.458	1.562	1.701	1.519	1.643
0.114	0.121	0.112	0.119	0.108	0.115	0.182	0.198	0.122	0.132
0.739	0.787	0.607	0.649	0.258	0.277	0.277	0.301	0.324	0.351
1.959	2.086	1.914	2.046	1.725	1.850	2.021	2.200	1.965	2.126
	46.840		47.051		47.220		47.894		47.608

* Less oxygen ≡ F.
** Based on 22 oxygens (1st column) and Σcations − (Na + K + Ba) = 14 (2nd column of each pair).
† Calculated positive charge per formula unit based on the 14-cation normalization procedure.
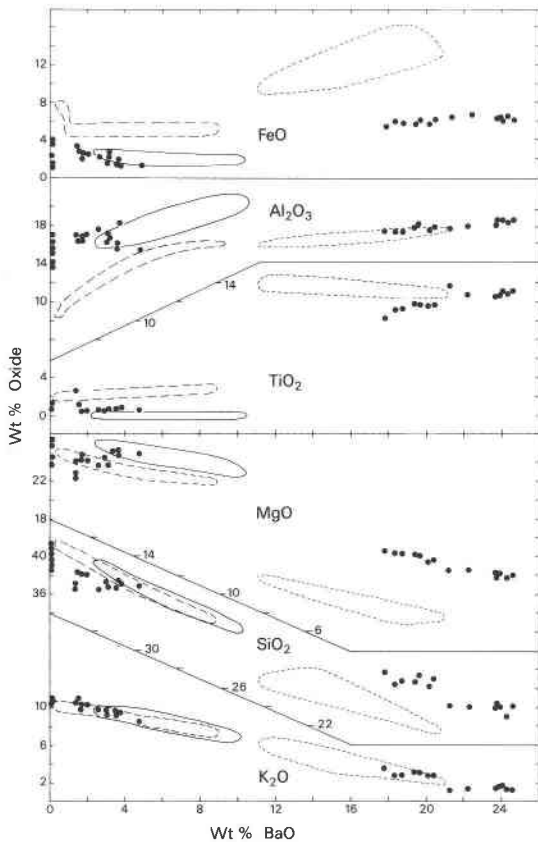
Fig. 5. Chemical variation in phlogopites in wt% oxides. Dots: Rogaland phlogopites, this work. Stippled line: Mansker et al. (1979). Solid line: Gaspar and Wyllie (1982). Broken line: Wendlandt (1977).
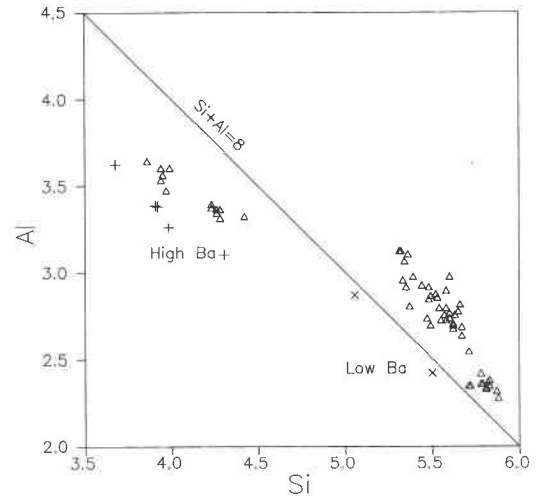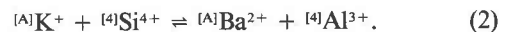

Fig. 6. Atoms of Si versus Al diagram for phlogopites. Triangles: Rogaland phlogopites of this work. Plus signs: data of Mansker et al.. Crosses: data of Wendlandt. All formula proportions are based on the 22-oxygen normalization.

$$^{[A]}K^+ + {}^{[4]}Si^{4+} \rightleftharpoons {}^{[A]}Ba^{2+} + {}^{[4]}Al^{3+}. \qquad (2)$$

In the Rogaland phlogopites, the amount of $^{[4]}Al^{3+}$ is more than sufficient to achieve charge balance for Ba^{2+} [Ba $< ({}^{[4]}Al - 2)$] in all of the phlogopites (see Table 1). However, the high-Ba phlogopites show an apparent deficiency in tetrahedral cations ($^{[4]}Si^{4+} + {}^{[4]}Al^{3+} < 8$ per 22 oxygens), whereas the low-Ba phlogopites do not (Table 1, Fig. 6), suggesting that the two groups obey distinct substitution schemes (Fig. 6). Ti substitutions will be discussed only for the high-Ba phlogopites.

It is suggested that Ti contents of biotite commonly increase with increasing metamorphic grade (Kwak, 1968), and this is supported by experimental results (Robert, 1976). The high-Ba, high-Ti phlogopites of Rogaland have probably indeed crystallized at high-grade conditions. However, Ti contents far exceed the 0.7 atoms Ti per 20 oxygens that was found experimentally at 1000 °C and 1 kbar by Robert (1976). The presence of Fe^{2+} seems to enhance Ti substitution (Czamanske and Wones, 1973), but this effect must be negligible for the Rogaland phlogopites given their high Mg/Fe ratios. If it is assumed that pressure does not have a large effect on Ti solubility, the presence of other cations must therefore enhance Ti contents.

Substitution schemes that involve Ti were reviewed by Dymek (1983):

Ti-Tschermak's:

$$^{[6]}R^{2+} + 2^{[4]}Si^{4+} \rightleftharpoons {}^{[6]}Ti^{4+} + 2^{[4]}Al^{3+} \qquad (3)$$

Ti-vacancy:

$$2^{[6]}R^{2+} \rightleftharpoons {}^{[6]}Ti^{4+} + {}^{[6]}\square \qquad (4)$$

Ti-oxy:

$$^{[6]}R^{2+} + 2OH^- \rightleftharpoons {}^{[6]}Ti^{4+} + 2O^{2-} + H_2. \qquad (5)$$

plotted) are much lower in TiO_2 (Solie and Su, 1987). The high-Ba phlogopites have a composition resembling the high-Ba biotites from Hawaiian nephelinites (Mansker et al., 1979) with respect to SiO_2, Al_2O_3, TiO_2, and K_2O, but have higher Mg/Fe ratios.

Substitution schemes for Ba-bearing phlogopite

For complex micas, it is generally impossible to derive a unique set of exchange vectors for components (Thompson, 1982) that correspond to crystallochemically valid substitutions. Even if Fe_2O_3 and H_2O are known, several equivalent sets of exchange components can be adopted to describe a single phase (Hewitt and Abrecht, 1986). Therefore, some knowledge of interatomic correlations is necessary to identify set(s) of exchange components and hence valid substitutions.

The negative correlation between K and Ba (cf. Fig. 5) reflects Ba substitution on the interlayer site of the phlogopites (Fig. 5). In contrast to A-site substitution of the univalent cations Rb^+, Cs^+ (Hazen and Wones, 1972), and NH_4^+ (Bos et al., 1988), the charge balance for Ba^{2+} is maintained by simultaneous substitution of Al^{3+} for Si^{4+} on the tetrahedral site, according to the scheme proposed by Wendlandt (1977):

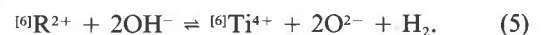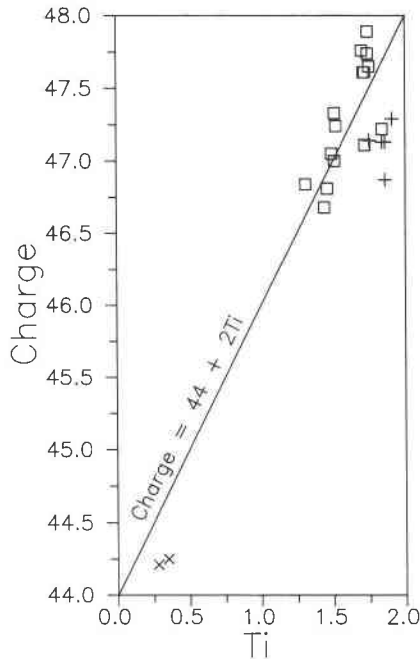Fig. 7. Atoms of Ti versus total cation charge for the high-Ba phlogopites from Rogaland (squares), Mansker et al. (plusses), and Wendlandt (crosses). All formula proportions based on the 14-cation normalization procedure.

Fig. 8. Atoms Ti versus (Fe + Mg) for the high-Ba phlogopites. Lines have inclinations −1 and −2 and correspond to Ti-oxy and Ti-vacancy substitutions respectively (squares: based on the 14-cation normalization procedure; triangles: based on the 22-oxygen normalization procedure). Plus signs represent data from Mansker et al. normalized on 14 cations.

Additionally, substitutions involving tetrahedral Ti might be considered. The possibility of $^{[4]}Ti$ in silicates is controversial (Hartman, 1969). Synthetic high-Ti OH-phlogopites do not contain tetrahedral Ti (Robert, 1976), whereas Kovalenko et al. (1968) reported $^{[4]}Ti$ in synthetic F-phlogopites. Farmer and Boettcher (1981) invoked the occurrence of $^{[4]}Ti$ as well as $^{[4]}Fe^{3+}$ in phlogopites in South African kimberlites. The high Ti content of the high-Ba biotites of Mansker et al. (1979) and Wendlandt (1977) and in those from Rogaland together with the low tetrahedral cation sums (Si + Al < 8 per 22 oxygens, Fig. 6) seems to support the existence of tetrahedral Ti. In this respect, it is interesting to note that all of these micas have formed in silica- and alumina-undersaturated environments. Crystallochemically, however, tetrahedral Ti in high-Ba biotites is unlikely. The electrostatic repulsion between Ba^{2+} and Ti^{4+} increases the lattice energy, and octahedral positions for Ti are strongly favored over the tetrahedral positions, since the latter are closer to the interlayer sites. Therefore, vacancy- or oxy-substitutions must be involved. Formula proportions normalized to a fixed anion framework are not affected by vacancies (Dymek, 1983). Low cation sums in the first column of the formula proportions in Table 1 may be attributed to the Ti-vacancy substitution (4). Normalization procedures that assume complete occupancy of the tetrahedral and octahedral sites are indifferent to variations in H_2O content (second column of the formula proportions in Table 1), and they may be used to calculate the total cation charge, which ideally equals
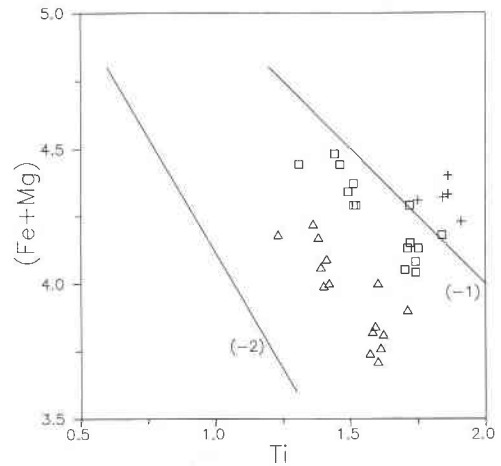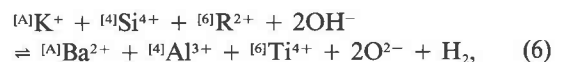
44 assuming an anion framework of 20 oxygens and 4(OH + F + Cl). Charge calculations considering all Fe as Fe^{2+} yield minimum values for the total charge (Table 1). The high-Ba phlogopites have a large excess charge that correlates well with 2Ti (Fig. 7), which points to substitutions (4) and (5) and rules out (3) as a dominant substitution.

A plot of Ti versus (Fe + Mg) per 22 oxygens (Fig. 8) yields a trend with a slope between −2 and −1 that is not conclusive evidence in favor of either substitution (4) or (5). When normalized to 14 cations, the data plot close to the line predicted by (5), but some combination of (4) and (5) is probably necessary to explain the substitution of Ti. The high oxide totals of the high-Ba phlogopites and the extremely dry granulite-facies conditions of formation support the concept of substitution schemes involving dehydrogenation reactions. Furthermore, if a dominant role for the Ti-oxy substitution is accepted, there is no need to invoke $^{[4]}Ti$, since on the basis of 14 cations, (Si + Al) exceeds 8 for all phlogopites.

The strong covariation of Ti and Ba in the Rogaland phlogopites suggests that combinations of substitution (2) with Ti-oxy substitution (5) and, to a lesser extent, with Ti-vacancy substitution (4) play a significant role. Adding (2) and (5) yields an overall substitution,

$$^{[A]}K^+ + {}^{[4]}Si^{4+} + {}^{[6]}R^{2+} + 2OH^-$$
$$\rightleftharpoons {}^{[A]}Ba^{2+} + {}^{[4]}Al^{3+} + {}^{[6]}Ti^{4+} + 2O^{2-} + H_2, \quad (6)$$

which ultimately leads to an anhydrous Ba-Ti end-member $BaMg_2TiSi_2Al_2O_{12}$.

The very small differences between Ahrens ionic radii of Ba^{2+} (1.33 Å) and K^+ (1.34 Å) on the one hand and Ti^{4+} (0.66 Å) and Mg^{2+} (0.68 Å) on the other do not indicate the necessity of an exact 1:1 covariation of Ba and

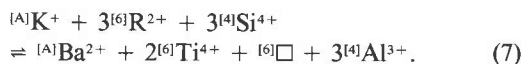**TABLE 2.** Substitution of $BaMg_2TiSi_2Al_2O_{12}$ in the high-Ba phlogopites

Spot:	B502	B512	B036	B046	B056
Phlogopite	26.61	20.80	9.79	5.97	8.45
$BaMg_2TiSi_2Al_2O_{12}$	57.94	63.50	74.85	82.95	81.14
"Eastonite"	9.20	8.19	6.86	6.45	6.93
Ti-vacancy	6.26	7.51	8.50	4.63	3.49
SSR		0.48	0.07	1.90	1.64	0.41

Ti. The composition of the phlogopites is probably controlled by localized buffering of Ba and Ti activities in fluids in grain-boundary films and in nearby minerals, and no unique overall substitution scheme is thought to control the chemical variation within the high-Ba phlogopites.

Least-squares mixing calculations were performed in order to recast the formula proportions of cations in the high-Ba phlogopites into linear combinations of $KMg_3Si_3AlO_{10}(OH)_2$ (phlogopite), $KMg_2AlSi_2Al_2O_{10}(OH)_2$ ("eastonite"), $KMgTi\square Si_3AlO_{10}(OH)_2$ (Ti vacancy) and $BaMg_2TiSi_2Al_2O_{12}$ (6). All Fe was assumed to be Fe^{2+} and was added to Mg, and all Na was added to K. Ideally, the squared sum of residuals (SSR) should be less than 1.0% since the analytical error is believed to be of this order of magnitude. In Table 2, results of the mixing calculations are given. SSR values exceed 1.0 in two cases owing to neglect of other minor substitution components, such as anandite ($BaFe_3Si_3FeO_{10}(OH)S$) and kinoshitalite ($BaMg_3Si_2Al_2O_{10}(OH)_2$). The proposed anhydrous Ba-Ti end-member constitutes up to about 81 mol% in the phlogopite solid solution of analysis B056. Using the end-member proportions in Table 2, the inferred structural formula for B056 is $(K_{0.14}Na_{0.05}Ba_{0.81})(Mg_{1.61}Fe_{0.45}Ti_{0.84}Al_{0.06}\square_{0.03})Si_{2.13}Al_{1.88}O_{12}((OH)_{0.38}O_{1.62})$.

Mansker et al. (1979) suggested the following substitution scheme as a 1:1:1 combination of (2), (3), and (4):

$$^{[A]}K^+ + 3^{[6]}R^{2+} + 3^{[4]}Si^{4+}$$
$$\rightleftharpoons {}^{[A]}Ba^{2+} + 2^{[6]}Ti^{4+} + {}^{[6]}\square + 3^{[4]}Al^{3+}. \quad (7)$$

However, the Ti-Tschermak's substitution (3) is not strictly valid for the Hawaiian biotites (Fig. 7). Both Mansker et al. (1979) and Wendlandt (1977) reported tetrahedral deficiencies (Fig. 6). Mansker et al. assumed contributions of large amounts of $^{[4]}Fe^{3+}$; Wendlandt assigned part of the Ti content to the tetrahedral sites. It is notable that these data may be explained by substitution schemes involving Ti-oxy contributions (Figs. 7 and 8), without invoking the existence of $^{[4]}Ti^{4+}$.

Detailed investigations of the structure and physical properties of the anhydrous Ba-Ti phlogopite end-member are in progress.

CONCLUSIONS

1. At least 75% of the K on the interlayer sites of phlogopites from Rogaland is replaced by Ba.

2. Analytical data for Ba-rich micas are best explained by assuming various amounts of Ti-oxy substitution, without invoking the presence of Ti on tetrahedral sites.

3. $BaMg_2TiSi_2Al_2O_{12}$ constitutes about 80 mol% of the natural biotite solid solutions from Rogaland.

4. The Ti content of the high-Ba phlogopites has been influenced by parameters other than temperature or Fe activity. The actual parameters cannot be identified from existing data.

5. The approximately 1:1 Ba-Ti coordination in the Rogaland high-Ba phlogopites is not crystallochemically controlled but reflects local availability Ba and Ti.

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