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Synthesis of a Rb analogue of $2M_1$ muscovite

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ABSTRACT

In the course of a study on the incorporation of Rb in muscovite, the Rb analogue of muscovite was synthesized at 600°C and 5 kbar. Rb_2CO_3, γ-Al_2O_3, and SiO_2 (cristobalite) were used as starting materials. Wet-chemical analyses and TGA data of the run products indicate that the composition is consistent with the ideal Rb end member. SEM photographs display well-crystallized micas as run products. The X-ray powder pattern can be satisfactorily indexed on the basis of a $2M_1$ cell, having $a = 5.215 \pm 0.003$, $b = 9.059 \pm 0.005$, $c = 20.59 \pm 0.01$ Å, $\beta = 96.540° \pm 0.003°$. The most likely space group is $C2/c$. The calculated density is 3.06 g·cm^{-3}. Compared with muscovite, the unit cell is enlarged mainly in the direction of the c axis, and the cell volume is enlarged by 3.3%. The IR-band positions of the Rb analogue of muscovite are similar to those of muscovite. On the basis of d spacings, the Rb end member can be easily distinguished from muscovite. By means of IR spectrophotometry, it can be easily distinguished from the NH_4 analogue of muscovite.

INTRODUCTION

Over the past 20 years, several studies on K-Rb exchange in rock-forming minerals have been reported. Several minerals have been studied: feldspars and feldspathoids (Lagache, 1968; Iiyama, 1968; Roux, 1971; Lagache and Sabatier, 1973), and phlogopite (Beswick, 1973; Volfinger, 1974). For muscovite, only the introduction of Rb as a trace element has been studied intensively (Volfinger, 1969, 1976).

Rb is often found in considerable amounts in hydrothermally altered granitic rocks and their aureoles (Vriend et al., 1985; Bussink, 1984) as well as in pegmatites (Černý and Burt, 1984). Muscovite, biotite, and feldspars are the most important host minerals for Rb in these rocks. Rb contents of several thousands of parts per million in pegmatitic muscovites are not uncommon. Luecke (1981) reported amounts up to 1 wt%. Khanna (1977) reported 6.98 wt% Rb in a muscovite from a pegmatite. K-Rb partition coefficients between micas and vapor depend on temperature (Beswick, 1973; Volfinger, 1976), and they may be of use as a geothermometer (De Albuquerque, 1975; Bernotat et al., 1976).

In the course of an investigation on the incorporation of Rb in muscovite, a Rb analogue of muscovite was synthesized. It is the purpose of this paper to describe the properties of this phase, herein informally referred to as Rb-muscovite, with SEM, chemical analyses, TGA, XRD, and IR spectrophotometry.

SYNTHESIS AND EXPERIMENTAL METHODS

For the synthesis of muscovite, several procedures are described in the literature. A variety of starting materials have been used, for example, KCl, $Al(OH)_3$, and $SiO_2 \cdot xH_2O$ (Gruner, 1939); $K_2O \cdot 6SiO_2$ and γ-Al_2O_3 (Yoder and Eugster, 1955; Chatterjee and Johannes, 1974); natural kaolinite and KOH (Velde, 1965, 1966); and K_2CO_3, γ-Al_2O_3, and SiO_2 (Chatterjee and Johannes, 1974).

Since the synthesis of muscovite from K_2CO_3, γ-Al_2O_3, and SiO_2 seems to be little problematic (Chatterjee and Johannes, 1974), we chose Rb_2CO_3, γ-Al_2O_3, and SiO_2 for starting materials for the synthesis of Rb-muscovite. Dried, extra pure Rb_2CO_3 (Merck, no. 7612), analytical grade γ-Al_2O_3 (Merck, no. 1095), and quartz (Merck, no. 7536) were used. The quartz was purified by hand-picking, because it contained small impurities of feldspars and mica. The pure quartz was heated for 3 h at 1500°C and 1 atm, resulting in a well-crystallized cristobalite. The starting materials were finely ground and mixed in an agate mortar, under acetone.

The synthesis of the Rb-muscovite was performed at 600°C and 5 kbar. The formation of the mica is according to the following reaction:

$$Rb_2CO_3 + 3\ \gamma\text{-}Al_2O_3 + 6\ SiO_2 + 2\ H_2O \rightleftharpoons 2\ RbAl_2Si_3AlO_{10}(OH)_2 + CO_2.$$

The synthesis was carried out in sealed Au capsules, containing about 200 mg of carbonate and oxide mixture and 50 μL of double-distilled water. Conventional cold-seal pressure vessels were used. The pressure medium around the Au capsule was Ar. The temperature is considered to be accurate to 1%, the pressure to 5%. Isobaric quenching to room temperature within a few minutes was achieved by blowing on the vessel compressed cold air. Run times of about 3 weeks produced well-crystallized micas. No other products were encountered. In a short run at 600°C and 15 kbar with a piston-cylinder apparatus, the Rb-muscovite can be formed besides appreciable amounts of corundum and Rb-feldspar.

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Fig. 1. (A) and (B) SEM photographs of synthetic Rb-muscovite.

Description of the mica

Optical and SEM description

Run products were examined under a polarizing microscope, which revealed very small, colorless mica flakes. The run products were too small for a well-oriented determination of the optical properties. SEM was used to get an impression of the morphology of the synthesized micas. Typical SEM pictures are given in Figures 1A and 1B. The crystals are usually thin, more or less hexagonal platelets, with a diameter of 1 to 4 μm, and a thickness of some tenths of a micrometer.

Chemical analyses

Rb, Si, and Al have been determined after a HF-$HClO_4$-HNO_3 and a $LiBO_2$-melt decomposition. Only samples composed of pure mica were used, and run products containing other phases (piston-cylinder runs) were not analyzed. Rb, Al, and Si were all determined by AAS. The results are given in Table 1. The values are in good agreement with ideal Rb, Al, and Si contents. Microprobe analyses (not reported here) gave semiquantitative results, owing to the small size of the micas.

Thermogravimetric analyses

To check for the presence of hydroxyl in the crystal and of H_3O^+ (which may be present in the interlayer), TGA analyses were executed. For comparison, an analysis of a synthetic muscovite (synthesized from K_2CO_3, γ-Al_2O_3, and SiO_2 at 600°C and 5 kbar) also was made. The muscovite loses 4.30 ± 0.2 wt% at temperatures up to 1000°C. The ideal weight loss of muscovite should be 4.52 wt%. Yoder and Eugster (1955) found values of 4.27 and 4.52 wt% for samples of a synthetic muscovite. For Rb-muscovite, a loss of 3.95 ± 0.2 wt% was recorded at temperatures up to 1000°C. The ideal weight loss of Rb-muscovite should be 4.05 wt%.

The TGA analyses are thus consistent with the presence of hydroxyl. The presence of significant amounts of H_3O^+ is not indicated. The hydroxyl groups of Rb-muscovite decompose mainly between 400 and 750°C.

TABLE 1. Chemical analyses (wt%) of the synthesized Rb-muscovite

	Ideal Rb end member	Acid decomposition (AAS)	$LiBO_2$-melt decomposition (AAS)
Rb	19.22	18.9 ± 0.3	19.4 ± 0.3
Si	18.95	—	19.0 ± 0.5
Al	18.20	—	18.3 ± 0.5

X-ray diffraction

The X-ray investigation of the Rb-muscovite was made with a Philips PW1050 diffractometer and an Enraf Nonius FR552 Guinier camera. Cu$K\alpha_1$ radiation was used (λ = 1.540 50).

The X-ray pattern of the Rb-muscovite resembles that of $2M_1$ muscovite in great detail. The Rb-muscovite was indexed on the basis of a $2M_1$ cell, which implies a space group $C2/c$ (Güven, 1971). Owing to the small size of the crystals, single-crystal techniques could not be applied. Cell parameters were calculated with a least-squares refinement program, on nine reflections. Si (JCPDS 27-1402) was used as an internal standard. Prediction by computer calculations of other reflections, which were not used in the refinement program, gave results that were in good agreement with observation, and calculated *hkl* values were consistent with values expected from the analogous muscovite reflections. It was concluded that it is possible to index the mica on a $2M_1$ cell with space group $C2/c$. The indexed X-ray diffraction pattern is given in

TABLE 2. X-ray pattern of Rb-muscovite

hkl	d_{calc} (Å)	d_{obs} (Å)	I/I_0 Diffractometer	I/I_0 Guinier
002	10.23	10.40	4	
004	5.12	5.20	4	12
020	4.53	4.52	16	30
110	4.50	4.48*	9	
022	4.14	4.13*	26	26
$\bar{1}13$	3.94	3.92	17	
023	3.77	3.73*	61	37
$11\bar{4}$	3.56	3.56	6	
006	3.409	3.41*	33	21
024	3.391			
025	3.036	2.99	15	
$13\bar{1}$	2.607	2.590*	53	85
116	2.596			
200	2.591			
$20\bar{2}$	2.582	2.580*	100	100
131	2.570			
$\bar{2}04$	2.425	2.430	6	
133	2.391	2.390	4	
040	2.265	2.261*	19	32
$\bar{2}21$	2.260			
222	2.152	2.155	16	
223	2.075	2.070	27	
044	2.071			
0,0,10	2.046	2.038	6	
046	1.887	1.885	2	
2,0,10	1.703	1.704	14	
060	1.510	1.509*	32	53
$\bar{3}31$	1.506	1.506	22	
262	1.303	1.300*		20

* Reflections used in the least-squares refinement.

Table 2. I/I_0 of the Guinier camera recording was determined with a densitometer of Joyce and Loebl, Inc. It may be noted here that the basal reflections are remarkably weak, especially for the diffractogram. A comparable observation was made by Chatterjee (1974). He noted that the basal reflections of synthetic, very fine grained (up to 2 μm) margarite were weaker than the equivalent reflections of coarser-grained natural margarite. He ascribed the effect to the very small grain size of the synthetic mica. It may be that the very fine grain size of the Rb-muscovite is also responsible for its relatively weak basal reflections. Incorporation of H_3O^+ would have the same effect, but TGA data showed that the presence of H_3O^+ is unlikely. As muscovite that was synthesized at the same conditions and with comparable grain size gives clearly stronger basal reflections, an effect of Rb in the alkali sites on the intensity of the X-ray lines cannot be ruled out.

IR spectrophotometry

An IR spectrum of Rb-muscovite was made with a Perkin-Elmer 580 IR spectrophotometer, using dried KBr tablets. In Table 3, the band positions for the Rb-muscovite are given and compared with published values for muscovite (Langer et al., 1981). The band positions of muscovite and Rb-muscovite are very similar. Band assignments (Langer et al., 1981) are also given.

TABLE 3. IR absorption maxima for synthetic Rb-muscovite and comparison with literature values for muscovite

Rb-muscovite wavenumber (cm^{-1})	Intensity*	Muscovite wavenumber** (cm^{-1})	Muscovite band assignments**
3630	vs	3637	Al–OH
1065	w	1065	Si–O
1040–1000	vs	1028–996	Si–O and Si–O–Si
929	ms	937	Si–O–^{IV}Al
829	ms	831	^{IV}Al–O?
800	ms	805	^{IV}Al–O–^{IV}Al
750	s	751	^{IV}Al–O–^{IV}Al
725	w	727	Si–O–^{VI}Al
690	w	700	Si–O–^{VI}Al
615	w	619	Si–O
530	vs	539	Si–O–^{VI}Al
475	vs	480	Si–O
410	s	410	
351	ms	353	

* w = weak; ms = medium strong; s = strong; vs = very strong.
** Langer et al. (1981).

Comparison with other muscovites

From the list of d values it appears that Rb-muscovite can be distinguished easily from muscovite. Observed d spacings are generally larger than those of muscovite (Yoder and Eugster, 1955; Chatterjee and Johannes, 1974). In Table 4 a comparison is made between published values of cell dimensions for muscovite and the obtained values for the Rb-muscovite. Compared with muscovite, the unit-cell of the Rb-muscovite is enlarged mainly in the direction of the c axis. Analogous behavior was noted by Hazen and Wones (1972) and Beswick (1973) for Rb-phlogopite. The increase in cell volume of Rb-muscovite relative to muscovite is 3.3%. The corresponding increase for Rb-phlogopite is 2.9% [as can be calculated from data of Beswick (1973)]. The NH_4-muscovites of Eugster and Munoz (1966) and Higashi (1982) are 1M micas, and the unit cells of these micas cannot be compared directly to the Rb-muscovite cell. The d spacings of basal reflections of these micas are, however, similar to those of Rb-muscovite basal reflections.

By means of IR spectrophotometry, Rb-muscovite can be distinguished easily from NH_4-muscovite (Eugster and

TABLE 4. Comparison between the cell dimensions of synthetic muscovites and Rb-muscovite

	1	2	3	4
a (Å)	5.189	5.1871	5.1883	5.215 ± 0.003
b (Å)	8.995	8.9927	8.9898	9.059 ± 0.005
c (Å)	20.097	20.1490	20.1516	20.59 ± 0.01
β	95°11′	95°46.78′	95°46.28′	96.540° ± 0.003°
V (Å^3)	—	935.09	935.14	966.4 ± 0.5

Note: Columns are (1) Yoder and Eugster (1955), synthetic muscovite; (2) Chatterjee and Johannes (1974), synthetic muscovite; (3) Chatterjee and Johannes (1974), synthetic muscovite; (4) This work, synthetic Rb-muscovite.

Munoz, 1966; Higashi, 1982), because of the absence of the characteristic NH_4-vibrations.

Calculated densities for muscovite from Table 4 are 2.83 $g \cdot cm^{-3}$. The calculated density of Rb-muscovite is 3.06 $g \cdot cm^{-3}$, an increase of 8.1%. For phlogopites, the corresponding increase is 8.2%, as can be calculated from data by Hazen and Wones (1972).

Conclusions

1. The Rb-muscovite is simple to synthesize at 600°C and 5 kbar and with the preparation of the starting mixture given in this paper.

2. Chemical analyses and hydroxyl content are in good agreement with values expected for the ideal Rb end member.

3. The X-ray pattern of the Rb-muscovite is analogous to that of $2M_1$ muscovite. The *d* spacings are generally larger. Rb-muscovite can be indexed on the basis of a $2M_1$ cell, and the space group is very likely *C*2/*c*.

4. In comparison with muscovite, the substitution of Rb for K results in lattice expansion mainly in the direction of the **c** axis. The cell volume is enlarged by 3.3%. The calculated density increases by 8.1% to 3.06 $g \cdot cm^{-3}$.

5. The IR spectrum shows a great similarity between the band positions of muscovite and Rb-muscovite.

6. Rb-muscovite can be distinguished easily from muscovite on basis of *d* spacings and from NH_4-muscovite by IR spectrophotometry.

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