FOUR CRYSTALLINE HYDRATES OF SODIUM METASILICATE

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A number of compounds of the general formula $Na_2SiO_3 \cdot nH_2O$ are reported in the literature. P. Groth[1] gives crystallographic measurements for $Na_2SiO_3 \cdot 9H_2O$, described by Fritzsche;[2] $Na_2SiO_3 \cdot 8H_2O$, described by von Ammon;[3] and $Na_2SiO_3 \cdot 5H_2O$, described by Peterson.[4] Erdenbrecher[5] reports the following: $Na_2SiO_3 \cdot 9H_2O$, rhombic, melting point 47° C.; $Na_2SiO_3 \cdot 6H_2O$, monoclinic, melting point 62.5° C.; and $Na_2SiO_3 \cdot 4H_2O$, hexagonal, melting point 85° C. Harman,[6] from a study of the system Na_2O–SiO_2–H_2O at 25° C., claims to have identified by Schreinemakes residue method the following compounds: $Na_2SiO_3 \cdot 9H_2O$, $Na_2SiO_3 \cdot 6H_2O$, $Na_2SiO_3 \cdot 2\text{–}1/2H_2O$, and Na_2SiO_3. The work of other investigators who have found some evidence of hydrates up to 14 is summarized by James G. Vail.[7]

In the present work crystals have been prepared of sufficient size and perfection to enable positive identification of the nine, eight, six and five hydrates of sodium metasilicate. Melting points, densities, photomicrographs, optical properties and crystallographic measurements for these four crystals have been obtained.

PREPARATION OF CRYSTALS

In the preliminary work a series of solutions were prepared covering a wide range of Na_2O, SiO_2, H_2O compositions. These were protected from the air and allowed to stand at room temperature on a table protected from vibration. After a period of time crystals would form, usually as masses of very minute individuals. These were drained as dry as possible and centrifuged in a high speed laboratory machine. In every case the crystals were analyzed for chemical composition and examined microscopically as a means of identification. Out of a total of 271 trials extending over a period of three and one-half years, only four hydrates of sodium metasilicate were found.

A crystal of the chemical composition $Na_3HSiO_4 \cdot 5H_2O$ was identified and may be the compound variously reported as the two and one-half, three and four hydrates of sodium metasilicate.

Much difficulty was experienced in obtaining crystals of sufficient

size and perfection for physical measurement. It was found necessary to use supersaturated solutions to obtain any appreciable rate of growth. Upon the slightest provocation there would separate a heavy mass of small feathery crystals, quite useless for accurate measurement. This necessitated many repeated trials and the development of a special technique before sufficiently good crystals could be obtained.

The method finally adopted was to obtain the mother liquor from which a heavy mass of crystals of the desired hydrate had separated. The mother liquor was heated and a portion of the crystals redis-

TABLE I

SOLID PHASE	COMPOSITION OF SOLUTION	
	Wt. % of Na_2O	Wt. % SiO_2
$Na_2SiO_3 \cdot 9H_2O$	12.85	1.24
$Na_2SiO_3 \cdot 8H_2O$	13.02	3.64
$Na_2SiO_3 \cdot 6H_2O$	25.60	2.91
$Na_2SiO_3 \cdot 5H_2O$	26.60	1.68

solved. The solution thus prepared was then divided among a number of beakers and placed inside of a large desiccator to cool. The solutions were protected from vibration by supporting the porcelain desiccator plate on three soft artgum rubber erasers. The desiccator in turn was supported on a three inch layer of absorbent cotton. The table carrying the desiccator was supported under each leg by a pyramid of four tennis balls. Other methods of protection from vibration were used but this method seemed to be the most satisfactory. When the solutions had cooled to near room temperature, a small carefully washed crystal of the desired hydrate was carefully introduced into each beaker. If the attempt proved successful, this seed would grow into a well developed crystal of from two to twenty millimeters greatest dimension. This growth required from one to twenty weeks depending upon conditions. Often, however, a mass of small crystals would separate so that the trial would have to be repeated. In most cases from twelve to eighteen months were required to secure desirable specimens.

The composition of typical solutions from which suitable crystals of each of the hydrates were grown is shown in Table I.

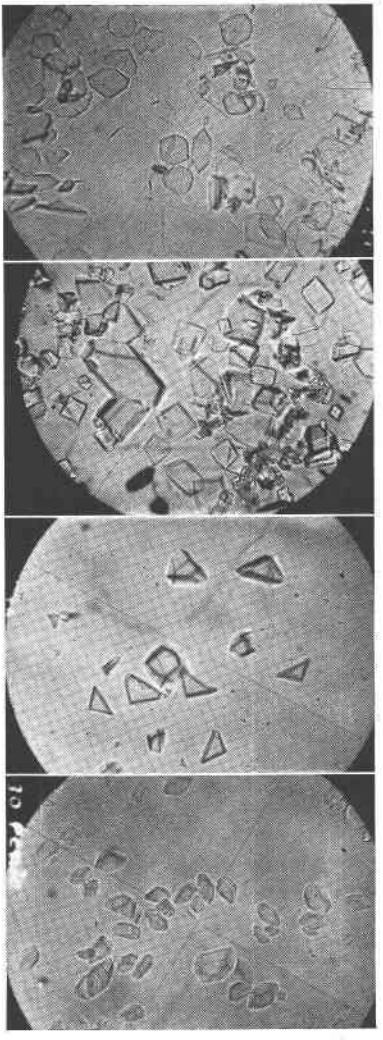

FIG. 1. Photomicrographs of the Four Crystalline Hydrates of Sodium Metasilicate.

Photomicrographs

Rapid cooling of a supersaturated solution accompanied by agitation yields a suspension of minute crystals. Photomicrographs showing the different hydrates are shown in Fig. 1.

Chemical Composition

All of these compounds are very alkaline. The *pH* of their solutions lie between those for Na_2CO_3 and NaOH when taken at equal normality. The crystals approach NaOH in hydroscopicity and like NaOH very quickly become carbonated when exposed to the air. These facts made it necessary to protect the crystals from the air as completely as possible and made the goniometric work to be described later very difficult.

Table II

		$Na_2SiO_3 \cdot 9H_2O$	$Na_2SiO_3 \cdot 8H_2O$	$Na_2SiO_3 \cdot 6H_2O$	$Na_2SiO_3 \cdot 5H_2O$
SiO_2	Calculated	21.14	22.56	26.09	28.31
	Found	21.08	22.56	26.07	28.27
Na_2O	Calculated	21.82	23.29	26.94	29.23
	Found	21.82	23.27	26.92	29.19
H_2O	Calculated	57.04	54.15	46.97	42.46
	Found	57.10	54.17	47.01	42.54

All crystals obtained showed a tendency to carry inclusions. Most of these could be removed by holding the crystals for several days in a thermostat at a temperature just below the melting point and recentrifuging. Chemical analyses on good specimens prepared in this manner are given in Table II.

Determination of Density

The crystals used in this work were freed from inclusions as described above. The densities were determined in a pyknometer using kerosene as the immersion liquid. In the case of the octahydrate the density was also determined by suspending a large crystal (40–50 grams) by a platinum wire and weighing in air and in kerosene. Because of possible microscopic inclusions the results were judged to be accurate to only the third decimal place and were not corrected to

density in vacuum. Table III gives the average for at least three closely agreeing determinations.

Determination of Melting Points

The melting points were determined by rotating the crystals in a thermostat and raising the temperature about .05° per day. Whenever any moisture appeared due to melted-out inclusions, it was removed by centrifuging and the purified crystals replaced. The results obtained are judged to be accurate to ± 0.05°C. They are given in Table III. The values obtained for the nine and six hydrates are somewhat higher than those given by Erdenbrecher, but since he used the warming curve method, his values would not be expected to be accurate to more than ± 0.5°C. Considering this fact there is good agreement.

Table III

Compound	Density at 20° C.	Melting points found °C.	Erdenbrecher melting points °C.
$Na_2SiO_3 \cdot 9H_2O$	1.646	47.85	47.0
$Na_2SiO_3 \cdot 8H_2O$	1.672	48.35	
$Na_2SiO_3 \cdot 6H_2O$	1.807	62.85	62.5
$Na_2SiO_3 \cdot 5H_2O$	1.749	72.20	

Optical Properties

The optical properties of the several hydrates have recently been determined by H. E. Merwin and reported by A. N. Winchell.[8] The data obtained on our materials are in substantial agreement with those reported by them.

The densities and indices of refraction do not show a regular increase with decreasing water content as would be expected. However, the changes are in the same sense for both properties and this affords a rough check on the observations, as shown below:

Crystal	Density	Mean Index of Refraction, $N=\alpha+\frac{\beta+\gamma}{3}$
		Observed
$Na_2SiO_3 \cdot 9H_2O$	1.646	1.455
$Na_2SiO_3 \cdot 8H_2O$	1.672	1.462
$Na_2SiO_3 \cdot 6H_2O$	1.807	1.474
$Na_2SiO_3 \cdot 5H_2O$	1.749	1.456

CRYSTALLOGRAPHY

$Na_2SiO_3 \cdot 9H_2O$: Orthorhombic crystals of $Na_2SiO_3 \cdot 9H_2O$ have been described by Nordenskiöld.[2] On crystals obtained in the course of the present work the following forms, listed in order of importance, were found: $a\{100\}$, $b\{010\}$, $o\{111\}$, $x\{241\}$, $k\{021\}$, $y\{421\}$ and $z\{310\}$. The last two had not been observed

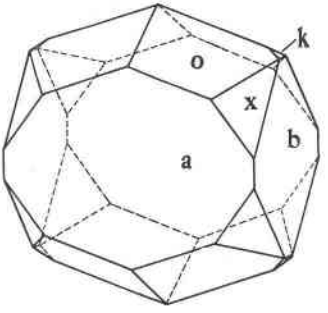

FIG. 2
$Na_2SiO_3 \cdot 9H_2O$
a {100}, x {241},
b {001}, k {021},
o {111},

before. Most of the crystals have the habit shown in Fig. 2. Some are tabular to {100}. The following table gives the coordinate angles for all the forms as obtained by measurement on the two-circle goniometer.

	FORM	MEASURED				CALCULATED			
		ϕ		ρ		ϕ		ρ	
b	{010}	0°	—	90°	—	—	—	—	—
a	{100}	89°	59′	90	—	90°	—	90°	—
o	{111}	55	20	31	3	—	—	—	—
x	{241}	35	53	59	15	35	52	59	23
k	{021}	—	3	34	22		0	34	24
y	{421}	71	17	64	14	70	56	64	30
z	{310}	77	27	90		77	1	90	—

From these measurements the axial ratio,

$$a:b:c = 0.6916:1:0.3424$$

is obtained. This is in fair agreement with the value 0.6888:1:0.3378 found by Nordenskiöld.

$Na_2SiO_3 \cdot 8H_2O$: Monoclinic crystals of $Na_2SiO_3 \cdot 8H_2O$ have

been described by von Ammon.[3] The crystals obtained in this work show a striking change in habit with change in the conditions of growth. From nearly congruent, slightly supersaturated, solution simple prismatic crystals with the forms $n\{120\}$, $r'\{\bar{1}01\}$ and $q\{011\}$, are grown. From solutions containing an excess of alkali, or from highly supersaturated solutions, flat plates parallel to $\{\bar{1}01\}$ with the forms $m\{110\}$, $q\{011\}$ and sometimes $n\{120\}$ and $f\{299\}$, as shown in Fig. 3 are produced. The form $\{299\}$ has not been reported, whereas numerous forms reported by von Ammon were not found on our crystals.

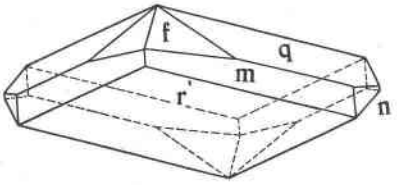

FIG. 3
$Na_2SiO_3 \cdot 8H_2O$ grown from a solution containing an excess of NaOH
m $\{110\}$, r' $\{\bar{1}01\}$, f $\{299\}$.
n $\{120\}$, q $\{011\}$,

The coordinate angles obtained by two-circle measurements are given below.

	Form	Measured				Calculated			
		ϕ		ρ		ϕ		ρ	
m	$\{110\}$	58°	52′	90°	—	—	—	—	—
n	$\{120\}$	39	38	90	—	39	37′	90°	—
r'	$\{\bar{1}01\}$	270	—	35	57′	270	—	—	—
q	$\{011\}$	32	52	40	20	32	40	—	—
f	$\{299\}$	45	23	45	15	45	16	45	27′

These measurements lead to the axial elements:

$$a:b:c = 0.6644:1:0.7148;\ \beta = 65°\ 23'$$

This result differs substantially from that obtained by von Ammon,[3] $a:b:c = 0.6352:1:0.6721$, $\beta = 70°\ 12'$, but the description of the crystals and the similarity of certain interfacial angles leaves no doubt as to the identify of the materials.

$Na_2SiO_3 \cdot 6H_2O$: Crystals of $Na_2SiO_3 \cdot 6H_2O$ have not been measured previously. In the present work monoclinic crystals of the hexahydrate of two very different habits were obtained. Fig. 4 shows the habit of crystals grown at room temperature with the

forms: $a\{100\}$, $m\{110\}$, $s'\{\bar{1}\bar{1}1\}$, $u\{2\bar{1}\bar{1}\}$, $c\{001\}$, $r'\{\bar{1}01\}$ and $t\{20\bar{1}\}$. They clearly belong to the sphenoidal class, (C_2), of the monoclinic system.

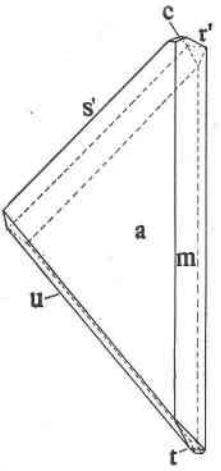

FIG. 4

$Na_2SiO_3 \cdot 6H_2O$ grown at room temperature

$a\ \{100\}$, $t\ \{20\bar{1}\}$,
$m\ \{110\}$, $s'\ \{\bar{1}\bar{1}1\}$,
$c\ \{001\}$, $u\ \{2\bar{1}\bar{1}\}$.
$r'\ \{\bar{1}01\}$,

Crystals grown at 50° C are short prismatic with the forms: $a\{100\}$, $m\{110\}$, $m'\{1\bar{1}0\}$, $c\{001\}$, $r'\{\bar{1}01\}$, $t\{20\bar{1}\}$ and $s'\{\bar{1}\bar{1}1\}$, the zone of the b-axis being most prominent.

The coordinate angles obtained by two-circle measurement are given herewith:

	Form	Measured				Calculated			
		ϕ		ρ		ϕ		ρ	
a	$\{100\}$	90°	2′	90°	—	90°	—	90°	—
m	$\{110\}$	28	3	90	—	—	—	—	—
m'	$\{1\bar{1}0\}$	151	59	90	—	151	57′	—	—
c	$\{001\}$	89	59	12	16′	90	—	12	9′
r'	$\{\bar{1}01\}$	269	53	19	43	270	—	19	35
t	$\{\bar{2}01\}$	269	51	42	49	270	—	42	49
s'	$\{\bar{1}\bar{1}1\}$	198	21	48	29	—	—	—	—
u	$\{2\bar{1}1\}$	220	51	54	52	220	50	54	47

The axial elements are:

$$a:b:c = 1.9211:1:1.0727;\ \beta = 77°\ 51'$$

$Na_2SiO_3 \cdot 5H_2O$: Although grown from very viscous solutions, many excellent crystals of $Na_2SiO_3 \cdot 5H_2O$ were obtained. They belong to the pinacoidal class, C_1, of the triclinic system. They do

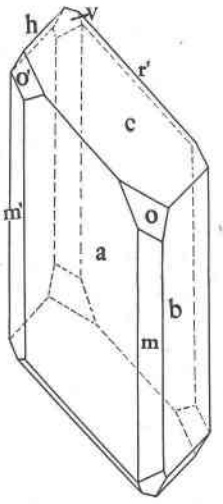

FIG. 5

$Na_2SiO_3 \cdot 5H_2O$ grown at 50° C.

$b\{010\}$,	$c\{001\}$,	$v\{\bar{1}21\}$,
$m\{110\}$,	$o\{111\}$,	$r'\{\bar{1}01\}$.
$a\{100\}$,	$o'\{1\bar{1}1\}$,	
$m'\{1\bar{1}0\}$,	$h\{0\bar{2}1\}$,	

not in any way resemble the supposedly monoclinic crystals of this composition obtained by Petersen[4] and measured by Hessenberg. Since the older description did not include density or optical properties it would be hazardous to try to reconcile these differences.

The crystals, shown in Fig. 5, are very constant in habit. The principal forms are, $c\{001\}$, $b\{010\}$ and $a\{100\}$. The others, $m\{110\}$, $m'\{1\bar{1}0\}$, $o\{111\}$, $o'\{1\bar{1}1\}$, $h\{0\bar{2}1\}$, $v\{\bar{1}21\}$, and $r'\{\bar{1}01\}$, are minor forms which may be lacking.

The following table gives the measured and calculated coordinate angles of all forms observed on $Na_2SiO_3 \cdot 5H_2O$.

Form		Measured				Calculated			
		ϕ		ρ		ϕ		ρ	
b	{010}	0°	00′	90°	00′	0°	00′	90°	00′
m	{110}	59	12	90	00	60	00	90	00
a	{100}	108	59	90	00	108	49	90	00
m'	{1$\bar{1}$0}	142	13	90	00	141	42	90	00
c	{001}	10	23	38	24	10	28	38	25
o	{111}	43	00	64	40	43	12	64	44
o'	{1$\bar{1}$1}					121	05	59	26
h	{0$\bar{2}$1}	174	55	58	43	174	58	58	42
v	{$\bar{1}$$\bar{2}$1}	224	27	59	06	224	15	58	24
r'	{$\bar{1}$01}	316	35	59	38	316	31	59	22

The axial elements are:

$a:b:c=0.7356:1:0.9005$; $\alpha=51°\ 52'$, $\beta=81°\ 47'$, $\gamma=70°\ 10'$

It is interesting to note the regular decrease in symmetry with decrease in water content in this series of hydrates:

$Na_2SiO_3 \cdot 9H_2O$	rhombic bipyramidal
$Na_2SiO_3 \cdot 8H_2O$	monoclinic prismatic
$Na_2SiO_3 \cdot 6H_2O$	monoclinic sphenoidal
$Na_2SiO_3 \cdot 5H_2O$	triclinic pinacoidal

Summary

Four definite hydrates of sodium metasilicate have been prepared and their physical and crystallographic properties determined.

A complete phase equilibrium study of the system Na_2O–SiO_2–H_2O is under way. The results of this work will be published at a later date.

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