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Experimental evidence on the substitution of Ti in biotite

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ABSTRACT

Various Ti substitutions in biotite were tested by hydrothermal syntheses of Fe and Mg biotites over the range of 600–800 °C at 1000-bars pressure and at the oxidation conditions of the methane-graphite buffer. Yields of greater than 95% biotite were obtained in a few experiments, but complete syntheses were generally not possible. Microprobe analyses of the run products indicate that (1) the Ti-Tschermak's substitution ($Ti + 2Al = R^{2+} + 2Si$) can be the dominant Ti substitution in both Fe and Mg biotites; (2) the Ti-vacancy substitution ($Ti + {}^{[6]}\square = 2R^{2+}$) can occur as the dominant Ti substitution in Mg biotite and in conjunction with other substitutions in Fe biotite; and (3) the experimental data do not support, but cannot rule out, the Ti-oxy substitution ($Ti + 2O^{2-} = R^{2+} + 2OH^-$). Specific substitution types appear to be governed by bulk composition and by the crystal-chemical constraints of the biotite structure.

INTRODUCTION

The phenomenon of Ti substitution in biotite has been investigated by many previous workers (e.g., Dymek, 1983; Guidotti et al., 1977; Labotka, 1983). In spite of these efforts, there is still no agreement on the kind of substitution, the crystallographic site of the Ti cation in the mica structure, or the extent of solid solution and its dependence on P-T-X-f_{O_2} conditions. Some doubts even exist about the valence of Ti in the structure. This inadequate understanding of the Ti substitution in biotite stems largely from the lack of conclusive experimental data, the scarcity of structure refinements on high-Ti micas, and the ambiguities in the interpretation of chemical analyses of natural phases.

An experimental investigation was undertaken to evaluate some of the various Ti-substitution mechanisms that have been proposed or appear to be possible in light of previous studies. Based on the natural evidence presented by Guidotti et al. (1977), Holdaway (1980), Bohlen et al. (1980), Labotka (1983), and Dymek (1983) and the experimental evidence from Forbes and Flower (1974), Robert (1976), Kovalenko et al. (1968), and Tronnes et al. (1985), the Ti exchange components included in Table 1 were chosen to be combined with a phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$), annite ($KFe_3AlSi_3O_{10}(OH)_2$), "eastonite" ($KMg_{2.5}Al_{0.5}Al_{1.5}Si_{2.5}O_{10}(OH)_2$), or siderophyllite ($KFe_{2.5}Al_{0.5}Al_{1.5}Si_{2.5}O_{10}(OH)_2$) additive component. Additional exchanges involving the interlayer site and exchanges generated as combinations of those in Table 1 are possible, but were not investigated.

Previous experimental work by Forbes and Flower (1974), Robert (1976), and Tronnes et al. (1985) demonstrates that Ti solubility in phlogopite increases with temperatures and decreases with pressure. Their studies, along with that of Kovalenko et al. (1968), suggest that the Ti-vacancy, Ti-Tschermak's, and Ti-oxy exchange vectors are valid substitution mechanisms. However, except for the data from Tronnes et al. (1985), these indications are based on inconclusive evidence. Because the micas in their run products were not analyzed chemically, the previous investigators had to assume biotite compositions based on initial bulk compositions and 100% synthesis. Given the relatively low solubility of TiO_2 in biotite (<10%), significant differences between the bulk composition and biotite composition can occur when yields are less than 100%. The data from Tronnes et al. (1985) on Mg biotites demonstrate that phlogopites with equal amounts of Ti-Tschermak's and Ti-vacancy substitution can form at high temperature. Their analyses and yields are consistent with both substitutions being valid. At lower temperatures, incomplete syntheses occur, and the proportion of the two substitutions varies with the Ti-vacancy substitution apparently being preferred in their Mg biotites.

EXPERIMENTAL PROCEDURE

A detailed description of the preparation procedures for starting materials is given in Hewitt and Wones (1975). Most Ti-bearing micas were synthesized directly from oxide mixes with excess H_2O in $Ag_{70}Pd_{30}$ capsules. Oxygen fugacities were defined by the graphite-methane buffer at a total pressure of 1 kbar and temperatures in the range of 600 to 800 °C. Some micas were grown from products previously synthesized unbuffered in René 41 bombs at total pressures of 5 to 6 kbar and temperatures between 500 and 600 °C. The majority of the biotites and some of the phlogopites were ground and rerun up to four times, usually at the same conditions. Changes in yield (estimated optically) and composition were determined for each crystallization interval.

In an attempt to increase the growth rate, size, and yield of the biotites, several experiments were performed using a $1m$ KCl or a $5m$ KOH solution instead of pure H_2O. The run products

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TABLE 1. Exchange components used in this investigation

Ti-Tschermak's (Ti-Tsch)	$^{[6]}Ti + 2^{[4]}Al = 2^{[4]}Si + ^{[6]}(Fe,Mg)$
Ti-vacancy (Ti-vac)	$^{[6]}Ti + ^{[6]}\square = 2^{[6]}(Fe,Mg)$
Ti-oxy	$^{[6]}Ti + 2O^{2} = ^{[6]}Fe + 2(OH)^{-}$
Ti-Al-oxy	$^{[6]}Ti + O^{2} = ^{[6]}Al + OH^{-}$
Ti-Si	$^{[4]}Ti = ^{[4]}Si$
$K^{[12]}\square$	$^{[4]}Si + ^{[12]}\square = K + ^{[4]}Al$
Tschermak's (Tsch)	$^{[4]}Al + ^{[6]}Al = ^{[4]}Si + ^{[6]}(Fe,Mg)$

obtained in initial syntheses using this method were then mixed with about the same amount of the corresponding starting material and intimately ground before being run again at the same temperature and pressure conditions and with the same fluid. This procedure was repeated up to four times.

Optical examination of the run products was performed by standard petrographic methods including dark-field microscopy for detection of minor amounts of additional phases. The refractive index, γ', was measured for several biotites at 25 °C using Na light (Table 2). X-ray powder-diffraction data were collected on an automated Philips diffractometer for use in the calculation of the cell parameters. Depending on the composition and crystallinity of the sample, between 11 and 24, usually between 15 and 20 reflections were used for the refinement. CaF_2 ($a = 5.4630$ Å) was used as an internal standard. All cell parameters (Table 3) were refined using the LSUCR program of Appleman and Evans (1973).

Because of the polyphase nature of all run products, stoichiometry of the micas could not be assumed, and they were analyzed using an ARL-SEMQ microprobe. Analytical data were reduced using the method of Bence and Albee (1968) and extrapolated to an ideal anhydrous sum of 96% using the fine-particle analysis techniques of Solberg et al. (1981). On the basis of the amount of scatter within one sample as well as the degree of reproducibility seen from a number of multiple analyses, the uncertainty of the analyses is estimated to be less than ±5% of the reported values for the elements K, Fe, Mg, Al, Si, and Ti. Multiple analyses of the same spot did not reveal any significant variations, and analyses across single grains did not indicate any zoning of the biotite flakes. All biotite formulas reported in the text and tables refer to analyses recalculated on the basis of an anhydrous biotite containing 22 oxygens.

RESULTS

The data in Table 2 represent the final compositions and yields for experiments that went through repeated crystallizations. Duplicate experiments, those with poor analyses, and the preliminary crystallizations are not shown. High-yield experiments (>90%) generally had biotite compositions that changed little over the sequence of crystallizations and are interpreted as stable, whereas those with low yields frequently showed significant changes in composition and should not be interpreted as final stable compositions. Yields of mica in the hydrothermal experiments were variable, but always less than 100%. The synthetic Ti-bearing Fe biotites coexist with sanidine, fayalite, and an oxide, either ilmenite or magnetite-ulvöspinel. Ti-bearing Mg biotites coexist with sanidine and rutile and/or geikielite. Orthopyroxene was found only in runs with Fe-Mg micas.

Multiple runs of the same samples often, but not always, resulted in the partial to nearly complete disappearance of the mica phase, although at the same time the remaining mica grains became larger. For example, the estimated biotite yields obtained from the starting composition annite + 0.5 Ti-vacancy were 90%, 75%, 30%, and 25–30% when the same sample was rerun four times at 800 °C. Phlogopites commonly showed neither increased growth nor a substantial change in the relative amounts of the coexisting phases.

The small number of experiments carried out with either a KCl or a KOH solution showed generally higher yields for biotite as well as larger crystals (Fig. 1). However, the KCl solution also favored the growth of large fayalite crystals, which were not observed with the KOH solution. Best yields were obtained from mixes starting with subequal amounts of previously grown biotites and oxide starting material. Only the annite + 0.5 Ti-Tschermak's starting composition was used for this type of experiment. Resulting biotite yields were always above 90%, some amounting to 98%, with K-feldspar as an additional phase.

Pleochroism was observed in all biotites and varies with composition. Low-Ti Fe biotites show greenish to colorless pleochroism; high-Ti Fe biotites show reddish-brown to light yellowish or brownish colors. The measured indices of refraction (γ') are in the range 1.679 to 1.703 (Table 2) and show a slight increase relative to annites (Wones, 1963; Hewitt and Wones, 1975), but no simple relationship with Ti content is observed, presumably because of the variety of substitutions affecting the composition.

Experiments with Ti-Tschermak's substitution

Consistently high yields (>75%) were obtained for both Fe and Mg biotites with amounts of the Ti-Tschermak's substitution as high as 0.5 atoms of Ti per formula unit (pfu; Figs. 2a, 2b). This is reflected by the analyzed compositions generally lying close to the starting compositions (Table 4). However, nearly all of these biotites show a Tschermak's substitution in the range 0.2 to 0.5 octahedral Al atoms pfu, depending on the starting composition. Octahedral vacancies are generally low but tend to increase with increasing Ti (Table 2). The highest TiO_2 content observed for the Ti-Tschermak's substitution mixtures was 4.5 wt% TiO_2 (0.55 atoms pfu).

No large differences were observed in the compositions obtained from biotites grown in a KOH or KCl solution as compared to those grown in pure H_2O. The former experiments yielded slightly higher Si and lower Fe contents, resulting in somewhat higher octahedral vacancies. However, no differences in the K contents were observed between these runs. An interlayer K deficiency of about 10% was observed in the majority of the analyzed synthetic biotites.

Experiments with Ti-vacancy substitution

For the Ti-bearing Fe biotites, the final yields for the Ti-vacancy substitution experiments decreased with time, were generally less than 50% (Fig. 2c), and tended to be

TABLE 2. Starting compositions and run data for synthetic Ti-bearing biotites

Run†	x	Fe/(Fe + Mg)	T (°C)	Run-time (d)	Est. yield vol%)	γ	K	Fe	Mg	Ti	$^{[6]}$Al	$^{[6]}\square$	$^{[4]}$Al	Si
A. Phlogopite-annite with Ti-Tschermak's substitution: $K_2(Fe,Mg)_{6-x}Ti_xSi_{6-2x}Al_{2+2x}O_{20}(OH)_4$														
118—2	0.25	1.00	600	72	90		1.83	5.36	—	0.27	0.31	0.06	2.63	5.37
280—1	0.25	1.00	650	30	75		1.72	5.39	—	0.24	0.33	0.04	2.35	5.65
182—2	0.25	1.00	700	61	85		1.86	5.54	—	0.24	0.30	−0.08	2.51	5.49
329—3	0.25	1.00	750	12	75		1.77	5.30	—	0.29	0.36	0.05	2.50	5.50
100—2	0.25	1.00	800	16	75	1.693	1.77	5.44	—	0.35	0.20	0.01	2.72	5.28
103—2	0.25	1.00	800	16	90	1.689	1.81	5.28	—	0.25	0.39	0.08	2.59	5.41
117—2	0.25	1.00	800	6	90	1.688	1.89	5.33	—	0.29	0.34	0.04	2.70	5.30
39—1	0.50	1.00	800	5	95		1.93	5.25	—	0.40	0.33	0.02	2.75	5.25
39—2	0.50	1.00	800	13	95	1.695	1.87	5.48	—	0.45	0.03	0.04	2.90	5.10
187—4	0.50	1.00	800	36	85		1.82	4.83	—	0.51	0.39	0.27	2.81	5.19
377—2*	0.50	1.00	775	(*)	90		1.78	4.94	—	0.44	0.41	0.21	2.65	5.35
377—3**	0.50	1.00	800	(*)	90		1.82	4.75	—	0.51	0.40	0.34	2.68	5.32
397—3**	0.50	1.00	775	(*)	97		1.78	5.19	—	0.43	0.24	0.14	2.65	5.35
392—3**	0.50	1.00	800	(*)	90		1.73	4.72	—	0.54	0.48	0.26	2.79	5.21
234—4	1.00	1.00	800	38	75		1.87	4.32	—	0.55	0.87	0.26	3.25	4.75
185—2	0.25	0.00	600	15	98		1.89	—	5.36	0.15	0.35	0.14	2.19	5.81
198—2	0.25	0.00	600	47	98		1.75	—	5.69	0.13	0.15	0.03	2.31	5.69
199—2	0.25	0.00	700	52	98		1.87	—	5.69	0.16	0.24	−0.09	2.29	5.71
205—2	0.50	0.00	700	52	95		1.84	—	5.36	0.08	0.60	−0.04	2.66	5.34
179—2	0.125	0.00	800	13	95		1.79	—	5.95	0.10	0.02	−0.07	2.19	5.81
54—1	0.25	0.00	800	4	98		1.95	—	5.58	0.23	0.10	0.09	2.41	5.59
191—2	0.50	0.00	800	29	90		1.78	—	5.51	0.19	0.35	−0.05	2.76	5.24
259—3	0.25	0.50	800	14	80		1.64	2.10	2.85	0.32	0.54	0.19	2.53	5.47
114—2	0.375	0.50	800	14	40		1.85	2.20	2.63	0.38	0.47	0.32	2.65	5.35
B. Phlogopite-annite with Ti-vacancy substitution: $K_2(Fe,Mg)_{6-2x}Ti_x\square_xSi_6Al_2O_{20}(OH)_4$														
290—1	0.25	1.00	750	28	85		1.73	5.77	—	0.27	0.00	−0.01	2.12	5.85
160—2	0.25	1.00	800	16	50		1.78	5.10	—	0.47	0.12	0.31	2.45	5.55
284—4	0.25	1.00	800	49	25		1.76	5.18	—	0.59	0.00	0.23	2.40	5.60
343—4	0.50	1.00	750	62	30		1.69	4.56	—	0.49	0.63	0.32	2.87	5.13
149—3	0.50	1.00	800	22	25		1.81	4.69	—	0.62	0.38	0.30	2.74	5.26
150—1	1.00	1.00	700	61	50		1.87	5.50	—	0.68	0.00	0.24	2.00	5.58
142—2	1.00	1.00	800	16	5		1.78	5.33	—	0.63	0.00	0.26	2.33	5.44
172—2	1.00	1.00	800	7	5		1.86	5.05	—	0.71	0.00	0.47	2.12	5.65
162—2	0.50	0.00	800	19	95		1.85	—	5.22	0.45	0.00	0.43	1.88	6.02
C. Eastonite with Ti-Tschermak's substitution: $K_2Mg_{5-x}Ti_xAlSi_{5-2x}Al_{3+2x}O_{20}(OH)_4$														
296—1	0.50	0.00	800	26	95		1.78	—	4.47	0.37	0.87	0.28	2.84	5.16
D. Phlogopite-annite with Ti-oxy substitution: $K_2(Fe,Mg)_{6-x}Ti_xSi_6Al_2O_{20+2x}(OH)_{4-2x}$														
175—2	0.25	1.00	800	6	40		1.86	5.66	—	0.37	0.00	0.04	2.26	5.67
120—3	0.50	1.00	600	72	60	1.665	1.90	5.44	—	0.48	0.00	0.16	2.43	5.49
128—2	0.50	1.00	700	49	10	1.699	1.97	5.11	—	0.62	0.00	0.32	2.70	5.25
119—1	0.50	1.00	800	6	40	1.703	1.90	4.69	—	0.77	0.10	0.43	2.74	5.26
325—2	0.75	1.00	750	63	5		1.68	4.44	—	0.71	0.46	0.38	2.85	5.15
174—2	0.50	0.00	800	20	90		1.70	—	5.18	0.36	0.13	0.33	1.87	6.13
E. Eastonite with Ti-oxy substitution: $K_2Mg_{5-x}Ti_xAlSi_5Al_3O_{20+2x}(OH)_{4-2x}$														
294—1	0.50	0.00	800	26	95		1.90	—	4.70	0.30	0.89	0.11	2.96	5.04
F. Phlogopite-annite with Ti-Tschermak's + Ti-vacancy substitution (1:1): $K_2(Fe,Mg)_{6-(3x/2)}Ti_x\square_{x/2}Si_{6-x}Al_{2+x}O_{20}(OH)_4$														
146—1	0.50	1.00	700	14	90		1.75	5.48	—	0.33	0.19	−0.01	2.44	5.56
140—1	0.50	1.00	800	10	75		1.84	5.31	—	0.44	0.15	0.10	2.62	5.38
133—1	1.00	0.00	800	10	90		1.88	—	4.64	0.49	0.51	0.35	2.70	5.30
G. Annite with $^{[4]}Ti = Si$: $K_2(Fe,Mg)_6Si_{6-x}Ti_xAl_2O_{20}(OH)_4$														
326—3	0.50	1.00	750	64	50		1.66	4.44	—	0.55	0.72	0.28	2.93	5.07
H. Phlogopite-annite with $^{[4]}Ti + O^{2-} = {}^{[4]}Al + OH^-$: $K_2(Fe,Mg)_6Si_6Ti_xAl_{2-x}O_{20+x}(OH)_{4-x}$														
347—2	0.50	1.00	750	15	85		1.78	5.70	—	0.59	0.00	0.14	1.79	5.78
348—2	0.50	1.00	800	7	80		1.79	5.71	—	0.62	0.00	0.16	1.75	5.76
I. Phlogopite-annite + 10 wt% rutile														
332—2	—	1.00	800	18	65		1.77	5.13	—	0.69	0.00	0.26	2.43	5.49
273—1	—	0.00	800	12	95		1.88	—	5.92	0.20	0.00	0.07	1.93	5.88

† Number after dash indicates number of regrinding-rerunning episodes.

* Samples were rerun with addition of ~50% of oxide starting mixture.

** Samples were run in KCl or KOH solution with addition of ~50% of oxide starting mixture.

higher for low-Ti starting compositions (Table 2). Compared to the Ti-Tschermak's samples, the TiO_2 contents were typically higher with a maximum value of 6.2 wt% (0.75 atoms pfu). Octahedral vacancies were generally in the range 0.2 to 0.5 atoms pfu, and no $^{[6]}$Al was present except in two samples grown from a mixture of composition annite + 0.5 Ti-vacancy and one sample grown from a composition of annite + 0.25 Ti-vacancy. In sam-

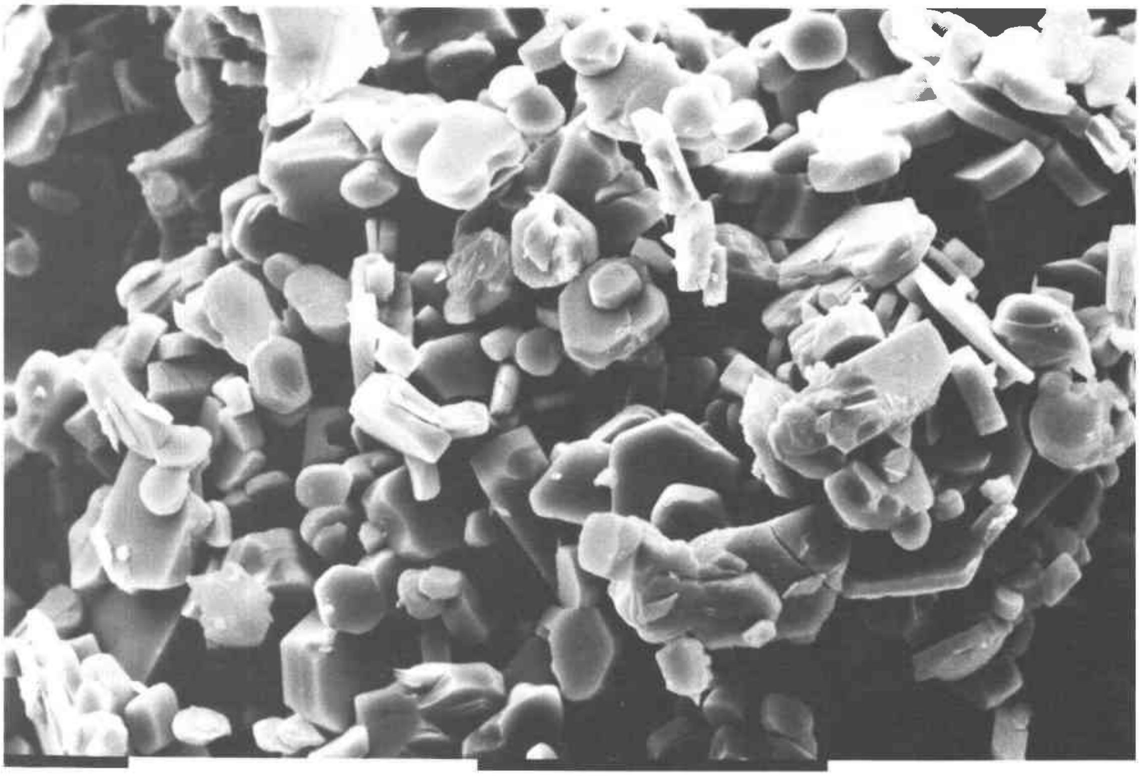

Fig. 1. SEM photograph of the synthetic biotites from run B397. The initial composition was annite + 0.5 Ti-Tschermak's substitution, and the estimated yield was 97% biotite. Run conditions were 775 °C and 1 kbar with a solution of 5*m* KOH. Scale bar is 10 μm.

ples with the starting composition annite + 1.0 Ti-vacancy, Si and Al were insufficient to fill the tetrahedral sites by 0.23, 0.23, and 0.42 atoms pfu, suggesting that some tetrahedral Ti may be present. The experiments with Ti-bearing Mg biotites had high yields, and the one that was analyzed contained approximately subequal amounts of $^{[6]}$Ti and octahedral vacancies.

Table 3. Cell parameters of synthetic Ti-bearing biotites

Sample	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å^3)
		A. Ti-bearing phlogopites			
54	5.326(2)	9.200(5)	10.303(2)	99.93(4)	497.22(19)
133	5.312(1)	9.196(2)	10.252(2)	99.89(2)	492.92(14)
162	5.322(1)	9.203(2)	10.247(2)	99.97(3)	494.29(13)
174	5.323(2)	9.187(3)	10.267(1)	100.20(3)	494.09(20)
198	5.320(2)	9.205(4)	10.307(2)	99.80(3)	497.33(19)
199	5.322(3)	9.197(6)	10.309(4)	99.98(4)	496.93(25)
205	5.319(2)	9.192(3)	10.303(3)	99.93(4)	496.14(19)
273	5.311(1)	9.214(2)	10.292(3)	100.08(4)	495.82(18)
296	5.309(3)	9.170(5)	10.266(4)	100.08(6)	492.07(28)
		B. Ti-bearing biotites			
99	5.386(3)	9.330(1)	10.262(1)	100.12(2)	507.68(22)
103	5.393(2)	9.316(3)	10.280(3)	100.22(3)	508.23(20)
128	5.386(3)	9.322(5)	10.221(5)	99.82(4)	505.72(32)
140	5.389(2)	9.331(3)	10.272(2)	100.13(3)	508.43(18)
149	5.394(1)	9.333(2)	10.195(2)	99.98(2)	505.45(12)
150	5.389(1)	9.325(2)	10.251(2)	100.42(3)	506.65(16)
160	5.421(4)	9.319(3)	10.237(4)	100.18(3)	508.95(27)
172	5.406(3)	9.323(3)	10.240(4)	99.97(9)	508.30(29)
175	5.403(4)	9.330(5)	10.286(6)	99.92(7)	510.81(42)
234	5.377(3)	9.297(3)	10.233(3)	100.18(3)	503.51(26)
325	5.378(1)	9.301(2)	10.193(2)	99.90(3)	502.29(14)
326	5.382(2)	9.305(2)	10.188(3)	99.97(3)	502.57(19)
332	5.385(3)	9.326(3)	10.231(2)	99.88(3)	506.16(24)
343	5.379(2)	9.336(4)	10.198(3)	100.10(4)	504.30(26)
347	5.394(2)	9.342(2)	10.257(2)	99.85(3)	509.24(19)
348	5.389(3)	9.349(4)	10.260(2)	99.98(4)	509.14(33)

Experiments with Ti-oxy substitution

Final yields for the Ti-oxy substitution experiments generally decreased with time (Fig. 2d) and when runs were repeated. Yields ranged from only traces of biotite up to 90% with higher yields being achieved for Mg-rich compositions and generally for Ti-poor starting compositions. The maximum TiO_2 content was 6.8 wt% (0.77 atoms pfu). Octahedral vacancies were present in all micas and ranged from 0.04 to 0.43 atoms pfu. $^{[6]}$Al was generally low but reached 0.46 atoms pfu in one experiment. In general, the final compositions of the phases in these experiments were farthest from the bulk compositions of the starting mixes, and the compositions of all the synthetic biotites in the study can be expressed satisfactorily in terms of the other Ti substitutions without need for a significant Ti-oxy component (Table 4).

The increasing Ti solubility with temperature was demonstrated with a starting mixture having the composition annite + 0.5 Ti-oxy. Biotites with 3.9 (0.48 atoms pfu (run 120), 4.8 (run 128) (0.62 atoms pfu), and 6.8 (0.77 atoms pfu) wt% TiO_2 (run 119) were obtained at temperatures of 600, 700, and 800 °C, respectively. Coexisting phases in all three samples were fayalite, sanidine, and ilmenite.

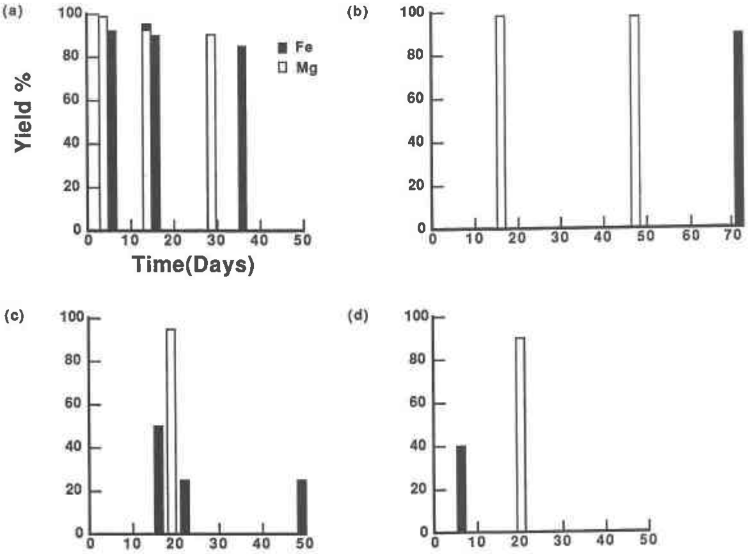

Fig. 2. Optically estimated yields vs. total synthesis time for synthetic biotites with bulk compositions representing the substitutions annite or phlogopite plus up to 0.5 Ti-Tschermak's at 800 °C (**a**) and 600 °C (**b**), up to 0.5 Ti-vacancy at 800 °C (**c**), and up to 0.5 Ti-oxy at 800 °C (**d**).

Experiments with other substitutions

The data are insufficient to make any definitive statements concerning the other substitutions, but there are no high-yield experiments resulting in compositions of micas that strongly support either Ti-Si or Ti-Al-oxy substitutions (Table 4), although, as previously mentioned, there is some evidence that the Ti-Si substitution may occur in compositions with low Al concentrations. (See experiments 150, 142, 172, 347, and 348.)

DISCUSSION

We do not claim that synthesis experiments of the type reported here represent equilibrium results or that the compositions synthesized necessarily represent stable phases. Clearly, the decreasing yields of some biotite compositions with time are good evidence that some of these phases are not stable under the conditions of synthesis. Similarly, the persistence of a phase with time provides no proof for the stability of that phase. However, the purpose of this paper is not to determine the phase relations of the Ti-bearing biotites, but only to evaluate several proposed substitutions.

A discussion of the role of Ti in micas is based upon certain assumptions concerning the valence of Ti. Although the octahedral coordination and 4+ valence for Ti have been widely accepted (Evans and Raftery, 1980), there are still no reliable data eliminating the possible occurrence of Ti^{3+} in biotite. Evans and Raftery, after having argued in favor of Ti^{3+} in phlogopites, gave a reinterpretation of their photoelectron studies on low-Ti phlogopites favoring Ti^{4+} (Evans and Raftery, 1982). The interpretations based on visible spectra are not unequivocal but suggest that most Ti is in a quadrivalent form (Robbins and Strens, 1972). On the basis of these considerations, we have assumed that all Ti in our synthetic biotites is present as Ti^{4+}.

A further difficulty arises because microprobe analyses do not yield data for Fe^{3+} or water contents. Some authors have proposed normalization procedures for the estimation of Fe^{3+} (e.g., Dymek, 1983), but such procedures, although suggestive, are not definitive. However, another approach may allow us to place limits on the amount of Fe^{3+} in our synthetic Ti-bearing biotites. Hazen and Wones (1972) argued that having approximately 10% of the Fe_{tot} as Fe^{3+} is necessary in annite for a stable structure because of the dimensional misfit between the octahedral and tetrahedral sheets. This requirement has been confirmed in experimental studies by Partin (1984) and Rebbert (1986). They were able to demonstrate by wet-chemical analyses on synthetic annites and siderophyllites, annealed at various hydrogen fugacities, that the proportions of Fe^{3+} are different for the two compositions when annealed at the same conditions. This is explained by assuming that two factors affect the Fe^{3+} content in biotite. First, there is the Fe^{3+} necessary for the fitting of the octahedral and tetrahedral sheets, as suggested by Hazen and Wones (1972). Second, there is the Fe^{3+} due to an oxidation substitution that is dependent on the oxygen fugacity in the system. Partin (1984) and Rebbert (1986) found that siderophyllite synthesized under reducing conditions at $f_{H_2} = 50$ bars contains less than 3% of the Fe_{tot} as Fe^{+3}, whereas annite synthesized under the same conditions contains 0.11 Fe^{+3}/Fe_{tot}. This sets an upper limit of 11% Fe^{3+} in our Ti-bearing biotites, which have been synthesized at even higher hydrogen fugacities (~ 160 bars) on the graphite-methane buffer. However, because the Ti-Tschermak's substitution has a steric effect that is similar to that of the Tschermak's substitution, there should be little or no need for Fe^{3+} in the

TABLE 4. Initial and final compositions of synthetic Ti-bearing biotites expressed as vector substitutions

	Ideal compositional vectors from phlog-ann						Actual compositional vectors from phlog-ann					
Run	$K^{[12]}\square$	Ti-Si	Ti-vac	Tsch	Ti-Tsch	Ti-oxy	$K^{[12]}\square$	Ti-Si	Ti-vac	Tsch	Ti-Tsch	Ti-oxy
Group A												
118	0	0	0	0	0.25	0	0.17	0	0.06	0.31	0.25	−0.04
280	0	0	0	0	0.25	0	0.28	0	0.04	0.33	0.15	0.05
182*	0	0	0	0	0.25	0	0.14	0	0	0.30	0.18	0.07
329	0	0	0	0	0.25	0	0.23	0	0.05	0.36	0.19	0.06
100	0	0	0	0	0.25	0	0.23	0	0	0.20	0.38	−0.03
103	0	0	0	0	0.25	0	0.19	0	0.08	0.39	0.20	−0.03
117	0	0	0	0	0.25	0	0.11	0	0.03	0.34	0.24	0.03
39	0	0	0	0	0.50	0	0.07	0	0.02	0.33	0.25	0.14
99	0	0	0	0	0.50	0	0.13	0	0.03	0.03	0.50	−0.08
187	0	0	0	0	0.50	0	0.18	0	0.27	0.39	0.30	−0.06
377	0	0	0	0	0.50	0	0.22	0	0.21	0.41	0.23	0.00
397	0	0	0	0	0.50	0	0.22	0	0.14	0.24	0.32	−0.03
390	0	0	0	0	0.50	0	0.18	0	0.34	0.40	0.23	−0.06
392	0	0	0	0	0.50	0	0.27	0	0.26	0.48	0.29	−0.01
234	0	0	0	0	1.00	0	0.13	0	0.26	0.87	0.26	0.04
185	0	0	0	0	0.25	0	0.11	0	0.14	0.35	−0.03	0.04
198	0	0	0	0	0.25	0	0.25	0	0.02	0.15	0.21	−0.10
199*	0	0	0	0	0.25	0	0.13	0	0	0.24	0.09	0.07
205*	0	0	0	0	0.50	0	0.16	0	0	0.60	0.11	−0.03
179*	0	0	0	0	0.13	0	0.21	0	0	0.02	0.19	−0.09
54	0	0	0	0	0.25	0	0.05	0	0.08	0.10	0.18	−0.03
191*	0	0	0	0	0.50	0	0.22	0	0	0.35	0.32	−0.13
259	0	0	0	0	0.25	0	0.36	0	0.19	0.54	0.18	−0.05
114	0	0	0	0	0.38	0	0.15	0	0.32	0.47	0.17	−0.11
Group B												
290*	0	0	0.25	0	0	0	0.27	0.03	0	0	0.20	0.05
160	0	0	0.25	0	0	0	0.22	0	0.31	0.12	0.28	−0.12
284	0	0	0.25	0	0	0	0.24	0	0.23	0	0.32	0.04
343	0	0	0.50	0	0	0	0.31	0	0.32	0.63	0.28	−0.11
149	0	0	0.50	0	0	0	0.19	0	0.30	0.38	0.28	0.05
150	0	0	1.00	0	0	0	0.13	0.42	0.24	0	0.07	−0.05
142	0	0	1.00	0	0	0	0.22	0.23	0.26	0	0.28	−0.14
172	0	0	1.00	0	0	0	0.14	0.23	0.47	0	0.13	−0.12
162	0	0	0.50	0	0	0	0.15	0.10	0.43	0	0.02	−0.10
Group C												
296	0	0	0	1.00	0.50	0	0.22	0	0.28	0.87	0.10	0
Group D												
175	0	0	0	0	0	0.25	0.14	0.07	0.04	0	0.20	0.06
120	0	0	0	0	0	0.50	0.10	0.08	0.16	0	0.27	−0.03
128	0	0	0	0	0	0.50	0.03	0.05	0.32	0	0.37	−0.12
119	0	0	0	0	0	0.50	0.10	0	0.43	0.10	0.37	−0.03
325	0	0	0	0	0	0.75	0.32	0	0.38	0.46	0.36	−0.03
174	0	0	0	0	0	0.50	0.30	0	0.33	0.13	0.02	0.01
Group E												
294	0	0	0	1.00	0	0.50	0.10	0	0.11	0.89	0.09	0.11
Group F												
146*	0	0	0.25	0	0.25	0	0.25	0	0	0.19	0.25	0.08
140	0	0	0.25	0	0.25	0	0.16	0	0.10	0.15	0.32	0.03
133	0	0	0.50	0	0.50	0	0.12	0	0.35	0.51	0.16	−0.02
Group G												
326	0	0.50	0	0	0	0	0.34	0	0.28	0.72	0.28	0
Group H												
347	0	0	0	0	0	0	0.22	0.43	0.14	0	0.01	0.02
348	0	0	0	0	0	0	0.21	0.49	0.16	0	−0.02	−0.01
Group I												
332	0	0	0	0	0	0	0.23	0.08	0.26	0	0.33	0.02
273	0	0	0	0	0	0	0.12	0.19	0.07	0	0.03	−0.09

Note: Vectors chosen are not unique (Hewitt and Abrecht, 1986), but were chosen specifically to compare various Ti substitutions.
* Adjusted to zero vacancies by subtraction from (Fe,Mg).

structure. Based on Partin's and Rebbert's data, we estimate the Fe^{3+} content of those biotites in this study with substantial Ti-Tschermak's substitution to be less than a few percent of the Fe_{tot}.

It was argued by Hewitt and Abrecht (1986) that a high-yield synthesis on composition for a specific substitution is a strong indicator of the validity of that substitution mechanism. Using this criterion, the data in Table

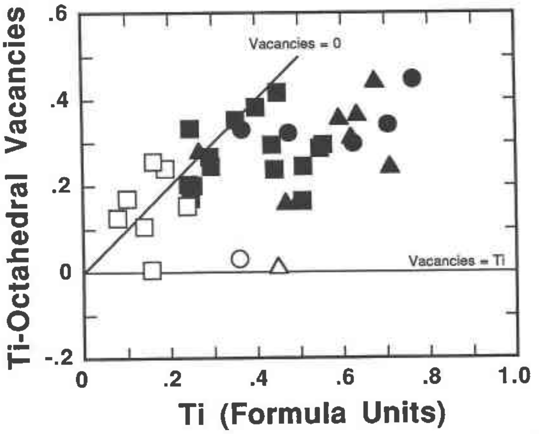

Fig. 3. Plot of the difference between Ti and the calculated octahedral vacancies vs. Ti content for synthetic biotites. Solid symbols are for experiments with annite as the additive component, and open symbols represent those with phlogopite as the additive component. Squares are for compositions with Ti-Tschermak's substitution, triangles for compositions with Ti-vacancy substitution, and circles for compositions with Ti-oxy substitution.

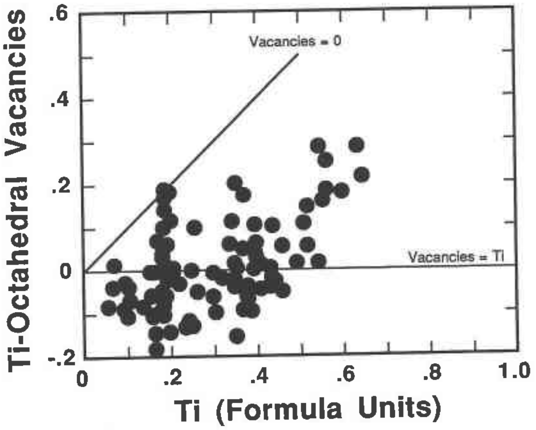

Fig. 4. Same plot as Fig. 3 but for natural biotites from pelitic rocks. Data from Guidotti et al. (1975), Tracy (1978), Speer (1981), Novak and Holdaway (1981), Labotka (1983), and Ruiz et al. (1978).

2 support the Ti-Tschermak's substitution in Fe and Mg biotites and the Ti-vacancy substitution in the Mg biotites, but give little evidence for the other substitutions. This conclusion is supported by the correspondence between starting compositions and biotite compositions for the Ti-Tschermak's experiments, allowing for the additional Tschermak's substitution in aluminous compositions, and the relatively poor agreement for the Ti-vacancy and Ti-oxy experiments in the Fe biotites (Table 4). The significantly higher yields obtained with phlogopitic starting compositions, regardless of the substitution type, suggest a better realization of the intended substitutions. However, the analyses reveal that only the experiments using phlogopite bulk compositions with Ti-Tschermak's and Ti-vacancy substitutions yield products with compositions close to the appropriate vectors.

Compositions of biotites grown from Ti-Tschermak's substitution–type mixes reveal some additional features. Generally, these biotites show a low vacancy content and an amount of $^{[6]}$Al proportional to the Al content of the starting mix. The $^{[6]}$Al can probably be attributed to the Tschermak's substitution for which there is considerable experimental evidence (Rutherford, 1973; Hewitt and Wones, 1975; Partin, 1984; Rebbert, 1986). It can also be interpreted that the Ti-Tschermak's substitution is acting to decrease the misfit between the octahedral and tetrahedral layers. For example, biotites grown from the starting composition annite + 0.25 Ti-Tschermak's show slightly lower yields and significant amounts of $^{[6]}$Al (e.g., samples 100, 103, and 117), whereas run 99 yielded 95% or greater biotite on the bulk composition of the mix (annite + 0.5 Ti-Tschermak's). Using the data of Hazen and Burnham (1973) to calculate mean T–O bond lengths and the data of Shannon (1976) to calculate mean M–O bond lengths, the d(O)/d(T) values for several starting compositions and some analyzed biotites are given in Table 5. Structures with d(O)/d(T) > 1.275 or <1.235 have been shown by Hazen and Wones (1972) to be unstable. The calculated values in Table 5 indicate that Fe^{3+}-free biotites having the bulk composition annite + 0.25 Ti-Tschermak's should not be stable, but compositions of annite + 0.5 Ti-Tschermak's or annite + 0.25 Ti-Tschermak's + 0.25 Tschermak's would be possible. These predictions are in good agreement with the observed compositions and yields. It remains to be explained, however, why all of these compositions are not stabilized by other chemical adjustments such as the increase in Fe^{3+} that occurs in annite.

Fe biotites grown from Ti-vacancy and Ti-oxy substitution–type mixes yield more ambiguous results. The low yields and compositions of these biotites indicate that the intended substitutions have only partially been realized. Octahedral vacancies are always present (0.23–0.47), but it is evident that, even if all octahedral vacancies are due to the Ti-vacancy substitution, there is still a considerable amount of Ti that has to be accounted for by other substitutions. Figure 3 shows clearly that (1) the Ti-Tschermak's experiments yield biotites with a strong tendency toward a low vacancy content; (2) the Ti-vacancy and Ti-oxy experiments with Fe biotites produce compositions with Ti significantly in excess of the octahedral vacancies; (3) the Ti-vacancy and Ti-oxy experiments with Mg bio-

Table 5. Calculated d(O)/d(T) values for different Ti-bearing biotite compositions

Annite + 0.25 Ti-Tschermak's	1.281
Annite + 0.5 Ti-Tschermak's	1.269
Annite + 0.25 Ti-Tschermak's + 0.25 Tschermak's	1.272
Run 99	1.271
Run 100	1.271
Run 103	1.271
Rub 117	1.269

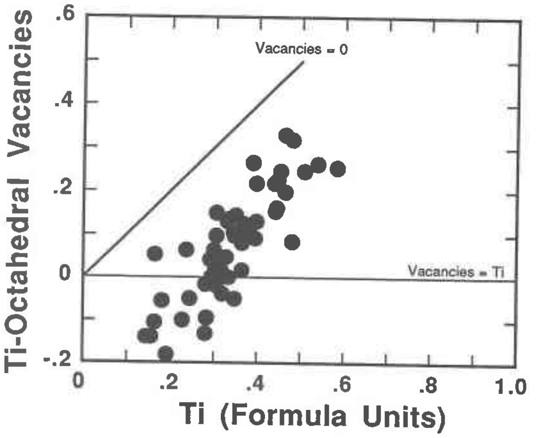

Fig. 5. Same plot as Fig. 3 but for natural biotites from granitic rocks. Data from Dodge et al. (1969), Dodge and Moore (1968), Czamanske and Wones (1973), Czamanske et al. (1977), and Barker et al. (1975).

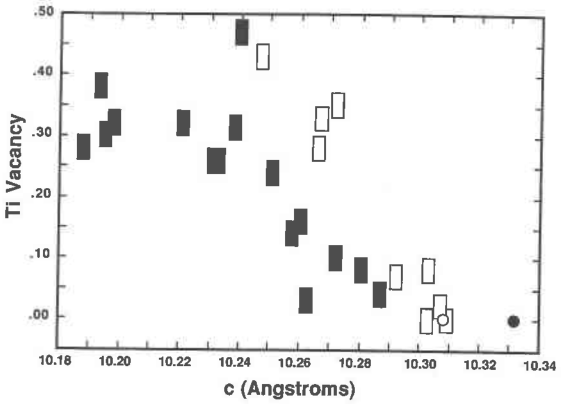

Fig. 6. Plot of the *c* dimension of synthetic biotites from Table 3 vs. the calculated amount of Ti-vacancy substitution from Table 4. Open symbols are for Mg-biotites, and the solid symbols are for Fe-biotites. The two circles are for pure annite and phlogopite as reported by Hewitt and Wones (1975).

tites show a tendency to have Ti equal to the vacancy content; and (4) the data all trend toward the origin, suggesting that the Ti-Tschermak's and Ti-vacancy substitutions can account for a significant portion of the Ti in the synthetic biotites, in natural biotites from pelitic rocks (Fig. 4), and in natural biotites from granitic rocks (Fig. 5). It is of interest to note that although there is no apparent relationship between Ti and octahedral vacancies in the biotites from granitic rocks, there are octahedral vacancies present in all samples plotted and the number of vacancies is remarkably constant.

The rather high yields for Ti-bearing Mg biotites and the proportionally high vacancy contents (Fig. 3) suggest that the vacancy substitution can occur in these micas without the need for other substitutions. The reason for this different behavior in biotites and phlogopites is speculative at this time. Differences in thermal stability might account for the variation, but even though many of our experiments were performed near the upper stability limit for annite (Eugster and Wones, 1962; Hewitt and Wones, 1981), some experiments were done at lower temperatures and yielded equivalent results. The greater tendency for the Ti-vacancy substitution in the phlogopites could be due to the structural restraints imposed on the biotite structure. The Ti-vacancy substitution in biotite may not shrink the octahedral sheet, because the small size of Ti^{4+} could be compensated by the large size of a vacancy as inferred from muscovite (r_{vac} = 0.9 Å; Güven, 1971) and K$_2$(Mg$_5\square$)Ge$_8$O$_{20}$F$_4$ (r_{vac} = 0.75 Å; Toraya et al., 1978). In fact, the size of the vacancy in a Ti-bearing biotite might be larger because of the greater attraction from a Ti^{+4} cation. Because the tetrahedral sheet in Fe biotite cannot expand (Hazen and Wones, 1972), the Ti-vacancy substitution therefore might not be compatible with a stable Fe biotite. This would not affect the structural stability of phlogopite, where simple tetrahedral rotation can make the tetrahedral layer larger or smaller as needed.

The cell-parameter data in Table 3 were analyzed for further insight into the reasons for the compositional effect on the Ti-vacancy substitution. A variety of parameters were plotted, but only the *c* cell parameters showed a significant variation with the amount of Ti-vacancy substitution (Fig. 6). The Mg biotites demonstrate a very regular decrease in *c* as the number of vacancies increase. The Fe biotites show an even greater change for a given number of vacancies, but are much more irregular in behavior, probably because the vacancy substitution is always accompanied by other substitutions. It is apparent that the Fe biotite structure has to adjust more than Mg biotite in order to accommodate an equivalent amount of Ti-vacancy substitution. The reasons why the greater adjustment is necessary are still problematic, but that it must occur is at least a good qualitative argument why the Ti-vacancy substitution is more difficult to achieve in the Fe biotites.

Another difference in Ti substitution between biotite and phlogopite is demonstrated by the greater Ti solubility in Fe biotite compared to phlogopite in natural pelitic systems (Fig. 7) and in the synthetic systems (Fig. 8). The inherent electron-configuration differences between Fe and Mg might provide a partial explanation. Unlike Mg, the transition metal Fe is more able to maintain local charge balance with higher-charged cations like Ti^{+4} by charge-transfer processes such as

$$\mathrm{Fe^{2+} + Ti^{4+} = Fe^{3+} + Ti^{3+}}.$$

The optical spectra of biotite suggest (Burns, 1970) this kind of transfer process may be occurring, but whether it could significantly affect Ti concentrations is highly speculative.

Micas grown from Ti-vacancy and Ti-oxy substitution–type mixes show similar composition trends (Table 4), although neither H$_2$O nor Fe^{3+} concentrations are available to be compared. This relationship is not unex-

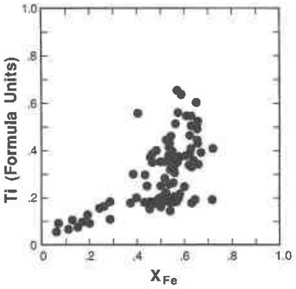

Fig. 7. Plot showing the variation of Ti content vs. mole fraction Fe in natural biotites from pelitic rocks. Data from the same sources as in Fig. 4.

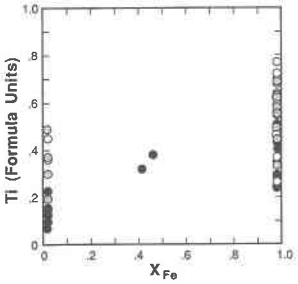

Fig. 8. Plot showing the variation of Ti content vs. mole fraction Fe in synthetic biotites from this study. Dark circles represent bulk compositions of phlogopite-annite + Ti-Tschermak's substitution; open circles, phlogopite-annite + Ti-vacancy or Ti-oxy substitutions; stippled circles, phlogopite-annite + other substitutions included in Table 1.

pected because all oxy substitutions can be formulated in terms of a vacancy substitution and a Fe-Ti oxide. For example, annite + 0.75 Ti-vacancy + $0.25Fe_2TiO_4$ = annite + 1.0 Ti-oxy + H_2O. Ulvöspinel-rich oxide phases along with sanidine and fayalite were common in Ti-rich run materials for these two substitution types. However, it must be remembered that the decomposition products of all Ti-bearing Fe biotites also involve sanidine (and/or feldspathoid) plus an Fe-Ti oxide that is dependent both on bulk composition and the oxidizing conditions of the system.

CONCLUSIONS

The inability to synthesize a composition—or, better, the instability of that composition once synthesized—is good evidence against the viability of the substitution under those conditions. Conversely, the synthesis of a phase on composition for some substitution and the persistence of that phase lend credence to the substitution scheme. Sequences of compositions along vectors representing the substitution also add support to the argument. These data do not provide the importance of a substitution because it can always be asserted that they may represent metastable equilibrium or disequilibrium compositions. However, when looked at in terms of the data on natural phase compositions, they not only seem to corroborate some earlier conclusions, but they shed some light on the complexity of the problem and help explain the apparent inconsistencies in previous attempts to evaluate the Ti substitution in biotite.

Based on observations of the yields of synthetic Ti-bearing micas and on comparisons of their compositions with regard to the starting bulk compositions, there is substantial experimental evidence that the Ti-Tschermak's exchange is a viable substitution mechanism in Fe and Mg biotites. There are also strong indications that the Ti-vacancy substitution occurs commonly in phlogopite and, possibly, to a lesser extent in Fe biotite. It is believed that structural constraints limit the exclusive occurrence of the Ti-vacancy substitution in Fe biotite and require an additional cosubstitution to enhance the fit between the tetrahedral and octahedral layers (e.g., Ti-Tschermak's, Tschermak's, $MgFe_{-1}$, or muscovite substitution). Our data do not indicate that the Ti-oxy exchange is an important substitution mechanism but are not definitive because the presence or absence of any oxy substitution cannot be shown in the absence of Fe^{3+} and water analyses. Even with those data, specific evidence for a particular oxy-substitution would be ambiguous (Hewitt and Abrecht, 1986). Considering the difficulties in the experimental evaluation of substitution types in complex Ti-bearing micas and the ambiguities inherent in such an evaluation based upon chemical analyses, even if complete, we believe that any conclusions beyond these statements are premature.

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REFERENCES CITED

Appleman, D.E., and Evans, H.T. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. U.S. Geological Survey Publication 73-003.

Barker, F., Wones, D.R., Sharp, W.N., and Desborough, G.A. (1975) The Pikes Peak batholith, Colorado Front Range, and a model for the origin of the gabbro–anorthosite–syenite–potassic granite suite. Precambrian Research, 29, 97–160.

Bence, A.E., and Albee, A.L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. Journal of Geology, 76, 382–403.

Bohlen, S.R., Peacor, D.R., and Essene, E.J. (1980) Crystal chemistry of a metamorphic biotite and its significance in water barometry. American Mineralogist, 65, 55–62.

Burns, R.G. (1970) Mineralogical applications of crystal field theory. Cambridge University Press.

Czamanske, G.K., and Wones, D.R. (1973) Oxidation during magmatic differentiation, Finnmarka Complex, Oslo area, Norway: Part 2, The mafic silicates. Journal of Petrology, 14, 349–380.

Czamanske, G.K., Wones, D.R., and Eichelberger, J.C. (1977) Mineralogy and petrology of the intrusive complex of the Pliny Range, New Hampshire. American Journal of Science, 277, 1073–1123.

Dodge, F.C.W., and Moore, J.G. (1968) Occurrence and composition of biotites from the Cartridge Pass pluton of the Sierra Nevada batholith, California. U.S. Geological Survey Professional Paper 600-B, B6–B10.

Dodge, F.C.W., Smith V.C., and Mays, R.E. (1969) Biotites from granitic rocks of the central Sierra Nevada batholith, California. Journal of Petrology, 10, 250–271.

Dymek, R.F. (1983) Titanium, aluminum and interlayer cation substitutions in biotite from high-grade gneisses, West Greenland. American Mineralogist, 68, 880–899.

Eugster, H.P., and Wones, D.R. (1962) Stability relations of the ferruginous biotite, annite. Journal of Petrology, 3, 82–125.

Evans, S., and Raftery, E. (1980) X-ray photoelectron studies of titanium in biotite and phlogopite. Clay Minerals, 15, 209–218.

——— (1982) Determination of the oxidation state of manganese in lepidolite by X-ray photoelectron spectroscopy. Clay Minerals, 17, 477–481.

Forbes, W.C., and Flower, M.F.J. (1974) Phase relations of titan-phlogopite, $K_2Mg_4TiAl_2Si_7O_{20}(OH)_4$: A refractory phase in the upper mantle? Earth and Planetary Science Letters, 22, 60–66.

Guidotti, C.V., Cheney, J.T., and Conatore, P.D. (1975) Interrelationships between Mg/Fe and octahedral Al content in biotite. Amerian Mineralogist, 60, 849–853.

Guidotti, C.V., Cheney, J.T., and Guggenheim, S. (1977) Distribution of titanium between coexisting muscovite and biotite in pelitic schists from northwestern Maine. American Mineralogist, 62, 438–448.

Güven, N. (1971) The crystal structure of 2M1 phengite and 2M1 muscovite. Zeitschrift für Kristallographie, 134, 196–212.

Hazen, R.M., and Burnham, C.W. (1973) The crystal structure of one-layer phlogopite and annite. American Mineralogist, 58, 889–900.

Hazen, R.M., and Wones, D.R. (1972) The effect of cation substitutions on the physical properties of trioctahedral micas. American Mineralogist, 57, 103–129.

Hewitt, D.A., and Abrecht, J. (1986) Limitations on the interpretation of biotite substitutions from chemical analyses of natural samples. American Mineralogist, 71, 1126–1128.

Hewitt, D.A., and Wones, D.R. (1975) Physical properties of some synthetic Fe-Mg-Al trioctahedral biotites. American Mineralogist, 60, 854–862.

——— (1981) The annite-sanidine-magnetite equilibrium. GAC-MAC Joint Annual Meeting, Calgary, Abstracts, 6, A-66.

Holdaway, M.J. (1980) Chemical formulae and activity models for biotite, muscovite, and chlorite applicable to pelitic metamorphic rocks. American Mineralogist, 65, 711–719.

Kovalenko, N.I., Kashayev, A.A., Znamenskiy, Y.B., and Zehuravleva, R.M. (1968) Entry of titanium into micas (experimental studies). Translated from Geokhimiya, 11, 1348–1357.

Labotka, T.C. (1983) Analysis of the compositional variations of biotite in pelitic hornfelses from northeastern Minnesota. American Mineralogist, 68, 900–914.

Novak, J.M., and Holdaway, M.J. (1981) Metamorphic petrology, mineral equilibria, and polymetamorphism in the Augusta quadrangle, south-central Maine. American Mineralogist, 66, 51–69.

Partin, E. (1984) Ferric/ferrous determinations in synthetic biotites. M.S. thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Rebbert, C.R. (1986) Biotite oxidation: An experimental and thermodynamic approach. M.S. thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Robbins, D.W., and Strens, R.G.J. (1972) Charge-transfer in ferromagnesian silicates: The polarized electronic spectra of trioctahedral micas. Mineraological Magazine, 38, 551–563.

Robert, J.L. (1976) Titanium solubility in synthetic phlogopite solid solutions. Chemical Geology, 17, 218–227.

Ruiz, L.J., Aparicia, A., and Garcia Cacho L. (1978) Chemical variations in biotites during prograde metamorphism, Sierre de Guadarrama, Sistema Central, Spain. Chemical Geology, 21, 113–129.

Rutherford, M.J. (1973) The phase relations of aluminous iron biotites in the system $KAlSi_3O_8$-$KAlSiO_4$-Al_2O_3-Fe-O-H. Journal of Petrology, 14, 159–180.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A-32, 751–767.

Solberg, T.N., Abrecht, J., and Hewitt, D.A. (1981) Graphical procedures for the refinement of electron microprobe analysis of fine-grained particles. Microbeam Analysis, San Francisco 1981, 160–161.

Speer, J.A. (1981) The nature and magnetic expression of isograds in the contact aureole of the Liberty Hill pluton, South Carolina. Geological Society of American Bulletin, 92, part I, 603–609; part II, 1262–1358.

Toraya, H., Iwai, S., Marumo, F., and Hirao, M. (1978) The crystal structures of germanate micas, $KMg_{2.5}Ge_4O_{10}F_2$ and $KLiMg_2Ge_4O_{10}F_2$. Zeitschrift für Kristallographie, 148, 65–81.

Tracy, R.J. (1978) High grade metamorphic reactions and partial melting in pelitic schists, west-central Massachusetts. American Journal of Science, 278, 150–178.

Tronnes, R.G., Edgar, A.D., and Arima, M. (1985) A high pressure–high temperature study of TiO_2 solubility in Mg-rich phlogopite: Implications to phlogopite chemistry. Geochimica et Cosmochimica Acta, 49, 2323–2329.

Wones, D.R. (1963) Physical properties of synthetic biotites on the join phlogopite-annite. American Mineralogist, 48, 1300–1321.

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