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## SODIUM BICARBONATE (NAHCOLITE) FROM SEARLES LAKE, CALIFORNIA

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### ABSTRACT

Sodium bicarbonate was found in large quantities in a well core drilled below the central salt crust of Searles Lake. It occurs in monoclinic crystals and twins, chiefly in a gaylussite marl. It is suggested that it owes its origin to the interaction of trona and calcium bicarbonate solutions, or formed perhaps during a period when Searles Lake was slightly colder than it is now.

### INTRODUCTION

The name "nahcolite" has been given to naturally occurring sodium bicarbonate ( $\text{NaHCO}_3$ ) by F. A. Bannister,<sup>2</sup> who reported it in an efflorescence from an old Roman underground conduit from hot springs at Stufe de Nerone, near Naples. Later the compound was reported by E. Quercigh<sup>3</sup> as an incrustation in a lava grotto, apparently mixed with thenardite and halite. In neither of these two reported cases was the mineral actually isolated in its pure state and thoroughly investigated. Natural sodium bicarbonate had been reported earlier by P. Walther<sup>4</sup> from Little Mogadi dry lake, 40 kilometers south of Mogadi Lake, in British East Africa, but no confirmatory evidence was given.

The presence<sup>5</sup> of free sodium bicarbonate in the salts of Searles Lake was suspected from the analyses of Searles Lake salts made in the laboratory of the American Potash and Chemical Corporation, Trona, California, and samples were sent to the U. S. National Museum for isolation of the pure mineral, but before this work could be begun, Well No. 34, drilled by this corporation, penetrated rich beds of sodium bicarbonate at various depths from 122 feet to the bottom of the well at 289 feet. The core of this well, as available for examination, began with the bottom of the central salt body of Searles Lake at 81 feet and continued through saline materials to a depth of 289 feet.

<sup>1</sup> Published with the permission of the Secretary of the Smithsonian Institution.

<sup>2</sup> Bannister, F. A.: *Min. Mag.*, **22**, 53-64 (1929).

<sup>3</sup> Quercigh, E.: *Rend. Acad. Sci. (Naples)*, (**4**) **7**, 19-25 (1937).

<sup>4</sup> Walther, P.: *Am. Mineral.*, **7**, 86-88 (1922).

<sup>5</sup> Letter from Dr. W. A. Gale, Director of Research, American Potash and Chemical Corporation.

The central salt body of Searles Lake consists of alternating beds of soluble saline minerals, chiefly halite, hanksite, trona, glaserite and borax. The insoluble carbonate is chiefly pirssonite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ ) which is almost universally present in these salts in small quantities. The central salt body terminates abruptly in a thin layer rich in

TABLE 1. OCCURRENCE OF NAHCOLITE IN WELL NO. 34  
SEARLES LAKE, CALIFORNIA

Depth (Feet)	
122-126	Coarse, square prisms, with glassy luster and fair cleavage, in part a pure crystalline mass, in part embedded in microcrystalline northupite. Shows some interstitial borax.
146-147	Coarse, glassy, striated crystals and reticulated twins, with felted, semi-silky interstitial nahcolite. Also a reticulated mat of medium size glassy, striated prisms. Also streaks of small matted crystals in fine crystalline northupite "marl."
170	Pure nahcolite, porous mass of twinned crystals, with a few embedded gaylussite crystals.
178-179	Reticulated mat of prismatic nahcolite crystals, with silky semifibrous areas and embedded larger reticulated twins. Also nests of fine matted crystals, with gaylussite, in marl.
183-186	Almost pure nahcolite; loose porous aggregates of twinned crystals, with vugs lined with glassy individuals. Sometimes indistinctly layered.
204-210	Small nests and streaks of reticulated prismatic crystals, with gaylussite, in clay. Not abundant.
216-217	
222-223	
228-229	Pure nahcolite as loosely matted glassy prismatic crystals.
259	Pure, white nahcolite of varying crystal size; fine to medium, granular, with long, silky shreds and more compact areas.
261-263	
263-272	Predominately a gaylussite "marl," made up of fine crystals of gaylussite. Nahcolite present in long bladed crystals and as scattered arborescent aggregates. Some of the gaylussite is altered to nahcolite, as silky, fibrous pseudomorphs.
272-278	Snowy, fine grained aggregate of nahcolite crystals with semi-silky luster, with pockets of clayey coarser nahcolite.
279-280	Pure, fine granular loosely coherent nahcolite.
281-283	Sparing nests of glassy reticulated crystals in northupite "marl."
283-284	Sparingly, porous, granular nests in marl.

trona, borax and northupite ( $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{NaCl}$ ). This is followed by finely laminated shales rich in gaylussite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 4\text{H}_2\text{O}$ ), often predominately this mineral, forming a gaylussite "marl."

In Well No. 34, the change from pirssonite to gaylussite is not as abrupt as usual, scattered pirssonite persisting 25 feet below the salt

crust. The other components of the central salt crust also persisted in scattered bodies below the salt; trona to a depth of 130 feet (but only in the absence of much gaylussite), borax to 115 feet, halite to 120 feet and hanksite only very sparingly to 110 feet. In the place of these ordinary salt crust minerals, two new ones appeared: burkeite ( $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ ) and nahcolite ( $\text{NaHCO}_3$ ). Burkeite was confined to those layers between 94 and 125 feet, usually conspicuously free of gaylussite but with trona and halite abundant, borax occasionally present and hanksite rare.

Nahcolite, on the other hand extends intermittently from 121 to 278 feet, but chiefly from 170 feet to the bottom of the core. At 121 to 122 feet, it occurs in a very thin bed associated with gaylussite, trona, thenardite and northupite, and at 145 to 146 feet with gaylussite, burkeite and thenardite. All other occurrences are in simple gaylussite or northupite marls free of other saline minerals. It is particularly abundant from 169 to 186 feet, from 203 to 210 feet and from 258 to 286 feet.

The individual occurrences of nahcolite in Well No. 34 are given in Table 1.

Besides the various forms of aggregated crystals, nahcolite was also noted in samples from 286 feet as hairy tufts of thin prisms in crystal cavities in marl left by the solution of gaylussite crystals. These hairy tufts, under the microscope, show the typical single and twinned crystal habits of coarser nahcolite.

#### CHEMICAL PROPERTIES

An abundance of pure material was available for analysis. Clear glassy crystals were selected from specimen U.S.N.M. No. 102,861. The mineral is easily soluble in water. Analysis by standard methods gave the results recorded in Table 2.

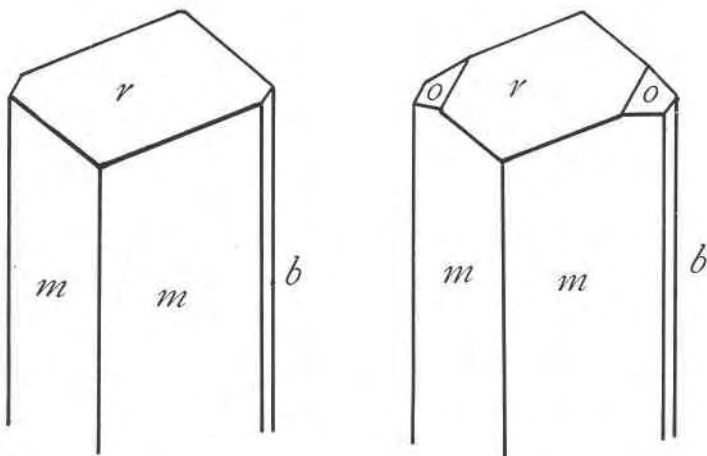
TABLE 2. ANALYSIS OF NAHCOLITE ( $\text{NaHCO}_3$ ),  
SEARLES LAKE, CALIFORNIA

<i>W. F. Foshag, Analyst</i>		
	Found	Theory
$\text{Na}_2\text{O}$	36.74	36.90
CaO	0.20	
$(\text{Fe, Al})_2\text{O}_3$	0.16	
$\text{CO}_2$	51.15	52.38
$\text{H}_2\text{O}$	10.76	10.72
Insol.	0.82	
	<hr style="width: 10%; margin: 0 auto;"/> 99.83	

*Pyrognostics.* Nahcolite is soluble in water, yielding a solution alkaline to phenolphthalein and to methyl red. It is also soluble in glycerine. The aqueous solution on heating gives off carbon dioxide. Before the blow-pipe, nahcolite fuses quietly, yields a white, crystalline bead, and colors the flame intense yellow.

#### CRYSTALLOGRAPHY

Many of the beds of nahcolite are made up of loosely friable crystal aggregates or porous masses with crystal lined vugs. The largest individuals, sometimes exceeding 2 centimeters in maximum dimension, are reticulated twins, embedded in smaller simpler crystals. Single crystals seldom exceed 1 centimeter in size. Although there is an abundance of crystals, good measurable individuals are rare, due to the prevalence of



FIGS. 1 and 2. Common habit of nahcolite single crystals, Searles Lake, California.

solution forms on the crystals but, as is often the case in readily soluble minerals, some faces seem unaffected. In the case of nahcolite, the clinopinacoid  $b$  remains bright,  $r(101)$  somewhat less so but the prisms and the orthopinacoid are very much rounded. The crystal measurements, therefore, are not of the highest order.

Simple crystals of nahcolite show little variation in habit. They are commonly prismatic,  $m(110)$  and  $r(101)$  are prominent,  $b(010)$  is narrow (Fig. 1). The pyramid  $o(111)$  is frequently present (Fig. 2). A termination more rarely met with is  $o(111)$  and  $s(\bar{1}01)$ , (Fig. 3).

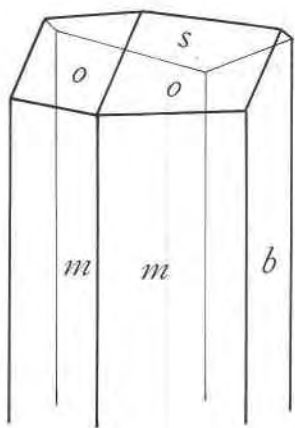


FIG. 3. Unusual termination of  $o(111)$  and  $s(101)$ . Searles Lake, California.

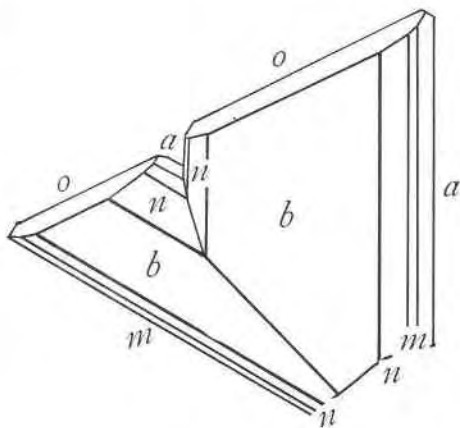


FIG. 5. Acute twin, crystal #4, nahcolite, usually found on complex twinned aggregates, ( $b$  projection). Searles Lake, California.

Twinning is very common; the twinning plane and the composition plane is  $r(101)$ . Both contact and penetration twins are found, often in combination with each other. Since the twinning is usually repeated, the twinned forms may become extremely varied. As is often the case with twins of this character, they show a decided flattening in the plane perpendicular to the composition plane, in the case of nahcolite the clinopinacoid  $b(010)$ .

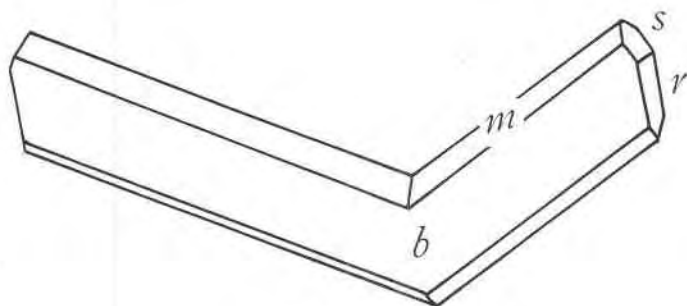


FIG. 4. Obtuse twin, crystal #15 nahcolite. A common habit in fine crystalline aggregates. Searles Lake, California ( $b$  projection).

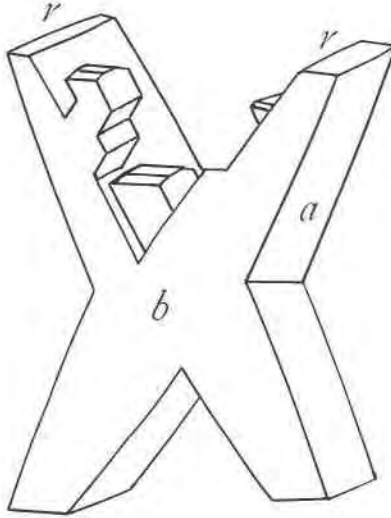


FIG. 6. Penetration twin, crystal #13, nahcolite, with subsidiary twinned individuals. Searles Lake, California (*b* projection).

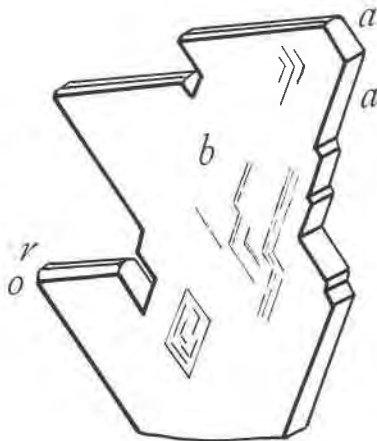
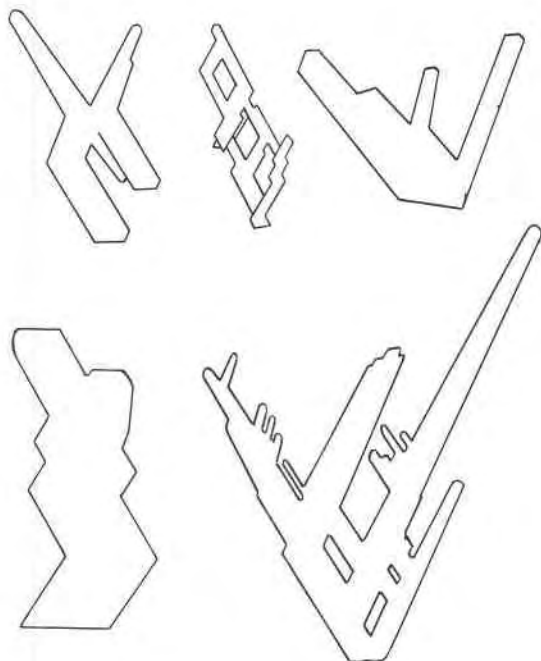


FIG. 7. Flattened repeated twin, crystal #14 nahcolite, frequent habit. Searles Lake, California (*b* projection).

The most common twin habit is a simple obtuse contact twin (Fig. 4) and is often found as complete individuals in the friable aggregates of loose crystals. The acute contact twin (Fig. 5) is usually attached and is, perhaps, simply the acute end of the penetration twins (Fig. 6), that frequently occur as larger individuals embedded in a finer crystalline matrix. Twins, like Fig. 7, are found in nests of loose crystals or in vugs. The possible permutations in these twin combinations are without number, Figs. 8 to 12 showing a few of the general types.



FIGS. 8-12. Camera lucida drawings showing varied twin habits, nahcolite, Searles Lake, California (*b* projection).

The crystallography of artificial  $\text{NaHCO}_3$  has already been determined by Schabus<sup>6</sup> and found to be monoclinic, with  $a:b:c=0.7645:1:0.3582$ .  $\beta=93^\circ 19'$ . The forms noted were:  $b(010)$ ,  $m(110)$ ,  $\omega(11\bar{1})$ ,  $i(121)$ ,  $o(111)$ ,  $a(100)$  and  $r(101)$ . A large number of the natural crystals from Searles Lake were examined, many were mounted for preliminary measurement but only 12 were completely measured because most crystals showed curved faces and could not be accurately adjusted on the goniometer. Since Schabus' measurements are presumably superior to mine, I have

<sup>6</sup> Groth, P.: *Chemische Kristallographie*, II Teil, p. 191.

calculated the gnomonic elements for nahcolite on the basis of Schabus' elements. The angle measurements on natural nahcolite from Searles Lake are given in Table 3.

TABLE 3. ANGLE MEASUREMENTS OF NAHCOLITE

Face	No.	Range	Average
<i>m</i> (110)	16	$\phi = 52^{\circ}19' - 52^{\circ}53'$	52°35'
<i>n</i> (120)	11	$\phi = 33^{\circ}11' - 34^{\circ}12'$	33°30'
<i>r</i> (101)	4	$\rho = 27^{\circ}39' - 28^{\circ}00'$	27°48'
<i>s</i> ( $\bar{1}$ 01)	2	$\rho = 22^{\circ}18' - 22^{\circ}22'$	22°20'
<i>o</i> (111)	8	$\phi = 55^{\circ}14' - 56^{\circ}10'$ $\rho = 32^{\circ}24' - 33^{\circ}9'$	55°25' 32°30'

The *x*-ray elements for sodium bicarbonate have already been determined by W. H. Zachariassen.<sup>7</sup> It is monoclinic with four molecules per unit cell.  $a = 7.51\text{\AA} \pm 0.04$ ,  $b = 9.70\text{\AA} \pm 0.04$ ,  $c = 3.53\text{\AA} \pm 0.03$ .  $\beta = 93^{\circ}19'$ . Space group.  $P2_1/n$ .

The crystallographic elements, together with the measured and calculated two circle angles are given in Table 4.

TABLE 4. NAHCOLITE—NaHCO<sub>3</sub>

Monoclinic, prismatic  $-P2_1/n$   
 $a:b:c = 0.7645:1:0.3582$ .  $\beta = 93^{\circ}19'$  (Schabus).  
 $p_0:q_0:r_0 = 0.4685:0.3576:1$ .  $\mu = 86^{\circ}41'$ .  
 $p_0' = 0.4692$ ,  $q_0' = 0.3589$   $X_0' = 0.580$ .

Letter	Form	Measured		Calculated	
		$\phi$	$\rho$	$\phi$	$\rho$
<i>b</i>	010	0°00'	90°00'	0°00'	90°00'
<i>m</i>	110	52 35	90 00	52 28	90 00
<i>n</i>	120	33 30	90 00	33 11	90 00
<i>r</i>	101	90 00	27 48	90 00	27 48
<i>s</i>	$\bar{1}$ 01	90 00	22 20	90 00	21 10
<i>o</i>	111	55 25	32 30	55 45	32 32

Forms found by Schabus on artificial sodium bicarbonate but not found on nahcolite are *i*(121) and  $\omega$ (11 $\bar{1}$ ).

#### PHYSICAL AND OPTICAL PROPERTIES

Nahcolite is colorless to white, sometimes gray or buff from included mud. The luster is vitreous, somewhat resinous on the cleavage. Fracture

<sup>7</sup> *Jour. Chem. Phys.*, **1**, 634-639 (1933).



conchoidal. Cleavage: domatic  $r(101)$  perfect; pyramidal (111) good; pinacoidal  $a(100)$  distinct.

The mineral is biaxial, negative,  $2V=75^\circ$  ca. Dispersion is weak,  $v$  greater than  $r$ . Cleavage plates (parallel to the perfect cleavage  $r$ ) show a well centered biaxial figure, indicating that the acute bisectrix is normal, or nearly normal to the cleavage. Plane of the optic axis is parallel to  $b(010)$ .  $Y=b$ .  $X \wedge c=27^\circ$ .<sup>8</sup> The cleavage fragments bounded by (111) and (100) and lying upon  $r(101)$  show parallel extinction.

The indices of refraction as determined by the immersion method, with independent determinations on the identical material by Dr. Mark Bandy, and the values for the artificial compound as given by Larsen and Berman and by Merwin are given in Table 5.

TABLE 5. INDICES OF REFRACTION—NAHCOLITE

Foshag	Bandy	Larsen and Berman <sup>a</sup>	Merwin <sup>b</sup>
$\alpha=1.375$	1.378	1.380	1.376
$\beta=1.505$	1.502	1.500	1.500
$\gamma=1.583$	1.583	1.586	1.582

<sup>a</sup> *Loc. cit.*

<sup>b</sup> In Winchell, *loc. cit.*

#### PARAGENESIS

The origin of nahcolite in the Stufe de Nerone and in a lava tunnel at Vesuvius can be easily explained by the action of  $\text{CO}_2$  and water vapor upon thermonatrite or trona. This is a method once much used to manufacture "baking soda." P. Walther believed that the nahcolite of Little Mogadi Lake was also due to the action of  $\text{CO}_2$  upon trona, since  $\text{CO}_2$  escaped from the playa muds in large quantities. Such an origin might be invoked for the Searles Lake mineral if a sufficient source of  $\text{CO}_2$  could be demonstrated.

Sodium bicarbonate, in open solutions, loses  $\text{CO}_2$  and passes eventually to trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ). It is this instability of  $\text{NaHCO}_3$  in solution that led R. Wegscheider<sup>9</sup> to explain its apparent absence in nature. The intimate association of nahcolite, gaylussite, and marls in Searles Lake suggests that it may perhaps owe its presence there to an interaction of trona and calcium bicarbonate (which finds its way into

<sup>8</sup> The value  $20^\circ$  given by Larsen and Berman (The Microscopic Determination of the Nonopaque Minerals. 2d ed., *U. S. G. S., Bull.* 848, p. 152) is in error. Robson in Winchell (Microscopic Characters of Artificial Minerals: 2d ed. 1931, p. 199) gives  $X \wedge c=27.5^\circ$ .

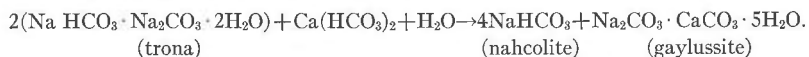
<sup>9</sup> In Doelter: *Handbuch der Mineralchemie*, 1, 193.

playa basins in small but continuing amounts through the agency of drainage) under conditions that do not allow the escape of carbon dioxide, as in playa muds.

A solution of calcium bicarbonate added to a solution of trona, precipitates abundant calcite, with the formation of sodium bicarbonate according to the reaction.



Or it may produce gaylussite after the reaction



Gaylussite is stable in strong trona solutions at ordinary temperatures. Such a reaction would, then, explain the presence of sodium bicarbonate.

There is a second and interesting possibility that may be suggested. In the system  $\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$ , trona is not stable below  $21.26^\circ$ ; <sup>10</sup>  $\text{NaHCO}_3$  (nahcolite) and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  (natron) are the stable phases. The temperature of the deep brines at Searles Lake is  $22.5^\circ$ . The position of the nahcolite in the lower beds of Searles Lake suggests the possibility that these salts were deposited during the Pleistocene period of glaciation, when, presumably, the waters were somewhat colder than they are today. A temperature drop of slightly more than  $1^\circ$  would bring about the deposition of nahcolite.

The writer desires to express his thanks to Dr. W. A. Gale of the American Potash and Chemical Corporation, for calling this interesting occurrence to his attention, and for transmitting to the U. S. National Museum the nahcolite bearing portion of the core.

<sup>10</sup> Hill and Bacon: *Jour. Am. Chem. Soc.*, **49**, 2487-2495 (1927).