TITANIUM SOLUBILITY IN SYNTHETIC PHLOGOPITE SOLID SOLUTIONS

J.-L. ROBERT

CNRS, Centre Recherches sur la Synthèse et la Chimie des Minéraux, Orléans (France) *
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ABSTRACT

Robert, J.-L., 1976. Titanium solubility in synthetic phlogopite solid solutions. Chem. Geol., 17: 213—227.

An experimental determination has been made of the solubility of Ti in phlogopite, in the system $K_2O-MgO-TiO_2-Al_2O_3-SiO_2-H_2O$. The fixation of Ti^{4+} in the phlogopite structure is considered to follow the substitutional model: $2Si^{IV}, Mg^{VI} \rightleftharpoons 2Al^{IV}, Ti^{VI}$. Titanium substitutes in octahedral sites and does not replace Si^{4+} in tetrahedral sites.

The solubility of Ti in phlogopite is very small at 600°C and 1,000 bar (0.07 Ti atom per formula unit); it increases up to 0.2 Ti atom per formula unit at 800°C and 1,000 bar, and 0.7 Ti atom per formula unit at 1,000°C and 1,000 bar.

Pressure reverses this trend and reduces the solubility (0.2 Ti atom per formula unit at 1,000°C and 7,000 bar.

The experimental results explain why Ti-rich phlogopites are usually encountered in lavas (lamproites), and also, why the Ti content of biotite increases with metamorphic grade. However, any use of the solubility of Ti in biotites as a geothermometer or a geobarometer would necessitate a determination of the influence of Fe on that solubility.

INTRODUCTION

Because of the small Ti^{4+} content in natural biotites, generally less than 2% by weight of TiO_2, the position of this ion in the trioctahedral mica structure is not clearly known. Most of the statistical examinations of empirical structural formulae suggest that Ti^{4+} is in octahedral position, replacing Fe^{2+}, Mg^{2+} or Al^{3+} (Oki, 1961; Kwak, 1968; Czamanske and Wones, 1973), however, some of them seem to indicate that Ti may be in tetrahedral positions substituting for Si^{4+} (Kunitz, 1966).

It is interesting then to examine these conclusions through a systematic synthesis of Ti-bearing micas under various hydrothermal conditions. The study permits not only the elucidation of the substitutional relation accom-

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*Address: CNRS, Centre de Recherches sur la Synthèse et la Chimie des Minéraux, Rue de la Férollerie, 45045 Orléans Cedex, France.

panying Ti incorporation in this mineral, but also the dependence upon temperature and pressure of the solubility of this element in phlogopitic micas.

The recent reports of Ti-rich micas in rocks of the granulite facies (Zakrutin and Grigorenko, 1968), in xenoliths in some volcanic rocks (Flower, 1971) suggest that the Ti content in micas varies considerably as a function of the physical conditions of their formation.

The present study deals with the experimental results on this problem in the system $K_2O-MgO-TiO_2-Al_2O_3-SiO_2-H_2O$. Because of the technical complication of oxygen fugacity control, the introduction of Fe was avoided in this preliminary stage of the study.

EXPERIMENTAL PROCEDURES

The study is based upon the crystallization under hydrothermal conditions of several oxide mixtures corresponding to different compositions in the system. The synthetic products are then examined in order to identify the crystalline phases present and to determine the compositional range of oxide mixtures which give only a single trioctahedral mica phase.

CHOICE OF THE COMPOSITIONS TO BE STUDIED

It is neither reasonable nor realistic for the purpose of the present study to attempt the investigation of the phase relations encountered in this six-component system. The study of Ti-phlogopites is efficiently accomplished by choosing appropriate compositions to give a single-mica phase.

This choice was guided by a crystallochemical consideration of Ti^{4+} incorporation in phlogopite and by the results obtained on the compositional variation of phlogopite solid solutions in the system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$ (Robert, 1976). The introduction of Ti into the phlogopite composition can probably be realized in one of the following ways.

(1) By the substitution of two Mg atoms by one Ti atom, with creation of one octahedral vacant site in the structure. This first type of substitution was already investigated by Forbes and Flower (1974) who succeeded in crystallizing the phase $K_2Mg_4TiAl_2Si_6O_{20}(OH)_4$ at temperatures superior to 1,100°C and very high pressures (7—30 kbar).

(2) By the substitution of one Mg atom by one Ti atom in the octahedral site, with simultaneous replacement of two Si atoms by two Al atoms in tetrahedral sites. This substitution may be expressed by $2Si^{IV}, Mg^{VI} \rightleftharpoons 2Al^{IV}, Ti^{VI}$ and leads to the theoretical end-member $K_2(Mg_5Ti)(Si_4Al_4)O_{20}(OH)_4$.

(3) By the substitution of one Si atom by one Ti atom in the tetrahedral sites. As it will be seen in the following pages, attempts to place Ti^{4+} in the tetrahedral position were unsuccessful.

Only the second type of substitution has been investigated in detail in the present work. The phlogopite solid solution in the system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$ has a considerable compositional range according

to the generalized structural formula on the basis O = 20 per formula unit:

$$K_2(Mg_{6-x-y}Al_x \square_y)(Si_{6-x+2y}Al_{2+x-2y})O_{20}(OH)_4$$
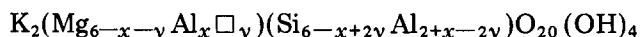
in which x designates the amount of the substitution $Si^{IV},Mg^{VI} \rightleftharpoons Al^{IV},Al^{VI}$ and y the amount of the substitution of the type $2Al^{IV},Mg^{VI} \rightleftharpoons 2Si^{IV},\square^{VI}$. The variation of these two parameters is dependent on temperature of synthesis. The possibility of presence of H_3O^+ in place of K^+ was excluded in this study.

The combination of the compositional range of non-titaniferous phlogopites and the substitutional types for Ti incorporation indicates that the most probable compositions of Ti-bearing phlogopites will exist within a conical volume in the tetrahedron $MgO-Al_2O_3-TiO_2-SiO_2$ (Fig.1, see p. 218). The base of the cone is the compositional range of Ti-free phlogopites in the TiO_2-free part of the system and the top of the cone is the theoretical end-member for the substitution studied indicated by T in Fig.1. This represents, in a very simplified manner, the chemical system of the present study. The K_2O content of the system was neglected in this representation because the compositions studied always contain sufficient amount of K_2O to give the micaceous phase alone. The H_2O content was omitted because the experiments were always performed in the presence of excess water.

STARTING MATERIAL FOR THE SYNTHESES

The starting materials used in this study were mixtures in appropriate proportions of the oxides SiO_2, Al_2O_3, MgO, K_2O and TiO_2. The mixtures of the first four oxides were prepared in the form of gels using ordinary procedures. For this purpose, the tetraethyl orthosilicate, nitrates of Al, Mg and K, ethanol and ammonium hydroxide of analytical pure reagents were used. Analytical-grade TiO_2 (anatase) was mixed intimately with these gels to obtain the desired composition. The accuracy of bulk compositions is estimated to be ± 5% of the calculated composition.

HYDROTHERMAL TREATMENT

About 30—100 mg of oxide mixture and about 15—50 μl of distilled water were introduced into a Au or Pt tubing of 2.5 or 4.8 mm external diameter. The tube is then sealed by arc-welding and placed in a pressure vessel. Runs at 600 and 800°C, 1,000 bar were performed in cold-seal pressure vessels and those at 1,000°C, 1,000 and 7,000 bar were realized in an internally heated pressure vessel using compressed Ar as the pressure medium.

During the experiments (2—10 days in general), the temperature showed a variation of ± 5°C around the desired value. In the case of the internally heated pressure vessel, this temperature variation was ± 10°C. The pressure of the experiment was checked at regular intervals by using a Bourdon-type pressure gauge in the case of the cold-seal pressure vessel and by a manganin resistance cell in the case of the internally heated bomb. The pressure of the run was maintained within 2% of the desired value.

IDENTIFICATION OF THE CRYSTALLINE PHASES IN THE PRODUCT*

The presence or absence of crystalline phases other than mica in run products was examined by observation under the microscope. Except in the cases of very high-temperature or -pressure crystallization, mica flakes are very small and constitute aggregates of random orientation. The average refractive index of these aggregates increases from 1.555 in magnesian phlogopite to about 1.575 in Ti-rich micas. Immersion liquids having a refractive index as close as possible to that of micaceous aggregates were used in optical examination. In this way the presence of 2—3% of other phases can be detected without difficulty if the grain size of the phase is not too small. The detection limit can be as high as 5% in the case of an impurity of very small grain size. When a mica phase is present alone, it has the bulk composition of the starting material.

In spite of the relative ease of the detection of minor crystalline impurities by the optical method, their identification is certain only by a combination of optical and X-ray observations. In most of the cases, X-ray powder diffraction permits the detection and identification of accessory phases in concentration of more than 5%.

The titaniferous oxides: rutile (TiO_2), geikielite ($MgTiO_3$)

At 1,000°C and 1,000 bar, rutile appears as prisms of about 5—10 μm in length. Under these conditions rutile commonly shows the characteristic "geniculated twin" associating two equal-sized individuals. In run products of high temperature, geikielite has small rounded grains of 1—6 μm in diameter; more rarely, some platty triangular grains are obtained. Both rutile and geikielite have a high birefringence and a high refractive index ($\bar{n} > 2$). When they have crystallized at 600°C or 800°C and 1,000 bar, the grains are small ($\leqslant 2$ μm) and it is not easy to distinguish one from the other by optical methods. However, morphological criteria were sometimes used: geikielite is present as small rounded grains, whereas rutile gives short sticks. X-ray identification of these minerals is possible only when they represent about 5% of the product. The peaks used for the identification of geikielite are at 2.22, 2.72 and 3.71 Å; for rutile they are at 2.49 and 3.26 Å. The observed values seem to indicate that these phases are stoichiometric, as is the case for spinel and corundum.

RESULTS

The experimental results obtained during this study are summarized in Table I and represented graphically in Figs. 1—4.

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*The abbreviations used to designate the phases:
Br = brucite; Cor = corundum; Fo = forsterite; Gk = geikielite; Ks = kalsilite; "L" = Al-free mica $K_2Mg_5Si_8O_{20}(OH)_4$; Lc = leucite; Phl = theoretical phlogopite; Phl ss = phlogopite solid solution; Qz = quartz; Rut = rutile; Sp = spinel.

TABLE I

Principal compositions used in the determination of the compositional range of titano-phlogopite and of its phase relations at 600°C and 1,000 bar. The compositions are given in mole% of oxides

Condensed starting material	K_2O	MgO	TiO_2	Al_2O_3	SiO_2	Phase assemblages
T: $K_2(Mg_5Ti)Si_4Al_4)O_{20}(OH)_4$						
Phl$_{95}$—T_5	7.17	42.65	0.36	7.53	42.29	Ti-Phl ss
Phl$_{93}$—T_7	7.18	42.57	0.50	7.68	42.07	Ti-Phl ss
Phl$_{90}$—T_{10}	7.19	42.45	0.72	7.91	41.73	Ti-Phl ss + Gk + Sp
Phl$_{75}$—T_{25}	7.27	41.82	1.82	9.09	40.00	Ti-Phl ss + Gk + Sp + (Lc)*
Phl$_{50}$—T_{50}	7.41	40.74	3.70	11.11	37.04	Ti-Phl ss + Gk + Sp + (Lc)
α: $K_2(Mg_{3.9}Al_{1.63}\square_{0.45})(Si_{5.25}Al_{2.75})O_{20}(OH)_4$						
α_{95}—T_5	8.08	31.94	0.40	17.69	41.89	Ti-Phl ss
α_{93}—T_7	8.07	32.08	0.56	17.54	41.65	Ti-Phl ss
α_{90}—T_{10}	8.05	32.30	0.81	17.56	41.28	Ti-Phl ss + Gk + Sp
α_{75}—T_{25}	7.99	33.37	2.00	17.18	39.46	Ti-Phl ss + Gk + Sp + (Lc)
α_{50}—T_{50}	7.90	35.10	3.94	16.57	36.49	Ti-Phl ss + Gk + Sp + (Lc)
γ: $K_2(Mg_{4.675}Al_{0.975}\square_{0.35})(Si_{5.725}Al_{2.275})O_{20}(OH)_4$						
γ_{95}—T_5	7.68	36.02	0.38	12.62	43.30	Ti-Phl ss
γ_{93}—T_7	7.68	36.07	0.54	12.68	43.03	Ti-Phl ss
γ_{90}—T_{10}	7.68	36.15	0.77	12.76	42.64	Ti-Phl ss + Rut + (Lc)
γ_{80}—T_{20}	7.68	36.40	1.54	13.06	41.32	Ti-Phl ss + Rut + (Lc)
γ_{70}—T_{30}	7.69	36.66	2.31	13.35	40.00	Ti-Phl ss + Rut + (Lc)
γ_{40}—T_{60}	7.69	37.43	4.61	14.22	36.05	Ti-Phl ss + Rut + Gk + (Lc)
β: $K_2(Mg_2Al_4)(Si_2Al_6)O_{20}(OH)_4$						
β_{90}—T_{10}	9.71	22.33	0.97	45.63	21.36	Ti-Phl ss + Sp + Cor + Rut + Ks
β_{80}—T_{20}	9.43	24.53	1.89	41.51	22.64	Ti-Phl ss + Sp + Cor + Rut + Ks
β_{70}—T_{30}	9.17	26.61	2.75	37.62	23.85	Ti-Phl ss + Sp + Cor + Rut + Ks
β_{60}—T_{40}	8.93	28.57	3.57	33.93	25.00	Ti-Phl ss + Sp + Cor + Rut + Ks
β_{50}—T_{50}	8.70	30.43	4.35	30.43	26.09	Ti-Phl ss + Sp + Gk + Rut + Lc
β_{40}—T_{60}	8.48	32.20	5.08	27.12	27.12	Ti-Phl ss + Sp + Gk + Rut + Lc
β_{20}—T_{80}	8.07	35.48	6.45	20.97	29.03	Ti-Phl ss + Sp + Gk + Lc
T	7.69	38.46	7.69	25.39	30.77	Ti-Phl ss + Sp + Gk + Lc

*( ): phase present in very little amount.

At 600°C and 1,000 bar (Table I)

As it is presently known (Robert, 1976), phlogopite does not have a constant composition in the system K_2O—MgO—Al_2O_3—SiO_2—H_2O. The structural formula of the mica derived from ideal phlogopite by the substitution $2Si^{IV},Mg^{VI} \rightleftharpoons 2Al^{IV},Ti^{VI}$ is: $K_2(Mg_5Ti)(Si_4Al_4)O_{20}(OH)_4$, (point T, Fig. 1).
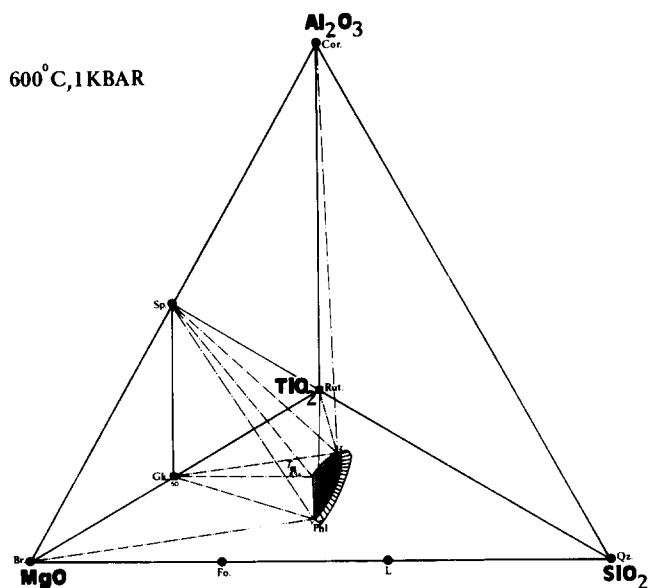
Fig.1. Phase relations observed concerning titanophlogopites at 600°C and 1,000 bar. The compositions are expressed in mole% of the oxides MgO—Al_2O_3—SiO_2—TiO_2. In this representation, TiO_2 is apical.
Br. = brucite; *Cor.* = corundum; *Fo.* = forsterite; *Gk.* = geikielite; *L* = Al-free mica $K_2Mg_6Si_8O_{20}(OH)_4$; *Phl.* = theoretical phlogopite; *Qz.* = quartz; *Rut.* = rutile; *Sp.* = spinel.
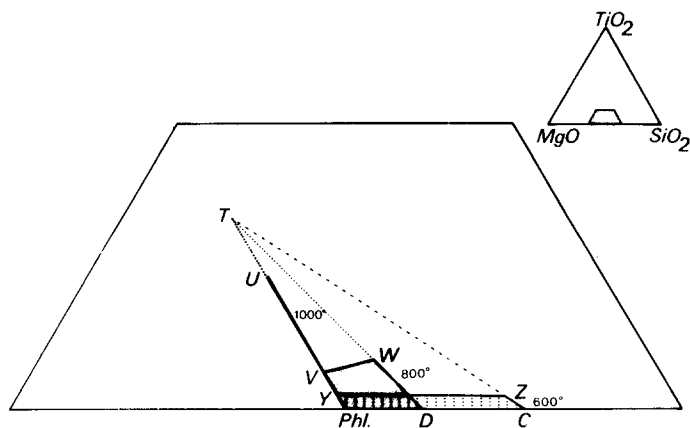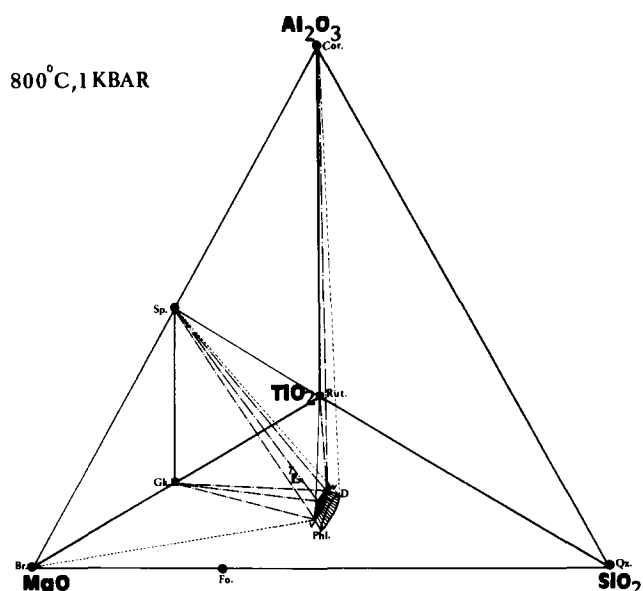

Fig.2. Schematic representation of the compositional range of titanophlogopite at 600° and 800° and 1,000°C and 1,000 bar, in a diagram MgO—TiO_2—SiO_2.
Phl. = theoretical phlogopite.

Fig. 3. Phase relations observed concerning titanophlogopites at 800°C and 1,000 bar. The compositions are expressed in mole% of the oxides MgO—Al_2O_3—SiO_2—TiO_2. In this representation, TiO_2 is apical.

Br. = brucite; *Cor.* = corundum; *Fo.* = forsterite; *Gk.* = geikielite; *Phl.* = phlogopite; *Qz.* = quartz; *Rut.* = rutile; *Sp.* = spinel.
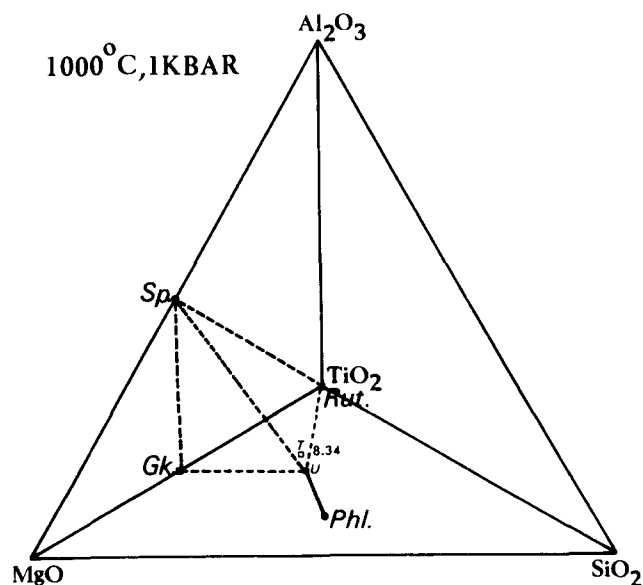

Fig. 4. Phase relations observed concerning titanophlogopites at 1,000°C and 1,000 bar. The compositions are expressed in mole% of the oxides MgO—Al_2O_3—SiO_2—TiO_2. In this representation, TiO_2 is apical.

Gk. = geikielite; *Phl.* = theoretical phlogopite; *Rut.* = rutile; *Sp.* = spinel.

The compositions studied form a conical volume defined by point T (top of the cone) and by the compositional range of Ti-free phlogopites (base of the cone). Some compositions outside of this conical volume have been investigated also to determine the phase assemblages present.

At 600°C and 1,000 bar, the solubility of Ti in phlogopites is very low. It attains only 0.07 ± 0.004 Ti a./f.u. (atom per formula unit). This maximum amount of Ti (0.67% by weight of TiO_2) does not vary significantly with the different values of x and y of the general formula of Ti-free phlogopites. Fig.1 depicts the solid solution in titaniferous phlogopites in the system at 600°C and 1,000 bar.

Around this small domain of a single-mica phase, the system is divided in the following phase domains as given in Table II (see also Fig.1). The assemblage (8): Ti-phlogopite solid solution—rutile occurs at very aluminous or very siliceous compositions. A wide compositional range of Ti-phlogopite may coexist with rutile alone, it is indicated by the grey surface in Fig.1.

The assemblages (1) and (2) have been obtained from very aluminous compositions. The composition of the Ti-phlogopite solid solution in these assemblages (1) and (2) can be estimated to be:

$$K_2(Mg_{3.98}Ti_{0.07}Al_{1.53}\square_{0.42})(Si_{5.16}Al_{2.84})O_{20}(OH)_4 \qquad \text{(point } Z \text{, Fig.1)}$$
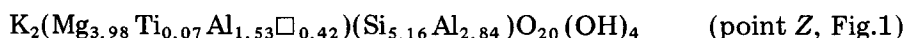
judging from the presence of corundum in these assemblages. In the Ti-free system, the composition of phlogopite solid solution in equilibrium with corundum was estimated to be:

$$K_2(Mg_{3.9}Al_{1.65}\square_{0.45})(Si_{5.25}Al_{2.75})O_{20}(OH)_4)$$
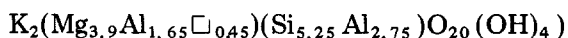
In the assemblages (3) and (4), Ti-phlogopite solid solution has the composition indicated above (point Z, Fig.1). For more magnesian compositions, assemblage (5) is obtained: Ti-phlogopite solid solution—geikielite—spinel. In this assemblage, the composition of the mica is quite variable. Towards Al-rich compositions it is limited by point Z, towards Mg-rich compositions by point Y. The composition of phlogopite corresponding to point Y is:
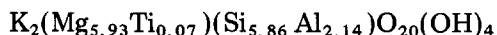
$$K_2(Mg_{5.93}Ti_{0.07})(Si_{5.86}Al_{2.14})O_{20}(OH)_4$$

TABLE II

Phase assemblages at 600°C and 1,000 bar for the system $K_2O-MgO-TiO_2-Al_2O_3-SiO_2-H_2O$

(1) Ti-Phl ss + Rut + Cor
(2) Ti-Phl ss + Rut + Cor + Sp
(3) Ti-Phl ss + Rut + Sp
(4) Ti-Phl ss + Rut + Gk   + Sp
(5) Ti-Phl ss + Gk   + Sp
(6) Ti-Phl ss + Gk   + Rut
(7) Ti-Phl ss + Gk
(8) Ti-Phl ss + Rut

which corresponds to the limit in solid solution between theoretical phlogo-
pite Phl and hypothetical Ti-phlogopite T. It is clear from an inspection of
Fig.1 and Table II, that the assemblage geikielite ($MgTiO_3$)—corundum
(α-Al_2O_3) is impossible under these conditions. The following assemblages
of three solid phases have been obtained in a systematic investigation of the
system MgO—Al_2O_3—TiO_2—H_2O at 600°C and 800°C, 1,000°C and 1,000 bar:

Br + Sp + Gk
Rut + Sp + Gk
Rut + Sp + Cor

In the case of crystallization of phase assemblages: mica + oxides, from

TABLE III

Principal compositions used at 800°C and 1,000 bar, to determine the compositional range
of titanophlogopite and of its phase relations

| Condensed starting material	K_2O	MgO	TiO_2	Al_2O_3	SiO_2	Phase assemblages
T: $K_2(Mg_5Ti)(Si_4Al_4)O_{20}(OH)_4$						
Phl_{95}—T_5	7.17	42.65	0.36	7.53	42.29	Ti-Phl ss
Phl_{90}—T_{10}	7.19	42.45	0.72	7.91	41.73	Ti-Phl ss
Phl_{85}—T_{15}	7.22	42.24	1.08	8.30	41.16	Ti-Phl ss
Phl_{80}—T_{20}	7.25	42.03	1.45	8.69	40.58	Ti-Phl ss
Phl_{75}—T_{25}	7.27	41.82	1.82	9.09	40.00	Ti-Phl ss + Gk + Sp + (Ks)*
Phl_{50}—T_{50}	7.41	40.74	3.70	11.11	37.04	Ti-Phl ss + Gk + Sp + (Ks)
D: $K_2(Mg_5Al_{0.75}\square_{0.25})(Si_{5.75}Al_{2.25})O_{20}(OH)_4$						
D_{95}—T_5	7.55	37.77	0.38	11.52	42.78	Ti-Phl ss
D_{90}—T_{10}	7.56	37.81	0.76	11.72	42.15	Ti-Phl ss
D_{85}—T_{15}	7.57	37.84	1.14	11.92	41.53	Ti-Phl ss
D_{80}—T_{20}	7.58	37.88	1.51	12.12	40.91	Ti-Phl ss
D_{75}—T_{25}	7.58	37.92	1.90	12.32	40.28	Ti-Phl ss
D_{50}—T_{50}	7.62	38.10	3.81	13.33	37.14	Ti-Phl ss + Gk + Sp + (Ks)
β: $K_2(Mg_2Al_4)(Si_2Al_6)O_{20}(OH)_4$						
β_{90}—T_{10}	9.71	22.33	0.97	45.63	21.36	Ti-Phl ss + Cor + Sp + Rut + Ks
β_{80}—T_{20}	9.43	24.53	1.89	41.51	22.64	Ti-Phl ss + Cor + Sp + Rut + Ks
β_{70}—T_{30}	9.17	26.61	2.75	37.62	23.85	Ti-Phl ss + Cor + Sp + Rut + Ks
β_{60}—T_{40}	8.93	28.57	3.57	33.93	25.00	Ti-Phl ss + Cor + Sp + Rut + Ks
β_{50}—T_{50}	8.70	30.43	4.35	30.43	26.09	Ti-Phl ss + Cor + Sp + Rut + Ks
β_{40}—T_{60}	8.48	32.20	5.08	27.12	27.12	Ti-Phl ss + Cor + Sp + Rut + Ks
β_{30}—T_{70}	8.26	33.88	5.79	23.97	28.10	Ti-Phl ss + Sp + Rut+Gk + (Ks)
T	7.69	38.46	7.69	15.39	30.77	Ti-Phl ss + Sp + Gk + (Ks)

*( ): phase present in very little amount.

hypothetical mica composition, K_2O is in excess. This excess of K_2O gives kalsilite when the bulk composition is very aluminous (assemblages (1)—(3)) and leucite when it is more magnesian (assemblages (4) and (5)). For the sake of clarity, the two phases have not been indicated on the figure.

INFLUENCE OF TEMPERATURE ON THE SOLUBILITY OF Ti IN PHLOGOPITE

At 800°C and 1,000 bar (Table III)

The compositional range of phlogopite without Ti observed at 600°C and 1,000 bar is reduced at 800°C and 1,000 bar (Robert, 1976). The most aluminous phlogopite, which also has the fewest octahedral ions, has the composition:

$$K_2(Mg_5Al_{0.75} \square_{0.25})(Si_{5.75}Al_{2.25})O_{20}(OH)_4 \qquad \text{(point } D, \text{ Fig.3)}$$
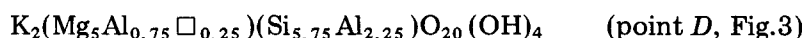
At 800°C and 1,000 bar, the solubility of Ti in phlogopite is much greater than that of 600°C and 1,000 bar. This solubility differs according to the different values of x and y in the general formula of Ti-free phlogopites. The theoretical phlogopite ($x = y = 0$) accepts 20 mole% of Ti-phlogopite T in solid solution (1.9 wt.% of TiO_2) whereas the most aluminous phlogopite ($x = 0.75$; $y = 0.25$) accepts 25 mole% of Ti-phlogopite T (2.4 wt.% of TiO_2). This fact is illustrated by Fig.2 which shows the compositional range of Ti-phlogopite at 600°C and 800°C, 1,000°C and 1,000 bar, in a diagram MgO—TiO_2—SiO_2. Thus, not only temperature, but also the proportion of SiO_2, Al_2O_3 and MgO in phlogopite has an influence on the solubility of the Ti-mica end-member T.

The phase relations of Ti-phlogopite at 800°C and 1,000 bar are very similar to those of 600°C and 1,000 bar. The assemblages as given in Table IV have been observed (Fig.3):

Most of the Ti-phlogopite-bearing assemblages at 800°C and 1,000 bar

TABLE IV

Phase assemblages at 800°C and 1,000 bar for the system K_2O—MgO—TiO_2—Al_2O_3—SiO_2—H_2O

|	Estimated composition of Ti-Phl ss
(1) Ti-Phl ss—Rut—Cor (2) Ti-Phl ss—Rut—Cor—Sp (3) Ti-Phl ss—Rut—Sp (4) Ti-Phl ss—Rut—Gk —Sp	$K_2(Mg_5Ti_{0.25}Al_{0.56} \square_{0.19})(Si_{5.31}Al_{2.69})O_{20}(OH)_4$ (point W, Figs. 2 and 3).
(5) Ti-Phl ss—Gk —Sp (6) Ti-Phl ss—Gk —Rut (7) Ti-Phl ss—Gk	variable from $K_2(Mg_5Ti_{0.25}Al_{0.56} \square_{0.19})(Si_{5.31}Al_{2.69})O_{20}(OH)_4$ to $K_2(Mg_{5.8}Ti_{0.2})(Si_{5.6}Al_{2.4})O_{20}(OH)_4$ \qquad (point V)
(8) Ti-Phl ss—Rut	variable

contain rutile. The compositional range of Ti-phlogopite associated with gei-kielite and spinel, geikielite and rutile or geikielite alone is limited to the curved line V—W in Fig.3. Just as at 600°C and 1,000 bar, there is excess of K_2O in the product when the oxide phases crystallize with a micaceous phase. This excess of K_2O gives kalsilite which is present with all the assemblages indicated.

At 1,000°C and 1,000 bar (Table V)

At these conditions only phlogopite of theoretical composition ($x = y = 0$) is stable in the system K_2O—MgO—Al_2O_3—SiO_2—H_2O (Robert, 1976). Compositions intermediate between Phl and T have been investigated. Theoretical phlogopite, $K_2Mg_6(Si_6Al_2)O_{20}(OH)_4$, accepts 70±5 mole% of Ti-phlogopite T, $K_2(Mg_5Ti)(Si_4Al_4)O_{20}(OH)_4$, in solid solution. The most titaniferous mica obtained is then:

$$K_2(Mg_{5.3}Ti_{0.7})(Si_{4.6}Al_{3.4})O_{20}(OH)_4$$
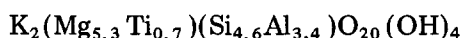
and contains 6.6 wt.% of TiO_2. It is indicated by point U in Fig.4. Beyond this limit of solubility of Ti, the assemblage Ti-Phl ss—Rut—Gk—Sp appears (Fig.4). The composition of Ti-Phl ss in this assemblage is:

$$K_2(Mg_{5.3}Ti_{0.7})(Si_{4.6}Al_{3.4})O_{20}(OH)_4$$
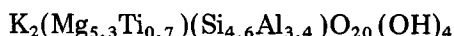
On the possibility of substitution $Si^{IV} \rightleftharpoons Ti^{IV}$

At 1,000°C and 1,000 bar, the solubility of Ti in phlogopite is very extensive. These conditions are favourable to test the possibility of replacing Si^{IV} by Ti^{IV} in the mica structure. This substitution gives a hypothetical mica $K_2Mg_6(Si_5Al_2Ti)O_{20}(OH)_4$. Some compositions lying between this mica and theoretical phlogopite have been investigated. None of them has given a

TABLE V

Compositions used in the determination of the compositional range of titanophlogopite at 1,000°C and 1,000 bar

Condensed starting material	K_2O	MgO	TiO_2	Al_2O_3	SiO_2	Phase assemblages
Phl_{90}—T_{10}	7.19	42.45	0.72	7.91	41.73	Ti-Phl ss
Phl_{80}—T_{20}	7.25	42.03	1.45	8.69	40.58	Ti-Phl ss
Phl_{70}—T_{30}	7.30	41.60	2.19	9.49	39.42	Ti-Phl ss
Phl_{60}—T_{40}	7.35	41.18	2.94	10.29	38.24	Ti-Phl ss
Phl_{50}—T_{50}	7.41	40.74	3.70	11.11	37.04	Ti-Phl ss
Phl_{40}—T_{60}	7.46	40.30	4.48	11.94	35.82	Ti-Phl ss
Phl_{30}—T_{70}	7.52	39.85	5.26	12.78	34.59	Ti-Phl ss
Phl_{20}—T_{80}	7.58	39.39	6.06	13.64	33.33	Ti-Phl ss + Sp + Gk + Rut
T	7.69	38.46	7.69	15.39	30.77	Ti-Phl ss + Sp + Gk + Rut

micaceous phase alone. The composition corresponding to
$K_2Mg_6(Si_5Al_2Ti)O_{20}(OH)_4$ gave the assemblage: Ti-Phl ss—Gk—Fo—Orthorhombic kalsilite.

These experiments show clearly that:

(1) The fixation of Ti in phlogopite occurs according to the substitution $2Si^{IV},Mg^{VI} \rightleftharpoons 2Al^{IV},Ti^{VI}$.

(2) The solubility of Ti in phlogopite increases greatly with increasing temperature.

Influence of pressure

All the previous results reported have been obtained at 1,000 bar. In order to assess the influence of an increase of pressure on the solubility of Ti, two kinds of runs were performed:

(1) At 600°C and 2,000 bar, results indicate an important decrease of the solubility of Ti, which becomes less than 0.1 wt.% of TiO_2.

(2) At 1,000°C and 7,000 bar, the maximum solubility of Ti is 20 mole% T into theoretical phlogopite. This solubility is similar to that of 800°C and 1,000 bar.

APPLICATION TO NATURAL FERROMAGNESIAN MICAS

The experimental results concerning the influence of temperature on the solubility of Ti in phlogopite may be compared to natural micas of various origins.

The model of substitution ($2Si^{IV},Mg^{VI} \rightleftharpoons 2Al^{IV},Ti^{VI}$) has been proposed by different authors, particularly by Oki (1961) for biotites from metamorphic rocks, and by Czamanske and Wones (1973) for biotites from granitic rocks. Nemec (1972) indicates a positive correlation between Ti and Al, and a negative one between Ti and Mg in micas of lamprophyres; these correlations are consistent with the proposed model. For comparison, ferromagnesian micas from metamorphic rocks are separated from those from igneous rocks.

Metamorphic rocks

A general phenomenon noted is the increase in Ti content of biotites with metamorphic grade. This fact has been observed by many authors, in different metamorphic series: Oki (1961) indicates an increase in Ti content with increasing metamorphic grade from 0.12 Ti a./f.u. (0.12 Ti atom/6 octahedral sites) to 0.37 Ti a./f.u. biotites from pelitic metamorphic rocks of the central Abukuma Plateau (Japan).

In the metamorphic series of the Wantabadgery—Adelong—Tumbarumba district (New South Wales, Australia), biotites from biotite—muscovite—quartz—cordierite—andalusite assemblages contain 0.25 Ti a./f.u. vs. 0.32—0.36 Ti a./f.u. in the assemblage where sillimanite appears. Engel and Engel (1960) have observed an increase in Ti content of biotites, from 0.35 Ti a./f.u. in the

upper amphibolite facies to 0.41 Ti a./f.u. in the lower granulite facies, in Adirondack paragneisses. Kwak (1968) demonstrated the same phenomenon in rutile-bearing schists of the almandine amphibolite facies from Sudbury, Ontario. Ti increases in biotites from 0.202 Ti a./f.u. at the beginning of the staurolite—quartz subfacies to 0.476 Ti a./f.u. at the end of the sillimanite—feldspar subfacies. Kwak (1968) proposes 475°C and 3.0—4.8 kbar, and 725°C and 5.5—7.5 kbar, as ranges of conditions of the genesis of these biotites. Zakrutin and Grigorenko (1968) indicate an average Ti content of biotites of 0.22 Ti a./f.u. (maximum 0.38) in the amphibolite facies and an average value of 0.48 Ti a./f.u. (maximum 0.67) in the granulite facies. Finally, exsolution of Ti and precipitation as titanium oxides from the mica structure could be an indication of retrogressive metamorphism (Rimsaite, 1964).

These examples clearly show the positive influence of the increase of metamorphic grade on the solubility of Ti in biotites. This observation is qualitatively in satisfactory agreement with the present experimental work. But the experiments have shown also that an increase of pressure would provoke the exsolution of Ti; the presence of Ti-rich biotites in rocks of the granulite facies seems to be in opposition with the experimental results. In addition, the values indicated for the Ti content of biotites in different facies seems too high according to the experimental data. It may be assumed that most of the natural micas concerned are saturated in Ti because they are generally accompanied by rutile or ilmenite. The extreme values given by Kwak (1968) for the Ti content of biotites from rocks of the amphibolite facies are 0.20 Ti a./f.u., and 0.48 Ti a./f.u. These solubilities have been obtained experimentally, in phlogopites, respectively at 800°C and 1,000 bar, and about 900°C and 1,000 bar. These temperatures are higher than those indicated by Kwak (1968). These differences may be resolved by the absence of an essential element, Fe, in the experimental system. The solubility of Ti in biotites of metamorphic rocks seems greater in the presence of Fe, at lower temperature and pressure than in Fe-free phlogopites. This assumption is supported by the observations of Rimsaite (1964) who found an increase in the solubility of Ti in phlogopites with increasing Fe content, and of Czamanske and Wones (1973) who noted a decrease of TiO_2 content of biotites with a decrease in their Fe content.

Igneous rocks

The Ti content of biotites from magmatic rocks is usually greater than that of biotites from metamorphic rocks (Velde, 1969). This difference is certainly due to difference in temperatures of crystallization of biotites, higher in the case of magmatic rocks.

Plutonic rocks. In granodiorites and quartz monzonites of the Sierra Nevada batholith, biotites contain an average of 0.30 Ti a./f.u. (Dodge et al., 1969). Recently, Czamanske and Wones (1973) have found (0.17 Ti a./f.u. in biotites

of granitic rocks, 0.35 Ti a./f.u. in biotites of granodioritic rocks, and 0.5 Ti a./f.u. in biotites from monzonitic rocks. This increase reflects the temperatures of crystallization of these rocks which increase from granitic to monzonitic rocks. The temperatures of crystallization indicated by the Ti content of biotites, estimated from experimental results (about 770°C for granitic rocks and at least 900°C for monzonitic rocks) may well be appropriate for these rocks. The general trend of Ti increasing with increasing temperature of formation corresponds well with the experimental results.

Volcanic rocks. The most titaniferous phlogopites may be encountered in K-rich lavas (Carmichael, 1967). The high-temperature and low-pressure crystallization of these rocks is unquestionable (presence of glass and leucite). Representative values of Ti content of such phlogopites are: 0.537 Ti a./f.u. in Spanish jumillite; 0.76 Ti a./f.u. in wolgidites and wyomingite of West Kimberley, Australia; and 0.84 Ti a./f.u. in fitzroyite of Australia (Carmichael, 1967). These values are consistent with the experimental results (0.7 Ti a./f.u. at 1,000°C and 1,000 bar).

Ultramafic rocks. Another type of occurrence of titaniferous mica is in ultramafic potassic rocks, such as those of Greenland (Upton and Thomas, 1973). In these rocks, phlogopite is associated with magnesian olivine, diopside and Fe—Ti oxides and contains 0.68—0.97 Ti a./f.u. According to the authors, the rocks have crystallized at an estimated depth of 3—4 km (about 1,000 bar).

Case of the xenoliths. Ti-phlogopite is sometimes present as xenocrysts in alkali basalts (Flower, 1971) and considered as coming from the upper mantle. The experiments have shown an important decrease in the solubility of Ti in phlogopite with increasing pressure (0.2 Ti a./f.u. at 1,000°C and 7,000 bar). Forbes and Flower (1974) have established the stability of a Ti-phlogopite $K_2(Mg_4 Ti)(Si_6 Al_2)O_{20}(OH)_4$ at very high pressures (up to 30 kbar) and very high temperatures. The existence of at least two kinds of titanophlogopites seems reasonable: one of high temperature and low pressure studied in the present work, and one of very high temperature and pressure.

CONCLUSION

The use of the solubility of Ti in ferromagnesian micas to determine with precision their conditions of genesis requires a knowledge of the influence of Fe on this solubility. In natural rocks, Fe seems to favour Ti incorporation in biotites. However, the present experimental study on the influence of the conditions of crystallization on the solubility of Ti in Fe-free phlogopite has shown that the temperature favours that solubility, whereas an increase of pressure provokes the exsolution of Ti between 600°C and 1,000°C. Therefore, Ti in ferromagnesian micas is a promising geothermometer as well as geobarometer.

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