# The crystal structure of thornasite, Na$_{12}$Th$_3$[Si$_8$O$_{19}$]$_4$(H$_2$O)$_{18}$: A novel interrupted silicate framework

YAPING LI,[1] SERGEY V. KRIVOVICHEV,[1,*] AND PETER C. BURNS[1,†]

[1]Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick, University of Notre Dame, Notre Dame, Indiana 46556-0767, U.S.A.

## ABSTRACT

The crystal structure of thornasite, Na$_{12}$Th$_3$[Si$_8$O$_{19}$]$_4$(H$_2$O)$_{18}$, $Z = 6$, rhombohedral, $a = 29.124(1)$, $c = 17.2602(9)$ Å, $V = 12,679.2(9)$ Å$^3$, space group $R\overline{3}c$, has been solved by direct methods, and refined to an agreement index ($R1$) of 5.7% calculated, based on 2266 unique observed reflections collected using Mo$K\alpha$ X-radiation and a CCD-based detector. The structure consists of a new interrupted silicate framework with composition [Si$_8$O$_{19}$]$^{6-}$. The framework density is 15.4 atoms per 1000 Å$^3$, which is typical for microporous aluminosilicate materials. The framework density, together with the presence of a three-dimensional network of channels in the structure, permit thornasite to be designated as a new member of the zeolite structure family. The framework consists of cubic cages and distorted six-membered rings linked via common edges. The circuit symbol is $(4^3 14^3)(4^3 6^2 14^3)_3(6.10.12)_3(6_2 10)_6$. Interruptions of the framework are caused by the presence of Th$^{4+}$ cations that are coordinated by eight O atoms. Na$^+$ cations and H$_2$O groups are located in channels through the structure. The theoretical parent framework for thornasite may be constructed by the insertion of two additional Si atoms in place of one Th atom. The theoretical framework density is 18.0 atoms per 1000 Å$^3$; the circuit symbol is $(4^3 10^3)(4^3 6^2 10)_6(4^3 6^2 8)_3(4^3 6.8.10)_3(4^2 6^2 8.10)_3(4^1 6^3 8.10)_3$.

## INTRODUCTION

Thornasite, a rare hydrous Na Th silicate, was described by Ansell and Chao (1987) from the floor of the De-Mix Quarry, Mont St. Hilaire, Quebec. It occurs as anhedral colorless to very pale green grains. Both single-crystal and powder diffraction patterns were reported to be of low quality due to the slightly metamict character of the mineral. We recently obtained superb crystals of thornasite from the same locality. These crystals do not appear to suffer from radiation-induced damage, and thus it was possible to fully determine the structure.

## EXPERIMENTAL METHOD

A crystal from De-Mix Quarry, Mont St. Hilaire, Quebec, was provided by Mr. Anthony Nikisher, Excalibur Mineral Co., New York. The crystal was mounted on a Bruker three-circle diffractometer equipped with a SMART CCD-based detector with a crystal-to-detector distance of 5 cm. A sphere of three-dimensional data was collected for the range $2.80° \leq 2\theta \leq 56.58°$ in 11 hours using frame width of $0.3°$ in $\omega$, with 10 seconds spent counting per frame. The unit-cell parameters were refined based on 7099 reflections using least-squares techniques. An empirical absorption correction was applied based on crystallographically equivalent reflections, with the crystal modeled as an ellipsoid. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from the *International Tables for X-ray Crystallography* of Ibers and Hamilton (1974). The data were corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. The SHELXTL Version 5.0 system of programs was used for structure determination and refinement. The details of the data collection, structure determination, and refinement are given in Table 1.

The reflection statistics indicate space groups $R3c$ and $R\overline{3}c$, with $R\overline{3}c$ preferred. The structure was solved by direct methods in space group $R\overline{3}c$. The final cycles of refinement included all atomic-positional parameters, anisotropic-displacement parameters for all atoms, and a weighting scheme of the structure factors, and converged to an agreement index ($R1$) of 5.7% calculated for the observed reflections ($|F_o| \geq 4\sigma_F$), and a goodness-of-fit of 0.87. Refinement of the structure in space group $R3c$ gave similar results, but anisotropic-displacement parameters for some Si and most O atoms were physically unrealistic. Ansell and Chao (1987) reported that thornasite is pyroelectric, in contradiction with space group $R\overline{3}c$. However, the crystallographic data of the current study do not suggest the structure is non-centrosymmetric; the pyroelectricity of thornasite reported previously may be associated with the metamict character and poor crystallinity of the studied samples.

Atomic coordinates and displacement parameters, calculated and observed structure factors, and selected interatomic distances, for thornasite are presented in Tables 2–4[1], respectively.

## RESULTS

### Description of the structure

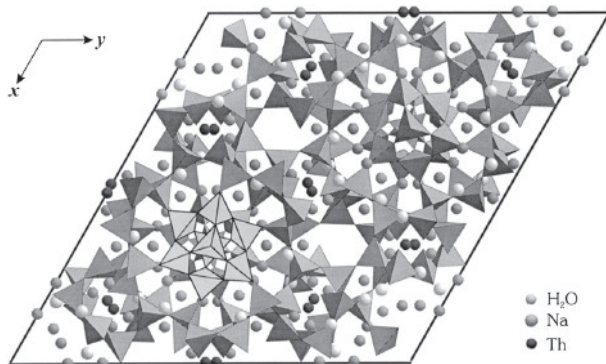The crystal structure of thornasite is shown in Figure 1. Silicate tetrahedra are linked into a three-dimensional framework with the stoichiometry [Si$_8$O$_{19}$]$^{6-}$, and a T:O ratio of 1:2.375.

\* Permanent address: Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg Russia

† E-mail: pburns@nd.edu

**TABLE 1.** Miscellaneous information for thornasite

| | | | |
|---|---|---|---|
| $a$ (Å) | 29.124(1) | Crystal size (mm³) | $0.20 \times 0.12 \times 0.10$ |
| $c$ (Å) | 17.2602(9) | Total reflections | 50,490 |
| $V$ (Å³) | 12,679.2 (9) | Unique reflections | 3511 |
| Space group | $R\bar{3}c$ | $R_{int}$, % | 12.4 |
| | | Observed $|F_o| \geq$ | |
| $F(000)$ | 9828 | $4\sigma_F$ | 2,266 |
| $\mu$ (mm⁻¹) | 5.93 | Final $R1$, % | 5.7 |
| $D_{calc}$ (g/cm³) | 2.68 | $S$ | 0.87 |
| Unit-cell contents: 6 [Na₁₂Th₃(Si₈O₁₉)₄(H₂O)₁₈] | | | |

*Note: $R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $S = [\Sigma w(|F_o|-|F_c|)^2/(m\text{-}n)]^{1/2}$, for $m$ observations and $n$ parameters.*



**FIGURE 1.** The crystal structure of thornasite viewed along [001]. One of the 4⁶ cubic cages is highlighted. The tetrahedra contain Si⁴⁺ ions. Labels for other cations are indicated in the legend.

[1]For a copy of Table 3, Document AM-99-055 contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (http://www.minsocam.org).

This ratio has not been previously observed for a framework silicate, although it is known for several silicates with double tetrahedral layers (Liebau 1985). Thus, thornasite represents a new type of silicate framework previously unknown among minerals and inorganic compounds.

There are six symmetrically independent Si atoms, each of which are tetrahedrally coordinated by O atoms. The $Si5O_4$ and $Si6O_4$ tetrahedra are linked via vertex-sharing to four other tetrahedra such that all of their vertices are bridging, whereas the $Si1O_4$, $Si2O_4$, $Si3O_4$, and $Si4O_4$ tetrahedra have three bridging and one non-bridging vertex each. This connectivity implies the structure is an interrupted framework, which is relatively rare in mineral structures. Only nine other minerals are known that have interrupted silicate frameworks (see Smith 1988; Rouse and Peacor 1994). The interruptions of the framework may be caused by various factors: (1) the presence of large cations, e.g., $Ca^{2+}$, $Ba^{2+}$, $Na^+$ (partheite, roggianite, wenkite, sarcolite, and ussingite), (2) the presence of $Be^{4+}$ (bavenite, leifite, and chiavennite), or (3) the presence of large clusters in the structural channels ($[Pb_4(OH)_4]^{4+}$ clusters in maricopaite). Thornasite belongs to the first group owing to the presence of relatively large $Th^{4+}$ cations. Indeed, all non-bridging O atoms in the silicate tetrahedra of the structure are bonded to the $Th^{4+}$ cations.

The coordination polyhedron of the single unique $Th^{4+}$ cation is a distorted tetragonal antiprism (Fig. 2), like that observed for large cations in the approximately dodecahedral sites in garnet. Th also occurs in this coordination polyhedron in the structure of ekanite, $ThCa_2[Si_8O_{20}]$, which contains unbranched single layers with composition $[Si_8O_{20}]^{8-}$ (Szymanski et al. 1982).

$Na^+$ cations and $H_2O$ groups are located in structural channels. Na1 and Na2 are coordinated by six and five O atoms, respectively. The $H_2O15$, $H_2O16$, and $H_2O17$ groups are bonded

**TABLE 2.** Atomic positions and displacement parameters (Å² × 10³) for thornasite

| Atom | Wyckoff position | $x$ | $y$ | $z$ | *$U_{eq}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Th1 | 18e | 0.15425(2) | 0.82091(1) | 1/12 | 16(1) | 17(1) | 17(1) | 14(1) | 1(1) | −1(1) | 9(1) |
| Si1 | 36f | 0.1684(1) | 0.9008(1) | -0.0861(2) | 16(1) | 16(2) | 20(2) | 12(1) | 5(1) | 1(1) | 7(1) |
| Si2 | 36f | 0.0641(1) | 0.8073(1) | -0.0689(2) | 17(1) | 14(2) | 19(2) | 17(2) | −1(1) | −2(1) | 8(1) |
| Si3 | 36f | 0.1595(1) | 0.9499(1) | 0.0598(2) | 16(1) | 16(2) | 13(2) | 17(2) | 2(1) | 0(1) | 7(1) |
| Si4 | 36f | 0.0991(1) | 0.7289(1) | -0.0929(2) | 14(1) | 17(2) | 12(1) | 13(1) | 1(1) | −1(1) | 6(1) |
| Si5 | 36f | 0.0645(2) | 0.9663(2) | 0.0512(3) | 43(1) | 36(2) | 39(2) | 60(3) | −3(2) | 0(2) | 22(2) |
| Si6 | 12c | 0 | 0 | 0.3415(6) | 53(2) | 39(3) | 39(3) | 79(6) | 0 | 0 | 20(1) |
| Na1 | 36f | 0.1486(4) | 0.8954(3) | 0.2413(4) | 66(2) | 114(7) | 76(5) | 30(3) | 3(3) | 8(4) | 65(5) |
| Na2 | 36f | 0.0287(3) | 0.8237(4) | 0.1184(5) | 81(3) | 60(4) | 141(7) | 53(4) | 9(4) | −4(4) | 59(5) |
| O1 | 36f | 0.1925(3) | 0.8713(4) | -0.0390(5) | 23(2) | 27(5) | 28(5) | 19(4) | 10(3) | 7(3) | 17(4) |
| O2 | 36f | 0.1629(4) | 0.9054(3) | 0.1074(5) | 26(2) | 45(6) | 16(4) | 17(4) | 0(3) | −4(4) | 17(4) |
| O3 | 36f | 0.1362(3) | 0.7548(3) | -0.0195(5) | 25(2) | 31(5) | 25(5) | 23(4) | −8(3) | −16(4) | 16(4) |
| O4 | 36f | 0.0769(3) | 0.8109(4) | 0.0204(5) | 24(2) | 19(4) | 38(5) | 15(4) | −4(4) | −2(3) | 16(4) |
| O5 | 36f | 0.0082(3) | 0.8033(5) | -0.0885(5) | 29(2) | 18(4) | 54(6) | 17(4) | −1(4) | 1(3) | 19(4) |
| O6 | 18e | 0.0587(4) | 2/3 | −1/12 | 26(3) | 22(5) | 11(6) | 41(8) | 11(5) | 6(3) | 6(3) |
| O7 | 36f | 0.0628(3) | 0.7563(3) | -0.1099(5) | 23(2) | 29(5) | 21(4) | 22(4) | −5(3) | −7(4) | 17(4) |
| O8 | 36f | 0.1086(3) | 0.8592(3) | -0.1150(5) | 22(2) | 17(4) | 19(4) | 24(4) | 5(3) | −4(3) | 3(4) |
| O9 | 36f | 0.1658(3) | 0.9465(3) | -0.0346(4) | 21(2) | 30(5) | 17(4) | 15(4) | 1(3) | −1(3) | 10(4) |
| O10 | 36f | 0.1998(4) | 0.9313(4) | -0.1628(5) | 29(2) | 29(5) | 40(5) | 18(4) | 17(4) | 13(4) | 18(4) |
| O11 | 36f | 0.1033(4) | 0.9466(5) | 0.0762(6) | 41(3) | 28(5) | 65(7) | 46(6) | 10(5) | 2(5) | 34(5) |
| O12 | 36f | 0.0960(6) | 0.0159(5) | -0.0067(8) | 71(4) | 66(9) | 49(8) | 89(11) | 23(7) | 8(8) | 22(7) |
| O13 | 6a | 0 | 0 | 1/4 | 30(6) | 0(8) | 0(5) | 89(19) | 0 | 0 | 0(3) |
| O14 | 36f | 0.0432(5) | 0.9822(6) | 0.1254(9) | 70(4) | 53(8) | 83(10) | 84(10) | −9(8) | 11(7) | 43(8) |
| H₂O15 | 18e | 0.2323(13) | 0 | 1/4 | 154(14) | 210(30) | 210(40) | 40(13) | 23(18) | 12(9) | 107(19) |
| H₂O16 | 36f | 0.0998(11) | 0.9422(10) | 0.2668(14) | 173(11) | 210(30) | 170(20) | 130(20) | 29(18) | −25(19) | 90(20) |
| H₂O17 | 18e | 0 | 0.8615(26) | 1/4 | 380(20) | 370(20) | 370(20) | 380(20) | −2(5) | −3(9) | 187(10) |
| H₂O18 | 36f | 0.3072(9) | 0.0421(7) | 0.3408(11) | 122(7) | 155(11) | 80(9) | 121(10) | −9(7) | 58(8) | 51(8) |

*Note: $U_{eq} = 1/3 \Sigma U_{ij}a_i^* b_j^* a_i b_j$ The anisotropic displacement factor takes are of the form: $-2\pi[h^2 a^{*} U_{11} + \cdots\cdots + 2hka^* b^* U_{12}]$.*

to Na cations, whereas $H_2O18$ is only H bonded into the structure; the closest Na atom is at 3.26 Å, which corresponds to a bond-valence of only 0.02 v.u., indicating that it is probably not a significant bond.

## Structural formula for thornasite

According to the crystal-structure determination (Table 5), the structural formula for thornasite is $Na_{12}Th_3[Si_8O_{19}]_4(H_2O)_{18}$, $Z = 6$. This differs from the formula $(Na,K)ThSi_{11}(O,H_2O,F,Cl)_{33}$ reported by Ansell and Chao (1987). These authors also obtained poor compatibility of the chemical and physical data; the compatibility index based upon the Gladstone-Dale relationship and parameters given by Mandarino (1976, 1979) was 0.096. The compatibility index based on the new formula calculated using the experimental density and refractive indices from Ansell and Chao (1987) is 0.067 according to Mandarino (1979).

## Structure and characteristics of the silicate framework

Description of silicate frameworks is usually done in terms of finite building units, from which they can be constructed (Liebau 1985; Smith 1988). The main building units needed to construct the structure of thornasite are shown in Figure 3. The vierer double rings of silicate tetrahedra $Si5O_4$ and $Si6O_4$, or cubic cages (Fig. 3a), are linked into infinite chains that are parallel to the $c$ axis. The cubes share each of their six 5-5 edges with the saddle-like distorted hexagonal rings (Fig. 3b). The resulting complex chains are linked via additional chair-like distorted hexagonal rings (Fig. 3c) as shown in Figures 3d and 4. Three adjacent chains are related to each other via a $3_1$ screw axis.

The circuit symbol for the thornasite framework (the shortest circuits of edges for the vertices) is $(4^3 14^3)(4^3 6^2 14)_3$ $(6.10.12)_3(6_2 10)_6$, which corresponds to four 4-connected and twelve 3-connected vertices. The existence of 14-membered rings in the circuit symbol results from interruptions of the framework.

The framework contains a three-dimensional system of cavities. One type of cavity (with approximate dimensions of $4.2 \times 4.6 \times 6.6$ Å$^3$) surrounds chains of cubic cages. A second type of cavity (with approximate dimensions of $4.6 \times 5.2 \times 5.9$ Å$^3$) forms channels running along [001] (the coordinates of the channel are 1/3, 1/3, $z$). Both types of cavities form a 3-dimensional system. The existence of cavities in thornasite is consistent with designation as a zeolite. The subcommittee on zeolites of the International Mineralogical Association (IMA) (Coombs et al. 1997) indicate that the framework in a zeolite "...contains
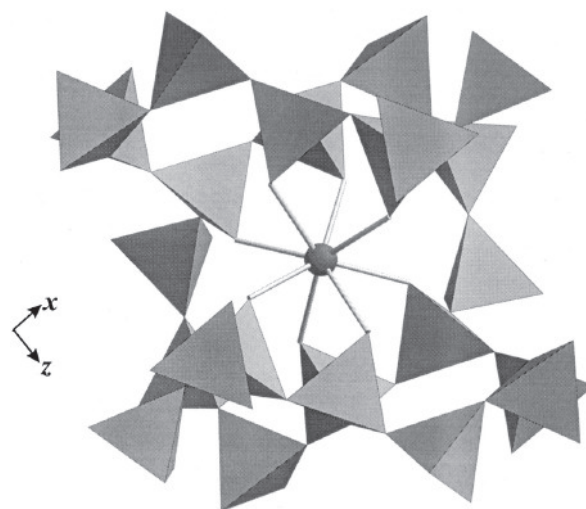


**FIGURE 2.** Coordination of the Th cation in the crystal structure of thornasite.

**TABLE 4.** Selected bond lengths (Å) and angles (°) for thornasite

| | | | | | | |
|---|---|---|---|---|---|---|
| Th1-O4 | 2.384(8) | Si4-O3 | 1.589(8) | Na1-O2 | 2.34(1) |
| Th1-O2 | 2.380(8) | Si4-O6 | 1.602(4) | Na1-O1a | 2.42(1) |
| Th1-O4a | 2.384(8) | Si4-O10c | 1.629(9) | Na1-H₂O16 | 2.45(3) |
| Th1-O2a | 2.380(8) | Si4-O7 | 1.637(8) | Na1-O8i | 2.49(1) |
| Th1-O3a | 2.475(8) | <Si4-O> | 1.614 | Na1-O3a | 2.56(1) |
| Th1-O3 | 2.475(8) | | | Na1-H₂O15e | 2.80(2) |
| Th1-O1a | 2.494(8) | Si5-O11 | 1.56(1) | <Na1-O> | 2.51 |
| Th1-O1 | 2.494(8) | Si5-O12d | 1.58(1) | | |
| | 2.433 | Si5-O14 | 1.59(1) | Na2-O4 | 2.34(1) |
| | | Si5-O12e | 1.61(1) | Na2-O3a | 2.40(1) |
| Si1-O1 | 1.579(9) | <Si5-O> | 1.59 | Na2-O9j | 2.53(1) |
| Si1-O10 | 1.601(8) | | | Na2-H₂O17 | 2.83(4) |
| Si1-O8 | 1.625(8) | Si6-O13 | 1.58(1) | Na2-O10j | 2.87(1) |
| Si1-O9 | 1.633(8) | Si6-O14f | 1.68(1) | <Na2-O> | 2.59 |
| | 1.600 | Si6-O14g | 1.68(1) | | |
| | | Si6-O14h | 1.68(1) | | |
| Si2-O4 | 1.577(8) | <Si6-O> | 1.66 | | |
| Si2-O5 | 1.608(9) | | | | |
| Si2-O8 | 1.626(8) | Si2-O5-Si3j | 148.9(6) | | |
| Si2-O7 | 1.629(9) | Si4k-O6-Si4 | 160.5(9) | | |
| | 1.610 | Si2-O7-Si4 | 129.8(5) | | |
| | | Si1-O8-Si2 | 127.0(5) | | |
| | | Si1-O9-Si3 | 129.7(5) | | |
| Si3-O2 | 1.580(8) | Si1-O10-Si4c | 153.1(7) | | |
| Si3-O11 | 1.62(1) | Si5-O11-Si3 | 145.8(8) | | |
| Si3-O5b | 1.623(9) | Si5l-O12-Si5m | 148.3(11) | | |
| Si3-O9 | 1.648(8) | Si6n-O13-Si6 | 180 | | |
| | 1.618 | Si5-O14-Si6o | 145.4(11) | | |

*Note:* a: $y - 2/3, x + 2/3, -z + 1/6$; b: $x - y + 1, x + 1, -z$; c: $-x + 1/3, -y + 5/3, -z - 1/3$; d: $y, -x + y + 1, -z$; e: $x, y + 1, z$; f: $x - y + 1, -y + 1, -z + 1/2$; g: $-x, -x + y - 1, -z + 1/2$; h: $y - 1, x, -z + 1/2$; i: $-y + 1, -x + 1, z + 1/2$; j: $y - 1, -x + y, -z$; k: $x - y + 2/3, -y + 4/3, -z - 1/6$; l: $x - y + 1, x, -z$; m: $x, y - 1, z$; n: $y, x, -z + 1/2$; o: $y, x + 1, -z + 1/2$.



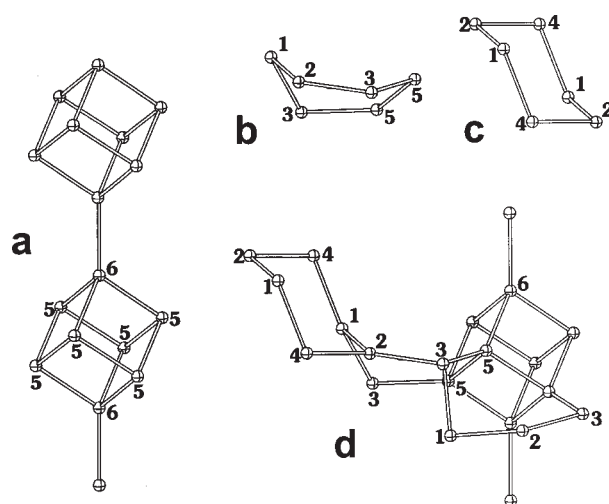**FIGURE 3.** Main building units of the silicate framework in thornasite. The numbers correspond to the Si atom designations in Table 2. Components (**a–d**) and their linkages are described in the text.

**TABLE 5.** Bond valence (v.u.) analysis for thornasite

| | Th1 | Si1 | Si2 | Si3 | Si4 | Si5 | Si6 | Na1 | Na2 | Σ |
|---|---|---|---|---|---|---|---|---|---|---|
| O1 | 0.41×2↓ | 1.13 | | | | | | 0.18 | | 1.72 |
| O2 | 0.56×2↓ | | | 1.13 | | | | 0.23 | | 1.92 |
| O3 | 0.44×2↓ | | | | 1.10 | | | 0.13 | 0.19 | 1.86 |
| O4 | 0.56×2↓ | | 1.13 | | | | | | 0.23 | 1.92 |
| O5 | | | 1.04 | 1.01 | | | | | | 2.05 |
| O6 | | | | | 1.07×2→ | | | | | 2.14 |
| O7 | | | 0.98 | | 0.96 | | | | | 1.94 |
| O8 | | 0.99 | 1.01 | | | | | 0.15 | | 2.15 |
| O9 | | 0.98 | | 0.93 | | | | | 0.14 | 2.05 |
| O10 | | 1.07 | | | 0.98 | | | | 0.06 | 2.11 |
| O11 | | | | 1.01 | | 1.19 | | | | 2.20 |
| O12 | | | | | | 1.10, 1.04 | | | | 2.14 |
| O13 | | | | | | | 1.19×2→ | | | 2.38 |
| O14 | | | | | | 1.10 | 0.84×3↓ | | | 1.94 |
| H₂O15 | | | | | | | | 0.07×2→ | | 0.14 |
| H₂O16 | | | | | | | | 0.17 | | 0.17 |
| H₂O17 | | | | | | | | | 0.06×2→ | 0.12 |
| H₂O18 | | | | | | | | | | 0 |
| Σ | 3.94 | 4.17 | 4.16 | 4.08 | 4.11 | 4.43 | 3.71 | 0.93 | 0.68 | |

*Note:* Values calculated using parameters from Brese and O'Keeffe (1991).

open cavities in the form of channels and cages. These are usually occupied by H₂O molecules and extra-framework cations that are commonly exchangeable." In thornasite the cavities contain Na⁺ cations and H₂O groups, although it is not known if they are exchangeable. The high-vacuum dehydration of thornasite at room temperature reported by Ansell and Chao (1987) is consistent with the zeolite character of the structure.

The framework density, 15.4 T atoms per 1000 Å³, is relatively low and is typical for microporous aluminosilicate materials (Smith 1988).

## Parent tetrahedral framework for thornasite

Most of the known interrupted tetrahedral frameworks correspond to unbroken parent frameworks that are observed in other structures. We could not find a parent framework for thornasite among known zeolite frameworks listed in Meier et al. (1996). However, the construction of a parent framework is useful in order to predict possible framework silicate configurations. The theoretical parent framework for thornasite was constructed from the thornasite structure by the insertion of two additional Si atoms in place of one Th atom. This operation corresponds to the addition of theoretical atoms designated Si7 and O15 to the list of atoms. The role of the O15 atom is to link two adjacent [Si7O₄] tetrahedra. This results in the conversion of the Si2, Si3, and Si4 silicate tetrahedra from 3-connected to 4-connected. Two Si1O₄ tetrahedra become 4-connected by their linking via their non-bridging O1 vertexes.

After estimating the approximate coordinates for the inserted atoms, the structure model was refined using the DLS program (Baerlocher et al. 1977). Following Han and Smith (1999a), we set ideal values for T-O, O-O, and T-T bonds equal to 1.63, 2.6618, and 3.1258 Å with weights of 2.0, 1.0, and 0.1, respectively. The atomic coordinates were refined to an *R* of 0.029 and are listed in Table 6. The relatively high *R* index may indicate low framework flexibility. The model gives a distorted Si1O₄ tetrahedron with one O-O distance about 3.0 Å. Thus, this model is an approximate model that may be realized in nature by a certain extent of declination of T-O, O-O, and T-T bonds from their ideal values (e.g., due to Al-Si substitution or symmetry reduction). Attempts to refine the unit-cell param-
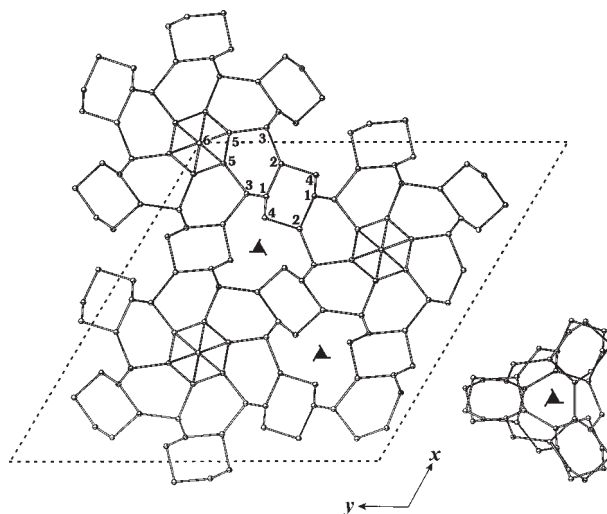


**FIGURE 4.** Organization of the silicate framework in thornasite. The numbers correspond to the Si atom designations in Table 2.
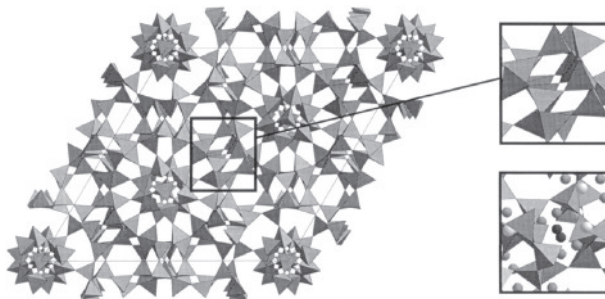


**FIGURE 5.** The parent theoretical tetrahedral framework for thornasite viewed along [001] (left). The structural fragment shown in the top-right box is the theoretical unbroken framework that corresponds to the interrupted framework observed in thornasite (lower-right box).

**TABLE 6.** Atomic coordinates for the theoretical parent framework for thornasite

| Atom | Wyckoff position | x | y | z |
|---|---|---|---|---|
| Si1 | 36f | 0.14929 | 0.87406 | −0.12599 |
| Si2 | 36f | 0.05921 | 0.80416 | −0.06110 |
| Si3 | 36f | 0.16382 | 0.93675 | 0.03935 |
| Si4 | 36f | 0.11278 | 0.72865 | −0.07356 |
| Si5 | 36f | 0.07038 | 0.96754 | 0.05209 |
| Si6 | 12c | 0 | 0 | 0.34505 |
| Si7* | 36f | 0.11131 | 0.84108 | 0.09539 |
| O1 | 18d | ⅙ | −⅙ | −⅙ |
| O2 | 36f | 0.16068 | 0.89979 | 0.11424 |
| O3 | 36f | 0.14877 | 0.73427 | 0.00254 |
| O4 | 36f | 0.08317 | 0.84284 | 0.01506 |
| O5 | 36f | −0.00550 | 0.77550 | −0.05135 |
| O6 | 18e | 0.73290 | 0 | ¼ |
| O7 | 36f | 0.08389 | 0.76431 | −0.06533 |
| O8 | 36f | 0.08412 | 0.84446 | −0.13554 |
| O9 | 36f | 0.16189 | 0.90314 | −0.03970 |
| O10 | 36f | 0.17979 | 0.92413 | −0.18678 |
| O11 | 36f | 0.11387 | 0.94748 | 0.05642 |
| O12 | 36f | 0.09949 | 0.02178 | 0.00000 |
| O13 | 6a | 0 | 0 | ¼ |
| O14 | 36f | 0.04185 | 0.98070 | 0.12394 |
| O15* | 18e | 0.46770 | 0.46770 | ¾ |

* Indicates atoms inserted into the thornasite structure to obtain a fully four-connected tetrahedral framework. The crystallographic parameters of the framework are the same as thornasite (Table 1).

eters gave unreliable results, probably because of the high complexity of the framework.

The theoretical parent framework of thornasite is shown in Figure 5 and may be compared with Figure 1. It may be described as consisting of chains of two different types that are shown in Figures 3a and 6a. Polyhedral building units and their
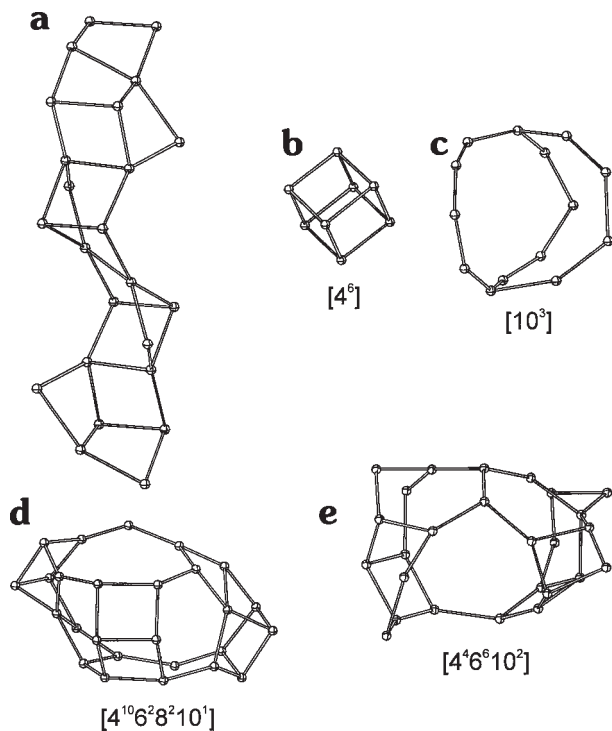


**FIGURE 6.** Main building units of the theoretical tetrahedral parent framework for thornasite. Circuit symbols are indicated, except for the chains in part a. See text for discussion of component linkages.

designations according to general rules given in Liebau (1985) and Smith (1988) are shown in Figures 6b–6e. The circuit symbol for the framework is $(4^3 10^3)(4^3 6^2 10)_6(4^3 6^2 8)_3$ $(4^3 6.8.10)_3(4^2 6^2 8.10)_3(4^1 6^3 8.10)_3$; note the absence of the 14-membered rings, in comparison with the broken framework of thornasite. The framework density is 18.0 T atoms per 1000 Å³.

Recently, theoretical 4-connected frameworks have received renewed interest (Han and Smith 1999a, 1999b, 1999c; Friedrichs et al. 1999) due to their importance in the study of zeolites and related materials. The new silicate framework of thornasite and its parent framework reported in this work provide insights into construction of new theoretical frameworks.

## REFERENCES CITED

Ansell, V.E. and Chao, G.Y. (1987) Thornasite, a new hydrous sodium thorium silicate from Mont St-Hilaire, Quebec. Canadian Mineralogist, 25, 181–183.
Baerlocher, Ch., Hepp, A., and Meier, W.M. (1977) DLS–76. A program for the simulation of crystal structures and geometric refinement. Insitut für Kristallographie und Petrographie, ETH, Zürich, Switzerland.
Brese, N.E. and O'Keeffe, M. (1991) Bond–valence parameters for solids. Acta Crystallographica, B47, 192–197.
Coombs, D.S., Alberti, A., Armbruster, Th., Artioli, G., Colella, C., Galli, E., Grice, J.D., Liebau, F., Mandarino, J.A., Minato, H., Nickel, E.H., Passaglia, E., Peacor, D.R., Quartieri, S., Rinaldi, R., Ross, M., Sheppard, R.A., Tillmanns, E., and Vezzalini, G. (1997) Recommended nomenclature for zeolite minerals: report of the subcommittee on zeolites of the International Mineralogical Association, Commission on New Minerals and Mineral Names. Canadian Mineralogist, 35, 1571–1606.
Friedrichs, O.D., Dress, A.W.M., Huson, D.H., Klinowski, J., and Mackay, A.L. (1999) Systematic enumeration of crystalline frameworks. Nature, 400, 644–647.
Han, Shaoxu and Smith, J.V. (1999a) Enumeration of four-connected three-dimensional nets. I. Conversion of all edges of simple three-connected two-dimensional nets into crankshaft chains. Acta Crystallographica, A55, 332–341.
———(1999b) Enumeration of four-connected three-dimensional nets. II. Conversion of edges of three-connected 2D nets into zigzag chains. Acta Crystallographica, A55, 342–359.
———(1999c) Enumeration of four-connected three-dimensional nets. III. Conversion of edges of three-connected two-dimensional nets into saw chains. Acta Crystallographica, A55, 360–382.
Ibers, J.A. and Hamilton, W.C., Eds. (1974) International Tables for X-ray Crystallography, IV. The Kynoch Press, Birmingham, U.K.
Liebau, F. (1985) Structural chemistry of silicates. Structure, bonding and classification, 347 p. Springer-Verlag, New York.
Mandarino, J.A. (1976) The Gladstone-Dale relationship. I. Derivation of new constants. Canadian Mineralogist, 14, 498–502.
———(1979) The Gladstone-Dale relationship. II. Some general applications. Canadian Mineralogist, 17, 71–76.
Meier, W.M., Olson, D.H., and Baerlocher, Ch. (1996) Atlas of Zeolite Structure Types (Fourth edition). 229 p. Elsevier, London.
Rouse, R.C. and Peacor, D.R. (1994) Maricopaite, an unusual lead calcium zeolite with an interrupted mordenite-like framework and intrachannel Pb₄ tetrahedral clusters. American Mineralogist, 79, 175–184.
Smith, J.V. (1988) Topochemistry of zeolites and related materials. 1. Topology and geometry. Chemical Reviews, 88, 149–182.
Szymanski, J.T., Owens, D.R., Roberts, A.C., Ansell, H.G., and Chao, G.Y. (1982) A mineralogical study and cristal-structure determination of nonmetamicht ekanite, ThCa₂Si₈O₂₀. Canadian Mineralogist, 20, 65–75.