

## Crystalline silica hydrates from leached silicates

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### Abstract

Most crystalline silica hydrates are layer structures. They are yielded by the leaching in acid of phyllosilicates lacking tetrahedral Al and in which the sheets are bounded on both sides by apical oxygens shared with both Si and cations. This permits cross-linking of the leached sheets by hydrogen bonds. Solid silica residues amorphous to X-rays are afforded by phyllosilicates in which the sheets are bounded on one side or on both sides by oxygens wholly bonded to Si, by inosilicates, and by tectosilicates with tetrahedral Si/Al  $\geq 2$ . Silica gels and sols are yielded by silicates containing isolated Si-O motifs and by tectosilicates with tetrahedral Si/Al  $< 2$ .

Two new crystalline silica hydrates afforded by the leaching of apophyllite (Silica-AP) and sanbornite (Silica-SN) are described. Supplementary data are given for Silica-X and Silica-GL. The supposed silica hydrates reported by leaching of hemimorphite, pectolite, scolecite, antigorite, chrysotile, heulandite, and glauconite are X-ray amorphous.

Silica residues amorphous to X-rays may contain sufficient order residual from the leached framework to influence their optical properties and their response when recrystallized hydrothermally at 175°C or by heating in air to 1000°C.

### Introduction

Many silicates are decomposed with the separation of silica through the action of acids or other reagents. The crystallochemical factors that influence the rate of attack and the physical appearance of the silica, as gelatinous, scaly, granular, or other forms, have been discussed by Murata (1943, 1946). Tschermak (1903, *et seq.*) found inflections in the dehydration curves of such residues and claimed the existence of numerous definite hydrates of silica. These phases were viewed as support for the silicic acid theory of the constitution of silicates as developed by him and by Clarke (1914). Tschermak's experimental evidence for the existence of the supposed hydrates did not find general acceptance, however, because of parallels drawn between the leached residues and chemically precipitated silica gels. The main arguments brought against him were the findings by Van Bemmelen (1896, 1908) and Zsigmondy (1911) that similar dehydration discontinuities were given by silica gels containing adsorbed water, attending variations in particle size and in experimental parameters, and the X-ray studies of Krejci and Ott (1931) and others that showed the silica gels to consist of poorly crystallized low-cristobalite. Tschermak (1914) did not

take kindly to the opposing interpretation of the dehydration data and referred to the criticism of Mügge (1908) as elevated thoughts without much factual support. Rinne (1913) concluded that new lines of evidence were needed to validate the reported hydrates. Summaries of the early state of knowledge of the supposed silica hydrates or silicic acids are given by Norton and Roth (1897), Himmelbauer (1914), Schwarz and Menner (1924), and Weiser (1935, p. 193-228).

The first X-ray work on a silica residue, done in 1927, proved it to be a definite crystalline hydrate,  $H_2Si_2O_5 \cdot I$ . The existence of at least 20 different crystalline silica hydrates has since been indicated by X-ray examination. These are listed chronologically in Table 1, which includes two new crystalline hydrates, Silica-AP and Silica-SN, found in the present study, and two phases, Silica-X and Silica-G, not formed by leaching and in which the presence of essential water is uncertain.

### Sample preparation

In the present study the silica residues leached from 29 different silicates (Table 2) were examined by X-ray and optical methods. The leaching usually

Table 1. Crystalline silica hydrates

Designation	Composition	Parent silicate	X-ray powder spacings	References
H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> -I		α-Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	3.87(10), 7.69(5), 5.67(5)	1, 2, 3, 4, 5
H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> -II		β-Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	5.48(10), 4.05(5), 3.55(5)	3, 6
Silica-GL	H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	BaFeSi <sub>4</sub> O <sub>10</sub>	3.78(10), 3.55(4), 8.2(2)	7, 8
Iler-I	? (wet)	Na polysilicate	3.69, 3.57, 7.48	9
Iler-II	? (dried 30°)	same	9.25, 3.49, 3.59	9
Iler-III	? (dried 110°)	same	3.70, 7.43, 3.59	9
Iler-IV	? (dried 400°)	same	3.41, 6.65, 3.68	9
Silica-X	Not known		3.38(10), 17.7(4), 4.33(4)	8, 10, 11
H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> -III		KHSi <sub>2</sub> O <sub>5</sub>	3.77(10), 3.17(7), 2.45(7)	12, 13, 14
H-magadiite	H <sub>2</sub> Si <sub>14</sub> O <sub>29</sub> ·5H <sub>2</sub> O	NaSi <sub>7</sub> O <sub>13</sub> ·3H <sub>2</sub> O	13.68(10), 3.42(7), 6.84(4)	15, 16, 17, 18
Silica-SH <sub>A</sub>	Not known	same	13.6, 6.66, 3.34	17
Silica-SH <sub>B</sub>	Not known	same	3.39, 5.50, 11.2	17
Silhydrite	H <sub>2</sub> Si <sub>3</sub> O <sub>7</sub> ?	same	14.50(10), 3.42(8), 3.14(3)	17
Silica-G	Not known		Near quartz	19
H <sub>2</sub> Si <sub>3</sub> O <sub>7</sub> -I		Na <sub>2</sub> Cu(Si <sub>3</sub> O <sub>7</sub> ) <sub>2</sub> ·5H <sub>2</sub> O	11.45(10), 4.31(8), 3.91(8)	20
H <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> -II		Na <sub>2</sub> Si <sub>3</sub> O <sub>7</sub>	10.04(10), 3.92(8), 3.81(5)	20
H <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> -I heated to 550°C			4.52(10), 4.30(8), 5.37(6)	20
Silica-AP	H <sub>2</sub> Si <sub>4</sub> O <sub>9</sub> ?	KCa <sub>4</sub> (Si <sub>2</sub> O <sub>5</sub> ) <sub>4</sub> F·8H <sub>2</sub> O	3.77(10), 7.56(4), 5.28(3)	8
Silica-SN	H <sub>2</sub> Si <sub>4</sub> O <sub>9</sub> ?	BaSi <sub>2</sub> O <sub>5</sub>	3.75(10), 5.99(4), 2.45(2)	8
Silica-SN heated to 125°C			3.76(10), 4.09(5), 3.63(3)	8

References : (1) Schwarz and Richter (1927); (2) Schwarz and Hennicke (1956); (3) Liebau (1964); (4) Wodtke and Liebau (1965); (5) Hubert et al. (1974); (6) Hubert et al. (1976); (7) Pabst (1958); (8) Present study; (9) Iler (1964); (10) Heydemann (1964); (11) Greenwood (1967); (12) Wey and Kalt (1967); (13) Le Bihan et al. (1971); (14) Johan and Maglioni (1972); (15) Eugster (1967); (16) Brindley (1966); (17) Gude and Sheppard (1972), d-spacings for SH<sub>A</sub> and SH<sub>B</sub> estimated from chart drawings; (18) Lagaly et al. (1974, 1975); (19) Flörke et al. (1976); (20) Guth et al. (1977).

was effected at room temperature in 0.1N HCl over periods of up to 30 days. Warm 3N HCl was employed with silicates very slow to leach. Washing was done first by repeated decantation and then in flowing water for 24 hours. The method of sample preparation was found to markedly influence the degree of order residual from the parent silicate framework. Retention of order seems favored by slow leaching in very dilute acid and by using relatively coarse grains, over 125 microns in size. Strong hot acid acting on a fine powder yields an X-ray amorphous residue. In some instances the development of the crystalline silica residue can be followed visually when the leaching is done on a dished-out slide under the microscope. The nature of the solvent employed also is a factor. Liebau (1964) found that α-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, when leached in sulfuric acid gave H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-I while methanol containing phenol or acetic acid gave H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-II.

The leached residues generally are quite plastic

and, when crystalline, are readily disordered by grinding. This is due to the fact that many of the crystalline residues are layer structures with weak interlayer bonding. X-ray powder data are best obtained by using leached powders without further crushing. In some instances the freshly prepared unwashed residues give faint and diffuse X-ray patterns that become strong when the residues are washed and dried.

#### Sample examination

Among the silicates listed in Table 2 only the residues from apophyllite, gillespite, and sanbornite gave strong X-ray powder patterns. The residues from hemimorphite, pectolite, scolecite, heulandite, antigorite, and chrysotile, reported by Tschermak (1905a, b, 1906) and Hillebrand (1906) to be definite hydrates on the basis of dehydration studies, were all found to be amorphous to X-rays. The crystalline residue reported by Smoluchowski (1936) from

glaucosite also was not verified. These residues showed an extremely broad, slightly skewed peak, usually centering in the range  $22^{\circ}$ – $23^{\circ}$   $2\theta$  ( $\text{CuK}\alpha$ ) in samples prepared at room temperature, and in the range  $21^{\circ}$ – $22^{\circ}$   $2\theta$  in samples heated at  $1000^{\circ}\text{C}$ . Some residues with such peaks showed a few faint additional sharp peaks, as noted in Table 2, that may represent mixtures of amorphous and crystalline phases.

A number of the residues amorphous to X-rays were found to be optically birefringent, with the optical orientation of the parent silicate but with greatly reduced indices of refraction, around 1.42–1.44. This feature was first described by Rinne (1902, 1913) in leached flakes of heulandite, stilbite, and brewsterite, although as found here, and earlier by Wyart (1933) in heulandite, the grains are X-ray amorphous. The flaky silica residue called bauerite produced by the leaching of biotite and vermiculite also has long been known to be optically biaxial (Fouqué, 1892; Rinne, 1911; Mehmel, 1937; Ruthruff, 1941), but it does not give an X-ray pattern. Leached clinocllore and hendricksite also are weakly biaxial with small  $2V$  and are X-ray amorphous. In the crystalline layer-structure hydrates afforded by the leaching of apophyllite (Silica-AP) and sanbornite (Silica-SN), the birefringence remains after the substances become amorphous to X-rays, by thermal disordering and dehydration at  $150^{\circ}\text{C}$ , and persists to high temperatures.

The optical anisotropism of X-ray amorphous residues presumably arises in partial order residual from the parent silicate framework. Residual traces of cations also appear to be a factor. Leaching of pectolite and antigorite continued long after the residues become amorphous to X-rays gradually decreases the birefringence virtually to zero. Inesite and biotite, however, remain faintly birefringent after prolonged leaching.

#### Thermal recrystallization

Some differences are found in the response of the silica residues when they are recrystallized under identical conditions (Table 2): by heating in air at  $1000^{\circ}\text{C}$  for 24 to 72 hours, or hydrothermally at  $175^{\circ}\text{C}$  for 3 to 30 days in a KOH solution buffered to pH 10. None of the residues recrystallized hydrothermally at  $91^{\circ}\text{C}$  or  $130^{\circ}\text{C}$ . The differences in response suggest a seeding effect through residual order, although no controlling structural theme is apparent. Traces of adsorbed or unleached cations, especially Al, may be a factor. Residual order also is

Table 2. Silica residues from leached silicates

Mineral	Unheated	Heated hydrotherm. at $175^{\circ}\text{C}$ , pH 10	Heated in air, $1000^{\circ}\text{C}$
Antigorite	ND	ND	ND
Apophyllite	Silica-AP	Silica-X	ND
Bannisterite	ND	ND	FD, quartz
Bementite	ND	Quartz	FD, cristobal.
Chabazite	ND	FD	Tridymite
Chrysotile	ND	Low-cristobal.	FD
Clinocllore	ND	Low-cristobal.	ND
Friedelite	ND	ND	FD
Gillespite	Silica-GL	FD	Cristobal.
Glaucosite	ND	-	-
Gmelinite	ND	Silica-X	ND
Gyrolite	FD	-	ND
Hardystonite	ND	-	-
Harmotome	ND	ND	ND
Hemimorphite	ND	ND	FD
Hendricksite	ND	ND	ND
Heulandite	ND	ND	ND
Inesite	ND	ND	Quartz
Johannsenite	ND	ND	FD
Lepidomelane	ND	Quartz	FD
Levyne	ND	-	Quartz
Nepheline	ND	-	-
Pectolite	ND	ND	ND
Sanbornite	Silica-SN	-	Cristobal.
Scolecite	ND	Silica-X	ND
Searlesite	FD	-	-
Stilbite	ND	ND	FD
Xonotlite	ND	ND	FD
Zeophyllite	ND	-	ND

Key: ND = No X-ray diffraction peaks  
FD = Faint unidentified X-ray diffraction peaks with amorphous material

suggested by the observation of Rinne (1896) that leached cleavage flakes of heulandite when recrystallized at red heat yielded single-crystal pseudomorphs of tridymite (?) that in their optical orientation preserve the sectoral twin boundaries of the parent crystal.

#### Silica-AP

The freshly-prepared, unwashed and hence still acid residue from the leaching of apophyllite gives a weak X-ray powder pattern. During prolonged washing in water the pattern sharpens and a strong but somewhat diffuse pattern is obtained after drying in air (Table 3). The pattern differs from those of earlier reported crystalline silica hydrates. This new hydrate is designated Silica-AP in allusion to the parent mineral. The leaching can be readily followed under the microscope, and is attended by the development of crack systems in the grains as described by Cornu (1905). The microcrystalline platy phase appears to be biaxial negative,  $2V$  large, with  $\alpha = 1.438$  and  $\gamma \sim 1.47$ .

Stepwise heating of samples to constant weight, with X-ray and optical examination, established an inflection in the weight loss curve at about  $130^{\circ}$ – $140^{\circ}\text{C}$  with accompanying loss of crystallinity. It is

Table 3. X-ray powder data for silica hydrates\*

Silica-AP		Silica-SN		Silica-X	
d	I	d	I	d	I
11.0	3	7.14	4	17.7	40
10.3	5	5.99	35	14.5	3
8.35	2	5.54	3	8.67	18
7.56	40	5.28	7	7.25	16
7.3	2	4.93	4	6.22	21
5.95	2	4.53	2	5.80	8
5.28	25	4.35	2	5.47	3
4.12	5	4.08	10	5.07	13
3.77	100	3.75	100	4.33	40
3.370	15	3.38	8	4.17	5
3.075	7	3.16	10	3.66	5
2.67	3	3.02	8	3.384	100
2.37	2	2.652	10	2.903	2
2.094	5	2.449	20	2.522	11
2.000	5	2.160	6	2.181	3
1.810	5	2.070	8	1.843	20
1.631	2			1.631	2

\* Diffractometer recording in Cu radiation, Ni filter  
Relative peak heights in arbitrary chart units.

difficult to locate the precise temperature of structural breakdown because the process is very sluggish. On average, only 2.15 percent H<sub>2</sub>O is lost during the structural breakdown, at 130°–140°C, and an additional 4.77 percent is lost gradually from 140°C to 1000°C. Cristobalite is formed at 900°C and 1000°C. It seems likely that some of the water resulting from structural breakdown is retained in the sample to high temperatures. On this basis the total water loss above 130°C corresponds to H<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>. On any basis the water content is too low to permit the [Si<sub>2</sub>O<sub>3</sub>]<sup>2-</sup> sheets of apophyllite to exist unmodified in Silica-AP and be compensated by a mechanism involving H.

Silica-AP also is afforded when apophyllite is leached in dilute sulfuric or acetic acids. The product from acetic acid is relatively fine-grained. A sample dried at 90°C broke down sluggishly in the range 130°–150°C with a loss of only 1.4 percent H<sub>2</sub>O. The X-ray pattern shows small differences in spacings and relative intensities from the HCl sample. Apophyllite is not attacked by mixtures of absolute methanol and glacial acetic acid. No changes were observed in the X-ray pattern of Silica-AP attending treatment with ethylene glycol. Natural alteration pseudomorphs of silica after apophyllite have been described from several localities (Bailey, 1941) and might represent Silica-AP.

#### Silica-SN

Leached sanbornite has been noted by Rogers (1932) and Douglas (1958) to leave an optically birefringent silica residue. A leached powder was found

here to give a strong X-ray powder pattern after washing and drying (Table 3). Optically, the contorted shred-like to platy phase is biaxial with  $\alpha = 1.438$  and  $\gamma = 1.456$ .

Dehydration studies made by heating samples dried at 105°C to constant weight, with accompanying X-ray examination, established a structural breakdown near 125°C, with the development of a more finely divided, very poorly crystallized phase admixed with amorphous material. The strongest lines of this phase are at 3.76(10), 4.09(5), and 3.63A(3). This phase broke down between 150°C and 400°C.

The initial breakdown of Silica-SN at about 125°C is not accompanied by a marked inflection in the dehydration curve. At 1000°C the sample converts to cristobalite. The total water loss between 105°C and 1000°C is 10.1 percent, of which 3.6 percent is lost up to the recrystallization at about 125°C. The water content of Silica-SN thus appears to be significantly less than the 13.0 percent required for H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, and to be near H<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>. The recrystallization product formed near 125°C may be a lower hydrate, but no quantitative data could be obtained.

The X-ray pattern of Silica-SN resembles that of H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-III, obtained by leaching of KHSi<sub>2</sub>O<sub>5</sub>. This phase breaks down to a lower hydrate near 200°C. The structure of KHSi<sub>2</sub>O<sub>5</sub> has shortened O–O distances associated with the hydrogen bond but otherwise is similar to the structure of sanbornite, described by Douglas (1958) in a different orientation.

#### Silica-X

When Silica-AP and the residues from gmelinite and scolecite are heated for 3 to 10 days at 175°C in a water solution of KOH buffered to pH 10, they are converted to Silica-X. It is accompanied by low-cristobalite with the amount of this increasing with the duration of the run. No recrystallization takes place at 130°C. Silica-X was first obtained by Heydemann (1964) and later by Greenwood (1967) by heating dried silica gel under similar conditions.

Silica-X is well crystallized as rectangular plates in sizes below 2 microns. It is birefringent with a mean index of refraction below 1.50 and probably has parallel extinction. Greenwood (1967) gives the mean  $n$  as 1.484. The X-ray powder pattern (Table 3) is characterized by a strong peak with a  $d$ -spacing of 17.7A. Silhydrite and H-magadiite also show a strong peak in this region (Table 1). Heated in air, Silica-X is stable at 400°C, but at 900°C breaks down into a

poorly crystallized unidentified phase or mixture. Conclusive evidence is lacking that Silica-X contains essential water.

#### Silica-GL

The structure of crystalline  $H_2Si_2O_5$  obtained by leaching of gillespite has been described by Pabst (1958). The symmetry and unit-cell dimensions differ from the other three reported modifications of  $H_2Si_2O_5$ . The phase is here designated as Silica-GL. Only a few diffuse X-ray powder lines (Table 1) were obtained here from a coarse leached powder. On heating, the powder pattern becomes increasingly diffuse above about 125°C and disappears below 200°C, correlating with a thermal break between 150°C and 200°C indicated by the dehydration data cited by Schaller (1929). The X-ray single-crystal observations of Pabst (1958) show that some order is retained at 405°C. The water content reported by Schaller corresponds to  $8SiO_2 \cdot 5H_2O$  or  $H_2Si_2O_5 \cdot \frac{1}{4}H_2O$ . Since the water content of the sample was found to vary with the humidity, the small excess over  $H_2Si_2O_5$ , probably is not significant.

#### Discussion

Hydrated or hydrous silica rather than anhydrous silica phases are afforded by the leaching of silicates. The parent silicate motifs, whether linked in 0, 1, 2, or 3 dimensions, are negatively charged and, after leaching, require neutralization by mechanisms involving  $H^+$  such as by hydrogen-bonding,  $H_3O^+$ , or the substitution of (OH) for O. The production of an anhydrous phase would require Si-O-Si sharing of all motif oxygens half bonded to Si. Geometrical factors would limit or prevent this polymerization in many structures without a more or less complete recrystallization of the leached framework. Partial polymerization is indicated in the formation of Silica-AP and in thermal recrystallizations to a lower hydrate.

Tentative generalizations based on the survey of Murata (1943, 1946) and the data of Table 2 can be made about the nature of the silica residues left by silicates decomposed by acids. Silicates with isolated Si-O motifs and tectosilicates with tetrahedral Si/Al < 2 decompose to yield silica sols or gels. Solid residues are left by the leaching of inosilicates, phyllosilicates, and tectosilicates with tetrahedral Si/Al  $\geq$  2. A few exceptions are known to these rules.

Whether the solid residues are crystalline or are amorphous to X-rays is another matter. Crystalline

silica hydrates are afforded only by phyllosilicates lacking tetrahedral Al. An apparent added requirement is that the  $Si_2O_5$  sheets of the parent phyllosilicate are bounded on both sides by oxygen ions that are shared half with Si and half with interlayer cations. This is the case with all of the parent silicates for which structural information is available: apophyllite, gillespite, sanbornite,  $KHSi_2O_5$ ,  $\alpha$ - $Na_2Si_2O_5$ , and  $\beta$ - $Na_2Si_2O_5$ . This structural feature would permit orderly stacking of the leached negatively charged sheets by interlayer hydrogen bonds or  $H_3O^+$  taking the place of the cations.

Solid residues amorphous to X-rays are afforded by phyllosilicates in which the sheets are bounded on one side or on both sides by oxygen ions wholly shared with Si—the basal layer of the  $SiO_4$  tetrahedra with the half bonded apical oxygens located inside or on one side of the sheet. In gyrolite and zeophyllite (Table 2) the detailed structure of the sheets is not known. Silicates containing such sheets do form orderly stackings, with or without interlayer cations, although the one-layer polar sheet structures are very poorly crystallized. The observed absence of crystallinity in their leached residues may be connected with the presence of tetrahedral Al, as discussed beyond, but this would not apply to silicates such as antigorite and chrysotile. Folding or curling of the leached polar sheets may be a factor. In any case the interlayer bonding would be relatively feeble, encouraging stacking disorder.

X-ray amorphous residues also are left by inosilicates, in which the difficulties of effecting a stable three-dimensional crystalline hydrate by a bonding mechanism involving  $H^+$  are compounded, and by tectosilicates with tetrahedral Si/Al < 2. Leaching of tetrahedral Al is disruptive of a (Si,Al) $O_4$  linkage, since the oxygen ions shared in the tetrahedral Si-O-Al bonds must be converted to (OH) to provide valence compensation, and this breaks the continuity of the linkage. With a high content of tetrahedral Al the framework is broken by acid treatment into small dispersible units (Schlecht, 1946).

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