

## MINERALOGICAL NOTES

### Some Notes on $\alpha$ -Spodumene, $\text{LiAlSi}_2\text{O}_6$

J. GRAHAM

Division of Mineralogy, CSIRO, Floreat Park, Western Australia, 6014

#### Abstract

Many spodumenes in polished section show a large variety of inclusions, some of them unusual minerals. The most common appear to be albite, plagioclase, and muscovite. It is suggested that X-ray reflections thought to indicate a low-symmetry space group for spodumene may be due to such phases in preferred orientations, and that these may also account for a good deal of the variation in spodumene analyses. Spodumene at Ravensthorpe in Western Australia is replaced by massive muscovite in three intergrown orientations related to the original structure; the chemical changes are discussed.

#### Introduction

As part of a study of the formation and alteration of  $\alpha$ -spodumene,  $\text{LiAlSi}_2\text{O}_6$ , a refinement of the crystal structure of this mineral was made some years ago on a fragment of almost ideal composition<sup>1</sup> (S32, Table 1) from a pegmatite at Mt. Marion in Western Australia. The three-dimensional structure analysis resulted in a conventional  $R$  of 0.048 in the centrosymmetric space group  $C2/c$ , including unobserved reflections at half background intensity. The parameters are in excellent agreement with those obtained by various authors (Clark, Appleman, and Papike, 1968, 1969; Peacor, private communication, 1970; Cameron *et al.*, 1973) but in common with these authors, space-group-forbidden reflections were observed.

At the Catlin Creek pegmatite, Ravensthorpe, Western Australia, spodumenes of various colors and differing composition occur. One area is characterized by "rotten spodumene," a dark green mica pseudomorph after spodumene. Even in fresh spodumene sectioned parallel to  $\{001\}$ , mica flakes can be seen optically aligned parallel to  $\{100\}$  and  $\{110\}$ , and it is possible to separate some mica from the spodumene by grinding and heavy-liquid separation. In other regions, alteration producing a white color is sometimes accompanied by an increase in sodium. Partial chemical analyses showed that low lithium figures were usually associated with high  $\text{K}_2\text{O}$  or high  $\text{Na}_2\text{O}$ ,

but not in sufficient quantity to make up the original stoichiometry.

It was of interest to know whether the spodumene itself could accommodate these changes in stoichiometry, or whether they were always due to the presence of additional phases.

#### Composition

A series of full and partial analyses was carried out on spodumenes and their decomposition products from Mt. Marion and Ravensthorpe, which together with published data on other spodumenes (Deer, Howie, and Zussman, 1963; Simpson, 1952) suggested a considerable variability of composition. Selected analyses from our series are shown in Table 1. Optical examination of powdered samples and of thin sections did not indicate any major degree of heterogeneity, although there was often alteration on partings and cleavages which made it necessary to hand pick material for analysis.

An attempt was made at the time of the structure analysis to detect differences due to chemical differences between Mt. Marion and Ravensthorpe spodumenes (analyses S32 and S30 in Table 1). Two-dimensional refinements showed identical positional parameters, so a difference Fourier was calculated from the  $hk0$  intensities,  $I_{S32} - I_{S30}$ . The lithium site was characterized by a weak positive region of charge and the aluminum site by a weak negative region, but the effect was very small, and the Fourier was on the whole remarkably flat. The meaning of this result de-

<sup>1</sup> All bulk analyses were carried out by Mr. C. E. S. Davis, to whom the author is deeply grateful.

TABLE 1. Analyses of Spodumene and Muscovite

	Spodumene				Muscovite
	S32	S30	S36	S38	S20
SiO <sub>2</sub>	64.3	63.8	62.23	63.19	52.5
Al <sub>2</sub> O <sub>3</sub>	26.0	26.7	26.7	27.4	29.2
Fe <sub>2</sub> O <sub>3</sub>	0.57	0.41*	0.19*	0.7*	2.04*
FeO	0.43				
MgO	0.01	0.04	0.07	0.01	2.40
CaO	0.06	0.09	0.62	0.34	0.08
K <sub>2</sub> O	0.03	0.09	0.83	0.36	9.9
Na <sub>2</sub> O	0.08	0.26	1.77	0.90	0.26
Li <sub>2</sub> O	7.55	7.72	6.06	6.82	0.02
H <sub>2</sub> O <sup>+</sup>	n.d.	n.d.	0.13	0.05	4.56
H <sub>2</sub> O <sup>-</sup>	n.d.	n.d.	0.94	0.59	0.59
	99.03	99.11	99.54	99.73	101.55
Musc.	0.3	0.9	8.5	3.6	97.4
Alb.	0.7	2.2	15.0	7.6	2.2
An.	0.3	0.4	3.3	1.7	0.4
Structural Formulae (Spodumenes corrected for feldspars and mica)					
S32	(Li <sub>0.97</sub> Fe <sub>0.01</sub> )(Al <sub>0.96</sub> Fe <sub>0.01</sub> )Si <sub>2.02</sub> O <sub>6</sub>				
S30	Li <sub>1.01</sub> (Al <sub>0.99</sub> Fe <sub>0.01</sub> )Si <sub>2.00</sub> O <sub>6</sub>				
S36	Li <sub>1.04</sub> Al <sub>1.01</sub> Si <sub>1.98</sub> O <sub>6</sub>				
S38	Li <sub>0.98</sub> Al <sub>1.03</sub> Si <sub>1.99</sub> O <sub>6</sub>				
S20	(K <sub>0.84</sub> Li <sub>0.01</sub> )(Al <sub>1.64</sub> Fe <sub>0.10</sub> Mg <sub>0.24</sub> )(Al <sub>0.61</sub> Si <sub>3.39</sub> )O <sub>10</sub> (OH) <sub>2</sub>				
*Total iron as Fe <sub>2</sub> O <sub>3</sub> . Analyst C.E.S. Davis.					

depends on the detailed structural formula assumed, but it seems clear that some Fe<sup>3+</sup> enters the aluminum site. This has since been confirmed by microprobe analysis of hiddenite from Spargoville in Western Australia<sup>2</sup> which contains approximately ½-1 percent Fe in solid solution. The result is fully explained if iron is distributed as shown in Table 1 for S32.

The variability of bulk composition, and the slight effects produced by it in the spodumene structure, suggested that spodumene crystals could be heterogeneous. This has been proposed before to explain the commonly observed excess of silica in the bulk analyses (Deer *et al.*, 1963).

An optical study of altered material suspended in a medium of R.I. 1.70 gave no indication of the presence of significant amounts of a second phase, although there was local staining at the edges of many grains and lamellar defects were nearly always observed. In polished section, however, the sample was obviously heterogeneous, and in fact contained about 10 percent feldspar and 2 percent mica. The

mica was often lamellar, but the plagioclase, which was on a much more massive scale, showed no obvious orientation relationships.

Polished sections of a number of spodumene crystals, including gem-quality hiddenite and kunzite, were examined microscopically and by microprobe. Every spodumene crystal examined contained some extensive veining and a variety of the following widely dispersed micro-inclusions (deduced from semi-quantitative microprobe data): albite, various compositions of plagioclase feldspars, muscovite (some Na with K), cassiterite, siderite with extensive Mn,Mg substitution, mangan-apatite, lithiophilite, silica, pentlandite (1 – 2μ only), prehnite, pollucite, new cesium mineral, and Na,Mn,Fe aluminosilicate. Mica, albite, and plagioclase were ubiquitous except in good areas of the gemstones. Because of the small size of most of the inclusions, analyses were only semi-quantitative, and some of the mineral identities are deduced. Errors could be introduced by the fact that the lithium content is not known.

In a sample from McPhee's Range in Western Australia<sup>3</sup> for which an analysis is available (Simpson, 1952), a cesium mineral was observed in rounded or dentate forms up to about 20 μ across. It also occurred in small veins in close association with muscovite, from which it could not be distinguished in polished section. The composition was similar to that of pollucite, but with calcium instead of some sodium, and a somewhat higher Al content. In polished thin section no grain could be found free of interference from spodumene, so optical properties could not be determined. Its Si(Li) spectrum is compared with that of pollucite in Figure 1.

In one specimen, two generations of spodumene were observed. No difference in composition could be detected in the electron microprobe, but the original spodumene fluoresced red under electron bombardment, while secondary spodumene in major veins (largely filled with albite) fluoresced blue.

It became evident from a series of partial analyses of more-or-less altered spodumenes that most of the potassium content is associated with muscovite alteration and most of the sodium and potassium with plagioclase feldspar. In performing a full analysis, it is essential to determine all elements on a single sample, as the heterogeneity can be observed on a macroscale, even when apparently clean regions are selected.

When muscovite and feldspar are allowed for,

<sup>2</sup> Kindly supplied by the Government Chemical Laboratories.

<sup>3</sup> Kindly supplied by The Government Chemical Laboratories.

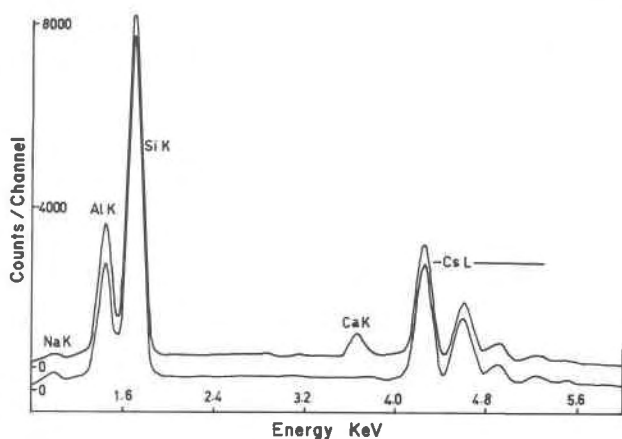
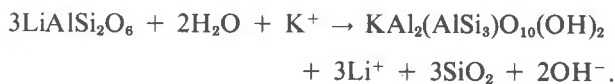


FIG. 1. Electron microprobe spectra of pollucite (lower) and the calcium-containing mineral from McPhee's Range spodumene. Calcium and cesium are positively correlated.

structural formulae from analyses such as those in Table 1 or in Deer *et al* (1963) are quite close to theoretical values; in particular, the excess of silica mentioned in Deer *et al* is usually considerably reduced. The formulae in the table are calculated to 6 oxygens. From the difference Fourier and from the change in the temperature factor of the lithium atom between samples, there is some isomorphous substitution for Li in the spodumene structure, but it is evidently very slight.

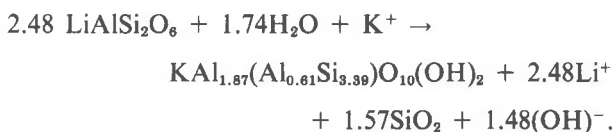
### The Transformation to Muscovite

A single-crystal diffraction pattern of the "rotten spodumene" from Ravensthorpe showed that it consisted of muscovite in three orientations, with the silicate sheets parallel respectively to {110} and {100} of the original spodumene. The pseudomorphous relationship suggests that the transformation to massive muscovite occurred by material exchange in solution, with little or no change in volume of the solid phases. An ideal reaction could be written

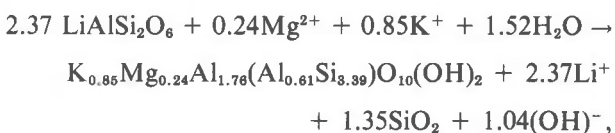


The silica and  $\text{OH}^-$  produced could be combined in some form of soluble silicic acid. However, a decrease in volume of the solid phases of about 20 percent is associated with this reaction.

The volume change would be reduced sufficiently by producing a silica-rich muscovite. Assuming a silica content equal to that observed (S20, Table 1) we may write



This reaction is accompanied by only a 2½ percent volume change, and the transport requirements are smaller. The metal-deficient octahedral layer is presumably unstable, so that the actual product at Ravensthorpe has magnesium replacing some of the aluminum and a reduced layer charge. One could produce the observed mica from ideal spodumene by the reaction



which would be accompanied by a volume increase of 2 percent. The alteration from spodumene to mica represents an increase in the proportion of alumina; the equations assume that no aluminum is introduced. They show that the amount of spodumene required for the transformation, and hence the overall change of volume of the solid phases, is a function of the detailed composition of the individual phases.

The structures of the two minerals and their orientation relationships suggest that the alteration to muscovite may be partly by a topotactic mechanism. A stylized (001) section of spodumene is shown in Figure 2a. In it, each quadrilateral represents an end-on view of a silicate chain (composition  $\text{SiO}_3^{2-}$ ) which runs the length of the crystal in the *c* direction. The (100) layering and the (110) cleavage are easily recognized. The mica structure may be stylized in a similar way (Fig. 2b).

If every alternate  $\text{SiO}_3^{2-}$  chain of spodumene is rotated through 180° about its long axis, and half of the non-bridging oxygens are converted to hydroxyls which remain in appropriate holes in the structure, the mica sheets can be built up on the spodumene (100) provided that the *M1* and *M2* cations rotate with the chain. This is a minor mode of occurrence of muscovite in "rotten spodumene," and is accomplished with relatively minor change of shape (12 percent expansion along spodumene [100], 9 percent along [010], and a contraction of 1 percent parallel to the chains along [001]). The *M1* cations are completely replaced by potassium at some stage during the process, and silica is lost to provide the necessary alumina enrichment and to compensate for the

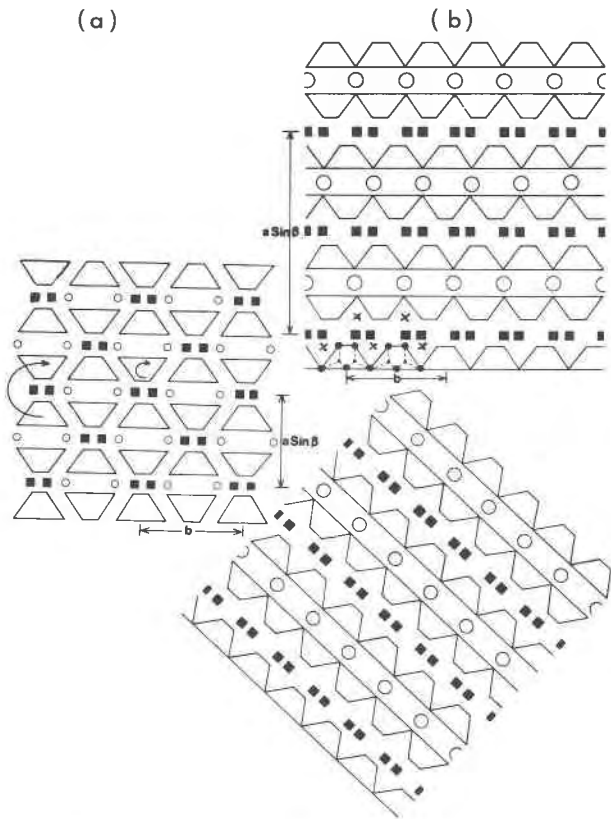


FIG. 2. Stylized structures of spodumene (a) and of mica (b) in the two orientations observed relative to spodumene. The silicate chains of the spodumene are perpendicular to the paper, and are represented by trapezia. The mica sheet is made up of similar chains sharing oxygens at the corners of the trapezium. Oxygens released by this sharing are converted to hydroxyls, a few of which are shown as crosses in (b). Squares are largely aluminum ( $M_2$ ) and small circles largely Li( $M_1$ ). In the mica, the larger circles are potassium.

volume increase of 21 percent which would occur if a 1:1 correspondence existed between the structures as suggested by this mechanism.

If every chain is rotated approximately  $46^\circ$  clockwise (or anti-clockwise), leaving the  $M_1$  and  $M_2$  cations approximately in their original spodumene positions, mica sheets parallel to (110) in spodumene are produced. This is the major orientation of the muscovite layers. A similar result, which requires somewhat smaller final adjustments, is obtained if pairs of silicate chains (the "I-beam" units of Papike *et al.*, 1973) rotate together about their common aluminum ions. Since this transformation is accompanied by a large expansion in the spodumene [110] direction (normal to the mica sheets) and a contraction along [1 $\bar{1}$ 0] (parallel to the mica sheets), it is not possible to build up extensive mica layers in any one

orientation, but the major orientations must alternate, giving the massive finely crystalline form observed.

Perhaps the most likely micro-inclusions, especially in gem-quality material, would be small quantities of petalite or eucryptite exsolved during the crystallization of  $\alpha$ -spodumene from the high temperature  $\beta$ -spodumene solid solution. Indeed it would be quite remarkable if such exsolution did not occur, given the formation of  $\alpha$ -spodumene by a double eutectoid as suggested by Roy, Roy, and Osborne (1950). The petalite structure consists of spodumene chains condensed to form a corrugated sheet somewhat different from the mica discussed in this paper (Liebau, 1961).

### The Space Group Problem

Most structure analyses of spodumene have been plagued by a number of space-group forbidden reflections which suggested a lower symmetry for spodumenes than for most other clinopyroxenes (Clark *et al.*, 1968, 1969; Peacor, private communication, 1970). We made many attempts to refine the structure in space groups  $C2$  and  $Cc$ , but no matter what displacements were applied to the atoms before refinement, they always returned to the same centrosymmetric positions. Only a few of the reflections could be interpreted as due to the Renninger effect, as the geometric criteria were not satisfied. Cameron *et al.* (1973) did not observe any forbidden reflections in precession photographs of spodumene from the same sample in which Clark *et al.* (1969) had observed up to ten. As shown in Table 2, a change in radiation or a change in rotation axis alters the reflections observed, and they are often associated with general radiation streaks which suggests that some may represent spots from an adjacent layer, but we could not exclude them with layer screens. Various tests, including the sensitive optical second harmonic generation (Kurtz and Perry, 1968), indicate centrosymmetry. The observations described in this paper suggested that the reflections could be artifacts due to the presence of a second phase. A  $b$ -axis Weis-

TABLE 2. Space-Group Forbidden Reflections from Mt. Marion Spodumene

Conditions	Reflections Observed
$c$ axis rotation, $CuK\alpha$	$\bar{5}01$ , $\bar{1}203^*$
$b$ axis rotation, $CuK\alpha$	Strong $\bar{2}01$ ; $\bar{2}03$ ; $\bar{2}05$ ; $201$ ; $20\bar{1}$ ; $20\bar{1}$ Weak $003$ ; $603$ ; $801$ ; $10,0,\bar{1}$ ; $40\bar{3}$ ; $\bar{4}0\bar{3}$ ; $10,0,1$
$b$ axis rotation $MoK\alpha$	$10,0,\bar{1}^*$ ; $\bar{2}0\bar{1}$ ; $201$ ; $\bar{2}03$

\* Reflection truncated.

senberg pattern from gem-quality kunzite still showed three forbidden reflections. This would require that any inclusions giving rise to the reflections must be coherent or finely dispersed; the kunzite did contain visible rutile needles, and the hiddenite was not free of inclusions. In any case, the variability of the non-space group reflections, and the good refinements which have been obtained, leave no obvious alternative to the  $C2/c$  symmetry.

### References

- CAMERON, M., S. SUENO, C. T. PREWITT, AND J. J. PAPIKE (1973) High temperature crystal chemistry of six pyroxenes. *Am. Mineral.* **58**, 594-618.
- CLARK, J. R., D. E. APPLEMAN, AND J. J. PAPIKE (1968) Bonding in eight ordered clinopyroxenes isostructural with diopside. *Contrib. Mineral. Petrol.* **20**, 81-85.
- , ———, AND ——— (1969) Crystal chemical characterization of clinopyroxenes based on eight new structure refinements. *Pyroxenes and Amphiboles: Crystal Chemistry and Phase Petrology, Mineral. Soc. Am. Spec. Pap.* **2**, 31-50.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1963) *Rock Forming Minerals*, Vols. 2 and 3, Longmans, London.
- EGGLETON, R. A. (1974) Nontronite intergrown with hedenbergite (abstr.). *Int. Crystallogr. Conf. Diffraction Studies of Real Atoms and Real Crystals, Melbourne*. Australian Academy of Science, Canberra.
- KURTZ, S. K., AND T. T. PERRY (1968) A powder technique for the evaluation of nonlinear optical materials. *J. Appl. Phys.* **39**, 3798-3813.
- LIEBAU, F. (1961) Untersuchungen an schichtsilicaten des formeltyps  $A_m(\text{Si}_2\text{O}_6)_n$  III. Zur Kristallstruktur von Petalit,  $\text{LiAlSi}_4\text{O}_{10}$ . *Acta Crystallogr.* **14**, 399-406.
- PAPIKE, J. J., C. T. PREWITT, S. SUENO, AND M. CAMERON (1973) Pyroxenes: comparisons of real and ideal structural topologies. *Z. Kristallogr.* **138**, 254-273.
- ROY, R., D. M. ROY, AND E. F. OSBORN (1950) Compositional and stability relationships among the lithium aluminosilicates: Eucryptite, spodumene, and petalite. *J. Am. Ceram. Soc.* **33**, 152-159.
- SIMPSON, E. S. (1952) *Minerals of Western Australia*, Vol. III, p. 585, Government Printer, Perth.

*Manuscript received, December 17, 1973; accepted for publication, March 20, 1975.*