The Crystal Structure of Tincalconite[1]

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Abstract

Tincalconite is trigonal, space group $R32$, with hexagonal unit cell $a = 11.09 \pm 0.03$, $c = 21.07 \pm 0.04$ Å and $Z = 9$. The crystal structure was determined for a synthetic crystal by interpretation of a three-dimensional sharpened Patterson synthesis and by use of the tangent method of Karle and Karle. The R index for 337 observed reflections is 0.06, and 0.07 for 398 including the non-observed ones.

The structure consists of discrete polyions $[B_4O_5(OH)_4]^{-2}$, contained in the cavities of a Na-polyhedra framework. The polyions are the same as in borax, and some structural relations between tincalconite, borax, and kernite can be emphasized. The framework of Na-polyhedra is the result of three dimensional sharing of faces, edges, and corners.

Introduction

Tincalconite is a hydrated sodium tetraborate, $Na_2B_4O_5(OH)_4 \cdot 3H_2O$. Except for only a few occurrences, natural tincalconite is known only as a fine-grained powder (Pabst and Sawyer, 1948), whereas artificial crystals have an octahedron-like habit. Hence most properties of tincalconite have been determined on synthetic crystals (Palache *et al*, 1951). Tincalconite is closely related to borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$. The reversible equilibrium tincalconite $\rightleftarrows$ borax and the relationships among tincalconite, borax, and kernite were fully explained by Christ and Garrels (1959). At normal conditions of relative humidity and temperature (*i.e.,* 60 percent relative humidity, 20–25°C), tincalconite and borax rapidly and reversibly convert to one another (Christ and Garrels, 1959).

The first consistent results for the chemical formula and the crystallographic data of tincalconite were given by Christ and Clark (1957) and Petch *et al* (1962) and later confirmed and extended in many other works (Christ and Garrels, 1959; Bray *et al*, 1961; Cuthbert and Petch, 1963a, 1963b). According to these studies, the correct chemical formula is $Na_2B_4O_5(OH)_4 \cdot 3H_2O$ instead of $Na_2B_4O_7 \cdot 5H_2O$ (on the assumption that tincalconite contains the same polyion as borax). The space group is not $R\bar{3}$ (Minder, 1935) but $R32$ and the sodium atoms lie on special positions surrounded by anions in either a regular

or an irregular arrangement. On the basis of the above considerations the crystal structure proposed by Invers (1948) looked unlikely.

Experimental

No known natural crystals are suitable for the structural study. Synthetic crystals of $Na_2B_4O_5(OH)_4 \cdot 3H_2O$ were easily grown from aqueous solutions of borax at nearly 80°C. A suitable tincalconite crystal was chosen and coated with cellulose acetate to prevent, as much as possible, rehydration and conversion into borax.

The lattice parameters were determined from the $hk0$ and $0kl$ Weissenberg photographs calibrated by superimposing single-crystal quartz reflections. The Laue-symmetry group determined from hkl Weissenberg photographs is $\bar{3}m$. The space groups consistent with the X-ray data are the following:

$$R3m \quad ; \quad R32 \quad ; \quad R\bar{3}m$$

The NMR spectrum (Cuthbert and Petch, 1963a) and the inspection of the Patterson synthesis showed space group $R32$ to be the most probable.

The cell dimensions are $a_h = 11.09(3)$, $c_h = 21.07(4)$ Å; the numbers in parentheses refer to the estimated standard deviations in terms of the last decimal place cited. Thus $11.09(3)$ indicates an *esd* of 0.03Å. The calculated density is 1.94 g/cm³, which compares to the specific gravity of 1.88 observed by Pabst and Sawyer (1948).

A total of 398 independent reflections were collected, 61 of which were below the observational limit. The intensities were measured by means of a microdensitometer from equiinclination integrated Weissenberg photographs taken around the c axis (l from 0 to 13) with Ni-filtered Cu radiation. The intensities were then corrected for Lorentz and polarization factors. The crystal used for the exposures had an irregular shape. No allowance was made for extinction or absorption corrections; however, the latter effect is almost negligible because of the crystal's low absorption

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coefficient μ ($= 24$ cm^{-1} for CuKα) and small size ($R_{min} = 0.02$, $R_{max} = 0.05$ mm).

Structure Determination and Refinement

A three-dimensional Fourier synthesis phased on positions obtained for the Na atoms from the partial resolution of the Patterson synthesis did not show unambiguously the remaining atomic positions. Normalized structure amplitudes (Table 1) were then calculated with scale and temperature factors as obtained by Wilson's method, and the structure was solved by application of the tangent formula (Karle and Karle, 1966).

In the attempt to obtain phases for 109 reflections with $|E| > 1$, the reflections (461), (093) and (330) were selected, with the first as the origin-de-

TABLE 1.   Measured and Calculated Structure Factors

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c

TABLE 2. Fractional Atomic Coordinates ($\times 10^4$), Anisotropic Thermal Parameters ($\times 10^4$)*, and Equivalent Isotropic Thermal Parameters according to Hamilton (1959)

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_H
Na(1)	0	6695(5)	50	38(6)	40(4)	7(2)	19	1(3)	1	1.38
Na(2)	0	0	50	29(7)	29	12(5)	14	0	0	1.43
Na(3)	0	0	928(5)	75(6)	75	21(4)	38	0	0	3.08
B_1	926(11)	2676(12)	3825(7)	22(11)	43(12)	4(5)	22(10)	2(5)	1(5)	0.94
B_2	2385(12)	585(12)	2882(9)	36(12)	24(12)	12(7)	19(10)	4(6)	4(6)	1.38
O(1)	0	5334(8)	0	4(9)	13(7)	7(4)	2	-5(4)	-3	0.66
O(2)	325(7)	2911(7)	2526(4)	31(7)	14(7)	10(3)	0(6)	-7(3)	7(3)	1.33
O(3)	2129(7)	421(7)	3503(5)	43(8)	19(7)	6(4)	15(6)	3(4)	2(3)	1.13
OH(4)	1281(7)	1942(7)	4290(4)	39(7)	17(7)	6(3)	21(5)	4(3)	2(3)	0.93
OH(5)	2630(12)	1794(8)	2577(5)	170(16)	54(9)	17(4)	86(11)	30(6)	21(4)	3.27
Ow(6)	885(8)	2223(9)	1339(4)	75(9)	66(10)	5(3)	44(8)	-9(4)	-4(4)	1.89
Ow(7)	0	8620(28)	0							

*The estimated standard deviations are given in parentheses. The temperature factors refer to the expression: $\exp[-b_{11}h^2+b_{22}k^2+b_{33}l^2+2(b_{12}hk+b_{23}kl+b_{13}hl)]$.

fining one. The generated phases were then refined by cyclic application of the tangent formula. A consistent set was employed for increasing to 150 the reflections with $|E| > 0.7$ that had known phases.

The R_{Karle}, R_{Drew}, α, and t criteria were employed (Kennard et al, 1971), where

$$R_{Karle} = \frac{\sum ||E_h| - |E_h|_{calc}|}{\sum |E_h|}$$

$$R_{Drew} = \frac{\sum_h |E_h| (1 - t_h)}{\sum_h |E_h|}$$

$$t = \frac{(A^2 + B^2)^{1/2}}{\sum_k |E_k| |E_{h-k}|}$$

$$A = \sum_k |E_k| |E_{h-k}| \cos (\varphi_k + \varphi_{h-k})$$

$$B = \sum_k |E_k| |E_{h-k}| \sin (\varphi_k + \varphi_{h-k})$$

$$\alpha = |E_h| (A^2 + B^2)^{1/2}$$

During the calculations a phase was considered as determined if $\alpha > 8$. The best R_{Karle} and R_{Drew} values of 0.28 and 0.25 respectively occurred in one of eight attempts. The map obtained from the properly phased E values confirmed the positions of the Na atoms located by the Patterson solution and showed all of the atoms, except one oxygen atom, Ow(7) and the hydrogen atoms. The atomic parameters and the individual isotropic temperature factors were refined using a modified full matrix least-squares program ORFLS (Busing et al, 1962). The $R = \sum ||F_o| - |F_c||/\sum |F_o|$ value after this refinement was 0.10.

A three-dimensional Fourier synthesis showed only a broad maximum suitable for Ow(7), a position where a later Fourier difference synthesis unambiguously located this atom. H positions were determined by inspection of interatomic distances.

Isotropic temperature factors of the H atoms were fixed at 3 Å² and inclusion of hydrogen atoms and Ow(7) reduced the R value to 0.08. Refinement was continued using anisotropic thermal parameters for all atoms except Ow(7) and the hydrogen atoms. The high value of the Ow(7) temperature factor (~ 17 Å²) can be explained structurally. The final R index for 337 observed reflections is 0.06 (or 0.07 for 398 including the non-observed ones). The final positional and thermal parameters are listed in Table 2. H positions are shown in Table 3. The atomic scattering factors used were those given by Cromer and Waber (1965).

TABLE 3. Fractional Atomic Coordinates for the Hydrogen Atoms ($\times 10^4$)

Atom			
H_1	1581	1411	4015
H_2	2383	2367	2859
H_3	684	2484	1766
H_4	425	2743	1151
H_5	515	8217	9747

Description of the Structure

The structure is illustrated in Figure 1; for clarity, this picture is a simplification of its overall three-dimensional character. The complete arrangement of the atoms in tincalconite can be obtained easily when projecting the structure on (010) of the C-centered orthohexagonal cell. Each of the three crystallographically independent sodium atoms is coordinated by six oxygen atoms (including OH, H_2O). Interatomic distances and bond angles are given respectively in Tables 4 and 5.

The oxygen atoms around Na(1) form a nearly regular octahedron. This Na(1) octahedron shares two hydroxyl corners OH(5) with two adjacent $BO_2(OH)$ triangles and two hydroxyl corners OH(4) with two adjacent $BO_3(OH)$ tetrahedra. It shares one edge, OH(4)-OH(4'), with the Na(2) polyhedron. This edge is 3.25 Å, the shortest one in the Na(1) octahedron, while the opposite edge OH(5)-OH(5') is the longest one (4.07 Å). Finally the Na(1) octahedron shares corners
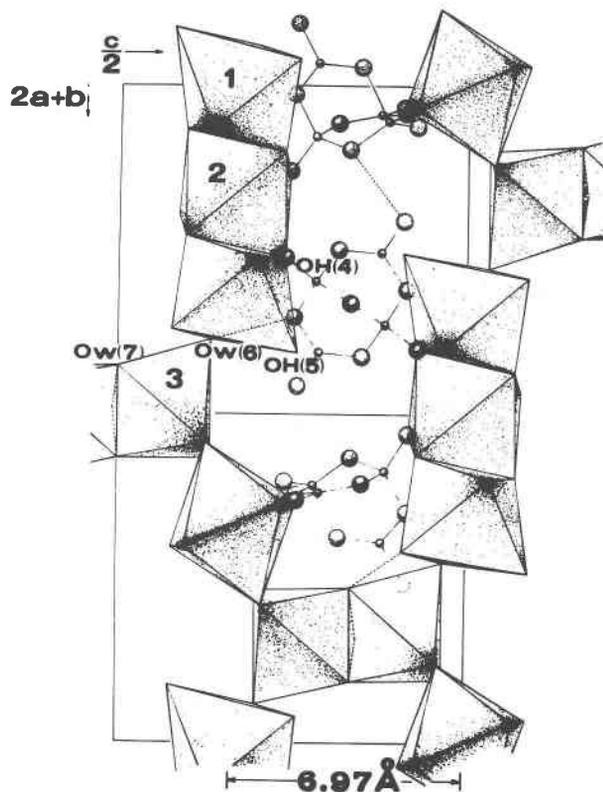
TABLE 4. Na-O Bond Lengths (Å) with Their Standard Deviations in Parentheses and Their Multiplicities in Braces

Na(1)-OH(4)	{x2}	2.483(7)	Na(2)-OH(4) {x6}	2.419(6)
-Ow(6)	{x2}	2.453(7)	Na(3)-Ow(6) {x3}	2.338(8)
-OH(5)	{x2}	2.442(8)	-Ow(7) {x3}	2.518(18)

with two Na(3) polyhedra through the two remaining water oxygens Ow(6).

The Na(2) atom is surrounded by six hydroxyls OH(4) with the cation-anion distance 2.42 Å; the shape of this polyhedron is a slightly distorted octahedral arrangement.

The Na(3) atom is surrounded by six water oxygen atoms. This polyhedron shares a face, built up by three Ow(7) water oxygens, with an equivalent Na(3') polyhedron and three corners Ow(6) with three Na(1) octahedra. This connection is rather unusual but already known (Corazza *et al,* 1967). The Na(3)-Na(3') distance is very long, 3.90 Å, compared with the distances for regular Na-ocathedra sharing one face, 2.80 Å. Moreover it is longer than those reported in the literature, 3.30 Å (Frevel, 1940; Miller, 1936; Grund and Preisinger, 1950), and 3.15 Å (Corazza *et al,* 1967). The increased distance and the irregularity of the Na-polyhedron are attributed to the electrostatic repulsion between the Na(3)-Na(3') cations and particularly to the stress of the "Na-chains" (Fig. 1). The Ow(7)-Na(3)-Ow(7') angle is 66.3°, whilst Ow(6)-Na(3)-Ow(6') is 106.8°. The Ow(7)-Ow(7') and Ow(6)-Ow(6') distances are respectively 2.75 and 3.75 Å.

These results are in good agreement with the conclusions of Cuthbert and Petch (1963b).

FIG. 1. Projection of tincalconite structure on (010) of the orthohexagonal cell. Dotted lines indicate some of the hydrogen bonds.

TABLE 5. O-Na-O Bond Angles (°) with Their Standard Deviations in Parentheses

O-Na-O	Angle	O-Na-O	Angle
Ow(6)-Na(1)-OH(5)	94.0(3)	OH(4)-Na(2)-OH(4')	85.55(2)
-OH(5')	89.3(3)	-OH(4")	84.57(2)
-OH(4)	83.6(2)	-OH(4"')	106.95(3)
-OH(4')	92.2(3)	OH(4^{IV})-Na(2)-OH(4^V)	163.35(4)
OH(5)-Na(1)-OH(5')	113.5(4)	Ow(6)-Na(3)-Ow(6')	106.82(3)
-OH(4)	164.2(3)	-Ow(7')	102.60(3)
OH(4)-Na(1)-OH(5)	82.6(2)	-Ow(7)	79.83(2)
-OH(4')	81.8(3)	Ow(7')-Na(3)-Ow(7)	66.33(2)
Ow(6')-Na(1)-Ow(6")	174.5(4)	-Ow(6)	123.90(3)
		Ow(7)-Na(3)-Ow(6)	179.92(4)
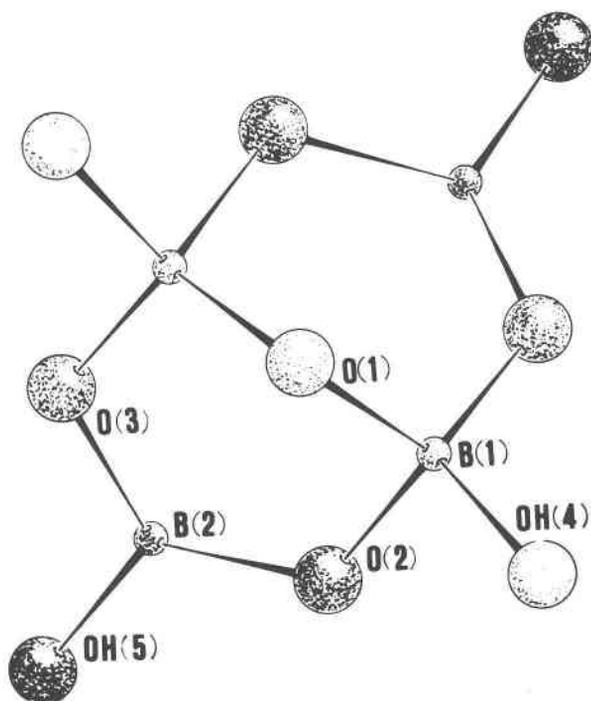
Fig. 2. $[B_4O_5(OH)_4]^{-2}$ polyanion in tincalconite.

Fig. 4. Projection of Na-octahedra in tincalconite on (001).

tances and bond angles are in good agreement with those given for the $[B_4O_5(OH)_4]^{-2}$ borax polyion (Table 6).

Hydrogen Bonds

No attempt to locate hydrogen atoms directly was made because of the low number of independent *hkl* reflections. However, from an inspection of the anion-anion distances we found some O-O distances less than 3.20 Å for oxygens not belonging to the same polyhedron (Table 7).

On the basis of O-O distance, the location of hydrogen atoms confirms Christ's rule that in the

In tincalconite the same boron-oxygen polyion occurs as in borax, and it is crossed by a two-fold axis in both structures. The polyion is formed by two symmetrical $BO_2(OH)$ triangles and two symmetrical $BO_3(OH)$ tetrahedra to give a compact group with composition $[B_4O_5(OH)_4]^{-2}$ (Fig. 2). Within the borate polyion, each of the $BO_2(OH)$ triangles shares O(3) and O(2) oxygens with the $BO_3(OH)$ tetrahedra, which are in turn connected to each other by the sharing of O(1). Interatomic dis-

Fig. 3. The structure of borax projected on (010). Some of the hydrogen bonds are shown by dotted lines (Morimoto, 1956).
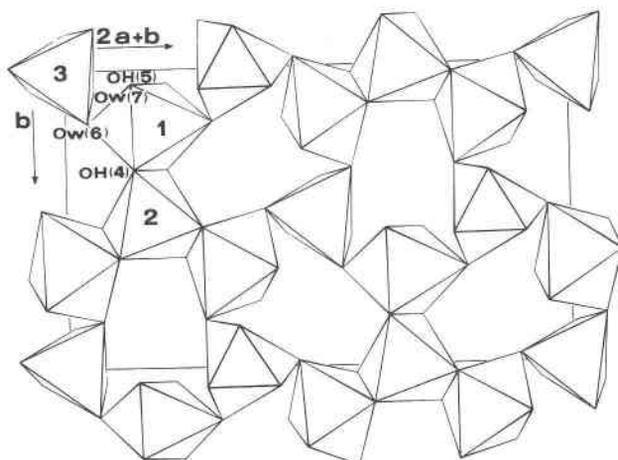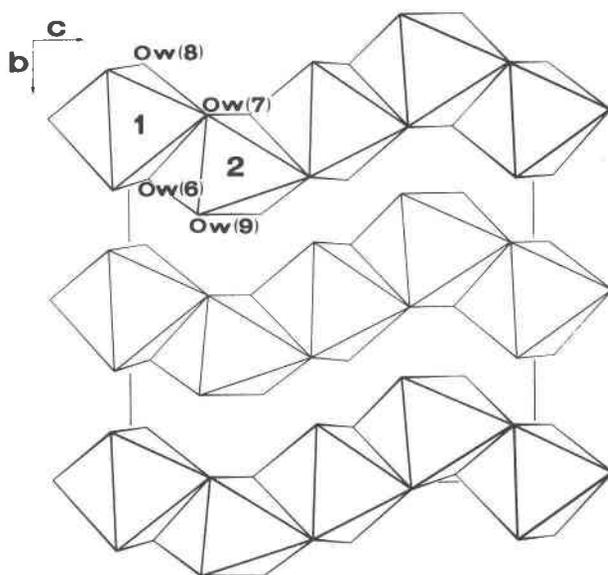

Fig. 5. Projection of Na-octahedra in borax on (100) (Morimoto, 1956).

TABLE 6. Comparison of B-O Distances and Angles in Borax and Tincalconite

	Borax N. Morimoto (1956)		Tincalconite This study	
Atoms	Distances(Å) or angles(°)	Atoms	Distances(Å) or angles(°)	
		B-O Distances		
B(1)-O(1)	1.47	B(1)-O(1)	1.460(12)	
-O(2)	1.46	-O(2)	1.468(12)	
-O(3)	1.54	-O(3)	1.507(13)	
-OH(4)	1.46	-OH(4)	1.454(13)	
B(2)-O(2)	1.36	B(2)-O(2)	1.358(14)	
-O"(3)	1.32	-O(3)	1.330(15)	
-OH(5)	1.40	-OH(5)	1.386(13)	
		O-B-O Angles		
O(1)-B(1)-O(2)	111.2	O(1)-B(1)-O(2)	109.3(7)	
O(1)-B(1)-O(3)	108.6	-O(3)	108.1(9)	
-OH(4)	110.2	-OH(4)	111.9(7)	
O(2)-B(1)-O(3)	108.5	O(2)-B(1)-O(3)	107.1(7)	
-OH(4)	111.5	-OH(4)	110.5(9)	
O(3)-B(1)-OH(4)	106.5	O(3)-B(1)-OH(4)	110.7(7)	
O(2)-B(2)-O"(3)	125.3	O(2)-B(2)-O(3)	122.9(10)	
-OH(5)	117.0	-OH(5)	120.1(10)	
O"(3)-B(2)-OH(5)	118.7	O(3)-B(2)-OH(5)	116.2(10)	

polyions of hydrated borates those oxygens not shared by two borons always attach a proton to form a hydroxyl group. So the hydrogen atoms were located at 1 Å from the oxygen atoms surrounding Na-polyhedra, along the vectors O-O reported below (Table 7).

Comparison of Tincalconite, Borax, and Kernite Structures

Christ and Garrels (1959) in their paper on sodium borate hydrates explain the apparently anomalous behavior found for the $Na_2B_4O_7$-H_2O system. For
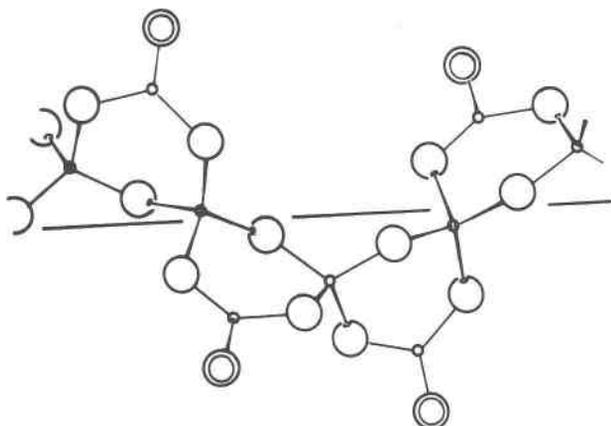

FIG. 6. Boron-oxygen chain running along the bisector of monoclinic angle in kernite (Cialidi *et al.,* 1967).

TABLE 7. O-O Distances less than 3.20 Å for Oxygens not Belonging to the Same Polyhedron in Tincalconite

OH(4)-O(3)	2.834(9) Å	Ow(7)-OH(5)	2.965(21) Å
OH(5)-O(1)	2.665(9)	Ow(6)-O(2)	2.758(10)
		Ow(6)-O(2)	2.845(9)

example, the reaction borax $\underset{+5H_2O}{\overset{-5H_2O}{\rightleftarrows}}$ tincalconite is easy and reversible, but the conversion borax-tincalconite into kernite is difficult. These authors state that this difficulty is related to a considerable activation energy for the conversion of borax-tincalconite into kernite, perhaps because kernite does not contain the same polyion $[B_4O_5(OH)_4]^{-2}$ as borax and tincalconite, but instead has infinite chains of composition $[B_4O_6(OH)_2]^{-2n}$, as was later confirmed experimentally (Cialdi *et al*, 1967; Giese, 1966).

In the light of structural results, the general arrangement of atoms in borax, tincalconite, and kernite can be compared. The borax structure, space group $C\,2/c$, is built up by chains along the c direction. One set of chains is composed of Na·$6H_2O$ polyhedra sharing edges with each other in the ac plane (Fig. 3). The other set of chains is formed by hydrogen-bonding between the discrete $[B_4O_5(OH)_4]^{-2}$ polyions which are located between the Na polyhedra and connected to them by hydrogen bonds.

In tincalconite and in borax, it is possible to identify similar structural units, but because of the lesser water content and closer packing of tincalconite, the following differences are noted (Figs. 1, 3, 4, 5).

1) The "Na-chains" in tincalconite are distorted compared to borax. The interaxial distance between two "Na-Na chains" in tincalconite is 6.97 Å (Fig. 1), whereas in borax it is 11.36Å (Fig. 3).

TABLE 8. Charge Balance of Oxygen Atoms in Tincalconite (Ionic Structure)

Atom	$B_\triangle$	$B_\square$	Na(1)	Na(2)	Na(3)	-H...	..H-	Total
O(1)...		2x3/4					2x1/4	2.00
O(2)...	1	3/4					2x1/4	2.25
O(3)...	1	3/4					1/4	2.00
OH(4)..		3/4	1/6	1/6		3/4		1.83
OH(5)..	1		1/6			3/4	1/4	2.16
Ow(6)..			1/6		1/6	2x3/4		1.83
Ow(7)..				2x1/6	2x3/4			1.83

2) Tincalconite shows a rotation of Na(3) polyhedra, forcing them to share one face. As mentioned above, the working conditions were close to the tincalconite-borax conversion, (60% R.H., 20–25°C). The high thermal parameter of Ow(7) must result from the instability of face-sharing between two Na(3) polyhedra. The transformation of tincalconite to borax can be considered as starting from the break of such face-sharing connections.

3) In tincalconite, hydroxyl groups are shared between $[B_4O_5(OH)_4]^{-2}$ polyions and Na polyhedra. Four OH groups belonging to the polyion are shared by four Na-polyhedra belonging to four different "Na chains" to build up the three-dimensional structure.

Under the assumption of an entirely ionic structure, the charge balance of oxygen atoms in borax can be compared with that of oxygen atoms in tincalconite, as shown in Tables 8 and 9. Distributing each hydrogen contribution as 3/4 to the linked oxygen atom and 1/4 to the unlinked one, the balance comparison between borax and tincalconite is satisfactory.

On the basis of the crystal structure determination (Giese, 1966; Cialdi *et al*, 1967), kernite is very different from borax and tincalconite. Indeed kernite is built up of boron-oxygen chains which can be considered as the polymerization reaction of borax polyions (Fig. 6),

$$n[B_4O_5(OH)_4]^{-2} = [B_4O_6(OH)_2]_n^{-2n} + nH_2O$$

Kernite has two crystallographically independent sodium atoms Na(1) and Na(2). Na(1) is surrounded by three water molecules and two oxygen atoms. Na(2) is surrounded by three oxygen atoms, one hydroxyl atom and one water molecule. Four such Na polyhedra are connected to form "islands"

which are in turn linked to boron-oxygen chains. Finally, although differences between borax and tincalconite exist, both are quite different from kernite because of the polymerization of the $[B_4O_5(OH)_4]^{-2}$ polyions and the "islands" of sodium-oxygen coordination. These features are the most important ones that explain the easy and reversible equilibrium of borax $\rightleftarrows$ tincalconite and the more difficult transformation of borax-tincalconite $\rightleftarrows$ kernite.

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TABLE 9. Charge Balance of Oxygen Atoms in Borax (Ionic Structure)

Atom	B$_\triangle$	B$_\square$	Na(1)	Na(2)	−H...	...H−	Total
O(1)...		2x3/4				2x1/4	2.0
O(2)...	1	3/4				1/4	2.0
O(3)...	1	3/4				2x1/4	2.25
OH(4)..		3/4			3/4	2x1/4	2.00
OH(5)..	1				3/4	2x1/4	2.25
O(6)...			1/6	1/6	2x3/4		1.83
O(7)...			1/6	1/6	2x3/4		1.83
O(8)...			1/6		2x3/4	1/4	1.92
O(9)...				1/6	2x3/4	1/4	1.92

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