Substitution Mechanisms and Solubility of Titanium in Phlogopites from Rocks of Probable Mantle Origin

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Abstract. Previously proposed substitution mechanisms for Ti in phlogopites, based on experimental studies and crystal chemistry, have been examined using data for 81 phlogopites from mantle-derived rocks (primarily as nodules in kimberlites and also from alkali basalts, lamprophyres and carbonatites), 49 phlogopites from high-K rocks with basaltic affinities, and from 32 phlogopites crystallized in high pressure experiments mainly on high-K rock compositions. For the majority of phlogopites from the kimberlite group and for all those crystallized in the experimental studies, the substitution of Ti can be represented by a combination of the mechanisms represented by $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$ and $Mg^{[VI]}2Si^{[IV]} \rightleftharpoons Ti^{[VI]}2Al^{[IV]}$. Some phlogopites in ultrapotassic rocks have only the former substitution mechanism. The Ti contents of phlogopites generally increase with decreasing octahedral site occupancy and decreasing $Si + Al^{[VI]}$. For the phlogopites crystallized in the experiments on high-K rocks, the solubility of Ti increases with increasing fO_2 and temperature, and possibly with decreasing pressure at constant fO_2. The effect of the composition of the liquids used in the experimental studies from which these phlogopites have crystallized has only minor effect on either the substitution mechanism or the solubility of Ti in phlogopites. This suggests that phlogopite in high-K rocks may be a potential geothermometer and possibly a geobarometer.

Introduction

Phlogopite is the only common mineral stable under mantle conditions which contains significant amounts of K. Many phlogopites from rocks believed to be of mantle origin contain often high TiO_2 contents (cf. Forbes and Flower 1974). This suggests that Ti-phlogopite may also be an important source of Ti in the upper mantle and Forbes and Flower (1974) have demonstrated that under mantle conditions such phlogopites have a greater stability range than phlogopites without Ti; thus providing a source of both K and Ti during breakdown of Ti-bearing phlogopite at mantle depths.

Phlogopite compositions from megacrysts and xenoliths in kimberlites, alkali basalts, carbonatites, lamprophyres, and particularly high-K mafic rocks have high but variable TiO_2 contents, often with marked differences between the cores (TiO_2-poor) and the rims (TiO_2-rich) (cf. Boettcher et al. 1979). The

high TiO_2 contents of phlogopites from these mantle derived rocks may reflect either a high Ti content inherent to the upper mantle or a result of metasomatic enrichment in the mantle producing phlogopites with higher TiO_2 contents in their rims than in their cores (Boettcher et al. 1979).

Whatever the source of the TiO_2 in the phlogopites in rocks derived from the upper mantle, a knowledge of the roles of pressure, temperature, fO_2, etc. in the solubility of Ti in the phlogopite as well as its modes of substitution is necessary to assess its potential as a geothermometer and geobarometer. Forbes and Flower (1974) synthesized Ti-rich phlogopite between 7–30 kb from a single starting composition [$K_2Mg_4Ti Al_2Si_6O_{20}(OH)_4$] containing about 10 wt.% TiO_2. At 30 kb they found this Ti-rich phlogopite was stable up to 1,350° C under excess H_2O (vapour) conditions and up to 1,500° C under vapour absent conditions, indicating a high solubility of Ti in phlogopite. These experiments did not establish the variation in solubility with T or P as only a single starting material was used. Using a series of starting materials, Robert (1976) determined the solubility of Ti in phlogopites between 600°–1,000° C at 1–7 kb which showed that the solubility increased greatly with temperature but decreased with pressure, reaching a maximum of 6.6 wt.% TiO_2 at 1,000° C and 1 kb.

Edgar et al. (1976) and Ryabchikov and Green (1978) studied a highly potassic biotite mafurite composition between 10 and 30 kb using various different amounts of H_2O and $H_2O + CO_2$ and different fO_2 conditions. These authors showed that the TiO_2 contents of phlogopites increased with increasing temperature, increased $\dfrac{Fe^{2+}}{Mg}$ and increased fO_2 (representing increased Fe^{3+}), and decreased with increasing pressure. Ryabchikov and Green (1978, Table 3) analysed a phlogopite at 30 kb, 1,300° C and with 2.4% H_2O and 5.9% CO_2 with 8.1% TiO_2. Edgar et al. (1976) concluded that for phlogopites coexisting with liquid, TiO_2 contents were such that $\dfrac{TiO_2 \text{ (liquid)}}{TiO_2 \text{ (phlogopite)}}$ increased with decreasing temperature and decreased with decreasing pressure and $\dfrac{Mg}{Mg+Fe}$ content of both phlogopite and liquid. They also suggested that TiO_2 substitutes more readily in Fe-rich phlogopites. From a study of phase relations in a rock of similar composition, Barton and Hamilton (1979) found that a phlogopite crystallized at 20 kb and 1,245° C had lower TiO_2 and higher Al_2O_3 contents than the phlogopites analysed by Edgar et al. (1976). They suggest that the mechanism of Ti substitution in their phlogopite was $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$ as proposed by Forbes and Flower (1974) whereas in the rock studied by Edgar et al.

(1976) the substitution may have been $Mg^{[VI]}2Si^{[IV]} \rightleftharpoons Ti^{[VI]}2Al^{[IV]}$, the mechanism proposed by Robert (1976).

Barton (1979) described phlogopites from several high-K lavas and found very differing Ti contents in phlogopites (and pyroxenes). He concludes that the bulk composition, particularly the Al contents, of the liquids from which these minerals crystallize, may affect the type of Ti substitution in the phlogopite structure.

These studies indicate that the degree of solubility of Ti in phlogopite as well as the mechanism of substitution is highly dependent on the composition from which they crystallized, and on the P, T and fO_2 conditions of their formation.

Mechanisms of Ti Substitution

A number of substitutions have been suggested for phlogopites, the commonest being $Mg^{[VI]} \rightleftharpoons Fe^{2+[VI]}$ (phlogopite-annite series) and $Mg^{[VI]}Si^{[IV]} \rightleftharpoons Al^{[IV]}Al^{[VI]}$ (phlogopite-eastonite series). Generally, in phlogopites from igneous rocks of high pressure origin, $Al^{[VI]}$ is less than $Al^{[IV]}$ with $Al^{[VI]}$ being accompanied by Si deficiency. In such phlogopites the muscovite molecule may be ignored. For Si-rich, Al-poor phlogopites Seifert and Schreyer (1971) proposed the substitution $Mg^{[VI]}2Al^{[IV]} \rightleftharpoons 2Si^{[IV]} \square^{[VI]}$.

Based on experimental studies, two mechanisms have been suggested for the substitution of Ti in phlogopites. Forbes and Flower (1974) proposed the substitution $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$. In contrast, Robert (1976) proposed the replacement of Mg by Ti in the octahedral site associated with the replacement of 2Si by 2Al in the tetrahedral site, e.g. $Mg^{[VI]}2Si^{[IV]} \rightleftharpoons Ti^{[VI]}2Al^{[IV]}$. The possibility of Ti substitutions involving tetrahedral sites has recently been discussed by Farmer and Boettcher (1981).

The replacement $Mg^{[VI]}2(OH)^- \rightleftharpoons Ti^{[VI]}2O^{2-}$ has been suggested for biotites (cf. Bohlen et al. 1980). As most phlogopite analyses used in this study were done by electron microprobe, values of H_2O, F and Cl are not known and therefore substitution involving $(OH)^-$ and O^{2-} could not be examined. However, if the low totals (93–97 wt.%) of the phlogopite analyses reflect, in addition to analytical uncertainties, variations in the H_2O, F and Cl contents in the (OH) site, which theoretically should be approximately 4 wt.%, a relationship between Ti contents and the totals should indicate the importance of coupled Ti substitutions involving the (OH) site. As no such correlation was found, we assume that such a substitution mechanism is probably unimportant. We also assume that anions in the (OH) site are about 4 wt.%, and accordingly have calculated structural formulae on the basis of 22 oxygen throughout.

Yoder (1957) and Wendlandt (1977), for example, have suggested K site substitutions in phlogopites. In the structural formulae of the high Ti-bearing phlogopites used in this study, the K-site deficiency is less than 0.2 and no correlation is found between this deficiency and Ti contents, suggesting that any substitutions involving the K site do not involve Ti.

For the majority of Ti-rich, Al-poor phlogopites Fe^{3+} has not been determined. Using the procedure of Carmichael (1967), Cundari (1973), and Sheraton and Cundari (1980), the presence of possible Fe^{3+} has been ignored in the structural formulae and Ti assigned to the tetrahedral site. This procedure suggests the substitutions can be written as $Si^{[IV]} \rightleftharpoons Ti^{[IV]}$ and $Mg^{[VI]}2Al^{[IV]} \rightleftharpoons 2Ti^{[IV]} \square^{[VI]}$ giving the hypothetical end-member molecules $K_2Mg_6Al_2TiSi_5O_{20}(OH)_4$ and $K_2Mg_5\square Ti_2Si_6O_{20}(OH)_4$ respectively. Robert (1976) has shown that the former end-member molecule is unstable at 1,000° C and 1 kb. Studies of synthetic Ti-garnets (Huggins et al. 1977) and Ti clinopyroxenes (Akasaka and Onuma 1980) show that the order of tetrahedral

site preference in these minerals is $Al > Fe^{3+} \gg Ti$. Using optical absorption spectra, Farmer and Boettcher (1981) suggest that the tetrahedral site preference in phlogopite is $Si > Al > Ti > Fe^{3+}$. Mössbauer spectra on synthetic ferriphlogopite [$K_2Mg_6Fe^{3+}Si_6O_{20}(OH)_4$] (Annerstern et al. 1971) and on a natural Al-poor phlogopite with minor TiO_2 ($Al_2O_3 = 9.97$ wt.%, $TiO_2 = 0.17$ wt.%) (Hogarth et al. 1970) show the presence of tetrahedrally coordinated Fe^{3+}. Unpublished Mössbauer spectra on a phlogopite from the high-K rocks of the Leucite Hills, Wyoming, with 11.8 wt.% Al_2O_3 and 2.2 wt.% TiO_2, shows that about 60 mol% of the Fe is Fe^{3+} and occurs in the tetrahedral site. This study suggests that the tetrahedral site deficiencies in Al-poor phlogopites in the Leucite Hills rocks can be attributed to the presence of Fe^{3+} rather than Ti.

The relationship between Ti and Si deficiencies and octahedral site deficiency in the structural formulae of phlogopites is shown in Fig. 1. Methods of calculating the structural formulae are given in the following section. The phlogopites plotted in Fig. 1 are from high pressure experimental studies, natural Ti-rich phlogopites ($TiO_2 > 3$ wt.%), from high-K mafic rocks, and from xenoliths of mantle origin. The broad trend of points between the end members $K_2Mg_5TiAl_4Si_4O_{20}(OH)_4$ (Fig. 1, Point A) and $K_2Mg_4\square TiAl_2Si_6O_{20}(OH)_2$ (Fig. 1, Point B), on which Ti occupies the octahedral site, indicates that in these phlogopites Ti is likely to occupy octahedral site. The fact that these phlogopites plot between the end-member molecules (Fig. 1) also suggests that Ti-rich phlogopites can be represented by these molecules. The scattering of points between the points A and B in Fig. 1 is particularly noticeable for phlogopites from the high pressure experimental studies where the phlogopites are small and more difficult to analyse than natural samples.

Procedure for Recalculating and Plotting Analyses

Analyses of phlogopites used in this study were subdivided into those in which the structural formula (O=22) showed Si<6 (Group I) and those with Si>6 (Group II). For both groups the analyses were further subdivided into those with a tetrahedral site deficiency in which Si+Al<8 with Si>6 (Group Ia), those with Si+Al>8 and Si<6 (Group Ib), those with Si+Al<8 with Si>6 (Group IIa), and those with Si+Al>8 with Si>6 (Group IIb). Very few analyses were in the last group and are not considered further.

For analyses in groups Ia and IIa, sufficient Fe^{3+} was recalculated from the total Fe (as FeO) and added to the Si+Al to fill the 8 tetrahedral sites, e.g. Si+Al+Fe^{3+}=8. From this value, Si+Al$^{[VI]}$ ($Al^{[VI]}$=0) was plotted against Ti (Figs. 2b, 4b, 5b). For the octahedral site occupancy (OSO) vs. Ti diagrams (Figs. 2a, 4a, 5a), the added Fe^{3+} was subtracted from the total Fe in the octahedral site, i.e. Mg+Mn+Ni+Ti+Fe^{2+} (adjusted for added Fe^{3+}). For analyses in group Ib, $Al^{[VI]}$ was added to Si and plotted against Ti (Figs. 2b, 4b, 5b) and, in these cases, the OSO value was simply the total of the octahedrally coordinated cations which were plotted against Ti (Figs. 2a, 4a, 5a).

Phlogopites Crystallized
in High Pressure Experiments

Analyses of phlogopites from high pressure (10–30 kb) experiments are mostly from high-K rock compositions with $K_2O > Na_2O$ and TiO_2 contents greater than that of peridotite. Most of these analyses are from biotite mafurite (Edgar et al. 1976, Ryabchikov and Green 1978); others are from an olivine ugandite (Edgar et al. 1980), and a madupite (Barton and Hamilton 1979). Unpublished phlogopite analyses from high pressure experiments on a katungite of composition similar to that given

Fig. 1. The relationships between Ti, 6-OSO (octahedral site occupancy), and 6-$(Si+Al^{[VI]})$ in the structural formula (22 O) of phlogopites belonging to group I (Si < 6). A and B are described in text. Data sources: o: experimental derived phlogopites, Edgar et al. (1976, 1980), Ryabchikov and Green (1978), Barton and Hamilton (1979), and unpublished data of experiments on katungite (Arima and Edgar). ●: natural phlogopites, Carmichael (1967), Dawson et al. (1970), Cundari (1973, 1975), Dawson and Smith (1973, 1975), Upton and Thomas (1973), Prinz et al. (1975), Velde (1975), Brooks (1978), Duda and Schminke (1978), Boettcher et al. (1979), Danchin (1979), Edgar (1979), Ehrenberg (1979), Griffin et al. (1979), Mitchell (1979), Roden and Smith (1979), Scott (1979), Wass (1979), Sheraton and Cundari (1980), Nixon et al. (1980), Kuehner et al. (1980)
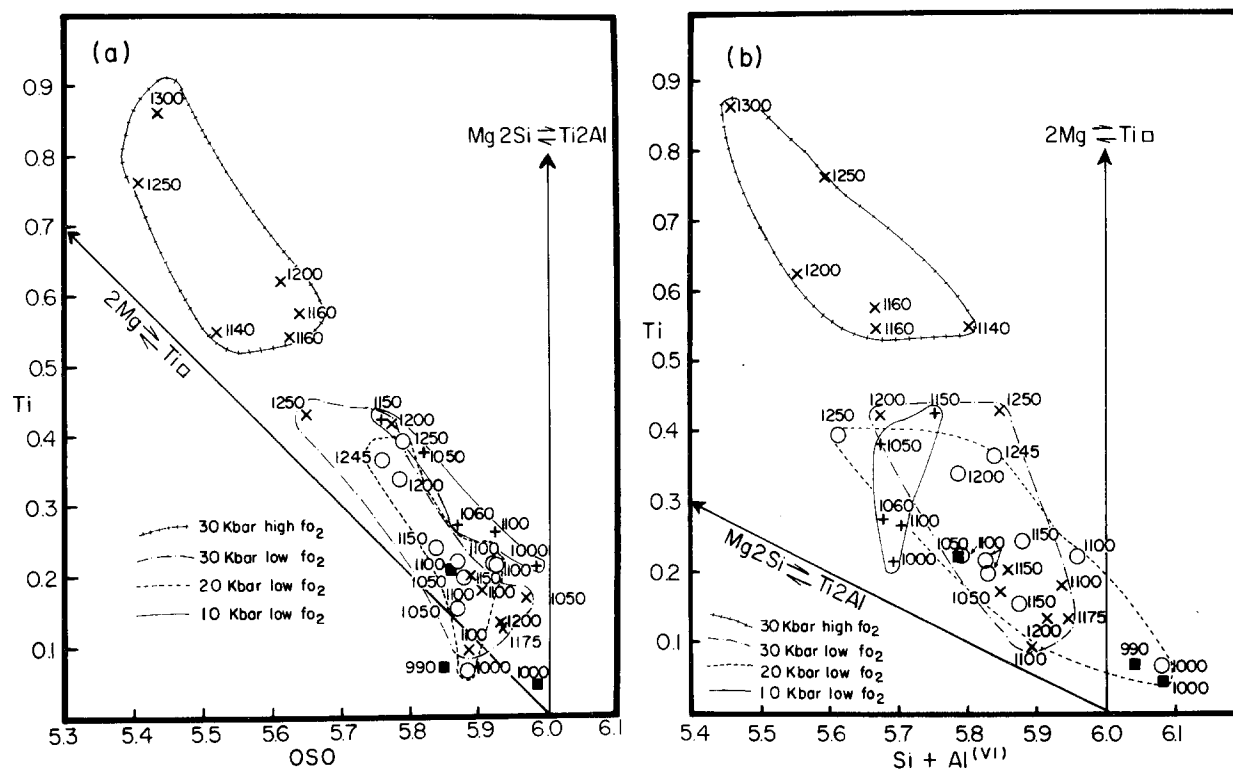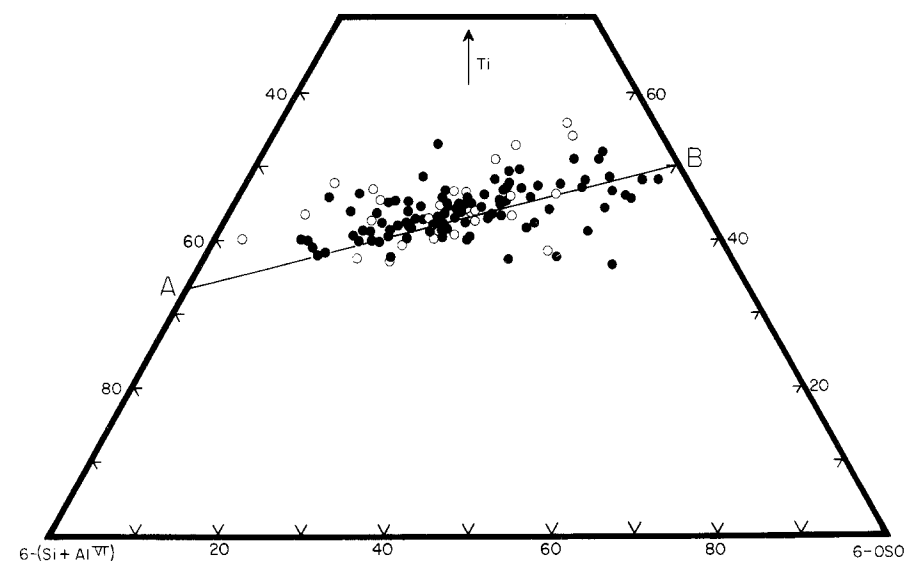

Fig. 2. The Ti vs. OSO (a) and Ti vs. $Si+Al^{[VI]}$ (b) relationships in the structural formula (22 O) of phlogopites produced in experimental studies. +: 10 kb, ■: 15 kb, o: 20 kb, ×: 30 kb. The data sources are those given in Fig. 1 and also Mysen and Boettcher (1975b) and Wendlandt and Eggler (1980)

by Holmes (1950) have also been used[1]. Mysen and Boettcher (1975b) give one phlogopite analysis from experiments on a peridotite spiked with phlogopite, and Wendtlandt and Eggler (1980) three analyses from a spinel lherzolite with added phlogopite. With one exception the phlogopites crystallized in these experiments do not occur on the liquidus but coexist with a variety of minerals commonly olivine, clinopyroxene, orthopyroxene, and occasionally garnet and ilmenite. Consequently the

phlogopites are usually not products of crystallization from a primitive liquid.

Figure 2 shows plots of Ti vs. $Si+Al^{[VI]}$ and Ti vs. OSO for phlogopites crysallized in high pressure experiments. Both plots show similar trends of decreasing $Si+Al^{[VI]}$ and OSO with increasing Ti. In terms of the substitutions proposed by Forbes and Flower (1974) and Robert (1976), the data follow neither trend. Although there are some discrepancies, both plots show an increase in Ti with increasing temperature. For the phlogopites crystallized in the 10 kb experiments (Fig. 2), the amount of $Mg^{[VI]}2Si^{[IV]} \rightleftharpoons Ti^{[VI]}2Al^{[IV]}$ substitution appears dominant with

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1 These analyses can be obtained from the authors

Table 1. Bulk compositions of rocks crystallizing phlogopites in experimental studies

Rock	K_2O	Al_2O_3	$\dfrac{Mg}{Mg+Fe}$	$\dfrac{Fe_2O_3}{FeO}$	TiO_2	SiO_2	No. of phlogopite analyses	Reference
Biotite mafurite	7.3	8.0	0.78	0.026	5.3	42.6	21	Edgar et al. (1976), Tables 1, 5) Ryabchikov and Green (1978, Tables 1, 3)
Olivine ugandite	1.74	9.91	0.77	0.378	1.85	43.98	2	Edgar et al. (1980, Tables 1, 8)
Madupite	7.19	7.85	0.77	67.1	2.31	43.56	1	Barton and Hamilton (1979, Tables 1, 3)
Katungite	3.02	7.54	0.70	3.0	3.84	38.05	4	Unpublished data
Peridotite +6% phlogopite	0.71	4.43	0.90	0.137	0.12	44.98	1	Mysen and Boettcher (1975a, Table 3, 1975b, Table 7)
Spinel lherzolite +10% phlogopite	1.02	4.84	0.91	0.110	0.18	43.7	1	Wendlandt and Eggler (1980, Tables 4, 5)

lesser amounts of substitution involving $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$. For phlogopites crystallized at higher pressures, both substitution mechanisms apply and appear to show some temperature dependence.

The only experimental data for phlogopites crystallized under high fO_2 conditions, comparable to those of the HM buffer, are those of Ryabchikov and Green (1978). These experiments are also the only ones with both H_2O and CO_2. In both plots these phlogopites have much larger Ti contents and much lower OSO and $Si+Al^{[VI]}$ values. The most probable cause of this is the fO_2 conditions under which these phlogopites were crystallized (Ryabchikov and Green 1978).

The bulk compositions of the rocks from which the phlogopites crystallized seem to have much less effect on the solubility of Ti in the phlogopite structure than do the physical conditions. The most important compositional variables affecting phlogopite crystallization in these rocks are listed in Table 1, together with the numbers of phlogopite analyses used in Fig. 2. Although most of the data are from high-K rocks rich in TiO_2, Al_2O_3 and with lower $\dfrac{100\,Mg}{Mg+Fe}$ than the spiked peridotite and spinel lherzolite composition, the SiO_2 contents are similar. Within the high-K rocks, differences in the bulk compositions do not appear to affect the Ti substitutions in the phlogopites (Fig. 2). The phlogopites crystallized from the spiked spinel lherzolite (Wendlandt and Eggler 1980) and peridotite (Mysen and Boettcher 1975a, b) samples have low Ti, $Si+Al^{[VI]}$ and OSO values which may reflect the low K, Ti and other Al available in these bulk compositions relative to those in the high-K rocks; thus inhibiting the crystallization of Ti-rich phlogopites. The linear trends shown in Fig. 2 and the apparent independence of these trends on the bulk compositions from which the phlogopites crystallized enhances the potential of Ti substitution in phlogopite being used as a geothermometer-geobarometer for high-K rocks.

The relationship between the P, T conditions and the Ti contents of phlogopites crystallized from the high-K rock compositions is more clearly shown in Fig. 3 where the Ti/OSO is plotted vs. temperature and the data contoured for pressure conditions. Figure 3 shows that the $\dfrac{Ti}{OSO}$ ratio increases with increasing temperature for a constant pressure, and decreases with increasing pressure for a constant temperature. As shown in Fig. 2, high fO_2 conditions produce very high $\dfrac{Ti}{OSO}$ ratios, with some overlap in the 20 and 30 kb data for low fO_2 condi-
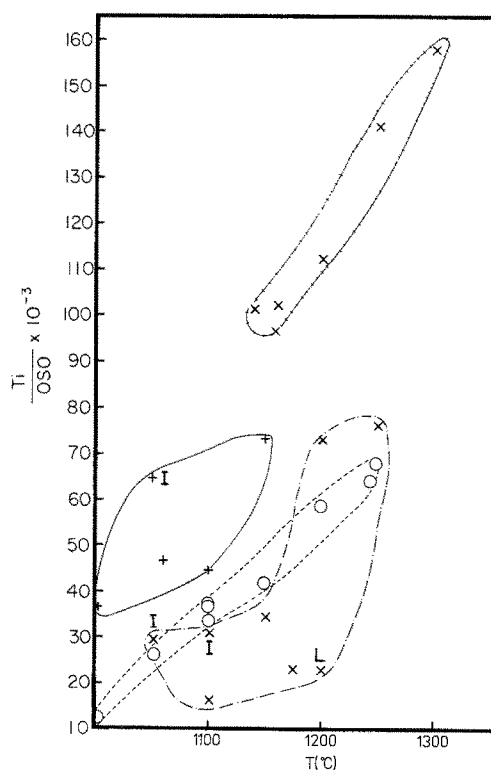

Fig. 3. The relationships between temperatures and $Ti/OSO \times 10^{-3}$ of phlogopites shown in Fig. 2. Pressures are contoured as in Fig. 2. *I*: phlogopites coexisting with ilmenite; *L*: phlogopites coexisting with liquid only

tions. Examination of the phases coexisting with phlogopite in the runs plotted indicates that the only major Ti-bearing mineral coexisting with phlogopite is ilmenite which occurs in the 10 kb, 1,050° C, in the 30 kb, 1,050° C and the 30 kb, 1,100° C runs. The only datum for phlogopite which coexists entirely with a liquid is for the run at 30 kb, 1,200° C with a $\dfrac{Ti}{OSO}$ ratio of 23.1×10^{-3}. As shown in Fig. 3, ilmenite and liquid are the only major Ti-bearing phases in these experiments. If these data are disregarded, the low temperature overlap of data in the 20 and 30 kb range is removed; producing a steeper curve for the 30 kb (low fO_2) data relative to those at 20 kb and similar slopes for the 10 and 20 kb (low fO_2) and 30 kb (high fO_2) data.
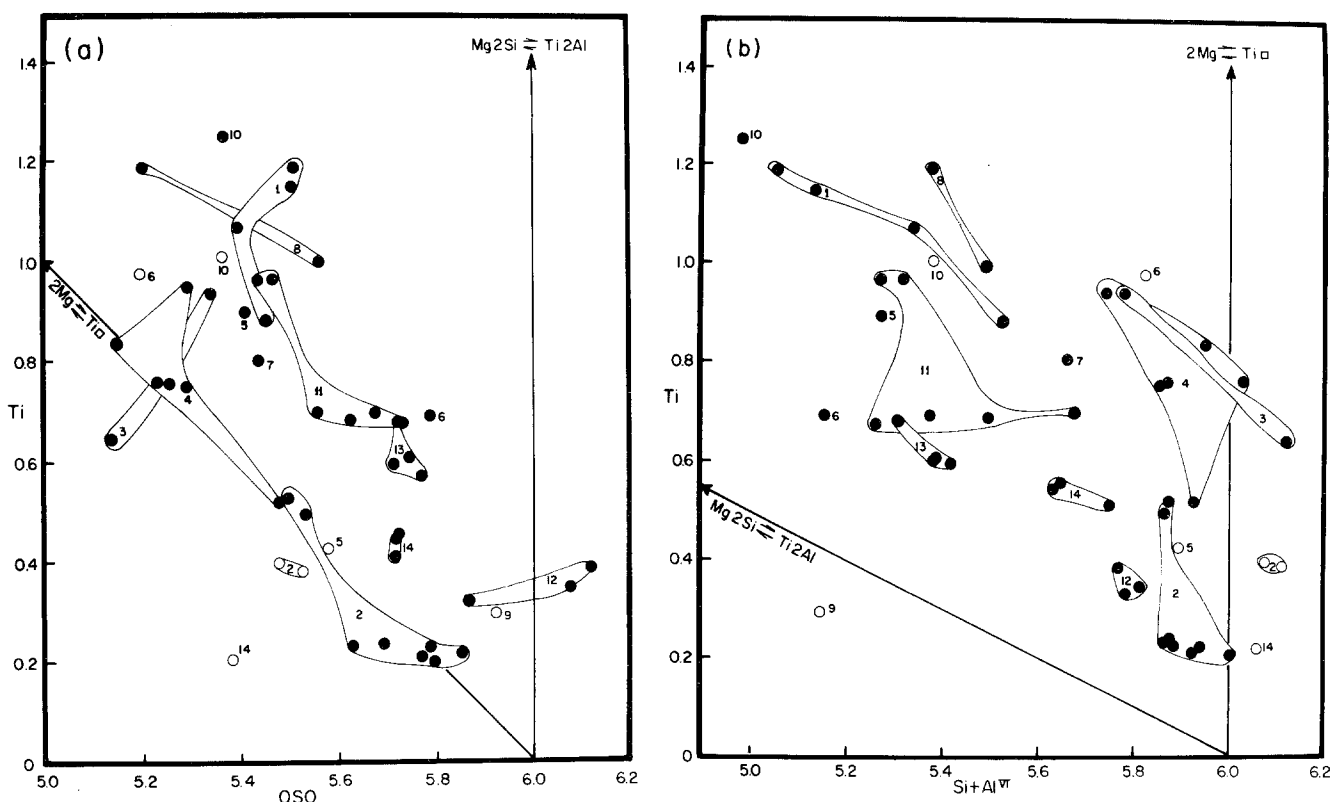
Fig. 4. The Ti vs. OSO (a) and Ti vs. Si+Al$^{[VI]}$ (b) relationships in the structural formula of phlogopites (22 O) occurring in high-K rocks. ●: phenocryst; o: groundmass. Data sources: _1_ Central New South Wales, Australia (Cundari 1973); _2_ Leucite Hills, Wyoming (Carmichael 1967; Kuehner et al. 1980); _3_ Murcia, Spain (Borley 1967, Carmichael 1967); _4_ West Kimberley, Australia (Prider 1939, Carmichael 1967); _5_ Lake Nyungu, Uganda (Edgar 1979); _6_ Gaussberg, Antarctica (Sheraton and Cundari 1980); _7_ Holsteinsborg, West Greenland (Brooks et al. 1978); _8_ Smokey Butte, Montana (Velde 1975); _9_ Alban Hills, Italy (Thompson 1977); _10_ Buell Park, Arizona (Roden and Smith 1979); _11_ Narssaq and Tugtutoq, South Greenland (Upton and Thomas 1973); _12_ Shonkin Sag, Montana (Nash and Wilkinson 1969); _13_ Laacher See, Germany (Duda and Schminke 1978); _14_ Vico, Italy (Cundari 1975)

Assuming from the limited data that the isobaric plots are linear (Fig. 3), the dependence of temperature on the $\frac{Ti}{OSO}$ ratios suggests their use as a potential geothermometer, provided an independent estimate can be made of the pressure and fO_2 conditions of phlogopite formation.

In the absence of any assemblages in natural rocks indicative of high fO_2 conditions, high fO_2 may possibly be assumed if the Ti contents are high and the OSO and Si+Al$^{[VI]}$ values are low (Fig. 2). Insufficient information is available to make an independent assessment of the pressure of crystallization on a P vs. $\frac{Ti}{OSO}$ plot analogous to that of Fig. 3, but the limited data suggest that at constant temperature the $\frac{Ti}{OSO}$ decreases with increasing pressure.

Phlogopites from High-K Rocks

Phlogopites in high-K rocks occur as phenocryst, groundmass and occasionally as xenocryst minerals. The phlogopites plotted in Fig. 4 have various SiO$_2$ (34–43 wt.%), Al$_2$O$_3$ (5–16 wt.%) and TiO$_2$ (5–16 wt.%) contents. Both Figs. 4a and b, showing Ti vs. OSO and Ti vs. Si+Al$^{[VI]}$ respectively, indicate two distinct trends. In Fig. 4a, Ti increases with decreasing OSO and suggests that the phlogopites from the rocks of the Leucite Hills, Wyoming; West Kimberley, Australia; and Murcia, Spain follow a different trend from those of central New South Wales, Austra-

lia; Buell Park, Arizona; Narssaq, Holsteinsborg and Tuqtutoq, W. Greenland; Laacher See, Germany; Alban Hills, Italy; and the Shonkin Sag laccolith, Montana. For some localities in which both phenocryst and groundmass phlogopites are present, e.g. Lake Nyungu, Uganda; Leucite Hills, Wyoming, and Gaussberg, Antarctica, the phenocryst and groundmass varieties follow different trends. Figure 4b suggests very similar trends, one with increasing Ti with decreasing Si+Al$^{[VI]}$, the other with increasing Ti and fairly constant Si+Al$^{[VI]}$. As shown in Fig. 4 one of the trends follows closely the 2Mg$^{[VI]}\rightleftharpoons$Ti$^{[VI]}$□$^{[VI]}$ substitution mechanism the other can be represented by both the substitutions 2Mg$^{[VI]}\rightleftharpoons$Ti$^{[VI]}$□$^{[VI]}$ and Mg$^{[VI]}$2Si$^{[IV]}\rightleftharpoons$Ti$^{[VI]}$2Al$^{[IV]}$. The latter substitutions are very similar to those for phlogopites crystallized under high pressure conditions (Fig. 2).

The two different trends in phlogopite substitution (Fig. 4a, b) from rocks of similar compositions may be attributed in some cases to differences in the depth (pressure) of crystallization of phlogopites in these rocks. The groundmass phlogopites from the biotite mafurite and leucitite from Lake Nyungu and Gaussberg (Fig. 4, points 5, 6) coexist with kalsilite and leucite respectively. For the biotite mafurite from Lake Nyungu, Edgar (1979) estimated the groundmass phlogopite equilibrated at a P_{H_2O} (=P_{total}) of 1–2 kb and 1,150°–1,180° C. If P_{H_2O} has approached P_{total} in the Gaussberg leucitite, the presence of leucite along with phlogopite in the groundmass suggests that the phlogopite may have formed at less than 5 kb P_{H_2O} (=P_{total}) as leucite is not stable above this pressure (Morse 1968). Further support for the pressure relationship to the substitution mechanism of
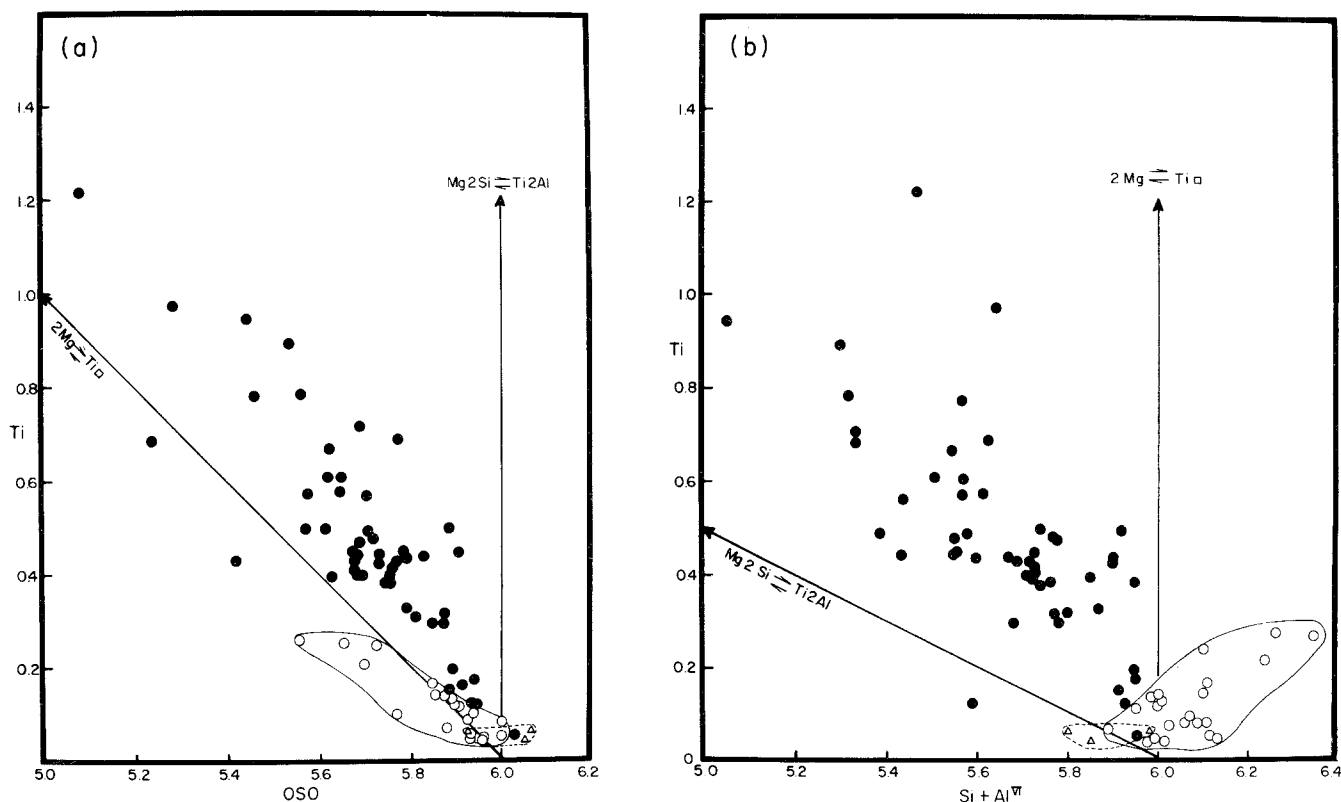
Fig. 5. The Ti vs. OSO (**a**) and Ti vs. Si+Al$^{[VI]}$ (**b**) relationships in the structural formula of phlogopites (22 O) in various mantle derived rocks. Data sources: △: "primary" phlogopites (Carswell 1975; Dawson and Smith 1975; Danchin 1979). ○: phlogopite from MARID suite (Dawson and Smith 1977), from glimmerite (Dawson and Smith 1975), and "core phlogopite" from kimberlite and their xenoliths (Boettcher et al. 1979). ●: phlogopite megacrysts in kimberlite (Dawson and Smith 1975; Mitchell 1979), inclusion of diamond (Prinz et al. 1975), xenolith in carbonatite (Dawson et al. 1970; Dawson and Smith 1973), from garnet peridotite xenolith in minette (Ehrenberg 1979), from garnet-granulite xenolith in kimberlite (Griffin et al. 1979), from garnet-peridotite xenolith in kimberlite (Danchin 1979), rim phlogopite (Boettcher et al. 1979), phenocryst and groundmass crystal of kimberlite and potassic lamprophyre (Scott 1979), xenolith of alkali basalt (Wass 1979), phenocryst and groundmass from lamprophyre (Nixon et al. 1980)

phlogopites is provided by cognate phlogopite inclusions in the Gaussberg rocks (Sheraton and Cundari 1980) which follow the substitution trend represented by the combination of $2Mg^{[VI]}\rightleftharpoons Ti^{[VI]}\square^{[VI]}$ and $Mg^{[VI]}2Si^{[IV]}\rightleftharpoons Ti^{[VI]}2Al^{[IV]}$ and coexist with groundmass phlogopites following the $2Mg^{[VI]}\rightleftharpoons Ti^{[VI]}\square^{[VI]}$ trend. Similarly the phenocrysts of phlogopites from Lake Nyungu (Edgar 1979) also have the same trend as the phlogopite inclusions from the Gaussberg rocks (Sheraton and Cundari 1980).

The phenocryst phlogopites from some of the rocks from the Leucite Hills and from West Kimberley have the same substitution trend as the groundmass phlogopites from Lake Nyungu and Gaussberg and, in both localities, coexist with leucite. This may imply that these phenocryst phlogopites were formed under relatively low P conditions in which $P_{H_2O}\approx P_{total}$. In the olivine orendite from the Leucite Hills, Kuehner et al. (1981) report phlogopite cores which have compositions which follow the substitution represented by the combined $2Mg^{[VI]}\rightleftharpoons Ti^{[VI]}\square^{[VI]}$ and $Mg^{[VI]}2Si^{[IV]}\rightleftharpoons Ti^{[VI]}2Al^{[IV]}$ trends and rims of quite different composition which have the $2Mg^{[VI]}\rightleftharpoons Ti^{[VI]}\square^{[VI]}$ substitution trend. As the cores of these phlogopites have probably crystallized at a higher pressure than the rims, differences in these zoned phlogopite compositions lend support to the concept that the groundmass phlogopites in the Lake Nyungu and Gaussberg samples may be of low pressure origin.

Barton (1979) pointed out the close relationship between the Al_2O_3 content of phlogopites and the chemistry of the rocks in which they occur. There is also a close correlation between the phlogopite chemistry and that of coexisting clinopyroxenes in many of these rocks. For the phlogopites plotted in Fig. 4, those from low Al_2O_3 (7–10 wt.%) rocks of the Leucite Hills, Murcia, West Kimberley, Holsteinsborg, Smokey Butte, Gaussberg and central New South Wales all have low Al_2O_3 contents. Rocks from these localities have very high K/Al (>0.9) and contain low Al_2O_3 clinopyroxenes with Al/Ti<2.

In contrast, the rocks from Buell Park, Alban Hills and Narssaq have higher Al_2O_3 (7–15.3 wt.%), lower K/Al (0.2–0.7) and contain phlogopites with higher Al_2O_3 and lower K/Al values, and high Al_2O_3 clinopyroxenes with Al/Ti values >2. Rocks from Shonkin Sag, Laacher See and Vico contain 13–20 wt.% Al_2O_3 with K/Al ratios of 0.2–0.5 and have phlogopites with the highest Al_2O_3 contents (producing an eastonite molecule when recalculated into end-member molecules) and also contain the most Al_2O_3-rich clinopyroxenes.

There is a tendency for increasing TiO_2 with decreasing tetrahedral site occupancy (Si+Al). Decreasing site occupancy might be accounted for by Fe^{3+} in the tetrahedral site $(Al\rightleftharpoons Fe^{3+})$. This tendency may imply that the presence of Fe^{3+} affects the solubility of Ti in phlogopites. Limited experimental data under different fO_2 conditions (Edgar et al. 1976, Ryabchikov and Green 1978) suggest that high fO_2 promotes the solubility of Ti in phlogopite. In natural magmas, the $\dfrac{Fe^{3+}}{Fe^{3+}+Fe^{2+}}$ ratios depend on the alkali contents as well as their P, T and fO_2 (Carmichael et al. 1974, Thornber et al. 1980). Although no data

are available for potassium, Mysen and Virgo (1978) and Seifert et al. (1979) have shown that tetrahedrally coordinated Fe^{3+} occurs in sodium-bearing silicate liquids with $Na/Fe^{3+} > 1$. If K has a similar effect, magmas with high K_2O and low Al_2O_3 contents would be expected to have higher $\frac{Fe^{3+}}{Fe^{2+}+Fe^{3+}}$ contents than less alkali-rich magmas formed under similar P, T and fO_2 conditions and hence be expected to crystallize phlogopites with higher Fe_2O_3 and TiO_2 contents.

The substitution mechanism proposed by Forbes and Flower (1974) based on high pressure experiments does not apply for all phlogopites in high-K rocks. Some of the phenocryst-groundmass data (Fig. 4) may imply that their trend is more common in phlogopites crystallized at low rather than high pressures, and by the fact that Forbes and Flower's substitution mechanism is not followed by any of the phlogopites produced in the experimental runs above 10 kb (Fig. 2). If Ti substitution mechanisms in phlogopites are pressure dependent, the two trends in Fig. 4 may imply that the rocks involved have crystallized under different pressure regimes.

Phlogopites from Kimberlites, Mantle Derived Xenoliths in Kimberlites, and Other Rocks

Phlogopites occur as megacrysts or groundmass minerals in this group of rocks and have TiO_2 contents ranging from 0.1 to 10.8 wt.%; the maximum value being from a phlogopite inclusion in a diamond in a xenolith in kimberlite (Prinz et al. 1975). Carswell (1975) distinguishes "primary" and "secondary" phlogopites in ultramafic xenoliths in kimberlites on the basis of their chemistry and textures; with the high TiO_2 phlogopites as "secondary". These "secondary" phlogopites may be products of mantle metasomatism (Boettcher et al. 1979), by late-stage alteration (Delaney et al. 1980), or as MARID micas (see Dawson and Smith 1977) formed by crystallization of kimberlitic magma under oxidizing conditions at relatively shallow depths (Dawson and Smith 1977).

Figure 5 shows the relationship of Ti and OSO and Ti and $Si+Al^{[VI]}$ for phlogopites from various types of xenoliths in kimberlites, alkali basalts, carbonatites and lamprophyres, all of which are of likely mantle origin. Three groups can be recognized.

(1) The "primary" phlogopites with low Ti values, Si and OSO values plotting close to the stoichiometric value ($OSO \sim 6.0$ and $Si + Al^{[VI]} \sim 6.0$).

(2) Phlogopites described as MARID (see Dawson and Smith 1977), phlogopites from glimmerites (Dawson and Smith 1975), and the cores of phlogopites analysed by Boettcher et al. (1979). For this group there is a trend of increasing Ti with decreasing OSO (Fig. 5a), and of increasing Ti with increasing $Si+Al^{[VI]}$ (Fig. 5b). The trend shown in Fig. 5a, together with the increasing Si content of these phlogopites with increasing Ti, indicates the substitutions are combinations of the type $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$ (Forbes and Flower 1974) and $Mg^{[VI]}2Al^{[IV]} \rightleftharpoons 2Si^{[IV]} \square^{[VI]}$ (Seifert and Schreyer 1971). This group contains low Al_2O_3 (> 1 Al< 2) and significant tetrahedral site deficiencies (Al $+Si < 8$) which may be due to Fe^{3+} in the tetrahedral site (Dawson and Smith 1977, Boettcher et al. 1979).

(3) Phlogopites which show increasing Ti with decreasing OSO (Fig. 5a) and $Si + Al^{[VI]}$ (Fig. 5b). Although there is considerable scattering in this group, both the $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$ and $Mg^{[VI]}2Si^{[IV]} \rightleftharpoons Ti^{[VI]}2Al^{[IV]}$ substitution mechanisms seem to be operative. Many phlogopites in this group have $Si+Al \approx 8$

and occasionally $Si+Al > 8$, producing the eastonite end member molecule. The K/Al ratio of these phlogopites is < 1. Figure 5 shows that the trends of this group are similar to both the experimentally produced phlogopites (Fig. 2) and those from the high-K rocks (Fig. 4) in that all three seem to follow the trend represented by the combination of the $2Mg^{[VI]} \rightleftharpoons Ti^{[VI]} \square^{[VI]}$ and $Mg^{[VI]}2Si^{[IV]} \rightleftharpoons Ti^{[VI]}2Al^{[IV]}$ substitution mechanisms. However, based on their Al_2O_3 contents and tetrahedral site deficiencies (8-Si-Al), this group can be distinguished from those of the high-K rocks.

The possibility of using Ti/OSO as a geothermometer for phlogopite-bearing kimberlites and their nodules of mantle origin, similar to that suggested for the high-K rocks (Fig. 3), cannot be assessed. In addition to the necessity for independent geothermometers and geobarometers the fact that phlogopites in kimberlites and their nodules may never have formed from a liquid, in contrast to the phlogopites crystallized experimentally, requires that a study be made of the effects of Ti incorporation in phlogopite caused by metasomatic (secondary) reactions rather than by liquid-solid (primary) reactions.

The only primary phlogopites in Fig. 5 for which geothermometric and geobarometric data are given are from a garnet lherzolite nodule from the Premier Mine, South Africa. Danchin (1979) suggests these phlogopites formed at $900°-1,115°$ C and 31–49 kb. When the Ti/OSO of these phlogopites are plotted on Fig. 3 they give pressures of about 30 kb (low fO_2) and temperatures around $1,000°$ C; values not far removed from those of Danchin.

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