

## SILHYDRITE, $3\text{SiO}_2 \cdot \text{H}_2\text{O}$ , A NEW MINERAL FROM TRINITY COUNTY, CALIFORNIA<sup>1</sup>

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### ABSTRACT

Silhydrite occurs at the Trinity County magadiite deposit where near-surface water leached sodium from magadiite. It is white, soft, and in monomineralic masses of crystals that are individually less than  $4 \mu\text{m}$  long. The crystals are birefringent (about 0.006) and have a mean index of refraction of 1.466. A measured density of 2.141 g/cc and a calculated Gladstone-Dale value of 2.116 are in fair agreement. Analysis of 10 grams of selected material gave:  $\text{SiO}_2$  88.93,  $\text{Al}_2\text{O}_3$  0.01,  $\text{Fe}_2\text{O}_3$  0.04,  $\text{FeO}$  0.02,  $\text{MgO}$  0.71,  $\text{CaO}$  0.11,  $\text{Na}_2\text{O}$  0.05,  $\text{K}_2\text{O}$  0.01,  $\text{H}_2\text{O}^+$  3.13,  $\text{H}_2\text{O}^-$  6.65,  $\text{TiO}_2$  0.01,  $\text{P}_2\text{O}_5$  0.00,  $\text{MnO}$  0.00,  $\text{CO}_2$  0.07,  $\text{Cl}$  0.01,  $\text{F}$  0.00, total 99.75 weight percent: composition  $3 \text{SiO}_2 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{Si}_3\text{O}_7$ . Treatment with  $\text{Na}_2\text{CO}_3$  produces a magadiite-like material; however, magadiite leached with dilute  $\text{HCl}$  yields a silica hydrate that differs from silhydrite. Heating studies show that silhydrite loses water at  $110^\circ\text{C}$  and  $165^\circ\text{C}$ , and becomes nearly amorphous up to  $900^\circ\text{C}$ . Prolonged heating at  $1,150^\circ\text{C}$  produces cristobalite. X-ray diffractometer powder data indicate an orthorhombic unit cell with  $a = 14.519(5) \text{ \AA}$ ,  $b = 18.80(1) \text{ \AA}$ ,  $c = 15.938(4) \text{ \AA}$ ,  $V = 4350(2) \text{ \AA}^3$ . The strongest lines of the pattern (in  $\text{ \AA}$ ) are: 14.50 (100)(100), 7.31 (22)(012), 7.07 (21)(121), 3.63 (27)(400), 3.54 (25)(401), 3.424 (82)(143), 3.143 (35)(015). Silhydrite is named for its composition.

### INTRODUCTION

Silhydrite ( $3\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) was discovered in 1969 while we were making a detailed mineralogical study at the Trinity County magadiite deposit. It is difficult to recognize in the field because silhydrite closely resembles the other white, soft, microcrystalline minerals that characterize this peculiar spring deposit. Laboratory techniques provide the data to clearly show that it is a distinct new mineral.

Single pieces range up to 3 or 4 cm in longest dimension, but most of the material is less than 5 mm across. We estimate that less than 100 kg of silhydrite are exposed at the deposit.

Synthetic crystalline silica hydrates, or those artificially derived from natural material by leaching, are well documented (Eugster, 1967; Iler, 1964; Pabst, 1958; Tschermak, 1905). Tschermak (1905) obtained "albitsäuer" ( $\text{H}_2\text{Si}_3\text{O}_7$ ) by controlled leaching of albite in dilute hydrochloric acid. The formulas of albitsäuer and silhydrite are identical but the X-ray diffraction data for albitsäuer may be different. The X-ray data vary according to the inherited structures of the

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

starting material, even though the synthetic silica hydrates may have the same composition. Silhydrite is not a natural replica of any synthetic product known to us. Field evidence and laboratory work on the Trinity County material indicate that leaching by near-surface water formed silhydrite from magadiite.

Silhydrite (sil hī/drīt) is named for its composition—silica and water. The name and the mineral have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material has been deposited with the U. S. National Museum, Washington, D. C., and specimen material will be held at the U. S. Geological Survey, Denver, Colorado.

#### OCCURRENCE

The magadiite deposit where silhydrite has been found is about 6 airline miles (10 km) east of relocated Trinity Center, and 1/4 mile (0.4 km) east of the East Fork of the Trinity River. A bulldozer-cut quarry exposes the magadiite in the SE 1/4 SE 1/4 sec. 30, T.

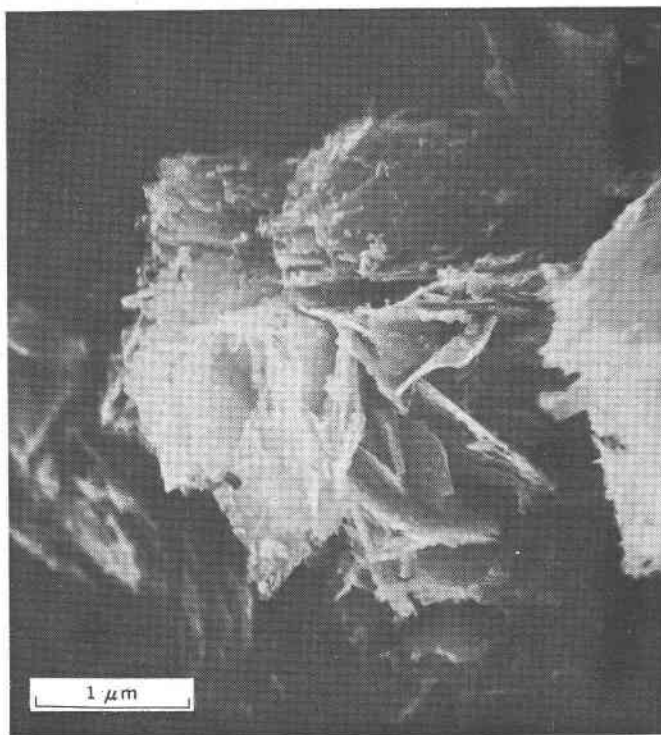


FIG. 1. Scanning electron micrograph of silhydrite by David E. Vaughn.

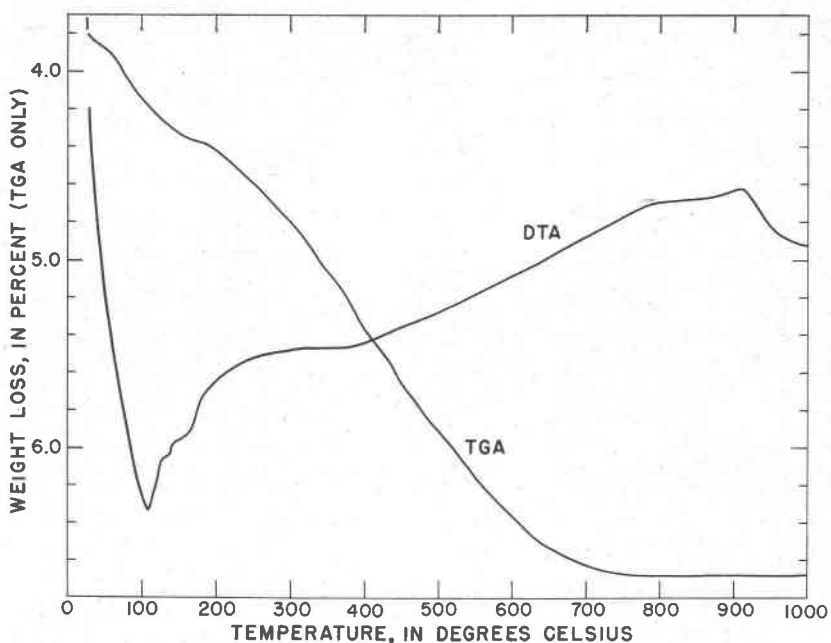


FIG. 2. Silhydrite thermal analysis curves. Thermogravimetric analysis (TGA) by William D. Long; differential thermal analysis (DTA) by William N. Lockwood.

37 N., R. 6 W., in the Bonanza King quadrangle, Trinity County, Calif.

Two earlier papers (McAtee *et al.*, 1968; Sheppard and Gude, 1969) and two abstracts (Eugster *et al.*, 1968; Gude and Sheppard, 1969) have set forth the geology and some of the mineralogy of the deposit. Briefly, serpentized ultramafic rocks of Mesozoic age are sheared and contain an irregular mass of talc-tremolite schist. Dacite, of probable Devonian age, forms a contact with the ultramafic rocks along the northern edge of the deposit. Magadiite has been precipitated from highly alkaline (pH = 10.3 to 10.9), cold (10°C), brine spring water that flows along the dacite contact and in the sheared talc-tremolite. The water has a composition close to that described by Feth *et al.* (1961) and Jones *et al.* (1967).

The deposit is exposed in a vertical bulldozed-quarry face that extends southwesterly 38 m in a quarter-circle arc from the dacite contact through the sheared talc-tremolite schist and ultramafic country rock. The face is 3 to 4 m high along most of the arc. Spring water seeps out of the face and in places runs in steady rivulets. A large mass of magadiite next to the dacite is exposed in a 2.5 by 3.7 m face

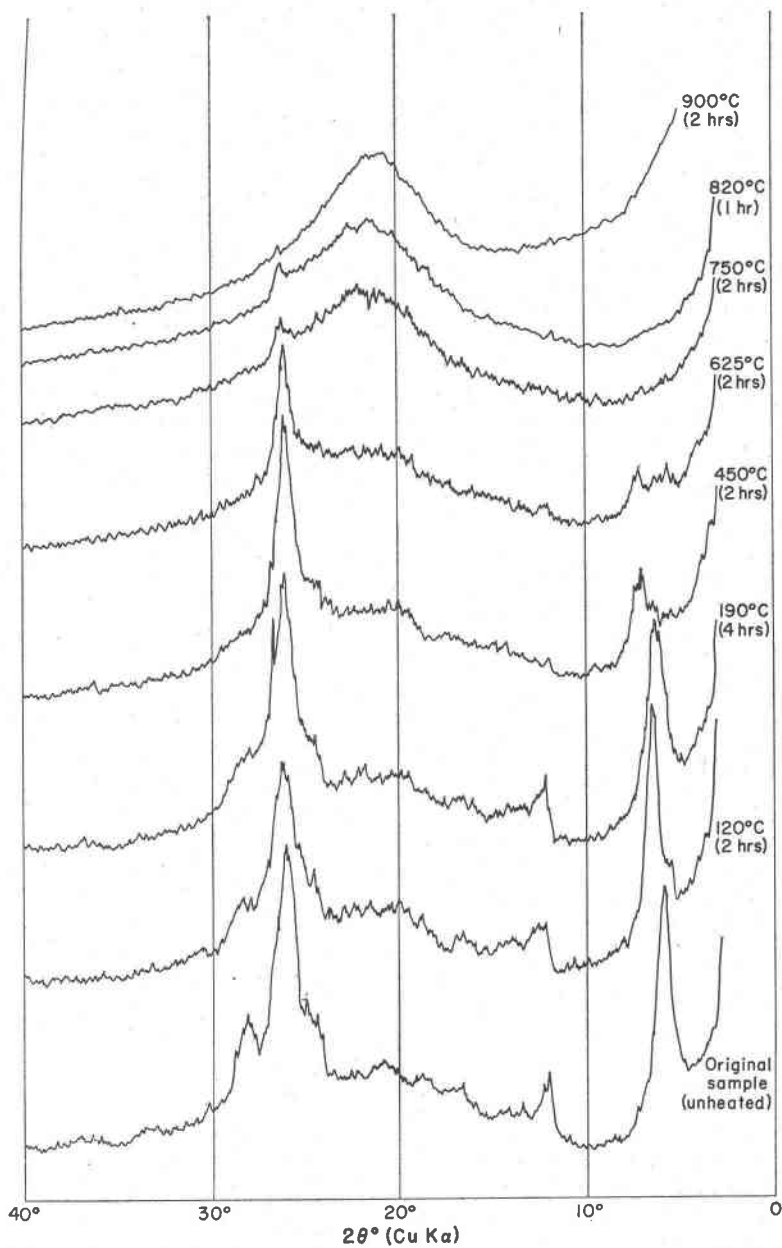


FIG. 3. Silhydrite X-ray patterns of static heating runs from  $20^\circ\text{C}$  to  $900^\circ\text{C}$ . Duration of heating runs shown in parentheses.

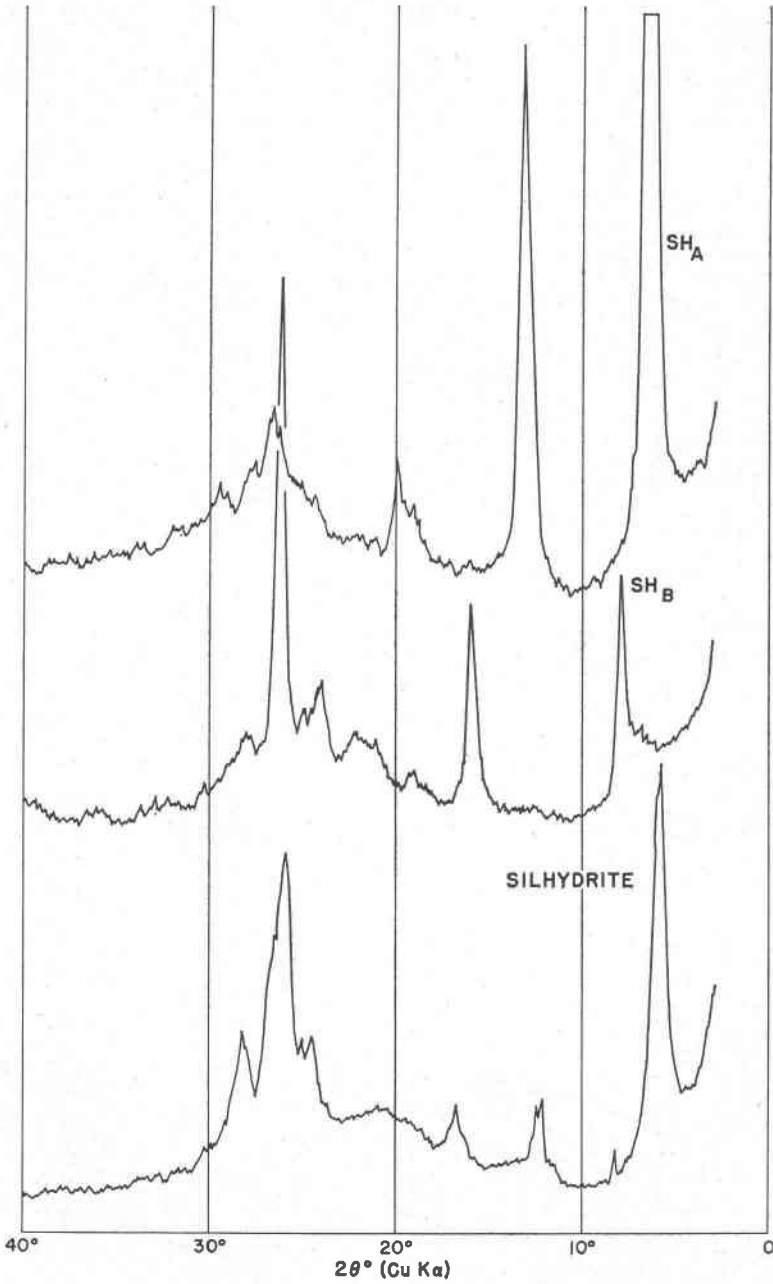


FIG. 4. Silhydrite and acid-leached magadiite X-ray patterns.  $\text{SH}_A$ , 10:1 HCl 1-hour leach;  $\text{SH}_B$ , 1:1 HCl 2-hour leach.

and is nearly monomineralic. Parts of this and smaller masses have slumped downslope to form the rubble in which silhydrite is found. Some relict magadiite was found with silhydrite in the largest rubble fragments. None of the other hydrous silicates that we have studied (Sheppard and Gude, 1969; and Gude and Sheppard, 1969) such as rhodesite, mountainite, and kenyaite is present with silhydrite. Soil detritus and hydrous iron oxide stains are found in minor quantities throughout the silhydrite fragments.

#### MINERAL CHARACTERISTICS

##### *General Appearance*

Silhydrite is white on a clean surface. Hydrous iron oxides stain fractures, crevices, and old surfaces of silhydrite. The mineral is distinctively punky, light in heft, and very porous when dry—a small piece up to 1 cm across can be moved by a light air puff. A fracture surface is rough and subconchoidal. Individual mineral grains are microcrystalline, none being larger than 4  $\mu\text{m}$  in the longest dimension. Silhydrite is insoluble in water.

##### *Physical Properties*

No mineral hardness can be measured; however, a dry specimen has a bulk hardness of about one on the Mohs scale.

A density of 2.141 (3) g/cc was measured on about 15 g of powdered material in a helium-air pycnometer using helium as the displaced fluid. This value is in fair agreement with a density of 2.116 g/cc calculated from the Gladstone-Dale formula. A bulk density of 0.65 (4) g/cc was obtained from a small cube. Thus, a piece of silhydrite will float on water for a few moments until it becomes water-logged.

##### *Optical Properties*

The observable optical properties of silhydrite are limited to mean values because of the small crystal size and the propensity of the material to form irregular aggregates.

A poorly preserved monoclinic morphology, relict after magadiite, may be seen in the scanning electron-microscope photograph (Fig. 1) (D. E. Vaughn, personal commun., 1970) of clots of silhydrite. Such material is optically similar to magadiite except that the mean index of refraction (1.466) for silhydrite is significantly less than that for magadiite (1.482). Silhydrite has a low (about 0.006) birefringence.

##### *Thermal Properties*

Silhydrite thermal properties are predictable from its simple com-

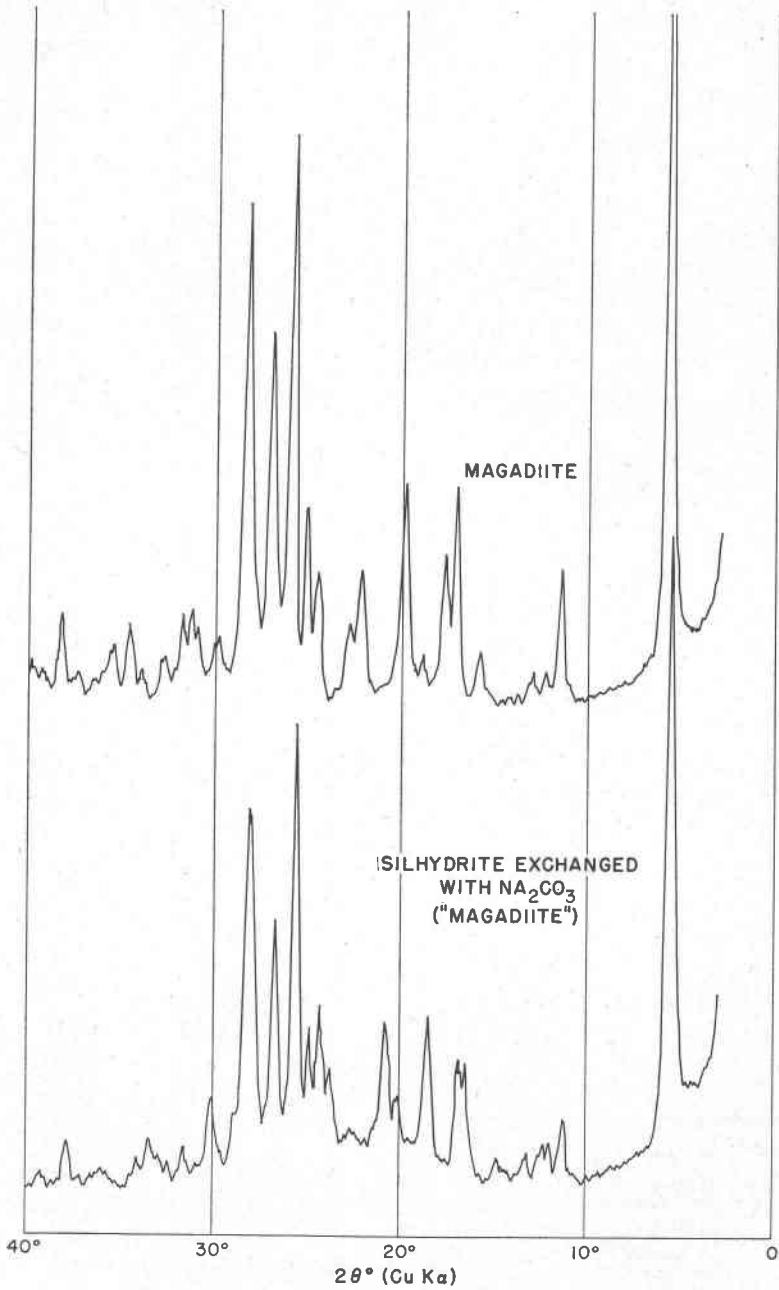


FIG. 5. Magadiite and sodium-exchanged silhydrate X-ray patterns.

position. We find from the TGA curve (Fig. 2) that two-thirds of the water rapidly leaves the mineral below 165°C, and the remaining one-third leaves at a slower constant rate from 165°C up to 750°C where no more loss can be detected. The DTA curve has a pronounced endothermic reaction at 110°C with perceptible shoulders up to about 200°C. The slope increases slightly at 400°C and stays at this rate up to 750°C. There is a hump at 900°C. A replicate DTA run shows all the same features.

Magadiite from Trinity County (McAtee *et al.*, 1968) has a DTA record with a threefold endothermic trough in the 100°–200°C range and a sharp exothermic peak at 750°–770°C. The higher temperature reaction for magadiite is consistent with the formation of tridymite, whereas silhydryte yields an amorphous material from DTA runs and

TABLE 1.--X-RAY DIFFRACTOMETER DATA FOR SILHYDRITE

<u>hkl</u>	<u>d</u> (calc) (Å)	<u>d</u> (obs) (Å)	<u>I</u>
100	14.52	14.50	100
020	9.40	9.38	10
012	7.34	7.31	22
121	7.07	7.07	21
003	5.31	5.31	16
400	3.630	3.627	27
401	3.539	3.540	25
143	3.420	3.424	82
015	3.143	3.143	35
318	1.834	1.833	9
167	1.827	1.827	13
606	1.789	1.789	6
109	1.758	1.758	5
039	1.704	1.705	5
646	1.672	1.674	5

## Orthorhombic

<u>a</u> (Å)	14.519(5)
<u>b</u> (Å)	18.80(1)
<u>c</u> (Å)	15.938(4)
<u>V</u> (Å <sup>3</sup> )	4,350(2)

Diffractometer, CuK $\alpha_1$  radiation,  $\lambda=1.54051\text{\AA}$ , 1° divergence slit, 0.002-inch receiving slit, 1/2° 2 $\theta$  per minute scanning speed, fluorite internal standard.



TABLE 2.--CHEMICAL AND SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF SILHYDRITE  
 [Columns 1, 2, 4: amounts in weight percent, except where noted.  
 Column 3: mole ratios]

	Chemical analysis			Spectrographic analysis	
	1	2	3		4
SiO <sub>2</sub>	88.93	89.31	2.73	Si	G
Al <sub>2</sub> O <sub>3</sub>	.01	.01	----	Al	.01
Fe <sub>2</sub> O <sub>3</sub>	.04	.04	----	Fe	.05
FeO	.02	.02	----	Mg	.2
MgO	.71	.71	----	Ca	.1
CaO	.11	.02	----	Na	L
Na <sub>2</sub> O	.05	.05	----	K	N
K <sub>2</sub> O	.01	.01	----	Ti	.005
H <sub>2</sub> O <sup>+</sup>	3.13	3.14	1.00	P	N
H <sub>2</sub> O <sup>-</sup>	6.65	6.68		Parts per million	
TiO <sub>2</sub>	.01	.01	----	Mn	5
P <sub>2</sub> O <sub>5</sub>	.00	----	----	B	20
MnO	.00	----	----	Ba	5
CO <sub>2</sub>	.07	----	----	Cr	2
Cl	.01	----	----	Cu	2
F	.00	----	----	Nb	L
Total	99.75	100.00		Ni	20
				Y	10
				Yb	1

1. Sample TC-10, Trinity County, Calif. Lab. serial No. D102547; analyst: Vertie C. Smith.
2. Analysis recalculated to 100 percent. CaCO<sub>3</sub> and NaCl removed from analysis.
3. Mole ratios.
4. Semiquantitative 6-step spectrographic analysis; analyst: Leon A. Bradley.  
 Results are to be identified with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, etc., but are arbitrarily reported as midpoints of these brackets, 1., 0.7, 0.5, 0.2, 0.15, 0.1, etc. The precision of a reported value is approximately plus or minus one bracket at 65 percent or two brackets at 95 percent confidence. G, greater than 10 percent; N, not detected, at limit of detection; L, detected, but below limit of determination.

separate heating studies taken up to 900°C. A specimen of silhydrite heated up to 1,150°C and held for 2 hours before quenching formed cristobalite.

The progressive collapse of the structure of crystalline silhydrite when statically heated 1 to 4 hours in batch runs is clearly shown by the diffractometer patterns in Figure 3. Some incipient structural re-ordering of poorly crystalline silica at temperatures above 625°C is evident from the pronounced diffraction hump at 22° 2θ. The eventual formation of cristobalite confirms this.

*X-ray Data*

All the X-ray data were collected by diffractometer from hand-packed powder holders or from collodion-membrane mounts. Measure-

ments for precise peak positions were made from an unoriented powder collodion mount with annealed fluorite (reagent grade  $\text{CaF}_2$ ) used as an internal standard. The minute ( $4 \mu\text{m}$ ) particle size precluded single-crystal X-ray studies on the available material.

A typical silhydrite diffractometer pattern made from the sample submitted for chemical analysis is shown in Figure 4 along with patterns for two artificially derived silica hydrates,  $\text{SH}_A$  and  $\text{SH}_B$ , both made from Trinity County magadiite. The  $\text{SH}_A$  was formed by leaching magadiite in dilute (10:1) HCl for 1 hour and then rapidly filtering and rinsing the residue. It has an X-ray pattern which most nearly matches the data for SH presented by Eugster (1967).  $\text{SH}_B$  invariably forms as a stable residue by a variety of acid leach methods—by prolonged treatment in very dilute HCl or EDTA, or by rapid leaching in strong HCl. The X-ray pattern for this artificial silica hydrate ( $\text{SH}_B$ ) matches the data for H-magadiite described by Brindley (1969).

Silhydrite has a diffractometer-pattern "family" resemblance (Figs. 4 and 5) to the various SH products as well as to magadiite and a magadiite-like sodium-exchanged silhydrite. All these hydrous silicates have a prominent reflection near  $6^\circ$  to  $8^\circ 2\theta$  and all have a nearly coincident peak at  $26^\circ 2\theta$ . A diffuse increase in background by incoherently scattered radiation from about  $12^\circ$ – $15^\circ$  up through  $30^\circ$ – $32^\circ 2\theta$  is present in all these patterns. Broadened peaks indicative of finely divided crystalline material are characteristic.

The tabulated X-ray data (Table 1) were prepared from repeated least-squares refinements by the U. S. Geological Survey Computer Program W-9214 using 15 peaks, from 8 carefully measured scans of the same sample mount. Several low-intensity broad peaks, too small to be measured accurately, were consistently noted in repeated runs but are not listed. The (100) reflection at  $14.5 \text{ \AA}$  shifts in position to smaller interplanar spacings (Fig. 3) as silhydrite dehydrates. The calculated orthorhombic parameters and all the reflection indices first derived by Akiro Kato (personal commun., 1970) are considered as provisional because the unit cell may have a lower symmetry. Calculated and observed values for the reflection peaks are generally in good agreement.

#### CHEMICAL ANALYSES AND PROPERTIES

About 10 g of material, free of stains and soil detritus and uniform in all other aspects, were selected for the chemical analysis in the Geological Survey standard silicate-analysis laboratory. This analysis, supplemented by a six-step semiquantitative spectrographic analysis,

gave the data for Table 2. The formula  $3\text{SiO}_2 \cdot \text{H}_2\text{O}$  ( $\text{H}_2\text{Si}_3\text{O}_7$ ) is derived from whole-number rounding of the mole ratios. There are remarkably few trace elements found by the spectrographic analysis, and the small amounts of minor components in the standard analysis can be ascribed to contamination from the soil that overlies the silhydrite.

The partial chemical analyses shown in Table 3 demonstrate the close relationships between magadiite and silhydrite through various exchange experiments that form artificial analogues of each natural end member. These data are less precise than the complete analysis; nevertheless, the cation-exchange behavior is clearly shown for the interrelated products. The ternary plot in Figure 6 combines data given by Sheppard, *et al.* (1970) for natural and synthetic sodium silicate hydrates with the new data of this paper.

## ORIGIN

The position of silhydrite in the magadiite deposit and its chemical

TABLE 3.--PARTIAL CHEMICAL ANALYSES OF SILHYDRITE, MAGADIITE,  
AND THEIR EXCHANGED PRODUCTS<sup>§</sup>

	1	2	3	4	5
$\text{SiO}_2$	91.5	94.5	78.7	79.0	80.5
MgO	.27	.22	.19	.57	.65
CaO	.02	.008	.008	.03	.03
$\text{Na}_2\text{O}$	.04	.08	5.48	5.12	4.40
$\text{K}_2\text{O}$	.005	.01	.01	.02	.01
L.O.I.	7.1	5.4	15.4	15.1	13.4
Exchange capacity <sup>§</sup>	38.2	----	----	59.7	----
Surface pH	5.5	----	----	10 (approx)	----

1. Silhydrite; Sample No. TC-10, Trinity County, Calif., Serial No. D142776.

2. Acid-leached (1:1 HCl) magadiite, ( $\text{SH}_B$ ); Serial No. D142773.

3. Re-exchanged (Sat.  $\text{Na}_2\text{CO}_3$ )  $\text{SH}_B$ ; Serial No. D142774.

4. Magadiite; Sample No. TC-3A, Trinity County, Calif., Serial No. D142772.

5. Exchanged (Sat.  $\text{Na}_2\text{CO}_3$ ) silhydrite; Serial No. D142777.

<sup>§</sup> All analyses reported in weight percent.  $\text{SiO}_2$  determined colorimetrically by H. H. Lipp. MgO, CaO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  determined by atomic absorption by Johnnie Gardner. L.O.I. ignited at 900°C by G. D. Shipley.

<sup>§</sup> Exchange capacity measured by H. C. Starkey by the ammonium chloride-batch method, reported in milli-equivalents per 100 grams (m.e./100 g).

and physical characteristics are convincing evidence that silhydrite formed from magadiite. Exposures at the deposit are limited to the two dimensions of the nearly vertical quarry face. Seasonal weather changes during the 4 years since our first visit have eroded and almost obliterated cleaned surfaces, especially where slope wash has draped over the silhydrite masses. Thus, observable relations between minerals *in situ* which were poor at best have now vanished.

We have not found silhydrite in direct contact with the main magadiite mass in the rubble. However, it appears that part of the magadiite body must have extended uphill from where we now see it. Erosion undercut the soft material which then slumped downslope where it was rapidly covered by forest litter and soil. Surface or near-surface water percolating through the humus gently leached the sodium from the magadiite leaving silhydrite as a more stable residual

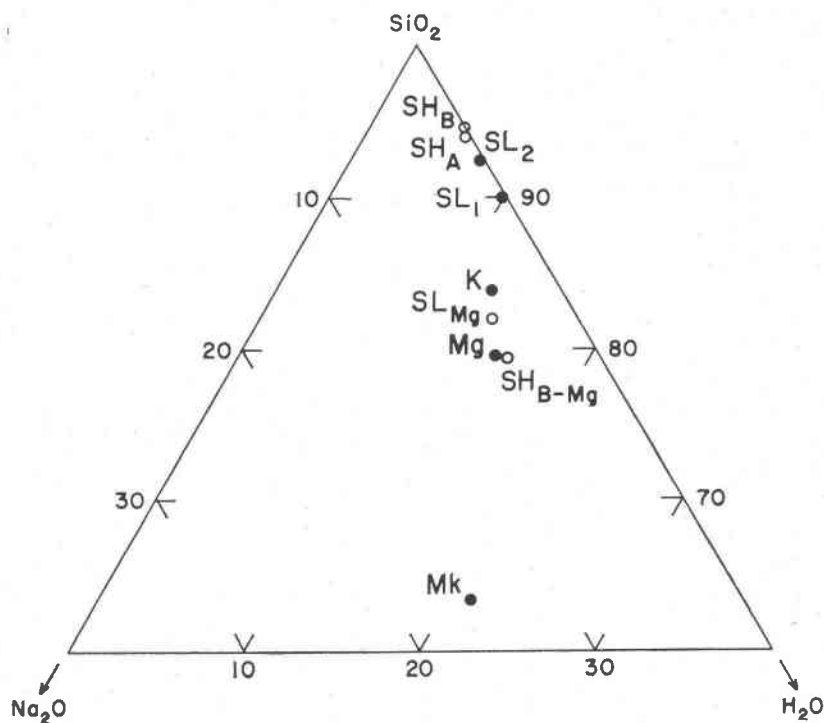


FIG. 6. Ternary diagram for the silica-rich part of the system  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ , in weight percent. Abbreviations: K, kenyaite; Mg, magadiite; Mk, makatite;  $\text{SH}_A$ , 10:1 HCl-leached magadiite;  $\text{SH}_B$ , 1:1 HCl-leached magadiite;  $\text{SL}_1$ , silhydrite, standard analysis;  $\text{SL}_2$ , silhydrite, partial analysis;  $\text{SL}_{Mg}$ ,  $\text{Na}^+$ -exchanged silhydrite;  $\text{SH}_{B-Mg}$ ,  $\text{Na}^+$ -exchanged  $\text{SH}_B$ . Symbols: ●, natural mineral; ○, synthetic product.

mineral. Both the position of silhydrite in the deposit and our knowledge of its exchange behavior preclude direct precipitation from solution as an origin. There is no evidence that silhydrite formed since the magadiite deposit was excavated.

## ACKNOWLEDGMENTS

Mr. Eugene Dohman, Trinite Mining Co., Shasta, Calif., kindly provided on-site accommodations and helped the authors at the magadiite deposit. Dr. David E. Vaughn, W. R. Grace Co., provided the scanning electron microscope photograph. Dr. Akiro Kato made the initial X-ray pattern-indexing. We wish especially to acknowledge the high-quality work of the supporting chemical and spectrographic analysts.

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