# Crystal chemistry of double-ring silicates: Structures of sugilite and brannockite

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## Abstract

The crystal structures of sugilite, $Na_2K(Fe^{3+},Mn^{3+},Al)_2Li_3Si_{12}O_{30}$, $a = 10.009(2)$ Å, $c = 14.006(3)$ Å, from the Wessels mine, Kalahari (South Africa), and brannockite, $KSn_2Li_3Si_{12}O_{30}$, $a = 10.002(2)$ Å, $c = 14.263(3)$ Å from the Foote mine, Kings Mountain (North Carolina, U.S.A.), were refined from X-ray single-crystal data. Both minerals crystallize in the space group $P6/mcc$ and belong to the double-ring silicates. Li occupies strongly angularly distorted tetrahedra, sharing two edges with $(Fe^{3+},Mn^{3+},Al)$ octahedra in sugilite and with Sn octahedra in brannockite. Na in sugilite exhibits distorted ninefold coordination, whereas the corresponding site in brannockite is vacant. Literature data of double-ring silicates are used to develop some general rules concerning the structural and chemical variation within this structure type.

## Introduction

Double-ring silicates (Figs. 1, 2) with the space group $P6/mcc$ comprise a series of compounds with the general formula[1] $^{VI}A_2^{IX}B_2^{XII}C^{XVIII}D^{IV}(T2)_3^{IV}(T1)_{12}O_{30}$ (Forbes et al., 1972).

Sugilite with the simplified composition $Na_2K(Fe^{3+},Mn^{3+},Al)_2Li_3Si_{12}O_{30}$ is known from three localities: (1) Iwagi Islet, southwest Japan (Murakami et al., 1976), (2) Wessels mine, Kalahari, South Africa (Dunn et al., 1980), and (3) from an unknown locality in the Central Provinces of India (Clark et al., 1980).

Large amounts of sugilite were found in the South African Wessels mine, where the mineral occurs in a massive fine-grained state. This sugilite is used as a gemstone because of its striking purple to magenta color (Waitzman, 1982; Zeitner, 1982; Henn, 1986). Kato et al. (1976) refined the crystal structure of sugilite from Iwagi Islet ($R = 4.7\%$) with the formula $^C(K_{0.81}Na_{0.19})^B(H_2O_{0.91}Na_{0.64})_2$ $^A(Fe^{3+}_{1.32}Na_{0.59}Ti_{0.06}Fe^{2+}_{0.03})_2{}^{T2}(Li_{2.12}Al_{0.59}Fe^{3+}_{0.29})_3^{T1}Si_{12}O_{30}$.

Closely related to sugilite are the Li-bearing double-ring silicates sogdianite, $K_{1.1}Na_{0.9}Li_{2.6}Fe^{2+}_{0.2}Fe^{3+}_{0.2}Al_{0.2}Ti_{0.4}$-$Zr_{0.8}Si_{12}O_{30}$ (Dusmatov et al., 1968), and darapiosite, $Na_{1.08}K_{1.23}Ca_{0.11}Li_{1.31}Zn_{1.1}Mn_{1.31}Zr_{0.46}Nb_{0.07}Si_{12}O_{30}$ (Semenov et al., 1975). The latter two minerals were found in the alkalic massif of Tadzhikistan, Central Asia. The crystal structure of sogdianite was refined to an $R$ value of 12.2% (Bakakin et al., 1975), and the formula was modified to $^CK^B(Na_{0.95}K_{1.05})^A(Zr_{0.8}Fe^{3+}_{0.6}Ti_{0.4}Fe^{2+}_{0.2})^{T2}(Li_{2.55}$-$Al_{0.15}\square_{0.30})^{T1}Si_{12}O_{30}$.

Brannockite, $KSn_2Li_3Si_{12}O_{30}$, is only described from the

Foote mine, North Carolina, U.S.A., and occurs as tiny colorless hexagonal plates, which can be distinguished from other coexisting minerals by their characteristic blue-white fluorescence under short-wave UV radiation (White et al., 1973).

Synthetic Li-bearing double-ring silicates with the compositions $K_3Mg_4LiSi_{12}O_{30}$ and $Na_3Mg_4LiSi_{12}O_{30}$ were studied by Nguyen et al. (1980). X-ray structure refinements on powders indicated that Li shares a tetrahedral site with Mg.

Crystal-structure studies on sugilite and brannockite, which are presented in this paper, were performed for two reasons: (1) to gain further information on the distortion of edge-linked $LiO_4$ tetrahedra and (2) to understand crystal-chemical and structural constraints of hexagonal double-ring silicates. The crystal structure of sugilite was reinvestigated because in the original study by Kato et al. (1976), the Li-bearing T2 site is up to 30% occupied by $Fe^{3+}$ and Al, whereas our microprobe analyses and structure refinement indicate that T2 in sugilite from the Wessels mine is almost entirely occupied by Li. In addition, anisotropic displacement parameters (temperature factors) are necessary to test whether the B site at ½, ⅔, 0 or a B′ site at ½, ⅔, $z$ (as in eifelite; Abraham et al., 1983) is occupied by Na. Kato et al. (1976) refined sugilite using only isotropic displacement parameters.

## Experimental details

A purple hand specimen from the Wessels mine composed of colorless, fibrous serandite-pectolite, idiomorphous sugilite up to 0.5 mm in diameter, and additional Mn-bearing minerals thus far not identified, was used to select hexagonal prisms of purple sugilite (sample deposited at the Museum of Natural History,

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[1] Preceding superscripts denote coordination numbers or crystallographic positions.

TABLE 1. Composition of sugilites

| | Wessels mine | | | |
| --- | --- | --- | --- | --- |
| | crystal 1* | crystal 2* | crystal 3** | Iwagi Islet† |
| | Oxides (wt%) | | | |
| $SiO_2$ | 72.38 | 72.23 | | 71.38 |
| $TiO_2$ | 0.00 | 0.00 | | 0.51 |
| $Al_2O_3$ | 5.88 | 2.51 | | 2.97 |
| $Fe_2O_3$ | 5.62 | 8.91 | | 12.76 |
| FeO | | | | 0.19 |
| $Mn_2O_3$ | 0.89 | 2.38 | | 0.00 |
| $Li_2O$ | 4.5 (calc.) | 4.5 (calc.) | | 3.14 |
| $Na_2O$ | 5.65 | 5.43 | | 4.37 |
| $K_2O$ | 4.71 | 4.68 | | 3.76 |
| $H_2O$ | | | | 0.93 |
| Σ | 99.63 | 100.64 | | 100.01 |

| | Calculated formula | | Refined | Calc. formula |
| --- | --- | --- | --- | --- |
| Basis | 30 O | 30 O | formula | 12 Si |
| Si | 12.060 | 12.108 | 12.00 T1 | 12.00 T1 |
| Al | 1.155 | 0.496 | 0.34 A | 0.59 T2 |
| $Fe^{3+}$ | 0.705 | 1.124 | | 1.61 A, T2 |
| $Mn^{3+}$ | 0.113 | 0.304 | | |
| $Fe^{2+}$ | | | | 0.03 A |
| Σ(Fe + Mn) | 0.818 | 1.424 | 1.66 A | 1.64 A, T2 |
| Li | 3.015 | 3.034 | 3.00 T2 | 2.12 T2 |
| Na | 1.825 | 1.765 | 1.96 B | 1.42 B, A, C |
| K | 1.001 | 1.001 | 1.00 C | 0.81 C |
| $H_2O$ | | | | 0.91 B |

* $Li_2O$ = 4.5 wt% (T2 site is fully occupied by Li) has been added to the microprobe analysis for matrix correction with a ZAF procedure. All Fe and Mn were considered as $Fe^{3+}$ and $Mn^{3+}$, respectively.
** Composition obtained from site-occupancy refinements allowing for Al and Fe on A and for Na and vacancies on B.
† Wet-chemical analyses by Murakami et al. (1976) used as constraints for the structure refinement of Kato et al. (1976).

TABLE 2. Details of X-ray data collection

| | Sugilite | Brannockite 1 big domain | Brannockite 2 small domain |
| --- | --- | --- | --- |
| Unique reflections | 622 | 1127 | 1107 |
| Reflections >6σ ($F_{obs}$) | 517 | 914 | 575 |
| θ limit (°) | <30 | <40 | <40 |
| Crystal size (μm) | 200 × 200 × 175 | 225 × 150 × 30 | |
| R (%) | 1.7 | 2.9 | 4.2 |
| $R_w$ (%) | 2.9 | 4.4 | 4.2 |
| a (Å) | 10.009(2) | 10.002(2) | |
| c (Å) | 14.006(3) | 14.263(3) | |

Intensity data were collected wtih an Enraf Nonius CAD4 single-crystal diffractometer (graphite-monochromatized MoKα radiation) with an omega scan mode. Both twin domains of a brannockite crystal were measured separately. Cell dimensions (Table 2) were refined from 18 automatically centered reflections with $19° > θ > 11°$. Intensities of all reflections with $h ≥ k$ and h,k,l positive were collected up to $θ = 30°$ for sugilite and up to $θ = 40°$ for brannockite. Reflections for which a prescan determined $[σ(I)/I] ≥ 1$ were flagged as weak. The final scan speed was calculated from the prescan to obtain $[σ(I)/I] = 0.03$. Reflections of the type hhl and h0l with $l ≠ 2n$ were considered as systematically absent and rejected; however, all crystals yielded low but significant intensities for the reflections 0 0 15 and 0 0 17, which are inconsistent with P6/mcc symmetry. Nevertheless, two low-intensity forbidden reflections were considered insufficient for choice of another space group. Similar violations were also found for osumilites (Armbruster and Oberhänsli, 1988). For the platy brannockite crystal, an empirical absorption correction was applied (psi scans). Data reduction, including background and Lorentz-polarization correction, was carried out with the SDP program system (Enraf Nonius, 1983).

Reflections allowed under P6/mcc were employed for the refinements using the sogdianite starting values of Bakakin et al. (1975) with the program system PROMETHEUS (Zucker et al., 1983). For brannockite, only those reflections were considered for which no overlap of twin-related domains was determined. Structure factors were weighted on the basis of counting statistics, applying a 6σ($F_{obs}$) cutoff. Neutral-atom scattering factors and real as well as imaginary parts of the anomalous dispersion corrections were used. In addition to positional and displacement parameters, occupancies of the sugilite A site were refined allowing for Fe and Al (Table 3). Fe and Mn cannot be distinguished in this type of site-occupancy refinement. Thus, the Fe occupation on the A site actually represents Σ(Fe + Mn). Final R values for brannockite are fairly high (Table 2), which is related to the irregular flakelike shape of the crystal and the resulting insufficient empirical absorption correction. Observed and calculated structure factors are compiled in Table 4.[2]

## RESULTS

Table 5 summarizes selected atom–atom distances and angles. The structure refinements indicate that the T2 position in sugilite and brannockite is occupied by Li. The fairly large T2 tetrahedron (Li–O: 1.970 Å (sugilite), 1.927 Å (brannockite)) is extremely distorted in its angles (Table 5 and Fig. 1), whereas the A site—which is occupied by

Bern, NMB-B5564). Crystals from the same hand specimen were also analyzed with an electron microprobe (Table 1). In comparison to other sugilite analyses from the Wessels mine (Clark et al., 1980; Dunn et al., 1980), this sample reveals strikingly high Al concentrations. The concentration of Fe, Mn, and Al varies from one grain to the other. In addition, most grains are also strongly zoned with respect to these cations.

Brannockite crystals were picked under UV light from a small rock piece wiht the assemblage quartz, albite, and white mica originating from the Foote mine, North Carolina, U.S.A. (sample deposited at the Museum of Natural History, Bern, NMB-B5563). A microprobe analysis of brannockite was not carried out because the results of White et al. (1973) indicated that brannockite from the Foote mine possesses the end-member composition $KSn_2Li_3Si_{12}O_{30}$.

Selected sugilite and brannockite crystals were studied on a precession camera to confirm the space group P6/mcc. This procedure showed that all brannockite crystals were twinned perpendicular to the (001) plane. On the basis of X-ray results, it cannot be decided whether the twinning is caused by the twin planes (210) or (140). On precession photographs with the c axis as precession axis, several sets of spots are common to both individuals of the twin. Reflections of the type 00l, 14l, 35l, 56l, 77l, 28l, 49l, 6 10 l, 07l, 3 12 l, 1 11 l, and 0 14 l in one twin domain (indices $h_1 k_1 l_1$) can be transformed with the matrix given below into the corresponding reflections of the second twin domain (indices $h_2 k_2 l_2$):

$$\begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix} = \begin{bmatrix} 8/7 & 3/7 & 0 \\ -3/7 & 5/7 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} h_1 \\ k_1 \\ l_1 \end{bmatrix}$$

[2] A copy of Table 4 may be ordered as Document AM-88-374 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 3. Fractional coordinates, displacement parameters, and site occupancies

| | Sugilite | Brannockite 1 | Brannockite 2 |
|---|---|---|---|
| **C (K)** | | | |
| $x$ | 0 | 0 | 0 |
| $y$ | 0 | 0 | 0 |
| $z$ | 1/4 | 1/4 | 1/4 |
| $B_{eq}$ | 1.52(1) | 1.42(2) | 1.59(5) |
| $U_{11}$ | 0.0164(4) | 0.0157(5) | 0.017(1) |
| $U_{22}$ | 0.0164 | 0.0157 | 0.017 |
| $U_{33}$ | 0.0196(7) | 0.00174(8) | 0.021(3) |
| $U_{12}$ | 0.0082 | 0.0079 | 0.0083 |
| **A** | 83 (1)% Fe, 17% Al | 100% Sn | 100% Sn |
| $x$ | 1/3 | 1/3 | 1/3 |
| $y$ | 2/3 | 2/3 | 2/3 |
| $z$ | 1/4 | 1/4 | 1/4 |
| $B_{eq}$ | 0.412(7) | 0.397(3) | 0.475(8) |
| $U_{11}$ | 0.0047(2) | 0.0046(1) | 0.0039(2) |
| $U_{22}$ | 0.0047 | 0.0046 | 0.0039 |
| $U_{33}$ | 0.0046(3) | 0.0045(1) | 0.0090(3) |
| $U_{12}$ | 0.0024 | 0.0023 | 0.0020 |
| **T2 (Li)** | | | |
| $x$ | 1/2 | 1/2 | 1/2 |
| $y$ | 1/2 | 1/2 | 1/2 |
| $z$ | 1/4 | 1/4 | 1/4 |
| $B_{eq}$ | 1.44(7) | 1.3(1) | 1.3(2) |
| $U_{11}$ | 0.017(2) | 0.019(4) | 0.014(6) |
| $U_{22}$ | 0.017 | 0.019 | 0.014 |
| $U_{33}$ | 0.016(3) | 0.008(3) | 0.015(8) |
| $U_{12}$ | 0.011(3) | 0.015(4) | 0.007(7) |
| **T1 (Si)** | | | |
| $x$ | 0.23633(5) | 0.23866(7) | 0.2384(2) |
| $y$ | 0.35620(5) | 0.35649(7) | 0.3564(2) |
| $z$ | 0.38678(3) | 0.39057(5) | 0.3905(1) |
| $B_{eq}$ | 0.566(7) | 0.316(8) | 0.36(2) |
| $U_{11}$ | 0.0066(2) | 0.0038(2) | 0.0033(5) |
| $U_{22}$ | 0.0071(2) | 0.0041(2) | 0.0036(2) |
| $U_{33}$ | 0.0057(2) | 0.0029(2) | 0.0058(5) |
| $U_{12}$ | 0.0036(2) | 0.0022(2) | 0.0017(5) |
| $U_{13}$ | 0.0005(1) | 0.0006(2) | 0.0006(5) |
| $U_{23}$ | 0.0006(2) | 0.0011(2) | 0.0007(5) |

| | Sugilite | Brannockite 1 | Brannockite 2 |
|---|---|---|---|
| **O1** | | | |
| $x$ | 0.1383(2) | 0.1318(3) | 0.1313(7) |
| $y$ | 0.3972(2) | 0.3977(4) | 0.3971(8) |
| $z$ | 0 | 0 | 0 |
| $B_{eq}$ | 1.36(3) | 1.14(4) | 1.2(1) |
| $U_{11}$ | 0.019(1) | 0.019(1) | 0.020(3) |
| $U_{22}$ | 0.019(1) | 0.016(1) | 0.020(3) |
| $U_{33}$ | 0.0062(7) | 0.003(1) | 0.008(3) |
| $U_{12}$ | 0.0081(8) | 0.008(1) | 0.008(2) |
| **O2** | | | |
| $x$ | 0.2232(2) | 0.2237(2) | 0.2234(5) |
| $y$ | 0.2774(2) | 0.2807(2) | 0.2800(5) |
| $z$ | 0.13775(9) | 0.1342(2) | 0.1351(3) |
| $B_{eq}$ | 1.24(2) | 0.97(3) | 0.92(6) |
| $U_{11}$ | 0.0130(6) | 0.0087(7) | 0.007(2) |
| $U_{22}$ | 0.0155(6) | 0.0128(8) | 0.011(2) |
| $U_{33}$ | 0.0161(5) | 0.0134(8) | 0.016(2) |
| $U_{12}$ | 0.0104(5) | 0.0081(7) | 0.007(1) |
| $U_{13}$ | 0.0005(5) | 0.0006(6) | 0.000(2) |
| $U_{23}$ | 0.0007(5) | 0.0004(6) | −0.001(2) |
| **O3** | | | |
| $x$ | 0.1665(1) | 0.1598(2) | 0.1592(4) |
| $y$ | 0.5091(1) | 0.5038(2) | 0.5040(4) |
| $z$ | 0.17032(8) | 0.1726(1) | 0.1733(3) |
| $B_{eq}$ | 0.92(2) | 0.58(2) | 0.54(5) |
| $U_{11}$ | 0.0106(6) | 0.0077(6) | 0.005(1) |
| $U_{22}$ | 0.0091(5) | 0.0050(6) | 0.005(1) |
| $U_{33}$ | 0.0117(5) | 0.0072(6) | 0.008(2) |
| $U_{12}$ | 0.0045(5) | 0.0033(5) | 0.001(1) |
| $U_{13}$ | −0.0013(5) | −0.0013(5) | −0.001(1) |
| $U_{23}$ | −0.0035(5) | −0.0036(5) | −0.002(1) |
| **B'** | 49(1)% Na | | |
| $x$ | 1/2 | | |
| $y$ | 2/3 | | |
| $z$ | 0.0134(7) | | |
| $B_{eq}$ | 1.7(1) | | |
| $U_{11}$ | 0.0175(8) | | |
| $U_{22}$ | 0.0175 | | |
| $U_{33}$ | 0.026(6) | | |
| $U_{12}$ | 0.00875 | | |

*Note:* Standard deviations are in parentheses. The displacement parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. $B_{eq}$ values are calculated according to Hamilton (1959); standard deviations of $B_{eq}$ are estimated as proposed by Shomaker and Marsh (1983).

($Fe^{3+}$, $Mn^{3+}$, and Al) in sugilite and by Sn in brannockite—reveals a rather regular octahedral environment. In both minerals, K resides in a large cavity (C site) situated between two double-ring units (Fig. 2). Sugilite refinements with Na at 1/2, 2/3, 0 (site symmetry 6̄) yielded an unreasonably large displacement parameter alaong $c$ (Fig. 3). Introduction of an additional degree of freedom in the refinement ($z$ parameter for Na) did not lead to a significant improvement of the $R$ values but did lead to more reasonable displacement parameters. Thus, it is suggested that Na in sugilite is disordered on a position of the type 1/2, 2/3, 0.0134 (site symmetry 3), which is to up to 49(1)% occupied, and that Na possesses distorted ninefold coordination. A similar coordination of Na has been found in the double-ring silicate eifelite (Abraham et al., 1983). The corresponding position in brannockite is vacant. Kato et al. (1976) suggested that in the Iwagi Islet sugilite, Na shares the B site with $H_2O$. Microprobe analyses of Wessels mine sugilite (Table 1) indicate that the B site is predominantly occupied by Na. In additiion, DTA-TGA

analyses of Wessels mine sugilite by Dunn et al. (1980) did not indicate the presence of volatiles.

When comparing the sugilite structure data given in this paper with the data of Kato et al. (1976), it is surprising that the cell dimensions and the T2–O and A–O distances agree within three standard deviations,[3] although both samples differ in chemical composition (Table 1). If the cation distribution ($Li_{2.12}Al_{0.59}Fe^{3+}_{0.29}$) on T2 suggested by Kato et al. (1976) is correct, the smaller ionic radii of $^{IV}Fe^{3+}$ (0.49 Å) and of $^{IV}Al$ (0.39 Å) in contrast to the ionic radius of $^{IV}Li$ (0.59 Å) (Shannon, 1976) should shorten the T2–O distance of their sample compared to the Wessels mine sugilite where T2 is occupied by Li only. In addition, the isotropic temperature factors $B_{eq}$ of T2 for sugilite and brannockite in this paper are 1.4 and 1.3, respectively (Table 3), whereas the corresponding value

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[3] Fractional coordinates of both sugilite structures are not compared, because the $z$ coordinate of O3 in the structure of Kato et al. (1976) is obviously misprinted.
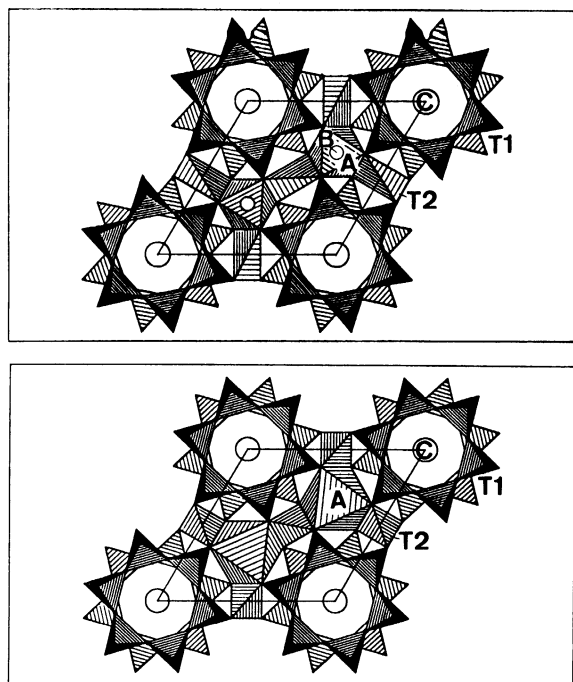
Fig. 1. Crystal structure of double-ring silicates projected along the $c$ axis (upper figure, sugilite; lower figure, milarite (Černý et al., 1980). In sugilite, the large T2 tetrahedra centered by Li are strongly angularly distorted, whereas the A octahedra (A site at ⅓, ⅔, ¼ occupied by $Fe^{3+}$, $Mn^{3+}$, and $Al^{3+}$) are fairly regular in their angles. In milarite, the small T2 tetrahedra centered by Be are fairly regular. However, the large A octahedra (Ca) are distorted. In this projection the double-ring units appear only as simple six-membered rings because the double rings are produced by a mirror plane perpendicular to the $c$ axis at $z = 0$. The B site at ⅓, ⅔, 0 in sugilite is occupied by Na.
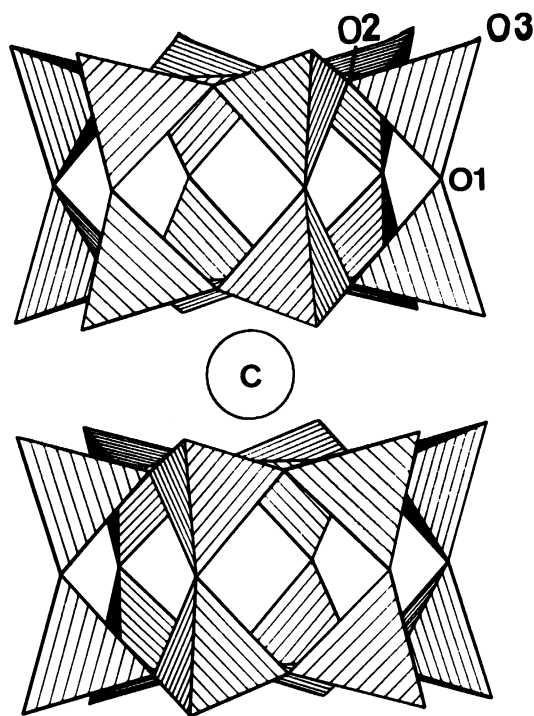


Fig. 2. Characteristic portion of the double-ring silicate structure projected perpendicular to the $c$ axis. Two double-ring units formed by T1 tetrahedra are stacked above each other, and the interspace is occupied by alkalies on the 12-coordinated C site.

for T2 in the Iwagi Islet sugilite (Kato et al., 1976) is 2.34. This high temperature factor may indicate that Kato et al. (1976) overestimated the scattering power of the cations on T2. The isotropic temperature factors for O1, O2, O3, T1, A, and C of Kato et al. (1976) are very similar to the $B_{eq}$ values obtained for the Wessels mine sugilite (this paper). Probably, erroneous wet-chemical analyses performed on pectolite-sugilite mixtures (Murakami et al., 1976) are responsible for the questionable cation assignment by Kato et al. (1976).

Although White et al. (1973) described brannockite to be hexagonal with the space group $P6/mcc$, their indexed powder pattern contains reflections (113, 405, 505, 409, 3.0.11, 0.0.13, 903, 663, and 11.0.3.) that violate $P6/mcc$ space-group symmetry. None of these reflections was observed for the single crystal investigated in this paper. However, if proper extinction rules are applied ($hhl$, $l = 2n$; $h0l$, $l = 2n$), most reflections can be alternatively indexed. These newly indexed powder data of White et al. (1973) were employed for cell-dimension refinement yielding $a = 10.018(1)$ Å, $c = 14.270(4)$ Å. The brannockite $a$ axis refined from these powder data is still sig-

TABLE 5. Selected interatomic distances and angles

|  | Sugilite | Brannockite 1 | Brannockite 2 |
|---|---|---|---|
| C–O2 (12×) | 2.994(2) | 3.055(3) | 3.044(6) |
| A | $(Fe^{3+},Mn^{3+},Al)$ | Sn octahedron | |
| A–O3 (6×) | 1.972(2) | 2.014(3) | 2.011(5) |
| O3–O3 (3×) | 2.681(2) | 2.682(2) | 2.661(7) |
| O3–O3 (3×) | 2.844(2) | 2.875(3) | 2.869(5) |
| O3–O3 (6×) | 2.815(2) | 2.919(3) | 2.923(5) |
| T1 (Si) |  |  |  |
| T1–O1 | 1.625(1) | 1.602(1) | 1.603(2) |
| T1–O2 | 1.620(3) | 1.620(4) | 1.621(6) |
| T1–O2 | 1.615(2) | 1.620(4) | 1.623(9) |
| T1–O3 | 1.577(1) | 1.594(2) | 1.602(4) |
| O1–T1–O2 | 108.1(2) | 109.8(3) | 110.4(5) |
| O1–T1–O3 | 108.0(1) | 111.4(1) | 111.7(3) |
| O2–T1–O1 | 110.8(1) | 110.1(3) | 110.3(5) |
| O2–T1–O3 | 111.4(1) | 108.2(2) | 107.6(3) |
| O2–T1–O2 | 104.0(1) | 105.0(1) | 104.5(3) |
| O3–T1–O2 | 114.4(1) | 112.2(2) | 112.2(3) |
| T2 (Li) |  |  |  |
| T2–O3 (4×) | 1.970(2) | 1.927(4) | 1.916(7) |
| O3–O3 (2×) | 2.681(2) | 2.682(2) | 2.661(7) |
| O3–O3 (2×) | 3.246(2) | 3.160(3) | 3.147(6) |
| O3–O3 (2×) | 3.649(2) | 3.541(3) | 3.520(5) |
| O3–T2–O3 | 86.8(1) | 88.2(1) | 87.9(2) |
| O3–T2–O3 | 111.0(1) | 110.1(1) | 110.3(2) |
| O3–T2–O3 | 135.7(1) | 133.5(1) | 133.5(1) |
| Na–O1 (3×) | 2.420(2) |  |  |
| Na–O3 (3×) | 2.733(8) |  |  |
| Na–O3 (3×) | 3.088(4) |  |  |
| T1–O1–T1 | 154.7(2) | 153.8(3) | 154.1(5) |
| T1–O2–T1 | 152.4(1) | 152.4(1) | 151.6(3) |
| T1–O3–T2 | 114.2(1) | 118.2(1) | 118.5(2) |

nificantly larger than the value of $a = 10.002(2)$ Å as obtained for both domains of the twinned crystal (Table 2). The experimental details for the collection of brannockite powder data (White et al., 1973) are not sufficient for a discussion about possible reasons for this discrepancy.

## STRUCTURAL VARIATION IN DOUBLE-RING SILICATES

Fairly precise structure refinements ($R$ values below 5%) are available for following double-ring silicates: milarite (Černý et al., 1980), osumilite (Hesse and Seifert, 1982; Armbruster and Oberhänsli, 1988), merrihueite (Kahn et al., 1972), eifelite (Abraham et al., 1983), sugilite (Kato et al., 1976, and this paper), and brannockite (this paper). In the following section, we will try to develop some general rules concerning the dependence of structural parameters on each other and on the chemistry of this class of compounds.

If comparing the Si-O distances in the above cited structures, it becomes evident that there is a strong variation of the T1–O3 distance, which is 1.577(1) Å in sugilite and reaches 1.635(1) Å in osumilite (Armbruster and Oberhänsli, 1988). However, in osumilites the T1 site is occupied by 85% Si and 15% Al. In all other double-ring silicates given in Table 6, T1 is occupied only by Si. For better comparison, the T1–O3 distances of osumilites were corrected for their Al content assuming a mean Si–O distance of 1.63 Å and a mean Al–O distance of 1.75 Å. Consequently, the observed values in osumilites are about 0.002 Å longer than the corrected ones for only Si occupation. Varying electrostatic bond strength (Pauling, 1960; Baur, 1970) around the O3 oxygen, liking the A octahedron to T2 and T1 tetrahedra, is responsible for the remaining variation in T1–O3 distances. For the calculation of the bond strength of O3, only the three closest cation neighbors were considered (A, T1, T2). Na on the B' site of sugilite and eifelite was neglected because the B'–O3 distance in these minerals is much longer than the distance between O3 and cations on A, T1, and T2. Linear-regression analysis of bond strengths ($S$) versus T1–O3 distances yielded

$$d_{T1-O3} = 1.377 + 0.1134S_{O3} \text{ with } R^2 = 97\%.$$



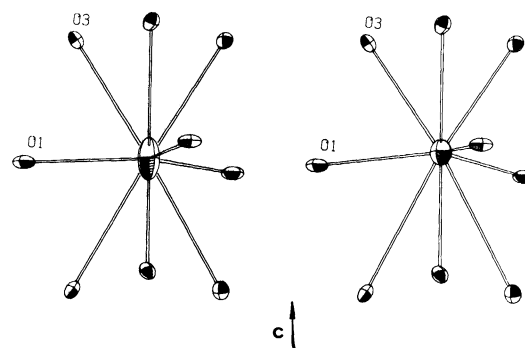Fig. 3. Coordination of Na in sugilite on the 9-coordinated B site. (Left) Na occupies the position ½, ⅔, 0 (site symmetry $\bar{6}$) and is at the same level along $c$ as O1. However, the displacement parameters are strongly elongated along the $c$ axis. (Right) Na is disordered along the $c$ axis (site symmetry 3) on ½, ⅔, 0.0134 and exhibits less anisotropic displacement parameters.

It is easily seen from Figure 1 that in double-ring silicates (Table 6), the length of the $a$ cell edge is dependent on the length of the shared edge between the T2 tetrahedron and the A octahedron and thus related to the lengths of the A–O3 and T2–O3 distances. In accordance with this observation, multiple linear-regression analyses with $a$ as the dependent variable and cation–oxygen distances as independent ones yielded the following equation as the best two-variable model ($R^2 = 98.4\%$):

$$a = 5.610 + 1.59d_{A-O3} + 0.63d_{T2-O3}.$$

The best two-variable model of multiple regression analysis with the $c$ axis as the dependent variable is given by the equation ($R^2 = 97.4\%$)

$$c = -1.600 + 1.126d_{T2-O} + 4.48d_{C-O}.$$

From Figure 2, the dominant influence of the C–O distance on the length of the $c$ cell edge becomes clear. The C position links two double-ring units that are stacked along the $c$ axis.

Large T2 tetrahedra show a strong angular distortion (sugilite and brannockite: Table 5) but are connected to fairly undistorted A octahedra. Small T2 tetrahedra (mi-

TABLE 6. Cell dimensions, selected bond distances, and bond strengths of double-ring silicates

| Mineral | Source | $a$ (Å) | $c$ (Å) | A–O3 (Å) | T2–O3 (Å) | T1–O3* (Å) | $S_{O3}$** | C–O2 (Å) | Ref.† |
|---------|--------|---------|---------|----------|-----------|------------|-----------|----------|-------|
| Milarite | Kings Mountain | 10.420 | 13.810 | 2.364 | 1.672 | 1.593 | 1.918 | 3.019 | 1 |
| Milarite | Vezna | 10.428 | 13.675 | 2.377 | 1.643 | 1.587 | 1.865 | 2.999 | 1 |
| Merrihueite | | 10.222 | 14.152 | 2.104 | 1.955 | 1.585 | 1.833 | 3.015 | 2 |
| Eifelite | | 10.137 | 14.223 | 2.077 | 1.989 | 1.580 | 1.767 | 3.035 | 3 |
| Osumilite | Antarctica | 10.086 | 14.325 | 2.118 | 1.767 | 1.630 (1.610) | 2.083 | 3.099 | 4 |
| Osumilite | Hayasaki | 10.150 | 14.286 | 2.154 | 1.764 | 1.635 (1.615) | 2.083 | 3.096 | 4 |
| Osumilite | Eifel B93 | 10.071 | 14.303 | 2.100 | 1.772 | 1.638 (1.618) | 2.113 | 3.120 | 4 |
| Sugilite | Wessels mine | 10.009 | 14.006 | 1.972 | 1.970 | 1.577 | 1.750 | 2.994 | 5 |
| Sugilite | Iwagi Islet | 10.007 | 14.000 | 1.976 | 1.971 | 1.577 | 1.82 | 3.000 | 6 |
| Brannockite | | 10.002 | 14.263 | 2.014 | 1.927 | 1.594 | 1.916 | 3.055 | 5 |

* Distances in parentheses corrected for 15% Al on T1.
** Pauling bond strength around O3.
† References are (1) Černý et al. (1980), (2) Kahn et al. (1972), (3) Abraham et al. (1983), (4) Armbruster and Oberhänsli (1988), (5) this paper, and (6) Kato et al. (1976).

larite) have minor distortions in their angles; however, the edge-sharing A octahedra are strongly compressed along the $c$ axis. Thus, Li, which accepts highly distorted coordination tetrahedra, is almost ideal in combination with cations favoring a regular octahedral environment within the double-ring silicate structure. On the other hand, large cations (like Ca) that allow fairly distorted octahedral coordination on A may be associated with cations that need rather regular tetrahedral coordination on T2. The charge of the cations on T2 and A is less important because the double-ring silicate structure offers several positions that may be partly occupied.

## ACKNOWLEDGMENTS

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