The Crystal Structure of Bikitaite, Li[AlSi$_4$O$_8$]·H$_2$O

VLADIMIR KOCMAN

Department of Geology, University of Toronto

ROBERT I. GAIT

Royal Ontario Museum

JOHN RUCKLIDGE

Department of Geology, University of Toronto, Toronto, Canada M5S 1A1

Abstract

The crystal structure of bikitaite, Li[AlSi$_4$O$_8$]·H$_2$O, has been determined from three-dimensional MoKα counter data by direct methods and refined by full matrix least-squares calculations using anisotropic temperature factors to an unweighted R-value of 0.037 for 824 observed reflections on a crystal from Bikita, Rhodesia. The cell parameters are: $a = 8.613(4)$, $b = 4.962(2)$, $c = 7.600(4)$ Å, $β = 114.45(1)^\circ$, space group $P2_1$, $Z = 2$.

There are three basic tetrahedral sites in the asymmetric unit of bikitaite, designated $T(1)$, $T(2)$, and $T(3)$. Refinement of the structure indicated (0.5 Al + 0.5 Si) in $T(1)$ and $T(3)$ and Si only in the $T(2)$ site. The mean bond lengths of the $T(1)$O$_4$ and $T(3)$O$_4$ tetrahedra are both 1.681 Å and the mean bond length of the $T(2)$O$_4$ tetrahedron is 1.610 Å. These bond lengths are very similar to those in comparable tetrahedra in other tektosilicates. The lithium atom in bikitaite is tetrahedrally coordinated by three oxygen atoms and a water molecule, with the mean bond lengths of the LiO$_4$ tetrahedron being 1.972 Å. With the exception of the oxygen in the H$_2$O molecule, all oxygens in the structure are bridging, forming zig-zag chains of tetrahedra parallel to [010]. These chains are joined together to form a three-dimensional network with one large channel containing Li and H$_2$O and with several smaller, empty channels.

Introduction

Bikitaite, a lithium-aluminosilicate from the lithium-rich pegmatites in Bikita, Southern Rhodesia, was described by Hurlbut (1957). Preliminary analytical, optical, and X-ray investigations (Hurlbut, 1957, 1958) have shown that the chemical formula of bikitaite is close to Li$_{0.95}$Al$_{1.10}$Si$_{1.95}$O$_8$·1.15 H$_2$O and that the mineral crystallizes in the monoclinic system with two possible space groups $P2_1$ or $P2_1/m$. Leavens, Hurlbut, and Nelson (1968) reported bikitaite in the lithium-rich pegmatites at King’s Mountain, North Carolina. Chemical analyses of samples from this locality have the nearly ideal composition of LiAlSi$_2$O$_8$·H$_2$O.

The first X-ray crystal structure studies of bikitaite were carried out by Appleman (1960) who reported the basic outline of the bikitaite structure in the space group $P2_1$. Accurate determination of the structure was prevented by the poor quality of crystals available at that time (Appleman, personal communication, 1972) and consequently structural details of Appleman’s refinement were never published. The thermal and chemical properties of bikitaite were studied by Phinney and Stewart (1961), who described dehydration and ion exchange properties of the mineral. Bikitaite has been synthesized at pressures between 1 to 2.5 kbar and at temperatures ranging from 300–350°C by Drysdale (1971).

Experimental

Excellent crystals of bikitaite (specimen #M27924 kindly provided for this study by the Royal Ontario Museum) were selected from the specimen. Crystals were examined under polarized light and by X-ray diffraction, and a crystal with well-developed faces, elongated along the $b$ axis, was chosen for the study. The crystal was cut in two; one part was saved for electron microprobe analysis, and the other part was used for determination of cell dimensions and data collection.
Several electron microprobe analyses of the single crystal were carried out using the ARL-EMX instrument at operating conditions of 15kV and 0.05 μA sample current. Diopside and anorthite were used as standards for Mg, Si, and Al. These data were processed by the EMPADR VII program written by Rucklidge and Gasparini (1969). Li₂O was determined by atomic absorption. Small amounts of Na, K, and Mg were reported in bikitaite by Hurlbut (1958), but a careful check using the electron microprobe revealed no Na or K. The small amount of Mg detected, 0.01-0.02 percent, was neglected. A summary of analytical and crystal data of bikitaite is given in Table 1.

Intensity data were collected up to sin θ/λ = 0.70 on a Picker FACS-1 four-circle diffractometer using Zr-filtered MoKα radiation. The dimensions of the crystals were 0.40 x 0.48 x 0.30 mm, and a total of 947 symmetry independent reflections were collected by the moving crystal-moving counter technique (2θ scan), using a scanning rate of 1°/min. with two stationary background counts of 40 sec. on each side of the peak. The threshold level for “unobserved” reflections was set to 3o F², and a total of 23 reflections were equal or less than this value. Absorption was low (μMoKα = 7.3 cm⁻¹) and no corrections were considered necessary. Corrections were made for Lorentz-polarization factors, and the data were put on an absolute scale by the K-curve and E-gen program. The distribution of E’s clearly indicated a noncentrosymmetric space group for bikitaite, thus confirming Appleman’s (1960) choice of P2₁:

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<th>Av.</th>
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Solution and Refinement of the Structure

A set of 181 E’s > 1.4 was chosen for the direct structural determination. The origin of the cell in space group P2₁ was specified according to Karle and Hauptman (1966) and Hauptman and Fisher (1971) by the means of 3 reflections with high E values. Three other reflections with high E’s were picked as starting phases a, b, c for the Σ₂ relationship and tangent formula refinement (Karle and Karle, 1966). All calculations were carried out by Larson and Drew’s (1968) ‘Tanfor’ program.

The calculated E-map using starting phases listed below revealed the whole structure.

### Table 1. Crystal Data and Chemical Analysis

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Six cycles of XFLS (Ellison, 1962) positional least-squares refinement using 9 atoms in the asymmetric unit decreased the R-value from an initial value of 0.36 to 0.15. The difference Fourier map calculated at this stage confirmed the positions of Li and O(7) (water molecule) which originally showed up in the ‘E-map’, but had been left out of the refinement. The addition of these to the atom list, together with another 3 cycles of isotropic refinement wherein Al was arbitrarily assigned to the T(3) site, lowered the R value to 0.076. This run, however, produced significantly different temperature factors for the tetrahedral sites T(1), T(2), and T(3), but the calculated mean bond lengths of the tetrahedra indicated that sites T(1) and T(3) are occupied by 0.5 Al + 0.5 Si, while site T(2) is occupied only by...
Si (Jones, 1968). Therefore a new scattering curve for \(T(1)\) and \(T(3)\) was calculated from \([f(\text{Al}) + f(\text{Si})]/2\) and a further 3 cycles of isotropic refinement lowered the \(R\) value to 0.052, and also reduced the spread of the isotropic temperature factors of the \(T\) sites. A summary of this refinement is shown in Table 2.

Three additional cycles of full matrix least-squares refinement with anisotropic temperature factors converged to the \(R\) value of 0.037 for 824 'observed' reflections and the value of the standard deviation of an observation of unit weight was 1.003. This quantity is given by \([\Sigma_{w}(F_o - F_c)^2/(NO - NV)]^{1/2}\) where \(w\) is the weight, \(F_o\) and \(F_c\) are the observed and calculated structure factors, \(NO\) is the number of observed structure factors and \(NV\) is the number of parameters varied in the last cycles of the refinement.

The weighting scheme used in the refinement was of the form \(w = 1/\sigma_{F_o}^2\), where:

\[
\sigma_{F_o} = 0.0565 F_o - 0.9285 + 9.608/F_o.
\]

The \(R\) value for all 947 reflections was 0.044. An attempt was made to establish the absolute configuration of the structure at the isotropic level (Ibers and Hamilton, 1965), but the results were rather inconclusive. The \(R\) values were 0.0480 for the configuration described in this paper (Table 3) and 0.0481 for the enantiomorph. The anomalous corrections for Si and Al (\(\Delta f = 0.1, \Delta f' = 0.1\)) were taken from Templeton (1962). A final difference Fourier map showed a few spurious peaks of height of about 0.6 \(e/\text{Å}^2\) in an overall background of about 0.3 \(e/\text{Å}^2\). Two peaks, in suitable positions, and approximately 1 Å apart from O(7) were considered to be hydrogen atoms. They were added to the atom list, given isotropic temperature factors of O(7), and positionally refined by one cycle of least-squares. The suggested coordinates of the hydrogen atoms are as follows: H(1) 0.303, 0.334, 0.474 and H(2) 0.455, 0.163, 0.467.

Scattering factors of neutral Si, Al, Li, and O used in the refinement were those reported by Cromer and Mann (1968). All calculations were carried out on IBM 360/65 and 370/165 systems at University of...
of Toronto Computer Center. The positional and thermal parameters of the structure with their standard deviations are shown in Table 3. All important bond lengths and angles and their standard deviations as calculated by ORFFE (1964) program are given in Table 4. A comparison of the observed and calculated structure factors (10 F_o, 10 F_c) and the phase angle α are listed in Table 5.

**Description of the Structure**

The structure, which is of a framework type, consists of infinite zig-zag chains of SiO₄ and (Si,Al)O₄ tetrahedra extending along two-fold screw axes parallel to the y-axis. These chains of tetrahedra are joined together to form large and small channels parallel to the y-axis. All T sites are tetrahedrally coordinated by four oxygen atoms and the resulting tetrahedra are linked together by sharing corners with equivalent tetrahedra in the y direction and with non-equivalent tetrahedra in the other directions. Since the 2y axis at 1/2, y, 1/2 is not occupied by any chain, the whole network forms one large channel centered on 1/2, y, 1/2 in which the Li atoms and H₂O molecules are located. Four smaller empty channels surround the large channel, so that for every large channel there are two small channels in the unit cell. The cross section of the large channel is about 5.5 x 6.5 Å and the diameter of the small channels is approximately 4 Å. Figure 1 is a three-dimensional view of the structure as plotted by the ORTEP (1965) program and Figure 2, which is a projection of the structure along the y axis, shows the distribution of the channels in bikitaite. Part of the structure projected along z is shown in Figure 3.

Each lithium atom is tetrahedrally coordinated by three oxygen atoms and a water molecule in such a way that only oxygens from Al-rich T(1) and T(3) tetrahedra participate in this bonding. This configuration maintains the charge balance of the structure. The Li-O bond lengths vary from 1.946 to 2.000 Å with an average length of 1.972 Å, which is in agreement with the average value of 1.974 Å found for this bond in LiOH·H₂O (Agron, Busing and Levy, 1972) and with the value of 1.98 Å given for tetrahedrally coordinated lithium compounds (Ondik and Smith, 1962). The water molecules in the structure are held in the large channel mainly by the longest coordination bonds in the LiO₄ tetrahedra (2.000 Å), but weak hydrogen bonding also is expected between the water molecules themselves. The O(7)–O(7') distance (water–water) is 2.95 Å, the hydrogen atom H(2') being 0.91 Å from O(7') and forming an O(7')...H(2')–O(7') angle of 173°. No contacts closer than 3.14 Å exist between the water oxygen and the rest of the silicate structure. Such a situation is not unknown (Baur, 1964, 1972; Hamilton and Ibers, 1968) and the hydrogen bonding of H(1) can be explained by extremely weak or bifurcated hydrogen bonds. Valence sum calculations carried out on the structure (Donnay, personal communication, 1972) and assuming no hydrogen bond for H(1) indicated that...
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**10 F and 10 F. Unobserved reflections marked by*, phase angle alpha in millicycles.**
all valence sums fall within the expected limits except O(7) which has a residual charge of \( \approx 0.24 \) v.u., a value which suggests that O(7) must participate in weak hydrogen bonding with either O(3) or O(4) or both. Clarification of the hydrogen bonding in bikitaite must await the results of a neutron diffraction study of the mineral. A thermogravimetric analysis of the mineral failed to reproduce the three-stage dehydration curve described by Phinney and Stewart (1961), who suggested that the water molecules were located at two different sites in the crystal structure. Figure 4 shows the DTA and TGA data which indicate a one-stage dehydration which is consistent with the crystal structure here described.

The Si/Al contents of the tetrahedra as predicted from bond lengths according to the linear model of Jones (1968) are Si\(_{1.0}\) for T(2), and Si\(_{0.5}\)Al\(_{0.5}\) for both T(1) and T(3). This curious combination of perfect order and perfect disorder is completely consistent with the chemical formula, and leads to some interesting observations. The oxygens of the T(2) tetrahedron are all in 2-fold coordination, forming bridges to T(1) or T(3) tetrahedra. On the other hand, in the T(1) and T(3) tetrahedra three of the oxygens are in planar 3-fold coordination, having a link to Li as well as to the adjacent Al\(_{0.5}\)Si\(_{0.5}\). The Li\(^+\) thus provides the necessary charge balance, as mentioned above, and in this way the structure forces both T(1) and T(3) cations to have an equal

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**Fig. 1.** A three-dimensional view of the bikitaite structure. Plotted with the ORTEP program, ellipsoids are drawn at 60 percent probability.
The shaded tetrahedra, at \( b \geq 1/2 \) share corners with the unshaded tetrahedra at \( b \leq 1/2 \). The apparent tetrahedral edge-sharing is an illusion of the projection (see Fig. 3). H\textsubscript{2}O is shown as large circles, Li as small circles occupying the large channels in the structure. The \( z \)-axis is parallel to the shaded tetrahedral "chains", the \( x \)-axis is horizontal.

It is perhaps instructive to tabulate the mean bond lengths of the bridging oxygens between the various types of tetrahedra, and to compare with similar types in low albite (Ribbe et al, 1969) and maximum microcline (Brown and Bailey, 1964).

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**Fig. 2.** The bikitaite structure projected along the \( y \)-axis. The shaded tetrahedra, at \( b \geq 1/2 \) share corners with the unshaded tetrahedra at \( b \leq 1/2 \). The apparent tetrahedral edge-sharing is an illusion of the projection (see Fig. 3). H\textsubscript{2}O is shown as large circles, Li as small circles occupying the large channels in the structure. The \( z \)-axis is parallel to the shaded tetrahedral “chains”, the \( x \)-axis is horizontal.

**Fig. 3.** Part of the bikitaite structure projected on the \( z \)-axis from \( c = +1/3 \) to \( c = -1/3 \). Only the tetrahedra are shown. The \( y \)-axis is vertical and the \( x \)-axis is horizontal.

**Fig. 4.** Differential thermal analysis and dehydration curve of bikitaite. Initial sample weight = 0.8344 g, heating rate 5\textdegree C/min. Both DTA and TG curves taken simultaneously on the “Derivatograph” (Orion, Budapest).
Bikitaite: Low Albite

| Twinning of Oxygen with Respect to Si and Al<sub>0.5</sub>Si<sub>0.5</sub> is to be Expected, but a Further Asymmetry Exists in the Al<sub>0.5</sub>Si<sub>0.5</sub>O<sub>5</sub>–O-Al<sub>0.5</sub>Si<sub>0.5</sub> Linkage Which Is Less Easily Explained. In This Case the Mean Length of One Arm of the Arrangement Is 1.678 Å, the Other 1.696 Å. The Influence of the Li on the O Position Is Negligible. This Is So Because in the Cases of the Coordination Triangle of Both O(1) and O(2), the T-Cation Which Is Further from O Is Closer to Li; Only in the Case of O(6) Is One T-Cation Closer to Both Li and O Together. Perhaps Some Asymmetry in the sp<sup>3</sup> Hybridization of Oxygen Is Responsible, but Beyond This the Authors Feel Unable to Comment.

Acknowledgments

The Authors Would Like to Thank Professor Gabrielle Donnay for Her Interest in This Study, as Well as Her Comments and Valence Sum Calculations. We Are Also Indebted to Dr. Klaus Dichtmann from Department of Chemistry, University of Toronto, for Valuable Discussions Concerning the Weighting Analysis.

The Study Was Supported by a Grant from National Research Council of Canada.

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Manuscript received, October 30, 1972; accepted for publication, August 13, 1973.