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THE CRYSTAL STRUCTURE AND THERMAL EXPANSION OF TUGTUPITE, $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$

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ABSTRACT

The crystal structure of tugtupite, ideally $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$, has been refined in space group $I\bar{4}$ to an R index of 0.023 for 621 observed reflections measured on an automated single-crystal four-circle X-ray diffractometer using Mo$K\alpha$ radiation. The framework T cations (T represents Al^{3+}, Be^{2+}, and Si^{4+}) are fully ordered, and this order lowers the cubic symmetry of many sodalite-group minerals to tetragonal symmetry for tugtupite, a sodalite-group mineral. The "sodalite" cage in tugtupite contains $[Na_4{\bullet}Cl]^{3+}$ clusters. Large Si–O–Be angles occur in this structure; smaller Si–O–Be angles occur in helvite-group minerals, because the cages contain $[(Mn,Fe,Zn)_4{\bullet}S]^{6+}$ clusters, whose large effective charge accounts for the smaller angles. The thermal expansion for tugtupite is modeled using the *DLS* program; the expansion is controlled mainly by rotations of the TO_4 tetrahedra, which are mainly caused by the expansion of Na–Cl bonds and nearly constant Na–O bonds.

Keywords: tugtupite, crystal structure, thermal expansion, sodalite group, helvite group.

SOMMAIRE

Nous avons affiné la structure cristalline de la tugtupite, dont la formule idéale est $Na_8[Al_2Be_2Si_8O_{24}]Cl_2$, dans le groupe spatial $I\bar{4}$ jusqu'à un residu R de 0.023 en utilisant 621 réflexions observées (diffractomètre automatisé, rayonnement Mo$K\alpha$). Les cations T de la trame (Al^{3+}, Be^{2+} et Si^{4+}) sont complètement ordonnés. C'est ce degré d'ordre qui réduit la symétrie cubique de plusieurs membres de la famille de la sodalite comme la tugtupite à une symétrie tétragonale. La cage typique de la sodalite contient, dans la tugtupite, un groupement $[Na_4{\bullet}Cl]^{3+}$. Les angles Si–O–Be sont grands dans la tugtupite; ils sont plus petits dans les minéraux du groupe de la helvite parce que le groupement $[(Mn,Fe,Zn)_4{\bullet}S]^{6+}$ de la cage possède une charge effective plus élevée. L'expansion thermique peut être reproduite par le logiciel *DLS*. L'expansion serait due surtout à la rotation des tétraèdres TO_4, qui dépend largement de l'expansion des liaisons Na–Cl, la longueur des liaisons Na–O demeurant à peu près constante.

(Traduit par la Rédaction)

Mots-clés: tugtupite, structure cristalline, expansion thermique, famille de la sodalite, famille de la helvite.

INTRODUCTION

Tugtupite is tetragonal and has the idealized formula $Na_8(Al_2Be_2Si_8O_{24})Cl_2$ (Danø 1966, Sørensen *et al.* 1971). The structure of tugtupite is isotypic with that of sodalite (cubic), as is that of minerals of the helvite group. The tugtupite framework may be regarded as intermediate in composition between the framework of sodalite $(Al_6Si_6O_{24})^{6-}$ and that of helvite $(Be_6Si_6O_{24})^{12-}$. The tetragonal symmetry of tugtupite is the result of T-cation ordering (T represents Al^{3+}, Be^{2+}, and Si^{4+}).

Danø (1966) determined the space group $I\bar{4}$ for tugtupite by utilizing precession and Weissenberg photographs, and the structure was refined with film data and the isotypic relationship with the sodalite structure. Interest in tugtupite arises primarily from the detailed structural effects that result from a framework that consists of three different T cations. In this study, we set out to refine the structure of tugtupite to obtain better structural parameters for comparison with structural data for sodalite- and helvite-group minerals (Hassan & Grundy 1983, 1984, 1985, 1989, 1991, Hassan *et al.* 1985). This comparison leads to an evaluation of the structural effects that arise from different T cations, interstitial cation (Na^+, Mn^{2+}, Fe^{2+}, Zn^{2+}), and anions (Cl^-, S^{2-}, OH^-, H_2O). An opportunity also arises to test the applicability of the d–p π bonding model to the sodalite-group minerals (*e.g.*, Cruickshank 1961, Brown *et al.* 1969, Gibbs *et al.* 1972). The thermal expansion of tugtupite also is rationalized in terms of its crystal structure, and the mechanism of expansion is compared to that in sodalite-group minerals (Hassan & Grundy 1984).

EXPERIMENTAL

The specimen of red tugtupite used in this investigation is from Ilímaussaq, Narssaq Kommune, South Greenland (Royal Ontario Museum #M32790). The chemical composition (Table 1) is taken from Danø (1966) because both samples are from the same locality; we assume that the composition of Danø (1966) is representative of our sample. Cell parameters, determined by least-squares refinement of fifteen high-angle reflections automatically centered on an automated four-circle single-crystal X-

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ray diffractometer, are presented in Table 1, together with other information pertaining to X-ray data collection and refinement.

The intensity data were collected from a cleavage fragment mounted on a Nicolet P3 diffractometer. Reflections allowable in space group $I\bar{4}$ (*i.e.*, $h + k + l = 2n$) were collected from two octants of reciprocal space to a maximum 2θ of 65°. A total of 1413 intensities were measured to give a data set of 647 unique reflections, of which 621 were classed as observed (Table 1). The data were corrected for Lorentz, polarization, background effects, and spherical absorption (Table 1). All crystallographic calculations were made using the XRAY76 Crystallographic Programs (Stewart 1976).

STRUCTURE REFINEMENT

Initially, the positional parameters and isotropic temperature-factors of Danø were used, including those for (fully ordered) Al, Be, and Si atoms, and atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968). A full-matrix least-squares refinement was made by varying the atomic positions, isotropic temperature-factors, and

TABLE 1. CHEMICAL COMPOSITION[1], CRYSTAL DATA[2], AND INFORMATION ON DATA COLLECTION FOR TUGTUPITE

Oxide	Wt. %	Cell contents[+]		Miscellaneous	
Al_2O_3	11.15	Al	2.03	a (Å)	8.640(1)
SiO_2	51.58	Si	7.98	c (Å)	8.873(1)
BeO	5.40	Be	2.00	V (Å^3)	662.4
Na_2O	25.52	Na	7.62	Density calc. (gcm^{-3})	2.34
K_2O	0.12	K	0.02	Crystal size (mm)	0.16 x 0.20
MgO	0.20	Mg	0.05		x 0.26
Cl	7.28	Cl	1.90	μ (cm^{-1})	9.56
S	0.33	S	0.09	μR	0.20
	101.58			Maximum 2θ	65°
O=Cl, S	1.99			0≤ h, k, l ≤	13
Total	99.59			Total no. of intensities	1431
				No. of unique reflections	647
Chemical Formula				No. of non-equiv. $\lvert F_o\rvert > 3\sigma\lvert F\rvert$	621
used in refinement				Final *R	0.023
$Na_8[Al_2Be_2Si_8O_{24}]Cl_2$				Final **R_w	0.030

[1] Chemical analysis from Danø (1966).
[2] Space group $I\bar{4}$; Z = 1; Radiation/monochromator = Mo/C; MoKα = 0.71069 Å.
*$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$; **$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$, w = 1.
[+] Based on Al + Be + Si = 12.0

TABLE 2. POSITIONAL, OCCUPANCY, AND ISOTROPIC THERMAL PARAMETERS (Å^2 x 10^4)

Atom	Site	Occ.	x	y	z	U_{iso}
Al	2(d)	1.0	0	1/2	3/4	76(4)
Be	2(c)	1.0	0	1/2	1/4	98(14)
Si	8(g)	1.0	0.0127(1)	0.2533(1)	0.4958(1)	74(1)
O1	8(g)	1.0	0.1504(3)	0.1343(2)	0.4417(2)	123(4)
O2	8(g)	1.0	0.3472(2)	0.0385(3)	0.6488(2)	119(4)
O3	8(g)	1.0	0.4256(2)	0.1486(2)	0.1377(3)	120(4)
Na	8(g)	1.0	0.1563(2)	0.1972(2)	0.1818(2)	188(3)
Cl	2(a)	1.0	0	0	0	234(3)

TABLE 3. ANISOTROPIC TEMPERATURE-FACTORS[1] (x 10^4)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	78(5)	78	74(8)	0	0	0
Be	86(18)	86	123(34)	0	0	0
Si	71(3)	63(3)	86(3)	-2(2)	-2(3)	-3(3)
O1	126(9)	116(9)	128(9)	46(7)	10(8)	1(7)
O2	107(8)	119(8)	132(9)	-3(6)	-35(8)	-4(8)
O3	112(8)	114(8)	135(9)	-1(6)	5(7)	38(8)
Na	206(7)	160(6)	199(6)	7(5)	24(5)	12(5)
Cl	228(4)	228	244(7)	0	0	0

[1] $U_{ij} = \exp[-2\pi^2(U_{11}h^2+U_{22}k^2+U_{33}l^2+2U_{12}hk+2U_{13}hl+2U_{23}kl)]$

TABLE 4. INTERATOMIC DISTANCES (Å), ANGLES (°), AND VALENCE SUMS (v.u.) FOR TUGTUPITE

AlO_4 Tetrahedron			BeO_4 Tetrahedron		
Al-O3	4 x	1.748(2)	Be-O2	4 x	1.631(2)
O3-O3	4 x	2.845(3)	O2-O2	4 x	2.633(3)
	2 x	2.872(3)		2 x	2.722(3)
Mean		2.854	Mean		2.663
O3-Al-O3	4 x	109.0(1)	O2-Be-O2	4 x	107.7(1)
	2 x	110.5(1)		2 x	113.2(1)
Mean		109.5	Mean		109.5
SiO_4 Tetrahedron			Na Coordination		
Si-O1		1.644(2)	Na-Cl		2.707(1)
-O1*		1.647(2)	-O1		2.370(3)
-O2		1.581(2)	-O2		2.303(3)
-O3		1.609(2)	-O2*		2.603(3)
Mean		1.620	-O3		2.396(3)
O1-O1*		2.672(3)	O1-Na-Cl		115.2(1)
-O2		2.587(3)	-O2		110.5(1)
-O3		2.640(3)	-O3		98.0(1)
O1*-O2		2.637(3)	O2-Na-Cl		122.8(1)
-O3		2.601(3)	-O3		99.5(1)
O2-O3		2.723(3)	O3-Na-Cl		106.1(1)
Mean		2.643			
			Bridging Angles		
O1-Si-O1*		108.6(1)	Si-O1-Si		140.8(2)
-O2		106.7(1)	Si-O2-Be		143.6(1)
-O3		108.5(1)	Si-O3-Al		135.3(1)
O1*-Si-O2		109.5(1)	T-T distances		
-O3		106.0(1)	Si-Al		3.100(1)
O2-Si-O3		117.2(2)	Si-Al		3.105(1)
Mean		109.4	Si-Be		3.051(1)

Bond-valence sums (v.u.)
Al = 4 x 0.769 = 3.076
Be = 4 x 0.509 = 2.035
Si = 0.947 + 0.940 + 1.123 + 1.041 = 4.051
Na = 0.25 + 0.216 + 0.259 + 0.115 + 0.201 = 1.041

O1 = 0.947 + 0.940 + 0.216 = 2.103
O2 = 1.123 + 0.509 + 0.259 + 0.115 = 2.006
O3 = 1.041 + 0.769 + 0.201 = 2.011

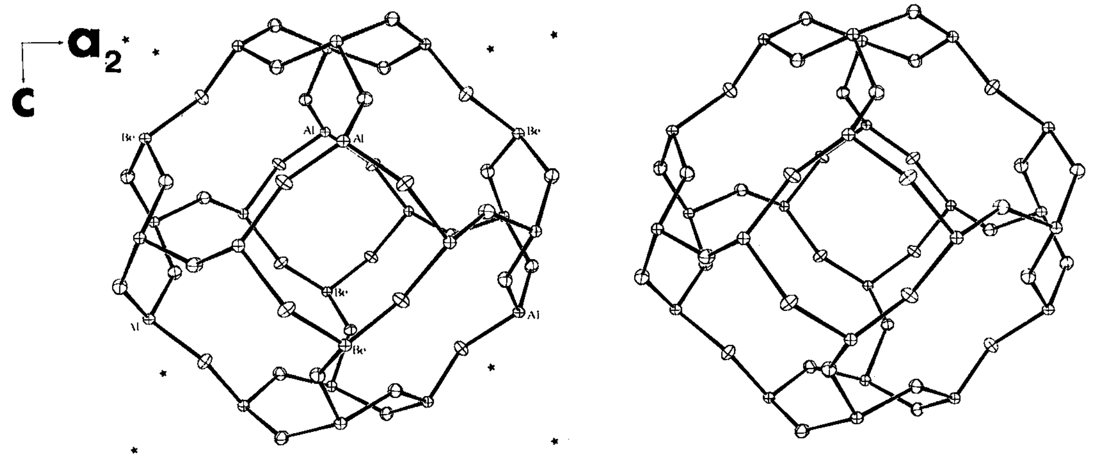

FIG. 1. Stereoscopic projection of the framework of tugtupite showing the "sodalite" cage and the ordering of the T cations. The Si and oxygen atoms are unlabeled.

a scale factor. The refinement of the structural model was constrained to the idealized chemical formula and resulted in an R index of 3.0% (Table 1). The isotropic temperature-factors were converted to anisotropic forms, and further cycles of refinement, with variations in all the refinable parameters, resulted in convergence to a final R index of 2.3%. The occupancy and temperature factors for both Na and Cl atoms were refined, and occupancy values of 1.00(1) were obtained for both atoms, which agree with the ideal chemical formula and are not significantly different from the chemical data of Danø (1966). A final difference-Fourier map was found to be featureless. The interatomic distances and isotropic temperature-factors for the atoms in the structure show nothing unusual, and the refinement was considered complete.

The atomic positions and isotropic temperature-factors are given in Table 2, anisotropic temperature-factors are listed in Table 3, and interatomic distances and angles are presented in Table 4. A copy of the structure factors is available at a nominal charge from Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DISCUSSION

The tugtupite structure

The cell parameters obtained for the red tugtupite used in this investigation [a = 8.640(1), c = 8.873(1) Å] differ from those obtained by Danø (1966) [a = 8.538(4), c = 8.817(4) Å], which are well outside the ranges in a (8.634 - 8.643 Å) and c (8.867 - 8.870 Å) given by Sørensen *et al.* (1971). Results of the present refinement [and the data of Sørensen *et al.*

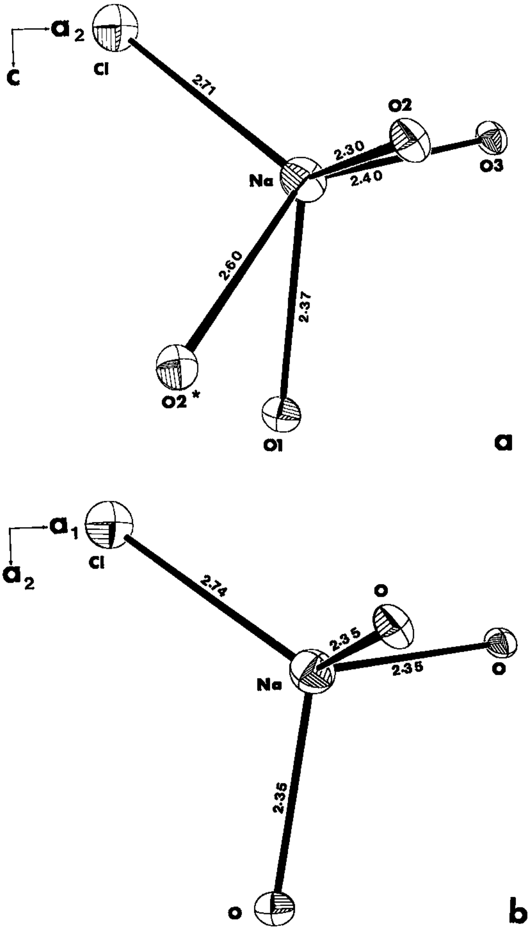

FIG. 2. Na atom coordinations: (a) five-fold coordination in tugtupite; (b) four-fold coordination in sodalite.

(1971)] do not indicate that the sample used in this study has a significantly different composition from the sample studied by Danø (1966), despite the apparent differences in cell parameters. In fact, the atomic positions are not significantly different from those of Danø (1966); however, significant differences occur in bond lengths because of the cell parameters used by Danø (1966). The *R* index obtained by Danø (1966) was 8.9% based on film data, isotropic temperature-factors, and Cu*K*α radiation.

The isotropic temperature-factors obtained by Danø (1966) are small because the crystal was probably not small enough (≈ 0.3 mm in diameter) for absorption to be negligible (μ = 86 cm^{-1}, Cu*K*α: Danø 1966). The crystal used in this study is smaller, and the absorption is quite low (Table 1). Furthermore, the isotropic temperature-factors obtained for tugtupite in this study (Table 2) are comparable to those of sodalite- and helvite-group minerals (Hassan & Grundy 1983, 1984, 1985), which suggests that our temperature factors are realistic.

The general structural features of tugtupite are similar to those of sodalite. The framework is characterized by four-membered rings in the faces of the unit cell, and these rings are linked to form six-membered rings about the corners of the unit cell (Fig. 1). The four-membered rings in the faces normal to the *a* axes have an ordered disposition of *T* atoms consisting of two Si, one Al, and one Be atom, whereas the four-membered rings in the faces normal to the *c* axis consist of Si atoms only. As a result of the linkage of the four-membered rings, all the six-membered rings have an ordered arrangement of *T* atoms consisting of one Al, one Be, and four Si atoms; the Be and Al atoms are diametrically opposite each other in the rings (Fig. 1). The cages contain Na and Cl atoms; the Cl atoms are at the corners and center of the unit cell. The final low *R* index can be taken to confirm the assumed full order of the three *T* cations Al, Be, and Si.

TABLE 5. COMPARISON OF FRAMEWORK GEOMETRY IN SOME SODALITE-GROUP MINERALS*

Mean Values	Tugt	Helvite[1]	OH-Soda	Soda	Grand mean
		SiO_4 Tetrahedron			
Si-O	1.620	1.629	1.616	1.620	1.621
O-O	2.643	2.660	2.638	2.644	2.646
		AlO_4 Tetrahedron			
Al-O	1.748	——	1.743	1.742	1.744
O-O	2.854	——	2.847	2.844	2.848
		BeO_4 Tetrahedron			
Be-O	1.631	1.634	——	——	1.633
O-O	2.663	2.668	——	——	2.666
		T-T Distances			
Si-Al	3.102	——	3.143	3.140	3.128
Si-Be	3.051	2.901	——	——	2.976
		Bridging Angles			
Si-O-Al	135.3	——	138.7	138.2	137.4
Si-O-Be	**143.6**	**125.0**	——	——	**134.3**
Si-O-Si	140.8	——	——	——	140.8

*Tugt = tugtupite; OH-soda = basic (hydroxy) sodalite; Soda = sodalite; [1]Mean values for helvite-group minerals (six structure refinements).

The Na atom is five-fold coordinated by one Cl and four O atoms in tugtupite (Fig. 2a), in contrast to its four-fold coordination in sodalite (Fig. 2b). However, the Na–Cl bond length (2.707 Å) in tugtupite is shorter than that in sodalite (2.736 Å). Of the four oxygen atoms bonded to sodium in tugtupite, three have a mean bond-distance (2.356 Å) similar to that in sodalite (2.353 Å). The fourth oxygen atom is further (2.603 Å), but it is within bonding distance in tugtupite because in sodalite the other oxygen atoms are much further (3.087 Å).

The BeO_4 and AlO_4 tetrahedra in tugtupite are close to being regular, with Be–O and Al–O distances of 1.631 Å and 1.748 Å, respectively. The SiO_4 tetrahedra are distorted. In the pure Si–O–Si linkage, the Si–O distances are 1.644 Å and 1.647 Å; this distance is 1.581Å with a Be linkage, and it is 1.609 Å with an Al linkage. The mean Si–O distance is 1.620 Å. Therefore, individual Si–O bond length does vary with the other cations in the Si–O–*T* linkage, but this effect is not observed for the mean Si–O bond lengths (see below). The satisfactory valence-sum calculations (Brown & Altermatt 1985) for the cations and anions in tugtupite also confirm that the three *T* cations, Al, Be, and Si, are completely ordered (Table 4).

Comparison of framework geometry in sodalite-group minerals

Tugtupite, helvite-group minerals, sodalite, and basic (hydroxy) sodalite provide an excellent opportunity to compare structural effects that arise from dissimilar cations (Si^{4+}, Al^{3+}, Be^{2+}) on the *T* sites and very different interstitial cations (Na^+, Mn^{2+}, Zn^{2+}, Fe^{2+}) and anions (Cl^-, S^{2-}, OH^-, H_2O). The pertinent bond-distances and angles of the framework are compared in Table 5.

The bond model of Brown *et al.* (1969) indicates that the Si–O bond length is affected by the *T* cation forming the Si–O–*T* linkage. This effect is observed for individual Si–O bonds in tugtupite (Table 4), but not in the other minerals (*cf.* helvite and sodalite, Table 5). The mean Si–O distances for the minerals considered in Table 5 are nearly constant despite the fact that the *T* atoms are different. The mean Al–O bond lengths also are identical and do not vary significantly among the minerals, as are the mean Be–O bond lengths (Table 5). Consequently, for the sodalite-group minerals, the mean *T*–O distances are constant, and such distances are not affected by different interstitial atoms or different *T* cations.

Among the minerals considered (Table 5), the principal difference is in the *T*–O–*T* bridging angles. The Si–O–*T* (*T* = Si, Al) angles are nearly equal, but the main difference occurs in the Si–O–Be angles in the helvite-group minerals and in tugtupite (Table 5). The value of the *T*–O–*T* angle has been proposed to be a qualitative measure of the degree of *d-p* π bonding in the silicate framework (Cruickshank 1961, Brown *et al.* 1969, Gibbs *et al.* 1972). A *T*–O–*T* bond angle of 18° corresponds to maximum *d-p* π interactions. Both Al and Si have 3*d* orbitals available for such interactions. However, Be atoms have no available orbitals of the correct symmetry to produce interactions of this type with the oxygen atom coordinating it. Therefore, a small Si–O–Be angle in helvite may be expected as a result of the smaller contribution to the bonding of the framework (Holloway *et al.* 1972); however, such a large Si–O–Be angle in tugtupite is surprising, but no simple explanation can arise from the *d-p* π bonding model.

The *T*-O-*T* angles in sodalite-type materials are probably controlled mainly by the interstitial ions. The greater the effective charge of the cage clusters, the smaller the *T*–O–*T* angle. The cage clusters in sodalite and tugtupite are $[Na_4 \cdot Cl]^{3+}$ and basic (hydroxy) sodalite contains $[Na_4 \cdot OH \cdot H_2O]^{3+}$ clusters. These clusters all have the same net charge (3+ valence units). However, in the helvite-group minerals, the $[(Mn, Fe, Zn)_4 \cdot S]^{6+}$ clusters are highly charged and have smaller sizes; thus their effective charge is much stronger than in the other minerals. Therefore, the $[(Mn, Fe, Zn)_4 \cdot S]^{6+}$ clusters strongly attract the oxygen atoms in the Si–O–Be linkages and give rise to small Si–O–Be angles in helvite-group minerals compared to Si–O–*T* angles in the other minerals, in particular, the Si–O–Be angles in tugtupite (Table 5).

Thermal expansion of tugtupite

Henderson & Taylor (1977) obtained data on thermal expansion of a red tugtupite from Kvanefjeld, Ilımaussaq, Greenland over the range of 20 to 905°C. These data indicate smooth variations in response to thermal expansion. The expansion is anisotropic, being greater along the *a* axes than along the *c* axis, as indicated by the decrease in *c*/*a* ratio with increasing temperature. A combination of tilting of the TO_4 tetrahedra, the presence of three types of *T* atoms, and the distortion of the SiO_4 tetrahedra does not allow unambiguous interpretation of the thermal expansion of tugtupite and its anisotropy in terms of the crystal structure (Henderson & Taylor 1977).

In this paper the thermal expansion of tugtupite is modeled using the *DLS* structure-modeling program (Villiger & Meier 1969) and thermal expansion data of Henderson & Taylor (1977). The high-temperature structure modeling assumes that the structures would adjust to a rise in temperature by rotation of TO_4 tetrahedral units as in sodalite (Hassan & Grundy 1984). Cell parameters at the various temperatures were fixed to the values obtained experimentally by Henderson & Taylor (1977), and the structures were fitted to these parameters. As in sodalite, the Na–O distances are expected to change little, and the geometry of the TO_4 tetrahedra is expected to remain relatively constant. The starting positional coordinates are taken from this work; the coordinates for the Na site are adjusted so that the three shorter Na–O distances are identical to those in sodalite. Structures were calculated at various temperatures in the range of 20 to 905°C, but here the structural parameters are given only for the struc-

TABLE 6. MODELED POSITIONAL PARAMETERS AT 20° C* and 905° C**

	20° C			905° C		
Atom	x	y	z	x	y	z
Al	0	1/2	3/4	0	1/2	3/4
Be	0	1/2	1/4	0	1/2	1/4
Si	0.0127	0.2534	0.4959	0.0158	0.2532	0.4959
O1	0.1495	0.1334	0.4424	0.1534	0.1339	0.4530
O2	0.3471	0.0380	0.6488	0.3463	0.0223	0.6501
O3	0.4257	0.1487	0.1378	0.4239	0.1495	0.1392
Na	0.1606	0.1918	0.1834	0.1818	0.2167	0.2050
Cl	0	0	0	0	0	0

*Cell parameters: *a* = 8.640, *c* = 8.873 Å; ***a* = 8.769, *c* = 8.976 Å.

TABLE 7. COMPARISON OF EXPERIMENTAL AND MODELED STRUCTURES

		This Work	20° C	905° C
Al-O3	4 x	1.748(2)	1.748	1.748
Be-O2	4 x	1.631(2)	1.631	1.631
Si-O1		1.644(2)	1.642	1.643
-O1*		1.647(2)	1.643	1.643
-O2		1.581(2)	1.580	1.580
-O3		1.609(2)	1.607	1.608
Mean		1.620	1.618	1.619
Si-O1-Si		140.8(2)	141.4	146.6
Si-O2-Be		143.6(1)	143.8	149.1
Si-O3-Al		135.3(1)	135.4	139.4
Na-O1		2.370(3)	2.355	2.355
-O2		2.303(3)	2.355	2.355
-O3		2.396(3)	2.355	2.355
Mean		2.356	2.355	2.355
-O2*		2.603(3)	2.596	2.487
Na-Cl		2.707	2.705	3.088

tures at 20 and 905°C (Table 6). Unit weights in the *DLS* refinement were found to be appropriate. The 20°C modeled structure is almost identical to the measured structure in this paper, except for a slight shift in the Na-site position (Table 6). With increase in temperature, the TO_4 geometry remains nearly constant, and three Na–O distances also are constant, but the Na–O2* distance becomes progressively shorter, from 2.596 Å at 20°C to 2.487 Å at 905°C as the 5-fold coordinated Na site becomes more regular (Table 7). Major changes occur in the bridging angles, which increase as the tetrahedra rotate with thermal expansion, and also the length of the Na–Cl bond increases from 2.707 Å at 20°C to 3.088 Å at 905°C (Table 7). The latter value is identical to that modeled for sodalite at 905°C (Hassan & Grundy 1984). Therefore, the mechanism of thermal expansion of the tugtupite structure involves the expansion of the Na–Cl bond lengths, which forces the Na atoms toward the center of the six-membered rings. Because the Na–O bond lengths are nearly constant, this mechanism causes the tetrahedra to rotate. An analogous mechanism of thermal expansion operates in the sodalite-group minerals (Hassan & Grundy 1984).

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