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STABILITY AND COMPOSITION OF K–Ti SILICATES, K–Ba PHOSPHATE AND K–Mg FLUORIDE AT 0.85–2.6 GPa: IMPLICATIONS FOR THE GENESIS OF POTASSIC ALKALINE MAGMAS

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ABSTRACT

The stability and compositions of K–Ti silicate ($K_2TiSi_3O_9$) and similar compounds, K–Ba phosphate [$K_6Mg_3Ba_2Ca(PO_4)_6$], and K–Mg fluoride [$(K,Na)MgF_3$], were determined between 0.85 and 2.57 GPa at 900–1400°C. Starting compositions of $K_4Ti_2Si_7O_{20}$ and $K_4Ti_7Si_{10}O_{36}$, equivalent to the K–Ti silicates stable near the solidus of natural lamproites at higher pressures, produced assemblages consisting of only $K_2TiSi_3O_9$ + rutile ± SiO_2. The phase $K_2TiSi_3O_9$ is the Ti analogue of the cyclosilicate wadeite ($K_2ZrSi_3O_9$). The K–Ba phosphate found in this study is of similar composition to that found in experimental studies of lamproites at high pressure, but has not been reported to occur naturally. The phase $KMgF_3$ is similar to that found in experiments in the system potassian richterite – phlogopite – F at 2 GPa, and is the K-analogue of the fluoroperovskite-group mineral neighborite. The relationships of the low-pressure K–Ti silicate formed in this study to those stable at high pressure (4–12 GPa) are discussed. The compounds found in this work appear to be stable in various forms in the lower crust and lithospheric upper mantle and can act as sources for the large-ion lithophile (K,Ba), and first- and second-period transition elements (Ti, Zr, *etc.*) characteristic of potassic alkaline magmas formed from metasomatized sources in the mantle.

Keywords: K–Ti silicate, K–Ba phosphate, fluoroperovskite-group mineral, wadeite, lamproite, upper mantle.

SOMMAIRE

Nous avons déterminé le champ de stabilité et la composition du silicate de K et Ti ($K_2TiSi_3O_9$) et de composés semblables, du phosphate de K et Ba [$K_6Mg_3Ba_2Ca(PO_4)_6$], et du fluorure de K et Mg [$(K,Na)MgF_3$] entre 0.85 et 2.57 GPa à 900–1400°C. Dans le premier cas, nos compositions de départ, $K_4Ti_2Si_7O_{20}$ et $K_4Ti_7Si_{10}O_{36}$, équivalentes aux silicates de K et Ti stables près du solidus de lamproïtes naturelles à pressions plus élevées, ont produit des assemblages contenant seulement $K_2TiSi_3O_9$ + rutile ± SiO_2. Le composé $K_2TiSi_3O_9$ est l'analogue titanifère du cyclosilicate wadéite ($K_2ZrSi_3O_9$). Le phosphate contenant K et Ba a une composition semblable à celle du phosphate synthétisé dans des expériences sur les lamproïtes à pression élevée, mais n'a pas encore été décrit dans la nature. Le composé $KMgF_3$ est semblable à ce que l'on trouve dans les expériences dans le système richtérite potassique – phlogopite – F à 2 GPa, et serait l'analogue potassique de la neighborite, minéral du groupe de la fluoropérovskite. Nous discutons des relations entre le silicate K–Ti de faible pression et les phases qui sont stabilisées à pression élevées (4–12 GPa). Les composés décrits ici semblent stables sous des formes variables dans la croûte inférieure et dans le manteau supérieur, et pourraient bien agir de sources des éléments lithophiles à large rayon (K,Ba) et des éléments de transition de la première et la seconde période (Ti, Zr, *etc.*) caractéristiques des magmas potassiques formés à partir de sources dans le manteau affectées par une métasomatose alcaline.

(Traduit par la Rédaction)

Mots-clés: silicate de K–Ti, phosphate de K–Ba, minéral du groupe de la fluoropérovskite, wadéite, lamproïte, manteau supérieur.

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INTRODUCTION

Lamproites are a clan of ultrapotassic peralkaline rocks characterized by enrichment in large-ion lithophile (K,Rb) and "incompatible" (*REE*, Sr, Ba, Ti, Zr, *etc.*) elements (Mitchell & Bergman 1991). The unusual geochemistry of the magmas leads to the crystallization of an exotic suite of alkali titanates and zirconates as accessory minerals. To explain the mineralogy and geochemistry of lamproites, Mitchell & Bergman (1991), Mitchell (1995) and Edgar & Mitchell (1997) have suggested that the mantle sources of lamproite magmas must contain titanates, zirconates and phosphates. Experimental studies of natural lamproite compositions at high pressures have shown that diverse alkali titanates and K–Ba phosphates are indeed near-solidus phases at 4–12 GPa, and could conceivably sequester K, Ba, Sr, *REE, etc.*, in metasomatized mantle (Mitchell 1995, Edgar & Mitchell 1997).

Little is known of the stability of alkali titanates and phosphates at high pressures and temperatures. The cyclosilicate wadeite ($K_2ZrSi_3O_9$) and hollandite-group minerals such as priderite [$(K,Ba)_{1-2}(Mg,Fe)_xTi_{6-x}O_{16}$] are stable throughout the lithospheric mantle up to pressures of 5 GPa (Arima & Edgar 1980, Dubeau & Edgar 1985, Foley *et al.* 1994). Recently, diverse K–Ti silicates and a K–Mg–Ba phosphate have been reported from experimental studies of SiO_2-rich lamproites from the Leucite Hills, Wyoming (Mitchell 1995), and Smoky Butte, Montana (Edgar & Mitchell 1997) at pressures of 5–12 GPa at 900° – 1900°C. A K–Mg fluoride was found in studies of the system potassian richterite – phlogopite – fluorine at 2 GPa by Edgar & Pizzolato (1995). Table 1 lists the compositions and suggested structural formulae of these compounds.

The objectives of this study are to investigate the stability of $K_4Ti_2Si_7O_{20}$ (referred to here as SiO_2-rich silicate) and $K_4Ti_7Si_{10}O_{36}$ (SiO_2-poor silicate), $K_6Mg_3Ba_2Ca(PO_4)_6$ (K–Ba phosphate) and $(K,Na)MgF_3$ at 0.85–2.57 GPa. Experiments were undertaken to determine whether these compounds exist at lower pressures (< 6 GPa) than those used in the experiments of Mitchell (1995) and Edgar & Mitchell (1997). In this study, we also compare the structure of the K–Ti silicates with those of other compounds between 1 atmosphere and 12 GPa and discuss their potential as reservoirs for large-ion lithophile elements (LILE) and other "incompatible" elements in the upper mantle and crust.

TABLE 1. EXPERIMENT STARTING COMPOSITIONS

Wt%	1	2	3		4
P_2O_5	-	-	35.72	Mg	20.55
SiO_2	54.71	44.56	-	K	26.71
TiO_2	20.78	41.47	-	Na	3.94
MgO	-	-	10.15	F	48.80
CaO	-	-	4.70		
BaO	-	-	25.73		
K_2O	24.51	13.97	23.70		

1 $K_4Ti_2Si_7O_{20}$; 2 $K_4Ti_7Si_{10}O_{36}$; 3 $K_6Mg_3Ba_2Ca(PO_4)_6$
4 $(K,Na)MgF_3$ (as elements)

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Mixtures of the stoichiometric compositions of the compounds listed in Table 1 were prepared from Analar or equivalent grade, pre-dried K_2CO_3, TiO_2, pure quartz (99.99 wt.%), CaO, $BaHPO_4$, $MgHPO_4{\bullet}3H_2O$, $Ca_5(PO_4)_3F$ as fluorapatite from Durango, Mexico, KF, MgF_2 and NaF. The starting materials were mixed by grinding dry or under acetone. Some mixtures were heated to above 900°C to dissociate K_2CO_3 and $MgHPO_4{\bullet}3H_2O$, quenched and desiccated. Optical and X-ray powder diffraction of such quenched starting materials showed them to consist of $K_2TiSi_3O_9$ and an inhomogeneous mixture of the starting materials. Crystalline K–Ba phosphate could not be identified in any of the quenched starting material.

All experiments were undertaken using a piston-cylinder apparatus 1.27 cm in diameter between 0.85 and 2.57 GPa at 900° to 1400°C. Pure Pt capsules were used for experiments above 1250°C, and $Ag_{50}Pd_{50}$ for experiments below this temperature. The pressure-transmitting assemblage was composed of talc plus Pyrex glass, heat being supplied by a graphite furnace. Temperature and pressure calibrations were made as described in Edgar *et al.* (1992). Temperatures were monitored using a $Pt_{90}Rh_{10}$ thermocouple. No correction was made for the effect of pressure on the emf of the thermocouple. Pressure was considered accurate to ±0.05 GPa, and temperature, to ±5°C of the stated value.

Products of each experiment were identified using a JEOL JXA–8600 electron microprobe at an accelerating voltage of 15kV and a beam current of 10 nA. Approximate modes of the products were estimated from back-scattered electron images. The experimental products were also examined by X-ray powder diffractometry.

PRIMARY AND QUENCH PRODUCTS

The distinction between primary and quench (metastable) crystals of each compound was based upon crystal morphology. Compounds coexisting with liquid quenched as glass were considered to be primary if they exhibited a euhedral habit, whereas quenched products are identified from their skeletal, bladed, dendritic or acicular habits.

$K_2TiSi_3O_9$ occurs as euhedral hexagonal crystals, 10–20 μm in length, in a matrix of smaller subhedral crystals of quartz and rutile and glass (Fig. 1). All crystalline phases formed from both SiO_2-rich and SiO_2-poor starting materials were considered primary. The K–Ba phosphate formed composite, rounded and blocky grains with maximum dimensions of up to 100 μm set

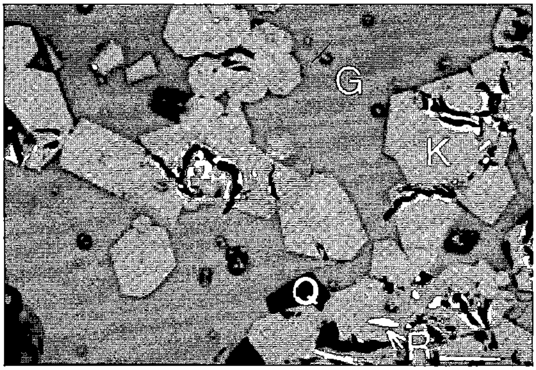

FIG. 1. Back-scattered electron image of K–Ti silicate (K), quartz (Q), rutile (R) and glass (G) produced from SiO_2-rich K–Ti silicate starting composition at 1.73 GPa and 1100°C. Scale bar: 10 μm.

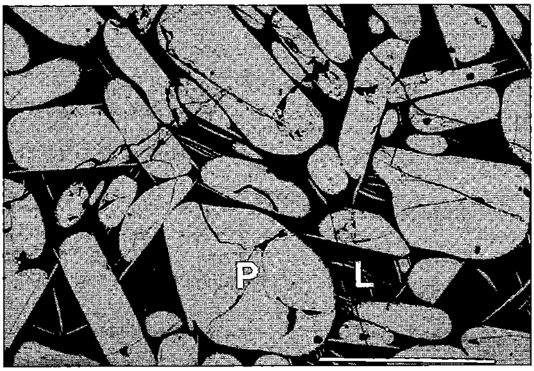

FIG. 2. Back-scattered electron image of K–Ba phosphate (P) and glass (L) produced from K–Ba phosphate starting composition at 2.57 GPa and 1200°C. Scale bar: 100 μm.

in glass (Fig. 2). Tiny stellate crystals were considered to represent quench material. $KMgF_3$ formed interlocking 10–100 μm crystals of uniform composition. Quench material of dendritic and bladed habit was observed in the minor amounts of interstitial glass.

EXPERIMENTAL RESULTS

K–Ti silicates

The results of the experiments on K–Ti silicate starting compositions are listed in Table 2. Within the P–T range of the experiments, neither of the starting compositions yielded products compositionally similar to the starting material and to the K–Ti silicates found in higher-pressure experiments on lamproite compositions. Instead, in all experiments, a K–Ti silicate corresponding to the formula $K_2TiSi_3O_9$ formed in association with rutile, quartz and glass.

Figure 3 shows phase relations for the SiO_2-rich starting composition ($K_4Ti_2Si_7O_{20}$) and demonstrates that assemblages are pressure-dependent, with an all-melt field existing below 1 GPa over a wide range of temperature. The melt-absent assemblage of $K_2TiSi_3O_9$ + rutile + quartz appears to be stable at all pressures above 3 GPa at temperatures ranging from 800 to 1300°C. Extrapolation of the phase relationships suggests that this solid assemblage will melt directly to a liquid at an pseudo-invariant point at about 0.5 GPa and 750°C. Table 2 and Figure 4 indicate that the SiO_2-poor starting material ($K_4Ti_7Si_{10}O_{36}$) yields the same $K_2TiSi_3O_9$ compound plus rutile and quartz. However, in contrast, the four-phase field involving melt is absent, and the solid assemblage melts directly to a liquid at all

TABLE 2. EXPERIMENTAL RESULTS - K-Ti SILICATES

P(GPa)	T (°C)	Time (Hours)	Phases Present
K-Ti Silicate (Si-rich)			
2.57	1050	4	Kts(67), Qtz(30), Rt(3)
2.57	1100	3	Kts(70), Qtz(25), Rt(3), L(2)
1.73	900	8	Kts(68), Qtz(30), Rt(2)
1.73	1000	6	Kts(64), Qtz(28), Rt(4), L(4)
1.73	1050	6	Kts(65), Qtz(26), Rt(4), L(5)
1.73	1100	6	Kts(66), Qtz(26), Rt(2), L(6)
1.73	1200	5	Kts(20), L(80)
0.85	860	8	Kts(70), Qtz(20), Rt(2), L(8)
0.85	900	8	Kts(17), Qtz(5), Rt(3), L(75)
0.85	1000	6	L(100)
K-Ti Silicate (Si-poor)			
2.57	1100	3	Kts, Qtz, Rt
2.57	1200	2.5	Kts, Qtz, Rt
1.73	900	8	Kts, Qtz, Rt
1.73	1000	6	Kts, Qtz, Rt
1.73	1100	6	Kts, Qtz, Rt
1.73	1200	2.5	L
0.85	900	8	L
0.85	1000	8	L

Kts = $K_2TiSi_3O_9$; Qtz = quartz; Rt = rutile; L = liquid; (x) = mode (vol.%)

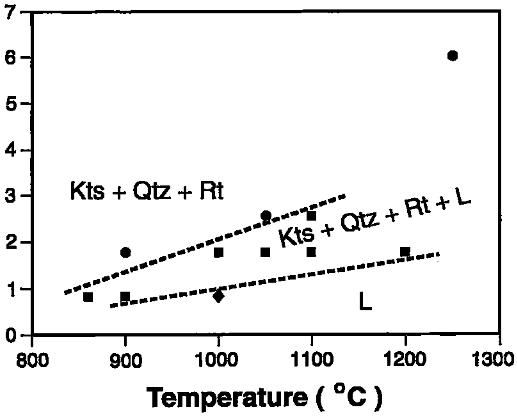

FIG. 3. Phase relations determined for the SiO_2-rich starting composition. Kts = $K_2TiSi_3O_9$, Qtz = quartz, Rt = rutile, L = liquid.

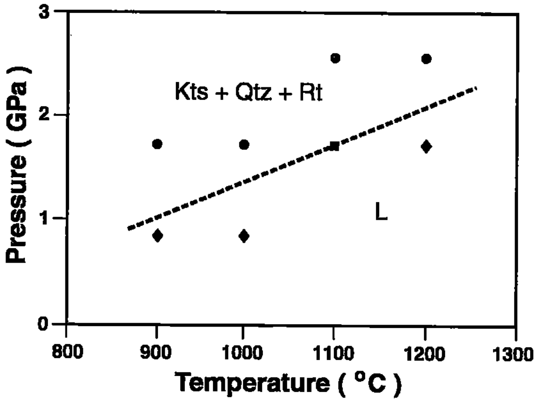

FIG. 4. Phase relations determined for the SiO_2-poor starting composition. Kts = $K_2TiSi_3O_9$, Qtz = quartz, Rt = rutile, L = liquid.

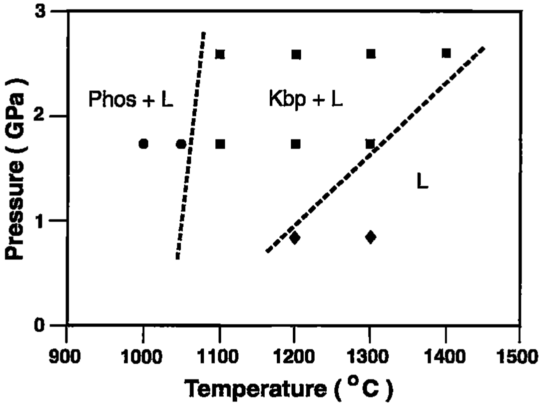

FIG. 5. Phase relations determined for the K–Ba phosphate starting composition. Phos = 2–4 phosphates, Kbp = $K_6Mg_3Ba_2Ca(PO_4)_6$, L = liquid.

temperatures. As this starting material contains about 20 wt.% more TiO_2 than the SiO_2-rich material, significantly more rutile (> 10 vol.%) occurs in the products of the experiments.

K–Ba phosphate

The products of the experiments on phosphate-bearing starting materials (Table 3, Fig. 5) are complex and difficult to characterize completely. For example, at 1.73 GPa and 1000°C, the products consist of several phosphate-bearing compounds distinguishable only by their composition and not by X-ray diffraction. Above 1100°C at 1.73 and 2.57 GPa, a single-phase K–Ba phosphate and melt coexist to <1200°C at about 1 GPa, and above 1400°C at 2 GPa. The complex phosphate assemblage found below 1050°C undoubtedly represents reaction of the K–Ba phosphate with melt.

TABLE 3. EXPERIMENTAL RESULTS - PHOSPHATE AND FLUORIDE

P(GPa)	T (°C)	Time (Hours)	Phases Present
K-Ba Phosphate			
2.57	1100	3	Kbp(85), L(15)
2.57	1200	3	Kbp(80), L(20)
2.57	1300	2	Kbp(75), L(25)
2.57	1400	2	Kbp(20), L(80)
1.73	1000	6	unidentified phosphate, L
1.73	1050	4	unidentified phosphate, L
1.73	1100	3	Kbp(20), L(80)
1.73	1200	3	Kbp(15), L(85)
1.73	1300	2	Kbp(10), L(90)
0.85	1200	4	unidentified phosphate, L(90)
0.85	1300	4	L(100)
K-Mg Fluoride			
2.57	1100	2	Kmf
2.57	1200	2	Kmf
2.57	1300	2	Kmf
2.57	1400	2	Kmf, L
1.73	1200	3	Kmf
1.73	1250	3	Kmf, L
1.73	1300	2	L
1.73	1400	2	L
0.85	1000	4	Kmf
0.85	1100	3	Kmf, L
0.85	1200	3	L
0.85	1400	2	L

Kbp = K-Ba phosphate; Kmf = (K,Na)MgF_3; L = liquid; (x) = mode (vol.%)

K–Mg fluoride

Phase relations for this compound are given in Table 3 and depicted in Fig. 6. The fluoride melts directly to a liquid at all pressures. Melting occurs at <1100°C at 0.85 GPa, and at <1400°C at 2.57 GPa.

COMPOSITIONS AND X-RAY DIFFRACTION

K–Ti silicates

Table 4 shows that the compositions of the K–Ti silicate formed from both SiO_2-poor and SiO_2-rich starting

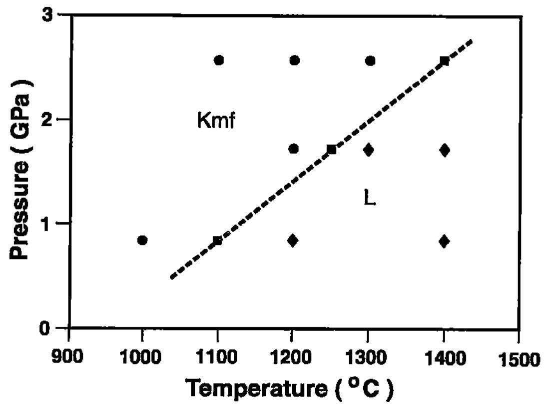

FIG. 6. Phase relations determined for the K–Mg fluoride starting composition. Kmf = (K,Na)MgF_3, L = liquid.

TABLE 4. REPRESENTATIVE COMPOSITIONS (WT%) OF K-Ti SILICATE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
P(GPa)	2.57	2.57	1.73	1.73	1.73	1.73	1.73	0.85	0.85	2.57	2.57	1.73	1.73	1.73
T(°C)	1050	1100	900	1000	1050	1100	1200	860	900	1100	1200	900	1000	1100
SiO_2	50.75	51.07	50.53	50.90	51.10	51.37	50.60	51.15	48.81	50.16	50.25	50.74	50.31	50.87
TiO_2	22.57	23.01	22.30	23.50	22.69	22.65	22.94	23.15	24.38	22.36	23.48	23.28	22.98	23.54
K_2O	25.98	25.67	25.91	26.03	25.95	25.83	26.54	25.65	25.55	25.80	25.29	25.59	25.19	25.55
Total	99.30	99.75	99.74	100.43	99.74	99.85	100.08	99.95	98.74	98.32	99.02	99.61	98.48	99.96
Structural Formula based on 9 oxygens														
Si	3.004	3.002	3.009	2.979	3.008	3.016	2.984	2.999	2.917	3.001	2.976	2.988	2.993	2.984
Ti	1.005	1.017	0.999	1.034	1.004	1.000	1.017	1.006	1.096	1.006	1.046	1.031	1.028	1.038
K	1.962	1.924	1.968	1.943	1.948	1.934	1.996	1.918	1.948	1.969	1.911	1.992	1.912	1.911

Compistions 1-9 and 9-14 from Si-rich and Si-poor starting material, respectively.

materials are identical and correspond closely to stoichiometric $K_2TiSi_3O_9$. Table 5 shows that the cell parameters and indexed X-ray pattern for $K_2TiSi_3O_9$ formed in this study are similar to those obtained on synthetic material prepared by Choisnet *et al.* (1973). On the basis of these data, and those of Arima & Edgar (1980) and Henshaw (1955), it is clear that $K_2TiSi_3O_9$ formed in our experiments is a hexagonal cyclosilicate isomorphous with wadeite ($K_2ZrSi_3O_9$).

K–Ba phosphate

The compositions of K–Ba phosphate formed during the experiments are similar to those of the starting material (Table 6). This observation suggests that the structural formula of the phosphate is $K_6Mg_3Ba_2Ca(PO_4)_6$, and is analogous to the formula of apatite calculated on an anhydrous basis. This conclusion is supported by the similarity of the X-ray-diffraction pattern to that of apatite. The synthesized phosphate is characterized by unusually high contents of K, Ba and Mg compared to common apatite. The compositions of glass co-existing with the K–Ba phosphate (Table 6) show a decrease in K_D (MgO) with increasing temperature.

TABLE 5. X-RAY DIFFRACTION DATA

$K_2TiSi_3O_9$			(K,Na)MgF_3		
	1	2		3	4
hkl	d	d	hkl	d	d
100	5.90	5.87	100	3.98	3.99
101	5.08	5.05	110	2.80	2.82
102	3.80	3.79	111	2.29	2.30
110	3.40	3.39	200	1.98	1.99
103	2.89	2.88	211	1.62	1.63
201	2.82	2.81	220	1.40	1.41
112	2.80	2.79			
211	2.17	2.16			
300	1.95	1.96			
214	1.65	1.65			
a(Å)	6.79	6.77		3.96	3.989
c(Å)	9.86	9.99			
$Å^3$	454.6	457.8		62.1	63.4

1 this study 1.73 GPa, 900°C; 2 Choisnet *et al.* (1973); 3 this study 2.557 GPa, 1300°C; 4 $KMgF_3$ Swanson *et al.* (1968). Diffractometer - Co Kα

K–Mg fluoride

Compositions of the K–Mg fluoride are similar to those of the starting material, show little variation (Table 7), and correspond to the stoichiometry (K,Na)MgF_3. X-ray powder patterns (Table 5) for this phase can be indexed on the cubic $KMgF_3$ structure (Swanson *et al.* 1968), indicating that the compound is a fluoroperovskite. In experiments containing glass, it is evident that Na is preferentially enriched in the liquid relative to the associated fluoride.

DISCUSSION

Potential fields of stability of K–Ti silicate compounds

Data from this study, Mitchell (1995), Edgar & Mitchell (1997) and Choisnet *et al.* (1973) demonstrate that particular K–Ti silicates form at particular pressures and temperatures, and that their formation is sensitive to bulk composition. From atmospheric to low pressures (1–3 GPa), the stable form of K–Ti silicate is probably the cyclosilicate $K_2TiSi_3O_9$. Naturally occurring $K_2TiSi_3O_9$ formed at low pressure has been reported by Mitchell & Steele (1992), intergrown with wadeite as a low-temperature – low-pressure mineral in a lamproite from Middle Table Mountain, Leucite Hills. Mitchell & Steele (1992) have suggested that despite the similarity in structure of the two minerals, they do not form significant solid-solutions with each other at low pressures (< 0.5 kbar). A Ba–K titanosilicate that is an intermediate member of a solid solution between $BaTiSi_3O_9$ (benitoite) and $K_2TiSi_3O_9$ has also been described as a product of the replacement of perovskite in the Hills Pond lamproite by Mitchell & Chakhmouradian (1999).

Above about 5 GPa to below 12 GPa, experiments on natural lamproite compositions have shown that the common stable K–Ti silicate phase is $K_4Ti_2Si_7O_{20}$; this may coexist with a rarer silica-poor phase, $K_4Ti_7Si_{10}O_{36}$ (Mitchell 1995, Edgar & Mitchell 1997). The structures of these titanosilicates are unknown, but possibly hexagonal on the basis of their habit (Mitchell 1995). Importantly, the compound $K_2TiSi_3O_9$ has never been encountered in any the experimental studies of natural

TABLE 6. COMPOSITIONS OF K-Ba PHOSPHATE

P(GPa)	2.57	2.57	2.57	2.57	1.73	1.73	1.73
T(°C)	1100	1200	1300	1400	1100	1200	1300
P_2O_5	36.73	35.42	33.90	33.50	33.49	33.67	33.15
MgO	9.29	8.39	3.58	2.88	3.31	3.61	2.84
CaO	5.84	7.38	11.40	11.13	11.44	12.05	11.12
BaO	25.91	24.70	28.80	29.81	29.17	28.37	30.62
K_2O	22.72	24.08	22.20	22.10	22.91	22.22	21.99
Total	99.49	99.97	99.88	99.42	100.32	99.92	99.72
Structural formula based on 24 oxygens							
P	6.030	5.990	6.002	5.992	5.692	5.956	5.996
Mg	2.760	2.460	1.116	0.912	1.038	1.124	0.904
Ca	1.248	1.604	2.554	2.534	2.578	2.098	2.546
Ba	2.024	1.934	2.360	2.482	2.404	2.322	2.564
K	5.778	6.050	5.923	5.992	6.146	5.992	5.992
Coexisting glass (melt)							
P_2O_5	38.82	37.10	35.19	35.58	35.54	37.25	35.89
MgO	19.35	16.18	14.15	13.27	13.87	16.34	13.54
CaO	6.82	8.07	5.99	6.96	6.78	6.14	7.16
BaO	20.98	21.26	23.35	20.84	22.10	20.02	22.39
K_2O	9.67	12.98	17.77	19.93	18.08	19.54	19.91
K_D(MgO)	0.48	0.52	0.25	0.22	0.24	0.22	0.21

lamproite over a very wide range of pressures (0.1 – 12 GPa) and temperatures. In this context, the study of Edgar *et al.* (1992) of the Smoky Butte lamproite from 0.8 to 3 GPa is especially relevant, as it demonstrated that K–Ti-titanates did not form as liquidus phase at these pressures, and the only Ti-rich phase to crystallize, at pressures of less than 1 GPa, was the Fe–Ti-oxide armalcolite. Attempts to synthesize $K_4Ti_2Si_7O_{20}$ at 6 GPa and 1400° – 1200°C from stoichiometric mixes of carbonates and oxides have been unsuccessful, as the reaction products consist of wadeite-structured $K_2TiSi_3O_9$ and coesite (Luth & Mitchell, unpubl. data).

The relationship between $K_2TiSi_3O_9$ and $K_4Ti_2Si_7O_{20}$ formed at high pressures using lamproite bulk compositions could be, in part, a function of silica activity as:

$$2(K_2TiSi_3O_9) + SiO_2 = K_4Ti_2Si_7O_{20}$$

However, even if this reaction is strongly pressure-dependent, it cannot explain the absence of the cyclosilicate as a low-pressure phase in the experiments on SiO_2-rich natural lamproites; other controls on its crystallization must be operating. Mitchell (1995) proposed a reciprocal relationship between TiO_2 and SiO_2, in which the Ti content increases with decreasing temperature and pressure for titanosilicates found in the experiments on Leucite Hills lamproite. For the K–Ti silicates formed in the relatively Ti-rich Smoky Butte lamproite, Edgar & Mitchell (1997) found this correlation to be weak and noted a systematic decrease in Zr with increasing Si. In experiments on lamproite from Oscar, West Kimberley (Mitchell, unpubl. data), K–Ti silicates do not form, and the high-pressure (5–8 GPa) suprasolidus phase assemblage is coesite, rutile and Ti-rich phlogopite. These data demonstrate clearly that the bulk composition of natural lamproitic liquids plays a major role in controlling the crystallization of titanosilicates. The experimental data show that their formation is preceded by the precipitation of coesite, which drives the remaining liquid to silica oversaturation. This in turn leads to increased Ti activity and titanate or K-titanosilicate formation. Unfortunately, why cyclosilicates such as $K_2TiSi_3O_9$ do not form remains an unresolved problem.

TABLE 7. COMPOSITIONS OF K-Mg FLUORIDE

P(GPa)	2.57	2.57	2.57	2.57	1.73	1.73	0.85	0.85
T(°C)	1100	1200	1300	1400	1200	1250	1000	1100
K	27.77	28.37	28.34	28.62	29.12	29.66	26.67	28.32
Na	3.44	3.07	3.03	2.77	2.30	2.31	4.14	3.12
Mg	20.40	21.76	20.47	20.22	20.65	20.28	20.54	20.13
F	47.45	47.05	47.88	47.45	46.63	46.54	48.14	47.15
Total	99.06	100.15	99.72	99.06	98.70	98.90	99.49	98.72
Structural formula based on 3 fluorines								
K	0.853	0.876	0.863	0.879	0.910	0.927	0.807	0.880
Na	0.180	0.162	0.157	0.145	0.122	0.123	0.123	0.165
Mg	1.008	1.085	1.003	0.999	1.039	1.019	1.001	1.005
Coexisting glass (melt)								
K	-	-	-	25.16	-	25.44	-	24.02
Na	-	-	-	5.43	-	4.74	-	6.78
Mg	-	-	-	21.97	-	21.23	-	22.67
F	-	-	-	48.19	-	48.03	-	45.92

At the highest pressures (12 GPa) used in experiments on Smoky Butte lamproite, K–Ti silicates were not formed (Edgar & Mitchell 1997). At this pressure at 1300° and 1400°C , a Ti-free silicate, $K_2Si_4O_9$, coexists with rutile and coesite, suggesting that K–Ti silicates may have an upper stability-limit of 10–12 GPa. This interpretation is in accord with the observed decrease in Ti (and Zr) with increasing Si in K–Ti silicates with increasing pressure. The compound $K_2Si_4O_9$ has been synthesized by Swanson & Prewitt (1983) and shown to be a wadeite-structured phase with Si in both tetrahedral and octahedral coordination, *i.e.*, $K_2{}^{VI}Si^{IV}Si_3O_9$. These data show that it is possible for wadeite-structured cyclosilicates to crystallize from lamproitic melts under some conditions.

Stability of K–Ba phosphate

K–Ba phosphate appears to be stable from 0.8 to 10 GPa on the basis of this study and that of Edgar & Mitchell (1997). Unlike the K–Ti silicates, its stability field does not appear to be influenced by bulk composition of the starting material, as it forms in simple synthetic systems and from natural lamproite compositions. The composition of the K–Ba phosphate and coexisting melt (Table 6) indicates that Mg acts as an incompatible element, with $0.2 < K_D{}^{Mg} < 0.5$. Thus, Mg contents of the melt are significantly higher than those of coexisting phosphate. The distribution of Mg is affected by both temperature and pressure, in contrast with the situation in most silicates under comparable P–T conditions, where Mg is buffered by ferromagnesian silicates.

Stability of K–Mg fluoride

This work, and that of Edgar & Pizzolato (1995), Zhao *et al.* (1994) and Mitchell (1997), show that cubic

$(K,Na)MgF_3$ is stable in a variety of bulk compositions, from 1 bar to at least 6.5 GPa at temperatures less than 1000°C. This study shows that the compound melts congruently. The compound $(K,Na)MgF_3$ has recently been found to occur in nature as a late-stage groundmass mineral in Oldoinyo Lengai natrocarbonatite (Mitchell 1997) and is the K-counterpart of neighborite ($NaMgF_3$).

Petrological implications

Compounds investigated in this study are rich in K, Ba, P, Ti, Mg and F, and can act as repositories for many of the "incompatible" elements characteristic of lamproitic and other potassic magmas. The experimental data demonstrate that these compounds are stable at pressures and temperatures equivalent to those occurring throughout the lower crust and the lithospheric mantle. If either of these regimes is subject to alkali metasomatism by mantle-derived alkaline magmas, it is conceivable that such compounds will form and host a wide suite of trace elements. The formation of such "metasomes" by mantle-derived fluids has been discussed by Haggerty (1989) and Thibault *et al.* (1992). Partial melting of such metasomatized host mantle can lead to incompatible-element-enriched magmas (Foley 1992, Mitchell 1995). Our experimental data show that K–Ba phosphate and "fluoroperovskite" can exist over a very wide range of pressures and temperatures. We infer that discrete metasomes defined by the occurrence of these compounds over a particular depth-range will probably not exist.

The K–Ti silicates that can provide a major host for K can play a significant role in controlling K-content of potassic volcanic rocks. Our data and those of Mitchell & Edgar (1997) suggest that any metasomatic effects induced by alkaline magmas in the lithospheric mantle will result in the formation of potassian titanian richterite and titanian phlogopite rather than $K_4Ti_2Si_7O_{20}$. Although $K_2TiSi_3O_9$ is stable from 1 bar to at least 6.5 GPa, it would appear that its formation is subject to significant bulk-composition controls. Thus, our data suggest that the upper asthenospheric mantle could contain metasomes enriched in $K_4Ti_2Si_7O_{20}$, and that similar compounds are unlikely to occur in the lithospheric mantle. The controls of the formation of these diverse K–Ti silicates obviously require considerable further investigation given that they are potentially major repositories for potassium in the upper mantle.

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