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THE HYDROTHERMAL CONVERSION OF MUSCOVITE TO KALSILITE AND AN IRON-RICH MICA

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ABSTRACT

Attempts to grow large single crystals of muscovite using muscovite cleavage plates as seeds and shredded muscovite as nutrient produced an iron-rich mica and considerable quantities of the $KAlSiO_4$ polymorph called kalsilite. This result is of interest since kalsilite is not a common mineral in nature. Optical data and *x*-ray measurements are presented for both the iron-rich mica and the kalsilite.

INTRODUCTION

Attempts to grow single crystal muscovite using muscovite seeds and nutrient in a steel lined autoclave produced an iron-rich mica and comparatively large quantities of the mineral kalsilite, the hexagonal form of $KAlSiO_4$. Kalsilite is relatively rare, although it may be more common than supposed since it is rather difficult to identify with assurance in thin section. Kalsilite was discovered in volcanic rocks from S.W. Uganda by Holmes (1942) and described by Bannister and Hey (1942), and first prepared in the laboratory by Rigby and Richardson (1947). Since that time additional work (Smith and Tuttle, 1957; Sahama and Smith, 1957; Smith and Sahama, 1957; and Tuttle and Smith, 1958) has done much to clarify phase relations in the system nepheline-kalsilite and polymorphism in $KAlSiO_4$. These studies indicate that at least seven different crystallized materials are possible. These include tetrakalsilite, orthorhombic $KAlSiO_4$, kalsilite, kaliophilite, disordered kaliophilite, a second orthorhombic phase with a smaller unit cell, and a new polymorph named tri-kalsilite (Sahama and Smith, 1957). The studies of Tuttle and Smith (1958) seem to indicate that sodium must be present in all stable phases mentioned above except kalsilite and the orthorhombic form of $KAlSiO_4$. Tri-kalsilite (Sahama and Smith, 1957) is found in a kalsilite-nepheline microperthite and hence it is probable that this kalsilite contains some sodium.

The system described here contained no appreciable quantities of sodium. At the temperatures and pressures used in these experiments kalsilite would appear to be the stable phase in the absence of sodium. This agrees with the results of Tuttle and Smith (1958) but not with the earlier studies of Rigby and Richardson (1947) which seemed to indicate that kalsilite must contain at least 1.5% Na_2O.

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* Operated for the Atomic Energy Commission by Union Carbide Corporation.

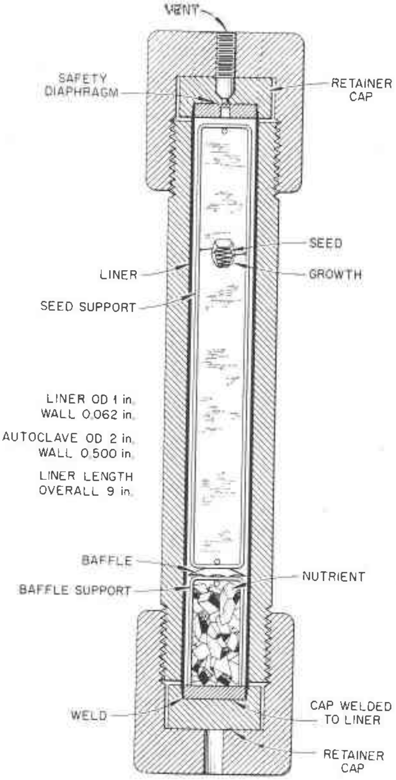

FIG. 1. Hydrothermal autoclave.

EXPERIMENTAL METHOD

Three hydrothermal runs were made using a one inch i.d. autoclave with a cold rolled steel liner. The autoclave was quite similar in design to those used by Bell Laboratories in their early quartz syntheses. (Fig. 1.) The following conditions were used:

Seeds and nutrient:	natural muscovite
Solvent:	KOH (1 N solution)
Partial fill:	70%
Temperatures:	
Seed area:	Approximately 410° C.
Nutrient area:	Approximately 425° C.
Estimated pressure:	1200 bars
Bomb liner:	Cold rolled low-carbon steel, 1″ o.d., $\frac{7}{8}$″ i.d.

Seeds were prepared from cleavage plates of natural muscovite, approximately $\frac{1}{2}$″ on an edge and 0.005″ thick. These plates were suspended in the upper portion of the liner, which during the run was the cooler

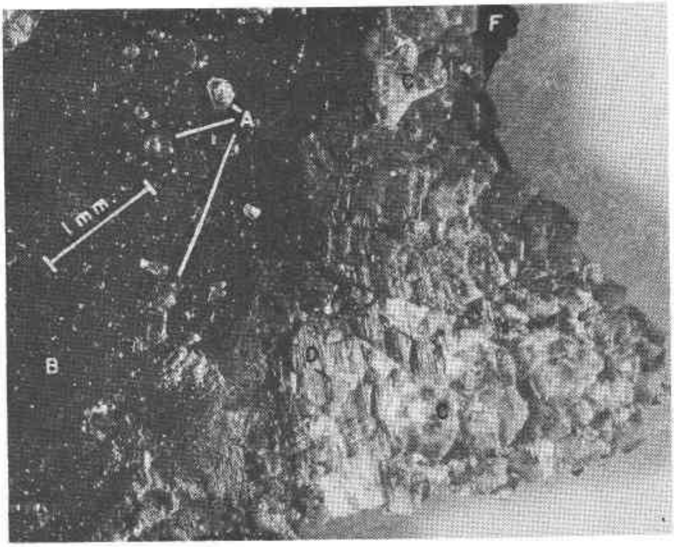

FIG. 2. Layered structure of converted muscovite seed plate.
A. Scattered crystals of kalsilite up to ½ mm. diameter.
B. Sheet of iron-rich mica.
C. Sheet of coalesced crystals of kalsilite; individuals up to 3.5 mm. diameter.
D. Thin layer of what appears to be partially digested muscovite at center of converted seed.
E. Sheet of coalesced crystals of kalsilite; individuals up to 3.5 mm. diameter.
F. Sheet of iron-rich mica.
G. Scattered crystals of kalsilite up to ½ mm. diameter.
(Note that layers E and G do not appear in this view.)

region of the system. Shredded pieces of muscovite were enclosed in a wire basket and placed at the base of the liner, which was the hotter region of the system. The seed and nutrient regions were separated by a perforated baffle placed convex upward and containing approximately 20% open space.

The ends of the liner were welded shut and a 70% partial fill of 1 N KOH solution added with a hypodermic syringe through a small hole drilled in one end cap. This fill hole was then easily welded shut. KOH was used as solvent rather than NaOH to reduce the number of components in the system, since the potassium mica was of interest. Runs were made lasting for twenty-one days, fourteen days, and twenty-nine days. A leak developed at some undetermined time during the first run of twenty-one days duration, probably rather early in the run since larger crystals of kalsilite were obtained in the second run of fourteen days. The final run of twenty-nine days duration was made to learn whether larger crystals of kalsilite could be grown. While this run produced more crystals of kalsilite, they were no larger than those produced in the preceding run.

EXPERIMENTAL RESULTS

Several general observations could be made from these experiments:

1. The original muscovite of the seed plates was largely converted to two new crystalline phases: an iron-rich mica and the mineral kalsilite.
2. The converted seed plates contained seven distinct layers consisting of kalsilite, the iron-rich mica, and a minor amount of unconverted muscovite. The nature of this layering is shown in Fig. 2. (Note that only five of the seven layers appear in the photograph which shows a converted seed plate broken across the layers.) It appears that during the conversion process the two outer sheets of iron-rich mica were formed at an early time in the run, and that the conversion of the remaining muscovite to kalsilite proceeded more slowly. The smaller, scattered crystals of kalsilite on the outer surfaces of the converted seed material probably did not start to grow until after at least some of the muscovite between the two iron-rich mica layers had been converted to kalsilite. The surficial kalsilite crystals almost certainly did not appear until distinct outer layers of the iron-rich mica had been produced.
3. The nutrient material which appeared largely converted to kalsilite, showed less development of the iron-rich mica than noted in the converted seed plates.
4. The iron-rich mica and also numerous small crystals of magnetite (black, octahedral, magnetic crystals) appeared more abundantly in the upper, cooler region of the liner.

The conversion apparently resulted from two major factors. First, the KOH solution attacked the cold rolled steel liner readily, yielding a solution rich in Fe^{+2} and Fe^{+3} ions. Second, the iron-rich mica appeared to be more stable under these conditions than the muscovite. The solvent was effective in attacking the muscovite, replacing the aluminum in the octahedral site with iron to produce some iron-rich mica and digesting the bulk of the muscovite to yield aluminum ions and SiO_4^{-4} groups which could then recombine with the potassium of the solvent and that produced during the disintegration of the muscovite to form kalsilite. The iron-rich mica appears to vary somewhat in its optical properties which may indicate that the replacement of aluminum by iron is incomplete. This is discussed further in the section dealing with optical data. The crystals of kalsilite which occur in the two inner layers are oriented with their *a*-axes lying within the plane of the original sheet. Many of the smaller crystals growing on the outer surfaces exhibit the same orientation; however, some grew with an *a*-axis normal to the surface and some were inclined to the surface (Fig. 3). There is some evidence for an

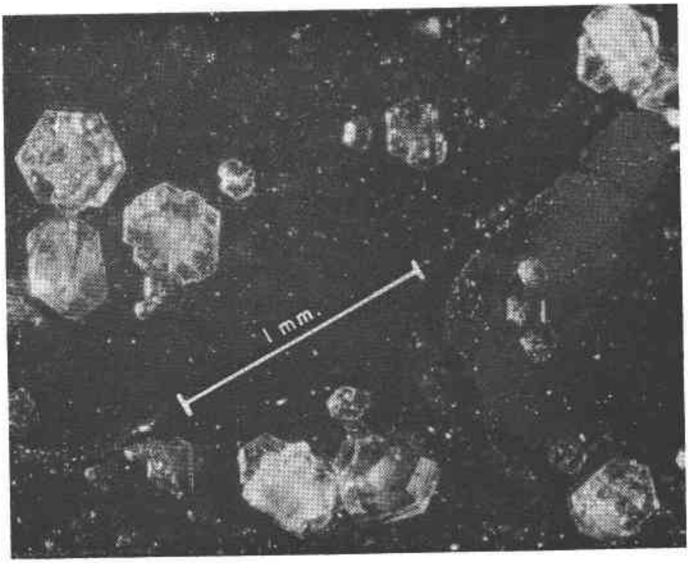

FIG. 3. Kalsilite crystals produced hydrothermally.

epitaxial relationship between the kalsilite and the mica. Crystals of kalsilite were also noted on the baffle plate, the upper end cap of the liner, and on the liner wall.

Numerous bubble inclusions are noted at the centers of most crystals, but the edges of the crystals are generally clear. Some of the bubbles are elongated or tubelike. Multiple growths are fairly common. In some cases, two or more individuals appear at distinct angles to each other. In other cases, a multiplicity of growth with only a slight angular divergence of axes results in tiny "rosette" shaped crystals.

The nature of the chemical reaction occurring during the synthesis of these materials may be expressed by a general chemical equation:

$$\underset{\text{(Muscovite)}}{KAl_2(Si_3Al)O_{10}(OH)_2} + Fe \xrightarrow[\text{(Temperature, Pressure)}]{\text{(KOH, }H_2O\text{)}}$$

$$\underset{\text{(Kalsilite)}}{KAlSiO_4} + \underset{\text{(Iron-rich mica)}}{K(Fe, Al)_2(Si_3Al)O_{10}(OH)_2} + \underset{\text{(Magnetite)}}{Fe_3O_4} + H_2$$

OPTICAL DATA

Optical data were determined for both the kalsilite and iron-rich mica formed during these runs. The kalsilite has the following optical properties:

Uniaxial negative	$\omega = 1.542 \pm 0.002$ $\epsilon = 1.538 \pm 0.002$	Colorless

These properties agree with those determined by Bannister and Hey (1942) in their original description of the mineral.

The iron-rich mica has the following optical properties:

Essentially uniaxial negative (Probably biaxial negative with 2V close to 0°)
$\alpha = 1.62 \pm 0.01$
$\beta = \gamma = 1.68 \pm 0.01$
Strongly colored and pleochroic. Black to greenish in macroscopic observation.
Pleochroism:
X = reddish brown
Y = Z = smoky green

Table 1 compares these values with reported indices of refraction for some other iron-bearing micas.

Table 1. Comparison of Indices of Refraction for Several Iron-Bearing Micas

Indices of Refraction	Iron-rich mica (±0.01)	Biotite	Lepidomelane	Annite
α	1.62	1.56–1.60	1.616–1.630	1.630
β	1.68	1.60–1.66	1.670–1.690	1.690
γ	1.68	1.60–1.66	1.670–1.690	1.690

The optical data on this material are somewhat variable, probably as a result of variations in the iron content. The determined value of α is uncertain because of the strong pleochroism and the plate-like nature of the material.

Physically, while this material retains the sheet structure of the original muscovite, it is considerably more brittle than muscovite or biotite. However, it still retains perfect basal cleavage and measurements of the value of α were made with difficulty. Also noted was the presence of variable quantities of an opaque material (probably magnetite) in intergrowth with the iron-rich mica.

Kalsilite Crystallography

To the best of the authors' knowledge, well-developed crystals of kalsilite have not been found in nature nor produced in the laboratory previously. Hence, identification has been generally based on the optical and x-ray measurements which are possible on materials which are anhedral. The kalsilite crystals grown here (Fig. 3) were of sufficient size to make some interfacial angle measurements with the two-circle goniometer (Table 2). These values are believed to be accurate within ±2°. Greater accuracy would be desirable, but does not appear possible with

TABLE 2. INTERFACIAL ANGLES FOR HYDROTHERMALLY PREPARED KALSILITE

Form	Miller Indices	$\rho \pm 2°$	$\phi \pm 2°$
Basal pinacoid	{0001}	0°	—
Hexagonal prism	{10$\bar{1}$0}	90°	60° intervals
Hexagonal dipyramid	{10$\bar{1}$1}	61°	60° intervals
Hexagonal dipyramid	{20$\bar{2}$3}	46°	60° intervals

the materials available. The crystal faces generally show a slight curvature which tends to give a range of values. Several crystals were measured which show four distinct forms.

These measured values of interfacial angles compare favorably with the values for the {10$\bar{1}$1} and {20$\bar{2}$3} forms computed using the values a_0 (5.17 Å) and c_0 (8.67 Å) determined by Bannister and Hey (1942). The ρ angle for the {10$\bar{1}$1} faces should be closer to 59°, and for the {20$\bar{2}$3} faces closer to 48°. The hexagonal dipyramid assigned the {10$\bar{1}$1} indices is rather well developed compared with the {2023} form which consists only of minute faces and which does not appear on all crystals.

The space group determined for kalsilite by Bannister and Hey (1942) is $P6_32$. The forms observed are possible forms in this crystal class.

X-RAY DATA

X-ray data were determined for the iron-rich mica and kalsilite obtained in these runs. A comparison of basal plane reflections for the iron-rich mica formed in these experiments, lepidomelane, biotite, and

TABLE 3. COMPARISON OF BASAL SPACINGS FOR SEVERAL MICAS

(hk·l)	Iron-rich mica[1]		Lepidomelane[2]		Biotite[3]		Muscovite[4]	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
00.1	10.04	100	10.1	100	10.1	100	10.0	100
00.2	5.06	50	5.04	20	4.58	20	5.0	60
00.3	3.37	100	3.36	100	3.36	100	3.34	80
00.4	2.51	95	2.51	40	2.51	40	2.48	40
00.5	2.033	45	2.01	80	2.00	80	2.00	70

[1] Copper radiation, Nickel filter, ($\lambda = 1.5418$ Å for K_α), diffractometer.

[2] ASTM X-ray Powder Data File, card number 2-0044, Molybdenum radiation, ($\lambda = 0.709$ Å), Nagelschmidt, 1937).

[3] ASTM X-ray Powder Data File, card number 2-0045, Molybdenum radiation, ($\lambda = 0.709$ Å), (Nagelschmidt, 1937).

[4] ASTM X-ray Powder Data File, card number 2-0055, Iron radiation, ($\lambda = 1.936$ Å), (British Museum).

muscovite is presented in Table 3. These results indicate that the iron-rich material is more similar to lepidomelane than to biotite. *X*-ray data for annite were not available. The recorded *x*-ray intensities were high for the even ordered reflections because a single plate of the iron-rich mica was mounted on a specimen holder to give only basal plane reflections, while the data shown for the other micas were taken from tabulations including all possible reflections.

Table 4 presents the *x*-ray powder photograph data for kalsilite. These results are very close to those of Smith and Tuttle (1957).

Smith and Sahama (1957) discussed order-disorder relations in kalsilite. The ordered form should either have a larger unit cell or be less symmetrical. Crystals of a kalsilite-nepheline microperthite from Kabfumu, (Belgian) Congo showed six additional diffuse reflections indicating that a new unit cell had to be taken at 30° to the usual cell. A rotation pattern about the *a*-axis of a single crystal specimen grown in these experiments was taken to determine whether the ordered or disordered form was present. Examination of the pattern showed no weak intermediate layer lines, indicating this sample to be of the disordered form.

TABLE 4. *X*-RAY DIFFRACTION PATTERN FOR HYDROTHERMAL KALSITE
Debye-Scherrer camera, Copper radiation, Nickel filter, 12 hours

d(Å)	I	*d*(Å)	I
4.34	S	1.959	MW
3.97	VS	1.931	M
3.12	VS	1.770	M
2.582	VS	1.662	S
2.483	S	1.622	S
2.435	S	1.575	VS
2.219	S	1.560	M
2.175	VS	1.491	VS
1.992	M	1.459	M

CONCLUSIONS

Muscovite was readily converted under hydrothermal conditions to the $KAlSiO_4$ polymorph, kalsilite, and an iron-rich mica, very similar to lepidomelane in optical properties and x-ray diffraction pattern. *X*-ray and optical data indicate that the kalsilite described here corresponds closely to the natural kalsilite described by Bannister and Hey (1942) and the synthetic preparations of other workers. A single crystal rotation photograph indicates the kalsilite prepared in these experiments to be the disordered form.

It has been suggested that kalsilite may be more common in nature than is apparent. The apparent ease with which muscovite is converted to iron-rich mica and kalsilite suggests that additional occurrences of kalsilite in nature may be found where basic dikes intrude muscovite-bearing rocks.

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