THE AMERICAN MINERALOGIST, VOL. 44, MARCH–APRIL, 1959

ON THE HYDRATES OF SODIUM CARBONATE, A CORRECTION, AND THE CRYSTALLOGRAPHY OF TRONA

A. Pabst, *University of California, Berkeley, California.*

Abstract

Reexamination of material earlier described as the hemipentahydrate of sodium carbonate, $Na_2CO_3 \cdot 2\frac{1}{2}H_2O$, proves it to be $Na_3H(CO_3)_2 \cdot 2H_2O$, trona. It is shown that all reports of the hemipentahydrate probably involved the same misidentification. A new setting of trona is based on the cell dimensions a_0 20.11Å, b_0 3.49, c_0 10.31, β 103° 8′, space group $I2/c$. This is reconciled with previous settings and a revised angle table and indexed powder pattern are given.

Many years ago the writer, Pabst 1930, published observations supposedly applying to the hemipentahydrate of sodium carbonate, $Na_2CO_3 \cdot 2\frac{1}{2}H_2O$. This hydrate had first been reported by Morel (1889) as crystallized slowly from a solution of Na_2CO_3 between 18 and 25° C. Blasdale (1923) reported this phase as crystallizing metastably at 25° C. over a large range of composition of aqueous solutions of the carbonates and chlorides of sodium and potassium.

Mr. H. S. Peiser (1957) has kindly pointed out that the supposed hemipentahydrate was probably the sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, trona. Fortunately the material used by Pabst (1930), mostly the products of crystallizations carried out in 1926, had been preserved and reexamination quickly showed that the material earlier described as the hemipentahydrate is, in fact, the sesquicarbonate as suspected by Peiser.

Morel (1889) reported a water content of 29.7 to 30.0 per cent and Blasdale (1923, p. 2937) reported percentages of water ranging from 29.90 to 32.10. Neither specified the method of analysis. The ideal water content of the supposed hemipentahydrate would be 29.82 per cent by weight. If the sesquicarbonate is heated so that only anhydrous Na_2CO_3 remains the combined weight loss due to water and carbon dioxide driven off would be 29.66 per cent. The unreported "water content" of the material designated hemipentahydrate by Pabst (1930) was estimated from ignition loss. It may be presumed that Morel and Blasdale made their "water determinations" in the same way.

Since the "hemipentahydrate" had been described as orthorhombic by Morel (1889), a description recorded by Groth (1908, p. 196), the monoclinic sesquicarbonate must be morphologically pseudosymmetric if these materials are identical. This feature had been noted by Ayres (1889), in describing crystals of artificial "trona," who said "The symmetry of these crystals may be viewed as almost orthorhombic" (see his Fig. 2, p. 65).

The optical characterization given by Pabst (1930) was defective. The optical orientation was only partly stated as "X=*c*." Had it been fully established, Z would have been found nearly normal to a face taken as (110), in conflict with the orthorhombic interpretation. The best values for the refractive indices of trona are probably those of C. W. Bunn, reported by Brown, Peiser and Turner-Jones (1949), $\alpha=1.418$, $\beta=1.492$, $\gamma=1.543$. Of the indices reported by Pabst (1930) for the supposed hemipentahydrate, $\alpha=1.435$, $\beta=1.492$, $\gamma=1.547$, the first is clearly in error. 2V calculated from the indices of Bunn is 75° 50′, in close agreement with the directly determined value, 76° 16′ (yellow), of Zepharovich (1888).

The density of the supposed hemipentahydrate was given by Pabst (1930) as 2.053 on the basis of pycnometer determination. It has been redetermined on the same material by means of a Berman balance and found to be 2.11, just below the calculated density of the sesquicarbonate, 2.13, given by Brown *et al.* (1949).

In attempting to reconcile the old measurements which had been fitted to Morel's orthorhombic elements with a monoclinic interpretation it was found necessary to reexamine the several settings and elements which have been assigned to trona. Trona crystals were first measured and recognized as monoclinic by Haidinger (1825). Later the elements of Zepharovich (1888) were most widely used and they appear in the 6th and 7th editions of Dana's System of Mineralogy. They differ only slightly from those given by Ayres (1889). Earlier settings that had been chosen by Rammelsberg (1855, p. 155) and by Des Cloizeaux (1874, p. 169) found no acceptance and will not be considered here. The crystal structure of trona was described by Brown, Peiser and Turner-Jones (1949) using another setting, adopted also by Bacon and Curry (1956) and by Candlin (1956). The relations of these settings with one based on a cell having the shortest possible *a* and *c* axes are shown in Fig. 1 and Table 1. From these it will be clear that the morphological setting hitherto used corresponds to half of a centered cell, whereas doubling the *a* axis of this setting corresponds to choosing the shortest and next shortest translation directions in the plane of symmetry as *c* and *a* respectively, the standard monoclinic setting. The space group designation, which is $C\,2/c$ for the cell chosen by Brown *et al.*, then becomes $I2/c$. One may also write $I2/a$ since the space group C_{2h}^{6} has two sets of glide planes.

Retabulation of the older goniometric measurements (Pabst, 1930) together with new measurements on crystals selected from the old material, on natural trona crystals from Searles Lake, California, and on newly prepared crystals of the sesquicarbonate (to be described below) as well as direct determination of the cell constants in the newly adopted

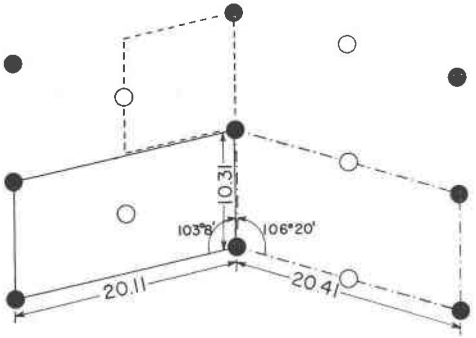

FIG. 1. The lattice of trona projected onto (010). Open circles represent lattice points displaced by $b/2$ from the level of those represented by solid circles. The C-centered cell of Brown, Peiser and Turner-Jones (1949) is shown by dot dash lines. The I-centered cell resulting from choice of the smallest possible a_0 and c_0 is shown by full lines and a cell corresponding to the axial elements of Zepharovich (1888) or of Ayres (1889) is shown by dashed lines. (See also Table 1.)

setting, all showed agreement within the limits of error with the axial elements for the new setting calculated from the cell constants given by Brown, Peiser and Turner-Jones (1949). Since the difference between these elements and those of Zepharovich involves differences in coordinate angles of more than half a degree, a new angle table has been calculated for trona, Table 2. The forms included in this table are those reported by Ayres plus {304} (old indices), a form referred to as prominent

TABLE 1. AXIAL ELEMENTS FOR SODIUM SESQUICARBONATE DIHYDRATE, TRONA, AND TRANSFORMATIONS

	Zepharovich (1888)	Brown, Peiser and Turner-Jones (1949)	Pabst (this paper), calculated from data of Brown *et al.* (1949)
	$a:b:c$ 2.8459:1:2.9696 $\beta=102°37'$	$a_0=20.41\pm0.03$ Å $b_0=\ 3.49\pm0.01$ $c_0=10.31\pm0.01$	$a_0=20.11\pm0.03$ Å $b_0=\ 3.49\pm0.01$ $c_0=10.31\pm0.01$
	Ayres (1889) $a:b:c$ 2.8426:1:2.9494 $\beta=103°29'$	$a_0:b_0:c_0$ 5.848:1:2.954 (2×2.924) $\beta=106°20'$	$a_0:b_0:c_0$ 5.763:1:2.954 (2×2.881) $\beta=103°8'$
Zepharovich or Ayres		$\bar{2}0\bar{1}/0\bar{1}0/001$	200/010/001
Brown *et al.*	$\bar{\tfrac{1}{2}}0\tfrac{1}{2}/0\bar{1}0/001$		$\bar{1}0\bar{1}/0\bar{1}0/001$
Pabst	$\tfrac{1}{2}00/010/001$	$\bar{1}0\bar{1}/0\bar{1}0/001$	

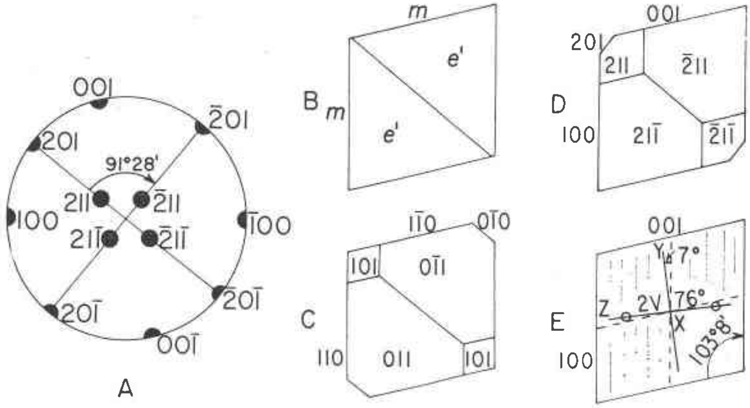

FIG. 2. A. Stereographic projection of the principal forms of trona on (010). B. End view of supposed hemipentahydrate as described by Morel (1889). C. End view of supposed hemipentahydrate as described by Pabst (1930), orthorhombic indexing. D. End view of trona as pictured by Ayres (1889). E. Cleavage and optical orientation of trona according to Zepharovich (1888) as seen in cross section normal to *b*.

on some crystals by Zepharovich, who also reported five other $\{h0l\}$ forms. In the course of the present study over 20 forms were identified, including a dozen $\{h0l\}$ forms not previously reported. However, the habit of both natural and artificial crystals was found to be similar to

TABLE 2. ANGLE TABLE FOR TRONA CALCULATED FOR NEWLY DERIVED ELEMENTS BASED ON *X*-RAY MEASUREMENTS OF BROWN, PEISER AND TURNER-JONES, (1949). COMPARE TABLE 1

Monoclinic; prismatic—$2/m$
$a:b:c=5.763:1:2.954$ β 103° 8′ $p_0:q_0:r_0=0.5126:2.8768:1$
$r_2p_2q_2=0.3476:0.1782:1$ μ 76°52′ p_0' 0.5264, q_0' 2.9540, x_0' 0.2332

Indices			ϕ	ρ	ϕ_2	$\rho_2=B$	C	A
Dana*	New	B.P.&T.-J.						
001	001	101	90°00′	13° 8′	76°52′	90°00′	—	76°52′
100	100	100	90 00	90 00	0 00	90 00	76°52′	—
304	302	$\bar{5}02$	90 00	45 39	44 21	90 00	32 31	44 21
101	201	$\bar{3}01$	90 00	52 8	37 52	90 00	39 00	37 52
$\bar{3}02$	$\bar{3}01$	201	−90 00	53 23	143 23	90 00	66 31	143 23
111	211	$\bar{3}11$	23 32	72 45	37 52	28 53	67 58	67 35
$\bar{1}11$	$\bar{2}11$	111	−15 30	71 56	129 20	23 38	75 52	104 43
211	411	$\bar{5}11$	38 22	75 8	23 9	40 44	67 17	53 8

* Indices as given in *The System of Mineralogy*, 7th ed., vol. II, p. 138, 1951 referred to the elements of Zepharovich (or Ayres). Compare Table 1.

TABLE 3. REINTERPRETATION OF INTERFACIAL ANGLES REPORTED BY PABST (1930) FOR THE SUPPOSED HEMIPENTAHYDRATE

Morel (Pabst, 1930)	Measured	Calculated	Zepharovich	Pabst	Calculated	
$101\wedge\bar{1}01$	57°57′	57°52′	$111\wedge\bar{1}1\bar{1}$	$211\wedge\bar{2}1\bar{1}$	57°46′	
$011\wedge0\bar{1}1$	47 44	*47 24	$\bar{1}11\wedge11\bar{1}$	$\bar{2}11\wedge21\bar{1}$	47 16	
$110\wedge1\bar{1}0$	76 27	†76 54	$001\wedge100$	$001\wedge100$	76 52	
$010\wedge011$	66 17	66 18	$\bar{1}01\wedge\bar{1}11$	$\bar{2}01\wedge\bar{2}11$	66 22	
$010\wedge110$	51 46	51 33	$\bar{1}01\wedge001$	$\bar{2}01\wedge001$	52 28	51 34
$010\wedge1\bar{1}0$	51 47	51 33	$10\bar{1}\wedge100$	$20\bar{1}\wedge100$	50 40	

* Should have been given as 47°26′ to correspond to Morel's measured value. Discrepancy is due to calculation from rounded value of *c/b*, 0.439.

† This angle is erroneously given by Groth (1908) as 71°54′ due to the misprint in Morel's report commented upon by Pabst (1930, p. 70).

the habits described by Zepharovich and Ayres except for the constant presence of the form $\{\bar{2}01\}$ (new indices) on the artificial crystals grown in solutions containing potassium, as shown in Fig. 2C.

It is now possible to reinterpret the angle measurements that had been fitted to the orthorhombic elements of Morel. In Table 3 the old measurements (Pabst, 1930, Table 1) are reproduced together with the revised interpretation. The first four angles listed do not differ by more than 8′ in the calculated values for the two settings. The error of the orthorhombic setting arises from the failure to recognize that the last two angles are not equivalent. The average of the ideal values of these angles matches closely the ideal value in the faulty interpretation. The pseudoorthorhombic cell obtained from the cell of Brown *et al.* by the transformation $\bar{1}01/\bar{1}0\bar{3}/0\bar{4}0$ or from the newly chosen cell by the transformation $102/10\bar{2}/040$, has the axial elements $a:b:c=0.793:1:0.437$, $\alpha=\beta=90°$, $\gamma=91°\ 28'$, very close to the orthorhombic elements given by Morel, $a:b:c=0.794:1:0.439$, $\alpha=\beta=\gamma=90°$. Evidently Morel made very good measurements.

Figure 2 shows the pseudoorthorhombic character of trona in stereographic projection, together with several (010) elevations and a diagram of the optical orientation as determined by Zepharovich (1889, p. 138). All other published observations on the orientation of trona are essentially in agreement with this.*

It is quite certain that the crystals described by Pabst (1930) as the hemipentahydrate of sodium carbonate and now shown to be the sesquicarbonate were the same as those described as the hemipentahydrate by

---

* The statement in Winchell's Elements of Optical Mineralogy, pt. II, 4th ed., 1951, page 126 that "$Y\wedge c=-17°$" clearly should be "$Y\wedge c=-7°$."

Blasdale (1923). They were obtained in the course of evaporation of an equimolal solution of sodium and potassium carbonates at 25° C., that is, within the range of compositions in which Blasdale obtained his "hemipentahydrate." Apparently the excess of CO_2 in the crystals entered the solution from the air since only neutral carbonates were used as starting materials.

The experiment of Morel was imitated by slowly evaporating solutions of Na_2CO_3 at room temperature, 24 to 28° C., slightly warmer than the temperature range of the original. Slow evaporation in crystallizing dishes protected only by a dust cover and with free access of air yielded clusters of the acicular sesquicarbonate crystals together with more or less equant crystals of the monohydrate (thermonatrite). In one series of crystallizations the crystals formed after a few days were redissolved by addition of a little water. This was repeated and upon the third and final evaporation of this lot abundant sesquicarbonate formed before any monohydrate.

Several studies, summarized by Seidell (1940, pages 1193–1198), have shown that the sesquicarbonate may be precipitated at very low concentrations of bicarbonate. At room temperature, under equilibrium, at extremely low bicarbonate concentrations, it may be accompanied by the decahydrate or possibly the heptahydrate. In only one trial was one of these, probably the decahydrate, obtained. It formed alone in clear, platy crystals by rapid precipitation from a solution of small volume and large surface area. The crystals effloresced rapidly in dry air, being transformed into pseudomorphs by coalescence of many clusters of the dehydration product arising at various points in each crystal. The process can be easily followed with a binocular microscope, and the pseudomorph of a suitably small, elongate, crystal makes a perfect powder preparation yielding an x-ray diffraction pattern showing only the lines of the monohydrate, thermonatrite.

The ASTM X-ray powder data file contains 3 cards for trona, 1-0938, 1-1077 and 2-0601. The first of these is stated to be for the decahydrate, though the material is named "trona" and the optical properties and density of trona are given on the card. The pattern recorded on card 1-0938 however, is not that of trona and presumably is that of the decahydrate. It coincides with the decahydrate pattern given under number 794 by Hanawalt, Rinn and Frevel (1938). Pattern number 793 of these authors, referred to $Na_2CO_3 \cdot 2\frac{1}{2}H_2O$, is the sesquicarbonate pattern. This was taken into the ASTM file as 1-1077 for trona implying a correction analogous to that here set forth. Table 4 records a powder pattern for trona indexed for all lines to 2.0 Å. The indexing has been checked by comparison with Weissenberg and precession patterns.

The false reports of the existence of $Na_2CO_3 \cdot 2\frac{1}{2}H_2O$ have given rise to

TABLE 4. *X*-RAY POWDER DIFFRACTION PATTERN OF SODIUM SESQUICARBONATE, TRONA. Cu RADIATION, Ni FILTER

Observations on trona from Searles Lake, California, and artificial material agree exactly. Calculated spacings for all possible lines with $d > 2.00$ Å, for cell of dimensions a_0 20.11 Å, b_0 3.49, c_0 10.31, β 103°8′; space group $I2/c$

hkl	$I_{obs.}$	$d_{obs.}$	$d_{calc.}$	*hkl*	$I_{obs.}$	$d_{obs.}$	$d_{calc.}$
200	ms	9.88 Å	9.79 Å	$\bar{4}04$			2.475
002	—	—	5.02	$\bar{5}12$			2.471
$\bar{2}02$			4.95	800	ms	2.447	2.448
	m	4.92					
400			4.90	213			2.441
202	vw	4.12	4.11	$\bar{8}02$	w	2.426	2.429
$\bar{4}02$	w	4.00	3.99	013			2.417
110	w	3.43	3.44	$\bar{6}11$			2.411
011			3.30	$\bar{4}13$			2.323
600			3.26	204			2.310
	ms	3.21					
$\bar{2}11$			3.20	213	m	2.259	2.262
402			3.17	611			2.238
310			3.08	710			2.183
	s	3.08			vw	2.186	
$\bar{6}02$			3.07	512			2.182
211			3.06	$\bar{7}12$	w	2.149	2.146
$\bar{1}12$			2.89	$\bar{6}13$	w	2.119	2.115
$\bar{4}11$			2.83	$\bar{1}14$			2.067
					w	2.060	
112	vw	2.79	2.79	$\bar{3}14$			2.057
$\bar{3}12$	mw	2.76	2.76	404			2.053
411	vs	2.659	2.645	$\bar{8}11$	m	2.040	2.039
510			2.606	413			2.038
					m	2.032	
$\bar{2}04$	w	2.587	2.578	802			2.027
				—			—
004			2.512		mw	1.996	
	mw	2.510					
312			2.508		mw	1.965	
602	vw	2.485	2.491		w	1.886	

and over 30 additional lines

confusing statements in several standard works of reference. In Winchells' *Microscopic Characters of Artificial Inorganic Substances*, 2nd ed., New York, 1931, the hemipentahydrate is described on page 200 largely on the basis of Pabst's faulty work and in a footnote it is suggested that "Larsen's data for 'trona' from Vesuvius may apply to this substance," a most unfortunate reversal of the situation as it is now revealed. In *The Barker Index of Crystals*, Volume 1, Part 2, Cambridge, 1951, the hemipentahydrate is described under number 0.369. This description is largely based on Groth, but, the misprint of an interfacial angle taken over by Groth from Morel (see second footnote to table 3 of this paper) not being recognized, new axial elements are calculated and a "correction" of Groth's elements which had been properly copied from Morel is given. These new elements correspond to no crystallographic measurements at all, not even to an orthorhombic interpretation of trona.

Equilibrium crystallization of $Na_2CO_3 \cdot 2\frac{1}{2}H_2O$ over a wide range of compositions at 0° and 15° C. in the system H_2O-NH_4Cl-Na_2CO_3 was reported by Mondain-Monval (1922) who referred to this phase as "carbonate de Morel." His work is the basis of Fig. 31, page 383, in the *International Critical Tables*, vol. IV, New York, 1928. Mondain-Monval did not report how he identified the phase but it may be confidently assumed that this was another case of failure to recognize the appearance of the sesquicarbonate.

REFERENCES

AYRES, EDWARD F. (1889), Notes on the crystallization of trona (urao): *Am. J. Sci.* (3), **38,** 65–66.

BACON, G. E., AND CURRY, N. A. (1956), A neutron-diffraction study of sodium sesquicarbonate: *Acta Cryst.*, **9,** 82–85.

BLASDALE, WALTER C. (1923), Equilibria in solutions containing mixtures of salts III. The system, water and the chlorides and carbonates of sodium and potassium at 25° IV. The system, water and the sulfates and carbonates of sodium and potassium at 25°: *Journ. Am. Chem. Soc.*, **45,** 2935–2946.

BROWN, C. J., PEISER, H. S., AND TURNER-JONES, MISS A. (1949), The crystal structure of sodium sesquicarbonate: *Acta Cryst.*, **2,** 167–174.

CANDLIN, ROSEMARY (1956), Thermal changes in the structure of sodium sesquicarbonate: *Acta Cryst.* **9,** 545–554.

DES CLOIZEAUX, A. (1874), Manuel de Minéralogie, vol. 2, Paris, 544 pages.

GROTH, P. (1908), Chemische Kristallographie, vol. 2, Leipzig, 914 pages.

HAIDINGER, WILLIAM (1825), Notice respecting trona, the native carbonate of soda from Fezzan: *Edinburgh Journ. of Sci.*, **2,** 325–332.

HANAWALT, J. D., RINN, H. W., AND FREVEL, L. K. (1938), Chemical analysis by *x*-ray diffraction: *Ind. & Eng. Chem.* (*Analytical Edition*) **10,** 457–512.

MONDAIN-MONVAL, P. (1922) Sur la préparation du chlorure d'ammonium: *Comptes Rendus*, **174,** 1014–1017, Sur la préparation du chlorure d'ammonium à basse température: *Comptes Rendus*, **175,** 162–164.

MOREL, J. (1889), Sur un nouvel hydrate de carbonate de sodium: *Bull. Soc. Fran. Min.* **12,** 546–548.

PABST, ADOLF (1939), On the hydrates of sodium carbonate: *Am. Mineral.* **15,** 69–73.

PEISER, H. S. (1957), (letter to A. Pabst, dated July 30, 1957).

RAMMELSBERG, C. F. (1855), Handbuch der Krystallographischen Chemie, Berlin, 410 pages.

SEIDELL, A. (1940), Solubilities of inorganic and metal organic compounds, Vol. I, 3rd ed., New York, 1698 pages.

v. ZEPHAROVICH, V. (1888), Ueber Trona, Idrialin und Hydrozinkit: *Zeits. Kryst.* **13,** 135–144.

Manuscript received June 13, 1958