TINCALCONITE CRYSTALS FROM SEARLES LAKE, SAN BERNARDINO COUNTY, CALIFORNIA

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Abstract

The discovery of small, well-formed crystals of tincalconite in drill cores from Searles Lake, San Bernardino County, California, is announced. The associated minerals are described and the results of goniometric and x-ray examination of tincalconite reported.

Introduction

The name tincalconite first appeared in print in 1878.[1] The statement in which it was contained reads as follows:—

> "Tincalconite (Shepard). Borax pulverulent et efflorescent, de Californie, 32p. cent d'eau."

This appeared in a section of the *Bulletin* headed "Extraits de diverses publications." Literature references are given for most of the extracts, all of which are concerned with new mineral names, but no reference si given with the extract on tincalconite which is quoted in full above. No trace has been found of any original publication by Shepard[2] on this material and it seems that such may never have been accomplished.

Mineralogists generally[3] considered the name tincalconite to apply to a variety of borax rather than to a distinct mineral. After half a century it was pointed out by Schaller[4] that "it is obvious" that Shepard's tincalconite "was the 5-hydrate of the borax series, $Na_2O \cdot 2B_2O_3 \cdot 5H_2O$ identical in composition with 'octahedral borax'." According to Schaller it is "not very abundant but rather widespread, coating both borax and kernite." It forms from borax, the 10 hydrate of the series, by partial dehydration or from kernite, the 4 hydrate, by hydration. So far it has been found only in powdery form.

Natural borax crystals such as are found embedded in the muds of Borax Lake in Lake County and Searles Lake in San Bernardino County, California, and numerous other localities are probably partly or wholly altered to the 5-hydrate and so should be considered pseudomorphs of tincalconite after borax. It is very easy to observe the process of partial

[1] *Bull. Soc. Min. France* **I**, 144 (1878).

[2] No initials are given with this name but it may be presumed that this was Charles Upham Shepard (1804–1886), an American mineralogist who was a most active and not always careful namer of minerals.

[3] Dana, E. S., System of Mineralogy, 6th ed. 887 (1892); Eakle, A. S. Minerals of California, Bull. **67,** Calif. State Mining Bureau, 170 (1914).

[4] Schaller, W. T., Borate minerals from the Kramer District, Mohave Desert, California: *U. S. Geol. Surv. Prof. Paper* **158-I,** 163 (1930).

dehydration in the laboratory. Perfectly clear, well formed crystals of the 10 hydrate are easily grown in the laboratory by evaporation of an aqueous solution at room temperature. If such crystals are left unprotected in a dry atmosphere they become dull, white and opaque within a few days or weeks. In some cases one can observe the whitened part extending from the surface into the clear borax crystal as a small bulbous or frond-like growth. This sort of change can be prevented or arrested by sealing the crystals in a small tube or coating them with shellac. It has been found possible to maintain crystals partly whitened and partly clear in a sealed tube for ten years or more.

DISCOVERY

Last summer one of us (D. L. S.) collected specimens from cores obtained by deep drilling at Searles Lake. One sample of a nine inch core was observed to contain numerous clear crystals suspected of being tincalconite. It was brought into the laboratory for further study and most of this report is based upon work on this sample.

GEOLOGICAL SETTING

Searles Lake is a salt body occupying a large basin in the northern part of San Bernardino County. There is water at the lake surface only in unusually wet seasons. A firm crust of salts covers an oval area of 11 or 12 square miles.[5] At the margins the salts are mixed with or covered by alluvial material. The total area of the playa zone, composed of salts and mixed alluvial material, is about 60 square miles. The salt body is exceedingly porous, consisting in large part of reticulated crystals with open spaces constituting more than 25%. These open spaces are occupied by a heavy brine which fills the numerous drill holes and is the chief raw material of the extensive chemical industries operated at the edge of the "lake."

According to Gale[6] the depth of the salt deposit is 60 to more than 100 feet, probably averaging 70 to 75 feet. The deepest of many wells whose records were reported by Gale penetrated salts to a depth of 85 feet. In recent years numerous borings carried to a greater depth have shown that there exists a deeper salt body under the muds that make up the bottom of the exposed salt body. These muds are 10 to 20 feet thick. Below them lies a "second" salt body sometimes referred to as the "lower structure." This lower salt body is some 40 or 50 feet thick.

[5] Gale, Hoyt S., Salines in the Owens, Searles, and Panamint basins, southeastern California: *U. S. Geol. Surv.*, *Bull.* **580**, 251–323 (1915)

[6] *Op cit.*, p. 273.

The core sample in which the tincalconite crystals were found was taken from deep well X-1, situated in sec. 23, R43E, T25S, slightly north of the center of the exposed salt body. This well penetrated to the bottom of the lower salt body at a depth of about 118 feet. Below this it penetrated dark muds with traces of various salts to about 121 feet, the limit of the boring. The core sample studied is 6 to 7 centimeters thick in its thickest portion and came from a depth of about 116 feet, that is from within a few feet of the bottom of the lower salt body.

TINCALCONITE CRYSTALS

The clear, colorless tincalconite crystals are scattered as isolated individuals or clusters of two or three through a thin layer, not over 2 centimeters thick, in the middle part of our core sample. The matrix is fine grained white salts not certainly identifiable with the unaided eye. In a few patches the ratio of volume of tincalconite crystals to matrix may be 1:2 or 1:3, but for the most part the ratio is 1:10 or less. The scattered crystals are easily separated from the matrix, often falling out when the core is broken. Not infrequently there is an open space partly surrounding the larger tincalconite crystals.

The great majority of the crystals lie within a rather narrow size range between one and three millimeters in maximum dimension. By weighing two counted lots of crystals it was found that the average weight of a crystal is just under three milligrams. Taking into account the shape and the density (reported below) it may be calculated that the average crystal is just under 2 millimeters from tip to tip. The largest crystals we have removed from the matrix are about 4 millimeters from tip to tip. Recently Mr. H. Stanton Hill[7] of Pasadena has found a tincalconite crystal that "would probably measure close to 1 cm. were it to be completely removed from its matrix."

The water content of the tincalconite crystals was estimated from the water loss of two small lots of clear crystals, heated to constant weight, care being taken not to drive off any other material by overheating. By a similar procedure it was shown that the common fully whitened borax corresponds closely in composition to tincalconite. For this purpose a large well formed borax crystal embedded in Searles Lake mud, which had been in the dry laboratory air 5 years, was used. The results of these tests, tabulated below, leave no doubt that both materials are essentially the pentahydrate.

	Weight per cent of H_2O
Ideal $Na_2B_4O_7 \cdot 5H_2O$	30.9
Tincalconite crystals	30.0
Whitened borax	29.8

[7] Letter to A. Pabst, dated January 7, 1948.

The specific gravity of small clear tincalconite crystals was determined by suspension in bromoform diluted with methyl alcohol and found to be 1.88. This agrees with the value 1.880 reported for "artificial crystals" by Schaller.[8] The optical properties were found to agree within the limits of error with those reported by Schaller for "artificial tincalconite."

The tincalconite crystals are very constant in habit. They are rhombohedral, invariably showing the forms $c\{0001\}$ and $r\{10\bar{1}1\}$ combined in such a manner as to closely resemble an octahedron. Other forms are lacking or appear only as minute truncations or strips. This habit is similar to that of artificial crystals which were long known as "octahedral borax." Figure 1 shows how close is this similarity. All the inter-
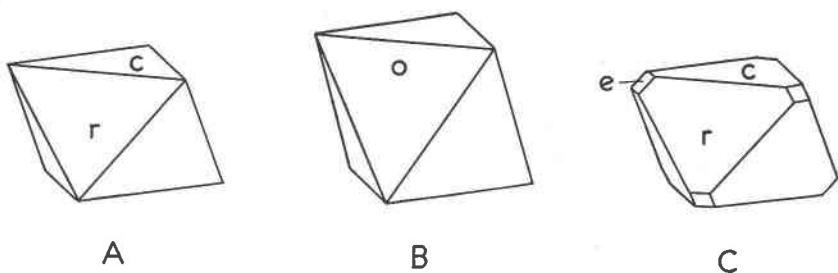

Fig. 1. A. Typical tincalconite crystals from Searles Lake.
$r\{10\bar{1}1\}$, $c\{0001\}$.
B. Ideal octahedron.
$o\{111\}$.
C. $Na_2B_4O_7 \cdot 5H_2O$ grown in laboratory.
$r\{10\bar{1}1\}$, $c\{0001\}$, $e\{01\bar{1}2\}$.

facial angles at the twelve like edges of an ideal octahedron are 70° 32'. In tincalconite the angle $r \wedge r$ is about $5\frac{1}{2}$ degrees more and the angle $c \wedge r$ is about 5 degrees less. This difference is scarcely discernible on crystals a few millimeters in dimension. On the other hand, all of the faces of an ideal octahedron are equilateral triangles whereas only the c faces of tincalconite are equilateral and the angle between edges of the r faces (this is also the interaxial angle of the rhombohedral axes) is about 12 degrees higher than the corresponding 60 degree angle on an octahedron. This can be noticed by careful inspection on even the smallest crystals.

Crystals of $Na_2B_4O_7 \cdot 5H_2O$ were grown in the laboratory from a water solution near 100° C. The small crystals first formed show the same habit as natural crystals but crystals grown to a larger size, 5 to 10 millimeters in maximum dimension, invariably show in addition small faces of the form $e\{10\bar{1}2\}$. With this form present the crystals also appear isometric,

[8] *Op. cit.*, p. 163.

the new form cutting all of the pseudo-octahedral corners and simulating a cube as shown in Fig. 1C.

Crystals of the pentahydrate were first measured by Arzruni.[9] He reported the same forms just mentioned and his measurements have been included in Groth's compilation "Chemische Krystallographie."[10] Unfortunately the column headings in Groth's table for calculated and measured angles are erroneous, except that the starred angle is given under the appropriate heading. All references to Arzruni's work herein are to the original publication only.

Four small tincalconite crystals and one laboratory grown crystal were measured on both two-circle and one-circle goniometers. The results showed that even selected natural crystals show such imperfections that precise angle measurements are not possible and that artificial crystals are no better. Arzruni reported variation of angle measurements over two or three degrees but gave values to minutes nevertheless. Table 1 shows a comparison of our results with those of Arzruni. Though no close agreement has been obtained a correction of Arzruni's results is not clearly indicated.

TABLE 1. INTERFACIAL ANGLES OF TINCALCONITE, $Na_2B_4O_7 \cdot 5H_2O$

	Average	Range	Number of observations	Arzruni	
				Measured	Calculated
$(10\bar{1}1 \wedge \bar{1}101)$	103°53′	103°18′–104°31′	12	103°38′	—
$(0001 \wedge 10\bar{1}1)$	65°37′*	64°52′– 66°50′	14	62°53′	65 11

* The angle ρ from two-circle measurements. The calculated angle $(10\bar{1}1 \wedge \bar{1}101)$ corresponding to this would be 104°8′, whereas the angle ρ calculated from the one-circle measurement of $(10\bar{1}1 \wedge \bar{1}101)$ would be 65°24′.

To check on the axial elements it is fortunately possible to draw upon other data. The cell dimensions of $Na_2B_4O_7 \cdot 5H_2O$ have been reported by Minder.[11] Table 2 gives axial elements derived from various sources. The agreement between our best values and Minder's best values happens to be fairly close. This should not be taken to indicate a precise determination.

[9] Arzruni, A., Ueber den sogenannten "octaëdrischen" Borax: *Pogg. Ann. der Physik*, **158**, (234), 250–252 (1876).

[10] Volume **2**, page 732, Leipzig (1908).

[11] Minder, W., Über den Bau einiger Hydrate von Natriumdiborat: *Zeits. Krist.*, **92**, 301–309 (1935). Minder entitles the section of his paper dealing with the pentahydrate "Tincalconite, $Na_2B_4O_7 \cdot 5H_2O$" suggesting that he may have used natural crystals. Through the courtesy of Dr. Werner Nowacki of Bern, Switzerland, where Minder did his work, it has been possible to ascertain that artificial material was used.

TABLE 2. AXIAL ELEMENTS OF TINCALCONITE, $Na_2B_4O_7 \cdot 5H_2O$

	c_h/a_h	a_h	c_h	α	a_r
Arzruni 1876 op. cit., p. 251	1.87			71°59′	
Minder 1935 op. cit., p. 305	1.850	11.3±0.1 Å	20.9±0.1 Å	72°36′*	9.54*
Minder 1935 op. cit., p. 304	1.887†	11.20†	21.13†	71°42′±5′	9.56±0.04 Å
This paper 1-circle measurement	1.892			71°35′	
This paper 2-circle measurement	1.911			71° 8′	

* Rhombohedral constants calculated from Minder's hexagonal cell.

† Hexagonal constants calculated from Minder's rhombohedral cell. Minder gives dimensions as Å. These should doubtless be interpreted as kX.

As indicated in Table 2 Minder reports separate cell constants for a rhombohedral and for a hexagonal cell, apparently derived from different rotation patterns. It is evident that his constants for the rhombohedral cell are more accurate. If a cell of these dimensions contains $3(Na_2B_4O_7 \cdot 5H_2O)$ the density should be 1.893, only slightly greater than the value 1.88 directly determined on both natural and artificial crystals.

Table 3 shows a record of a powder pattern of tincalconite crystals from Searles Lake made with copper radiation. It may be seen that all observed lines due to spacings over 1.75kX are accounted for and that the agreement of the spacings is such as to give at least a rough check on Minder's cell dimensions. The table also shows the intensities recorded by Minder for certain of these lines in a rotation pattern on the rhombohedron edge. All of the lines he recorded in this range of spacings are found on the powder pattern. There is substantial agreement also with the powder pattern of $Na_2B_4O_7 \cdot 5H_2O$ given on card 2233 of the original ASTM card file of powder patterns. The line 3.93 on our pattern is not recorded on the ASTM card and may be open to suspicion. On the other hand a corresponding line was also observed on a tincalconite pattern made with Fe radiation and there are no good grounds for attributing it to impurity.

The indexing of the pattern clearly shows that the lattice is rhombohedral. No systematic extinctions indicating glide planes are noted. Taking account of etch figures on $\{10\bar{1}1\}$ indicating absence of symmetry planes Minder concluded that the possible space groups are $C^2_{3i} - R\bar{3}$ and $D^7_3 - R32$. He excluded $C^4_3 - R3$ on morphological grounds and gave preference to group $R\bar{3}$. Observations here reported are not at variance

TABLE 3. POWDER x-RAY DIFFRACTION PATTERN OF TINCALCONITE COMPARED
with x-RAY DATA ON ARTIFICIAL $Na_2B_4O_7 \cdot 5H_2O$

Tincalconite					Artificial $Na_2B_4O_7 \cdot 5H_2O$		
Hexagonal indices *hkil*	Rhombohedral indices *hkl*	Calculated spacings*	Powder pattern Cu K_α radiation spacing	intensity	Minder‡ Cu rot. pattern intensities	ASTM card 2233† d	I
$10\bar{1}1$	100	8.815	8.83	7	st.st.		
$2\bar{1}\bar{1}0$	$1\bar{1}0$	5.599	5.60	5	m.st.	5.6	0.13
$02\bar{2}1$	$11\bar{1}$	4.736	4.73	5		4.72	0.13
$20\bar{2}2$	200	4.407	4.42	9	st.st.st.	4.40	0.60
$01\bar{1}5$	221	3.874	3.93	6 (broad)			
$3\bar{1}\bar{2}1$	$2\bar{1}0$	3.611	3.61	3	m.st.		
$12\bar{3}2$	$21\bar{1}$	3.463	3.47	7		3.44	0.53
$30\bar{3}0$	$2\bar{1}\bar{1}$	3.233	3.22	2			
$21\bar{3}4$	310	3.011	3.03	2	st.§	2.99	0.20
$11\bar{2}6$	321	2.974					
$30\bar{3}3$	300	2.938 ⎱	2.94	10	st.st.	2.94	1.00
$03\bar{3}3$	$22\bar{1}$	2.938 ⎰					
$22\bar{4}0$	$20\bar{2}$	2.799	2.79	5		2.76	0.13
$4\bar{1}32$	$3\bar{1}0$	2.606 ⎱	2.60	6 (broad)	m.	2.60	0.33
$22\bar{4}3$	$31\bar{1}$	2.601 ⎰					
$40\bar{4}1$	$3\bar{1}\bar{1}$	2.408	2.412	4		2.40	0.06
0009	333	2.347	2.350	2			
$31\bar{4}5$	410	2.269	2.278	2	st.	2.26	0.13
$40\bar{4}4$	400	2.203 ⎱	2.205	8	st.st.	2.19	0.67
$22\bar{4}6$	420	2.194 ⎰					
$41\bar{5}0$	$3\bar{1}2$	2.116	2.112	1			
$13\bar{4}7$	430	2.008	2.022	7	st.st.st.	2.01	0.33
$02\bar{2} \cdot 10$	442	1.950	1.954	5		1.94	0.27
$50\bar{5}2$	$4\bar{1}\bar{1}$	1.908	1.912	2			
$63\bar{3}0$	$3\bar{3}0$	1.866	1.866	4	m.st.	1.84	0.13
$41\bar{5}6$	510	1.814 ⎱					
$62\bar{4}2$	$4\bar{2}0$	1.806					
$33\bar{6}3$	$41\bar{2}$	1.804 ⎬	1.811	7+	st.	1.80	0.40
$22\bar{4}9$	531	1.799					
$32\bar{5}7$	520	1.791 ⎰					
$50\bar{5}5$	500	1.763	1.771	3	m.		
			1.662	4		1.65	0.07
			1.618	2−			
			plus about 30 more lines.				

* For planes in rhombohedral cell, $a_r = 9.56$, $\angle\alpha = 71°42'$, found by Minder, *op. cit.*, p. 304

† Card marked "H" to indicate that data are from Hanawalt of Dow Chemical Co.

‡ For planes in the zone [001] only. As observed on a Cu rotation pattern [001], Minder's Tabelle IV, *op. cit.*, p. 305.

§ Misprint in Minder's Tabelle IV, $21\bar{3}3$ for $21\bar{3}4$.

with these conclusions but there is some doubt whether the scant morphological data justify any preference among the three space groups permitted by the x-ray and etch figure evidence.

Associated Minerals

The core in which the tincalconite crystals were found has a layered structure so that one might speak of a "stratigraphy" of the core. Unfortunately there is no evidence to indicate what is top or bottom of the core and so the sequence of the layers remains in doubt. Three layers are readily discernible, each making up about one third of the total thickness of 6 or 7 centimeters but the layers vary somewhat in thickness, possibly due to local compaction of the initially very porous material. The "stratigraphy" of the core is essentially:

A. Whitened prismatic borax, up to 5 mm. long, much pore space, a very few grayish tincalconite crystals

B. Fine-grained, white, salts in which are embedded numerous clear tincalconite crystals

C. Reticulated mass of lath-like trona crystals.

Layer A is partly banded due to crystal size variation, but this is not persistent laterally. The layer consists almost wholly of whitened borax. This is in fact tincalconite pseudomorphous after borax as mentioned above. Microscopic examination shows that the pseudomorphing tincalconite is fairly coarse, up to 0.2 mm. or more in dimensions. All the larger fragments show spindly voids arranged at 60° to each other in (0001). In one finer band of borax there are a few grayish equidimensional tincalconite crystals up to 1 mm. in diameter. This tincalconite has copious inclusions of northupite, up to 0.05 mm., and gaylussite, up to 0.01 mm., certainly identifiable by crystal form and optical properties. A trace of trona adheres to the surface.

The change from layer A to layer B is rather abrupt, the whitened borax at the boundary being somewhat finer. The dense white to yellowish salt of layer B encloses numerous clear crystals and clusters of tincalconite which reach up to 4 or 5 millimeters in maximum dimension and were described above. The clear euhedral tincalconite crystals always enclose sharp octahedrons of northupite up to 0.06 mm. from tip to tip and some oval spaces, voids, bubbles or enclosed brine. It was found that each tincalconite crystal of average size (2 mms.) encloses several score northupite crystals. Even so the contamination is only a fraction of one per cent.

The groundmass of layer B consists largely of fine grained tincalconite with embedded laths of trona. There is often a bit of open space about the large tincalconite crystals. By increase in size and abundance of trona this layer grades into layer C which consists almost wholly of reticulated

trona laths, up to 3 mms. or more in length, with a good deal of open space. The trona is very clean and vitreous and rather uniform in habit with the forms {100}, {$\bar{1}$11} and {001}, flattened parallel to the front pinacoid and elongated along the b axis.

All of the minerals found with the tincalconite are well known in the Searles Lake deposits. They constitute only a small part of the full assemblage of minerals known from this locality. A list of the minerals in the Searles Lake saline deposits is given in Table 4. This is an amplifica-

TABLE 4. MINERALS OF THE SEARLES LAKE SALINE DEPOSITS

Discovered at Searles Lake		Year of discovery	Common in oceanic salt deposits	Common in other lacustrine salt deposits
Hanksite	$9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$	1885	Calcite	Trona
Sulphohalite	$2Na_2SO_4 \cdot NaCl \cdot NaF$	1888	Gypsum	Nahcolite
Northupite	$MgCO_3 \cdot Na_2CO_3 \cdot NaCl$	1896	Anhydrite	Natron
Pirssonite	$CaCO_3 \cdot Na_2CO_3 \cdot 2H_2O$	1896	Halite	Gaylussite
Tychite	$2MgCO_3 \cdot 2Na_2CO_3 \cdot Na_2SO_4$	1905	Glauberite	Thenardite
Searlesite	$NaB(SiO_3)_2 \cdot H_2O$	1914	Glaserite	Mirabilite
Schairerite	$Na_2SO_4 \cdot Na(F, Cl)$	1931		Ulexite*
Burkeite	$2Na_2SO_4 \cdot Na_2CO_3$	1935		Borax
				Tincalconite

* Found at Searles Lake according to Dr. Joseph Murdoch. (Letter to A. P. dated February 5, 1948.)

tion and rearrangement of a list published by H. S. Gale,[12] minerals found since 1915 being added and the minerals grouped to show the mineralogical peculiarities of the Searles Lake assemblage and to suggest its relations with other salt lake deposits and with oceanic salt deposits.

FORMATION OF THE TINCALCONITE

The mode of occurrence suggests that the tincalconite crystals formed directly from solution. The hole from which the core was taken is filled with brine. The composition of this brine varies only slightly with depth and is very similar to the brines whose composition was reported by H. S. Gale.[13] A sample from a depth of 115 feet has a specific gravity of 1.304, temperature 74° F. (23.3° C.) and the following composition:[14]

[12] *Loc. cit.*, p. 297. Besides these minerals quartz, sulfur, realgar, and a few other sulfides have been found with the Searles Lake salts. The brines also show a sulfide content reported as Na_2S.

[13] *Op. cit.*, p. 276.

[14] Letter from J. Ryan to D. L. Sawyer, dated 11-29-47.

KCl	3.04%	Na_2SO_4	5.87%
$Na_2B_4O_7$	1.96	NaCl	16.32
Na_2CO_3	6.60	Na_2S	0.35

Unfortunately it is not possible to state from experimental data with which crystalline phases such a solution would be in equilibrium.

If a solution of sodium tetraborate is crystallized at room temperature it yields the decahydrate. The pentahydrate is formed by crystallization from the pure aqueous solution only above 61° C. From solutions containing other ions the pentahydrate forms at lower temperatures.[15] If sulfate ion is also present the pentahydrate forms down to 49.3° C., at that temperature being in equilibrium with solution together with the decahydrate and Na_2SO_4 (thenardite). If both sulfate and ammonium ions are present it forms down to 41.7° C., at that temperature being in equilibrium with solution together with the decahydrate, Na_2SO_4 and $(NH_4)_2B_4O_7 \cdot 4H_2O$. Presumably in the presence of still other ions $Na_2B_4O_7 \cdot 5H_2O$ may crystallize directly from solution at still lower temperatures. This may have occurred in the crystallization of tincalconite at Searles Lake.

[15] International Critical Tables, vol. IV, pages 239, 346 and 331, New York (1928).