

Conversion of muscovite at high pressures and temperatures

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INTRODUCTION

Previous communications (Markov et al., 1966; Markov et al., 1968) established that certain trioctahedral micas (phlogopite, biotite, and lepidomelane) are unstable at high pressures and decompose.

A characteristic feature of these potassium-containing minerals is that although the mean density of the mineral associations formed during decomposition is greater than that of the initial micas, the potassium in these associations is incorporated in minerals of relatively low density (not more than 3 g/cm³).

This characteristic of potassium-containing minerals enabled us to draw certain inferences regarding their behavior at depth and the causes of removal of potassium into the outer layers (Markov et al., 1968).

This paper continues our work on the behavior of potassium-containing minerals at high pressures and temperatures. The investigations were performed on muscovite — one of the dioctahedral micas.

The conversions of muscovite were studied at a pressure of 66 kbar in the range 900-2000°C.

INITIAL MATERIAL

As the initial material we took pure, inclusion-free transparent crystals of muscovite (4 x 4 cm) from one of the Mamsk deposits. Table 1 gives the chemical composition of the initial muscovite. The refractive indices, measured in a refractometer, were as follows: Ng = 1.602, Nm = 1.599, Np = 1.566 (all ± 0.001). The density was measured by the immersion method: 2.81 ± 0.02 g/cm³. Table 2 gives the interplanar spacings.

SPECIMENS AND EXPERIMENTAL PROCEDURE

To create high temperatures in the pressure chamber we used internal heating. A stack of muscovite plates, cut from a crystal, was placed

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TABLE 1. Chemical composition of initial muscovite.

SiO ₂	—43.35
TiO ₂	— 0.22
Al ₂ O ₃	—35.45
Fe ₂ O ₃	— 0.91
FeO	— 1.06
MnO	— traces
MgO	— 3.29
CaO	— 0.75
H ₂ O ⁺	— 4.75
H ₂ O ⁻	— 0.30
Na ₂ O	— 0.57
K ₂ O	— 6.92
F ⁻	— 0.15
99.72	
F=0	—0.06
Total =99.66	

Analyst M.G. Zamurueva, Institute of Geology, USSR Academy of Sciences.

TABLE 2. Interplanar spacings of initial muscovite.

d*	J	d*	J
4.741	w	1.436	v.w.
4.311	s	1.404	w
3.741	avg.	1.340	s
3.391	avg.	1.325	avg.
3.231	s	1.311	avg.
3.121	v.w.	1.288	s
2.931	avg.	1.264	avg.
2.801	avg.	1.238	s
2.731	avg.	1.213	w
2.521	v.s.	1.196	w
2.431	w	1.149	w
2.341	avg.	1.123	avg.
2.161	w	1.110	avg.
2.091	avg.	1.096	w
1.971	s	1.080	v.w.
1.847	w	1.071	v.w.
1.792	w	1.060	w
1.712	w	1.053	w
1.633	v.s.	1.045	w
1.584	avg.	1.035	w
1.542	avg.	1.009	avg.
1.509	w	0.997	avg.
1.490	v.s.	0.989	avg.

*The X-ray photographs were corrected relative to NaCl.

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in the cylindrical cavity of a tubular graphite resistance furnace. The remaining space was filled with powder of the same muscovite so that the tablet height was 3 mm; on the end faces the furnace was sealed by graphite plugs. Before the experiment was begun, about 0.02 g of a saturated solution of KHCO_3 was introduced into the pressure chamber.

The experiments were performed by the quenching method; the procedure consisted of the following cycle: pressure rise - temperature rise - residence at this temperature - quenching - pressure reduction. The residence time at the maximum temperature was 5 min.

The temperature and pressure in the chamber were determined on the basis of independent calibrations (Markov et al., 1965; Ryabinin et al., 1963). The pressure was determined to within $\pm 8\%$, the temperature to within $\pm 5-7\%$. As shown by Markov et al. (1966), with this type of heater design, a considerable temperature gradient is created in the specimen, so that the latter displays a cold zone (at the ends) and a hot zone (near the heater). Calibrations enable the temperature to be determined in both zones.

Processing of the specimens after the experiment was as follows: microscopic investigation of faces and thin sections, measurement by the immersion method (Petrov, 1965) of the optical constants and densities of accessory minerals, and recording and processing of the powder patterns. The accessory minerals were identified from all these data.

RESULTS

Like trioctahedral micas, in the investigated temperature range (the parameters of the principal experiments are given in Table 3) muscovite undergoes a number of conversions. The character of the development of the accessory minerals in the specimens is illustrated by sketches (fig. 1) of thin sections from axial cross sections. The numbers of the sketches correspond to the numbers of the experiments in Table 3.

Below 1050°C the initial muscovite displays no changes during the experiment. In those

TABLE 3. Parameters of experiments on muscovite (pressure 66 kbar).

Expt. no.	Temperature		Time, mm	Medium
	Cold zone	Hot zone		
1	940	1120	5	KHCO_3
2	1290	1540	5	KHCO_3
3	1660	1980	5	KHCO_3

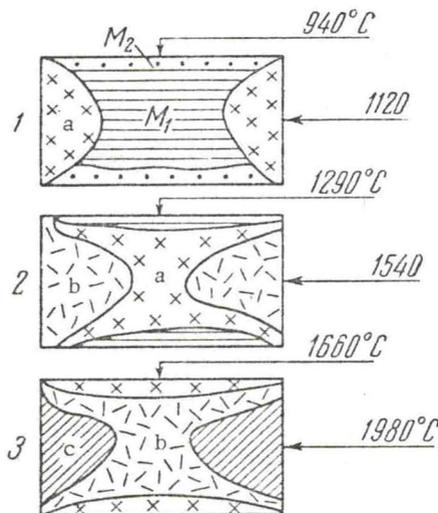


FIGURE 1. Scheme of location of neogenic phases in axial cross sections of specimens from experiments 1, 2, and 3 (table 3).

M_1 - crystal of initial muscovite
 M_2 - powder of initial muscovite

a - accessory mineral of "a" type
 b - accessory mineral of "b" type
 c - accessory mineral of "c" type
 (explanation in text)

The figures near each sketch are the temperatures in the cold and hot zones of the specimens.

parts of the specimen where the temperature is above 1050°C , muscovite is replaced by a neogenic formation of the "a" type. Figure 1, 1 shows a sketch of a thin section, whose cold zone had a temperature of 940°C (relict muscovite was retained in this zone). In the hot zone of the specimen the temperature reached 1120°C , and an association of the "a" type was observed. The boundary between the relict muscovite and the "a" material corresponds approximately to an isothermal surface of 1050°C .

In thin sections under the microscope, "a"-type neogenic material is brown. In the sector of immediate contact with muscovite we see that this material is an association of several minerals. This sector displays pointed (up to 0.01 mm) inclusions and round (0.016 x 0.008 mm) and elongated platy (0.04 x 0.008 mm) grains. If the boundary of the "a"-type neogenic association runs perpendicular to the cleavage of the initial muscovite, we observe development of accessory minerals at the cleavage planes of the mica ahead of the main front of muscovite replacement. Table 4 shows the densities and refractive indices of the minerals of this association. Table 5 (col. a) gives the interplanar spacings calculated from the powder pattern of "a" material.

TABLE 4. Refractive indices and densities of decomposition products of muscovite ("a" association).

	Platy mineral	Isotrop. weakly birefring.	Kyanite*
Refractive index	Ng' = 1.735 Np' = 1.725	Ng' = 1.558 ± 0.003 Np' = 1.549	Ng = 1.728 Nm = 1.722 Np = 1.713
Density, g/cm ³	3.60 ± 0.02	2.82 ± 0.02	3.56-3.68

*Larsen and Berman, 1965; **AlI ± 0.003.

TABLE 5. Interplanar spacings of "a"-type neogenic association.

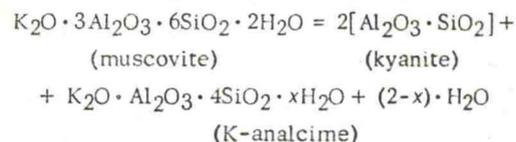
a		b		c		a		b		c	
Association "a"		K ₂ O·Al ₂ O ₃ ·4SiO ₂ ·H ₂ O**		Kyanite***		Association "a"		K ₂ O·Al ₂ O ₃ ·4SiO ₂ ·H ₂ O**		Kyanite***	
d*	l	d	l	d	l	d*	l	d	l	d	l
5.02	4	5.67	10	—	—	2.22	3	2.22	4	—	—
4.65	7	4.92	2	—	—	2.15	1	—	—	2.16	6
4.50	2	—	—	—	—	1.98	6	—	—	1.95	10
4.33	2	—	—	4.35	6	1.93	8	1.90	6	—	—
3.99	—	—	—	—	—	1.86	1	1.87	4	—	—
4.05	5	—	—	—	—	1.77	1	—	—	1.76	6
3.83	1	—	—	—	—	1.75	1	1.74	8	—	—
3.68	5	—	—	—	—	1.59	5	—	—	1.60	6
3.52	2	3.46	10	—	—	1.56	1	—	—	—	—
3.38	6	—	—	3.33	8	1.52	1	—	—	1.50	2
3.28	4	—	—	—	—	1.51	1	—	—	—	—
3.21	7	—	—	3.14	8	1.47	1	—	—	1.48	6
2.97	10	2.94	8	—	—	1.39	4	1.41	6	1.40	4
2.68	10	2.68	2	2.69	6	1.37	10	1.36	6	1.38	10
2.61	5	—	—	—	—	1.34	2	—	—	1.34	6
2.54	4	2.51	4	2.52	7	1.33	1	—	—	—	—
2.36	3	2.42	2	2.37	8	1.30	1	—	—	—	—
2.31	1	—	—	—	—	1.29	1	—	—	—	—

*Corrected with respect to NaCl; **Barrer, Baynham, 1956; ***Seki, Kennedy, 1964.

Comparison of all the data enables us to infer that one of the minerals formed is kyanite (for comparison Table 4 gives the literature values of the density and refractive index of kyanite - Larsen and Berman, 1965); col. c of Table 5 gives its interplanar spacings (Mikheyev, 1957). From the other lines on the powder pattern we can assume that a second mineral formed by breakdown of muscovite is the potassium analog of analcime (K₂O·Al₂O₃·4SiO₂·H₂O).¹ Column b (table 5) gives the interplanar spacings of this mineral from data of Barrer and Baynham (1956). Unfortunately, a search revealed no literature on the density and re-

fractive indices of this mineral (the report by these authors mentions only that the mean refractive index is ~1.490), so that its identification from X-ray data cannot be taken as final.

Thus at a pressure of 66 kbar in the range 1050-1350°C, muscovite decomposes, probably by the following scheme:



(Since the water content of K-analcime is not accurately known, we do not know whether free water is formed during breakdown of muscovite.)

Above 1350°C the kyanite + K-analcime

¹An artificial mineral synthesized by Barrer and Baynham, 1956.

940°C

1120

1290°C

1540

1660°C

1980°C

of location of neogenic phases sections of specimens from 1, 2, and 3 (table 3).

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ry mineral of "a" type ry mineral of "b" type ry mineral of "c" type ation in text)

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association becomes unstable and is converted to a new association of minerals ("b" type, fig. 1). Development of "b" accessory minerals begins on the side of the hot zones, when their temperature reaches 1350°C. Figure 1 (2) gives a sketch of a thin section in which the temperature of the cold zones was 1290°C. An "a" association (kyanite + K-analcime) was retained in these zones. On the hot-zone side (temperature about 1540°), the kyanite + K-analcime association was replaced by a "b" neogenic association. The boundary between these associations in the thin section corresponds approximately to an isotherm of 1350°C.

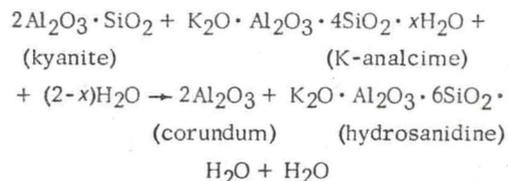
In transmitted light, in thin sections the neogenic "b" material has a bright yellowish color. It consists of a fine flaky mass, in which we clearly observe individual acicular crystals of size 0.008 x 0.12 mm. The needles are transparent and sometimes display sharp transverse fissures (fig. 2). In addition to needles, the fine flaky material contains fairly large (up to 0.015 mm) crystals (round, rhombic, rectangular), optically identical with these needles. In polarized light the fine flaky mass clearly consists largely of a mixture of two minerals (of size not more than 0.02 x 0.005), one of which (the minor) is characterized by gray interference colors, the other mineral being yellow-brown. Table 6 shows the refractive indices and densities of the "b" neogenic material.

Table 7 gives the interplanar spacings calculated from the powder patterns of the acicular mineral (col. a) and the fine flaky material adjoining the needles (col. c).²

²Specimens for the X-ray photographs were selected from the thin section itself.

The X-ray data for the acicular mineral agree closely with those for corundum (table 7, col. b), and the X-ray data for the adjoining material largely agree with those for hydrosandine $KAlSi_3O_8 \cdot H_2O$ ³ (table 7, col. d). However, like the optical data, several strong lines on the powder pattern of the mixture, absent in the group of lines of hydrosandine, indicate the presence of a third mineral in the "b" association, but it cannot be identified from the available data.

The refractive indices and the density of the acicular mineral agree closely with those of corundum, but the refractive indices and densities of the double-refracting mineral agree satisfactorily with those of hydrosandine (table 6). Although the "b" association contains a small amount of the third mineral, we assume that during conversion this mineral is not in equilibrium, and a second conversion takes place as follows:



A corundum + hydrosandine association is observed in the specimens up to 1800°C. Sectors of the thin section above 1800°C contained a fine flaky micaceous mass ("c" type neogenesis). Figure 1 (3) shows a sketch of a thin section of a specimen whose cold zone had a temperature of 1660°C, and whose hot zone

³An artificial mineral synthesized at high pressures (Seki and Kennedy, 1964).

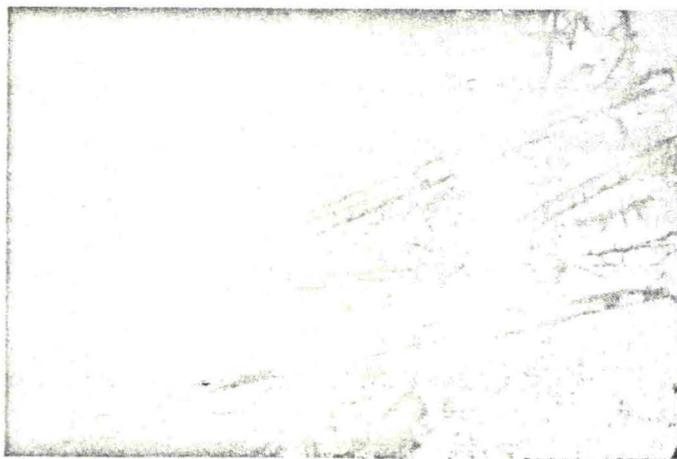


FIGURE 2. Replacement of an "a" accessory mineral (the dark field in the figure) by a "b" accessory mineral (light field - elongated corundum crystals clearly visible).

Transmitted light; x 20

TABLE 6. Refractive indices and densities of accessory minerals of "b" association.

	Acicular mineral	Corundum	Double-refracting mineral	KAlSi ₃ O ₈ ·H ₂ O***	Weakly double-refracting mineral
Refractive indices	Ng' = 1.771* Np' = 1.765*	Ng = 1.767 Np = 1.759	Ng' = 1.548* Np' = 1.537*	Ng = 1.545 Np = 1.535	Ng' = 1.570* Np' = 1.564*
Densities (g/cm ³)	3.95-4.05	3.95-4.10	2.55-2.65	2.58	2.6-2.7

*All +0.003; **Larsen and Berman, 1965; ***Seki, Kennedy, 1964.

TABLE 7. Interplanar spacings of minerals of "b" association.

a		b		c		d	
Acicular mineral		Corundum**		Material adjoining needles		KAlSi ₃ O ₈ ·H ₂ O***	
d*	l	d	l	d*	l	d	l
				4.65	10	7.67	0.5
				4.01	8	4.61	0.3
				3.88	4	3.96	3.0
						3.85	3.3
3.48	10	3.44	3	3.30	3		
				3.25	2		
2.94	4			2.96	10	2.957	10
2.69	2			2.67	10	2.667	8.9
2.55	10	2.54	6			2.518	1.0
2.37	3	2.37	4				
				2.31	3	2.308	1.5
				2.22	5	2.241	6.4
						2.211	1.7
2.09	10	2.08	9	2.09	1		
				1.94	4	1.924	1.3
				1.86	3	1.848	1.3
1.73	8	1.74	5	1.75	2	1.746	0.3
						1.715	0.4
				1.70	1	1.703	0.5
1.60	10	1.599	10	1.60	3		
						1.591	1.3
						1.560	0.7
				1.54	5	1.541	1.0
				1.51	2		
1.40	6	1.401	6				
1.37	8	1.374	7	1.37	1		
				1.33	7	1.334	1.0
						1.321	0.3
				1.28	1	1.283	0.8
						1.260	0.3
1.23	3						
						1.216	0.3
						1.203	0.3
						1.184	0.3

*Corrected relative to NaCl; **Mikheyev, 1957; ***Seki, Kennedy, 1964.

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2O·Al₂O₃·4SiO₂·xH₂O + (K-analcime)

l₂O₃ + K₂O·Al₂O₃·6SiO₂· (hydrosandine)

H₂O + H₂O

hydrosandine association specimens up to 1800°C, section above 1800°C con- micaceous mass ("c" type re 1 (3) shows a sketch of a ecimen whose cold zone had 560°C, and whose hot zone

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reached 1980°C. The corundum + hydrosandine association is retained in the cold zone, but "c" type neogenic material is observed in the hot zones. The boundary between the zones of formation of these associations corresponds approximately to the 1800°C isotherm.

The neogenic fine flaky mineral is similar in appearance to mica, but has X-ray data similar to those of muscovite. However, further research will be required to determine whether this association is equilibrium or consists of a "quenched phase."

CONCLUSIONS

Study of conversions of muscovite at 66 kbar in the range 900-2000°C revealed that muscovite is unstable at 1050-1350°C and breaks down into kyanite and K-analcime.

In the range 1350-1800°C the kyanite + K-analcime association is converted to an association consisting of corundum, hydrosandine, and a third (unidentified) mineral, which is apparently not in equilibrium.

In those parts of the thin section where the temperature was above 1800°C, fine flaky micaceous material was observed. The available petrographic data do not enable us to decide whether this material is formed by replacement of the corundum + hydrosandine association, or is a quenching phase formed from the melt as the specimen cools.

From the geological point of view, interest attaches to the kyanite + K-analcime association, first observed in our experiments, because it indicates the important part played by kyanite in geological processes. This might expand present ideas on the geochemistry of aluminum in abyssal processes.

Since the presence of potassium in corundum and kyanite is improbable, and the other minerals of the "a" and "b" associations have relatively low densities (less than 3 g/cm³), the results confirm the previously determined pattern (Markov et al., 1966; Markov et al., 1968) of behavior of potassium-containing minerals at high pressures and temperatures. This is further confirmation of our hypotheses on the causes of removal of potassium into the outer layers of the earth.

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