

MAKATITE, A NEW HYDROUS SODIUM SILICATE MINERAL
FROM LAKE MAGADI, KENYA¹

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ABSTRACT

Makatite was found in cores of trona from three drill holes in the Evaporite Series of Lake Magadi, Kenya. The makatite occurs as white spherulites or radiating acicular aggregates that fill or partly fill cavities in coarsely crystalline trona. Makatite commonly makes up 5–20 percent of the core and locally replaces trona. Erionite, magadiite, anorthoclase, gaylussite, and organic material are associated with the makatite. Makatite is length slow, shows parallel extinction, and has the following indices of refraction: $n_{\min.} = 1.472$, $n_{\max.} = 1.487$. Measured specific gravity is 2.072. Analysis on 1.2 grams of material from which trona had been removed by ultrasonic treatment in distilled water gave: SiO₂ 61.04, Al₂O₃ 0.15, Fe₂O₃ 0.11, MgO 0.04, CaO 0.28, Na₂O 14.76, K₂O 0.09, H₂O⁺ 12.71, H₂O⁻ 8.12, TiO₂ 0.14, sum 97.44 weight percent. The low total is probably due to an organic impurity. The composition can be expressed as Na₂Si₄O₉·5H₂O or as NaSi₂O₃(OH)₃·H₂O if H₂O⁺ is arbitrarily assigned to (OH) groups and H₂O⁻ to (H₂O). Differential thermal analysis shows sharp endothermic peaks at 80°, 100°, and 185°C; broad endothermic peaks at 530° and 810°C; and a broad exothermic peak at 675°C. The unit cell is orthorhombic, $a = 16.840 \pm 8 \text{ \AA}$, $b = 10.256 \pm 4 \text{ \AA}$, $c = 19.146 \pm 7 \text{ \AA}$, $V = 3,306.9 \pm 1.5 \text{ \AA}^3$. Strongest lines of the X-ray diffractometer powder pattern in \AA are: 9.04 (53) (011), 8.41 (29) (200), 5.09 (100) (203), 4.217 (29) (303, 400), 3.419 (36) (030), 3.381 (29) (500), 3.127 (35) (231), 3.015 (21) (033), 2.996 (57) (116), 2.882 (42) (225). The name is from the Masai (Kenya) word, *emakat*, which means soda—in allusion to the high sodium content of the mineral.

INTRODUCTION

The mineral described herein was first recognized by Hay (1968, p. 257–259) during an investigation of chert in the deposits of Lake Magadi, Kenya. Hay found white acicular crystals intergrown with bedded trona at a depth of 94 feet in drill hole B from the northcentral part of Lake Magadi (Fig. 1). The material gave a distinctive but unidentifiable X-ray diffractometer powder pattern, and the optical data suggested a zeolite. A chemical analysis and X-ray investigation showed, however, that the mineral is a new hydrous sodium silicate. This is the third new hydrous sodium silicate mineral to be reported from the deposits of Lake Magadi. The other two, magadiite (NaSi₇O₁₃(OH)₃·3H₂O) and kenyaite (NaSi₁₁O_{20.5}(OH)₄·3H₂O), were described by Eugster (1967).

Makatite (mä' kätite) is named for the Masai (Kenya) word, *emakat*, which means soda, in allusion to the high sodium content of the mineral. The name and mineral have been approved by the Commission on New

¹ Publication authorized by the Director, U.S. Geological Survey.

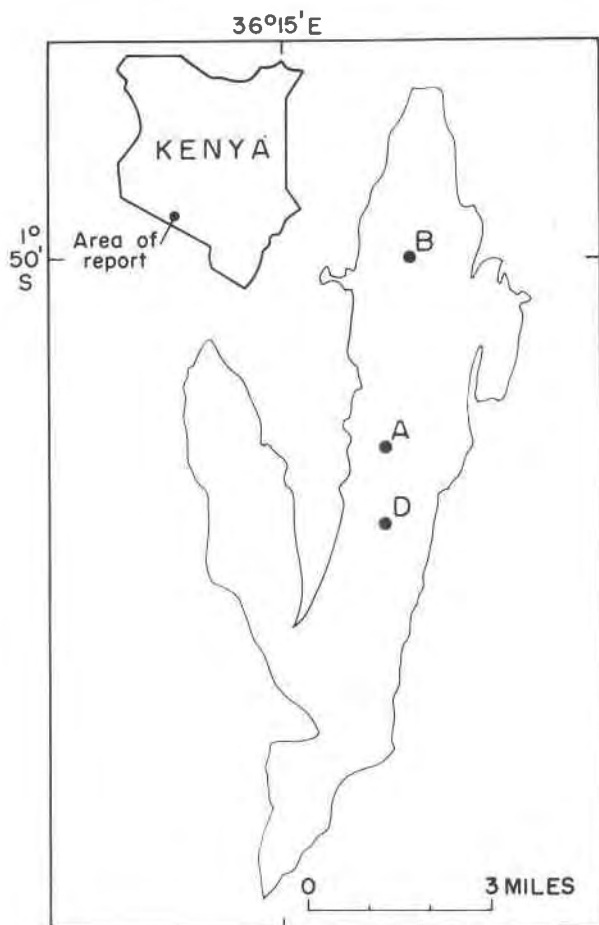


FIG. 1. Map of Lake Magadi showing the locations of drill holes where makatite was found. Minerals and Mineral Names, International Mineralogical Association. Type material has been deposited at the U.S. National Museum, Washington, D. C.

OCCURRENCE

Lake Magadi, Kenya, is a sodium carbonate-bicarbonate lake that is currently precipitating trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and halite. It is intermittently dry except for brine pools along the margin (Baker, 1958). The lake is underlain by the Evaporite Series, a thick deposit of trona and interbedded tuffaceous claystone. Trona has been mined from Lake Magadi since 1916 (Baker, 1958, p. 69).

Makatite was found in cores from three holes (Fig. 1) drilled in 1953 for the Magadi Soda Company. Logs and descriptions of the cores were given by Baker (1958, p. 41-43). Carbon-14 dates for trona in drill hole B are 4,600 years B.P., 5,750 years B.P., and 10,100 years B.P. for samples at depths of 36, 70, and 156 feet, respectively (Hay, 1968, p. 257). Thus, the Evaporite Series is of Holocene age whether the base is chosen at 112 feet as suggested by Eugster (1969) or at 157 feet as suggested by Baker (1958) and Hay (1968).

The distribution of makatite and associated silicate minerals in the Lake Magadi cores was determined by X-ray diffractometer powder study of water-insoluble residues. Trona and other water-soluble minerals were removed from crushed cores by ultrasonic treatment in distilled water. Core from drill hole B was sampled more thoroughly than core from the other holes. The distribution of makatite and associated silicate minerals from core of drill hole B is shown in Table 1. In drill hole B,

TABLE 1. MINERALOGY OF WATER-INSOLUBLE RESIDUES FROM CORE OF DRILL HOLE B, LAKE MAGADI, KENYA^a

Depth (in feet)	Lithology	Mineralogy	Depth (in feet)	Lithology	Mineralogy
2	Trona	Fp	82.5	do	Mg
12	do	Fp	84	Trona	Mg
14	do	Fp, Mi	88.5	do	Mk
16	do	Mg, K	90	do	Mk
20	do	None	92.25	do	Mk
36	do	None	92.75	do	Mk
42	do	None	93.5	do	Mk
46	do	Mk	94	do	Mk, Fp
49	do	Mk, Mg, E	94.5	do	Mk
52	do	Mg, Fp	95	do	Mk
54	Clay and trona	E, Mi	95.5	do	Mk
58	Trona	Mk, Mg	96	do	Mg, Mk, Fl
60	do	Mk, Mg	108	Clay and trona	E, Fp, Fl
63	do	Mg	112	Claystone	E, Fp
65	Claystone	E, Fp, A	114	do	P, Fp, A, C, Mi
70	Trona	Mg	115	do	Fp, E
72	do	Mg, Fp	137.75	Chert	Q
74	Clay and trona	Fp, Mg, E	157	Trona	Q, Fp
78	Trona	Mg, K, Fp	165	Claystone	Q, Fp, E, Fl, A
80.5	do	Mg, Fp	173	Tuff	E, A
81.5	Trona and halite	Mg, K			

^a Mineralogy determined from X-ray diffractometer patterns of powdered samples. Abbreviations: A, analcime; C, clinoptilolite; E, erionite; Fl, fluorite; Fp, anorthoclase; K, kenyaite; Mi, mica; Mg, magadiite; Mk, makatite; P, phillipsite; Q, quartz. Minerals listed in order of decreasing abundance.

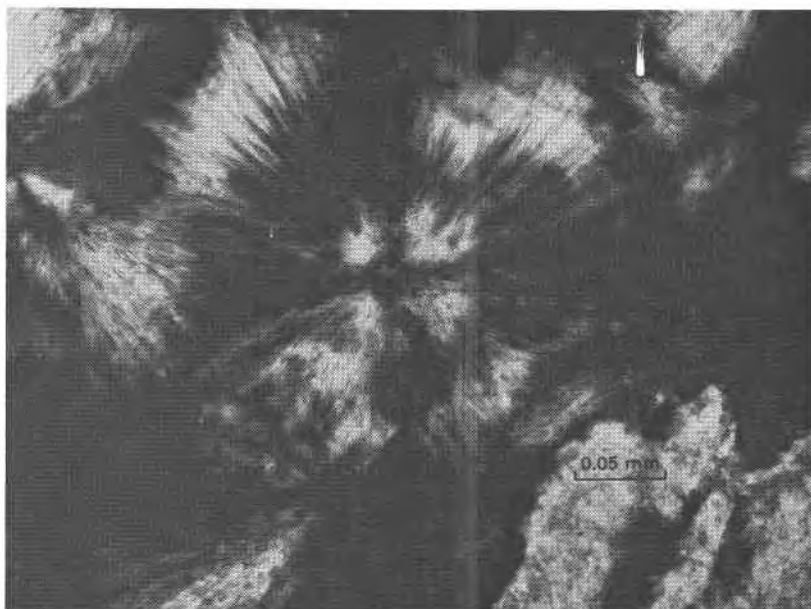


FIG. 2. Photomicrograph of spherulitic makatite. Crossed nicols.

makatite occurs at depths of 46–60 feet and 88.5–96 feet. Makatite is commonly associated with magadiite in the upper sequence, but it is generally the only water-insoluble mineral in the lower sequence. Gaylussite, anorthoclase, and erionite also occur locally with makatite in the same core samples, but it is unknown whether these minerals or magadiite are intimately associated with the makatite. The makatite content of the core samples ranges from less than 1 percent to about 50 percent, although the common range is 5–20 percent. Makatite was also identified in trona at a depth of 31 feet in drill hole A and at a depth of 27 feet in drill hole D (Fig. 1).

OPTICAL AND PHYSICAL PROPERTIES

The makatite occurs as white spherulites or radiating acicular aggregates that fill or partly fill cavities in the coarsely crystalline trona. Makatite is length slow and shows parallel extinction. Indices of refraction are $n_{\min.} = 1.472 \pm 0.001$ and $n_{\max.} = 1.487 \pm 0.001$. Other optical parameters could not be measured because the crystals were too small. The spherulites are 0.05–0.3 mm in diameter (Fig. 2). Electron micrographs show that individual crystals are 0.05–2.0 μm wide and commonly 5–30 μm long. Makatite commonly replaces trona and is locally pseudomorphous after bladed trona. The pseudomorphs are spongy in appearance because of the spherulitic character of the makatite. Specific gravity

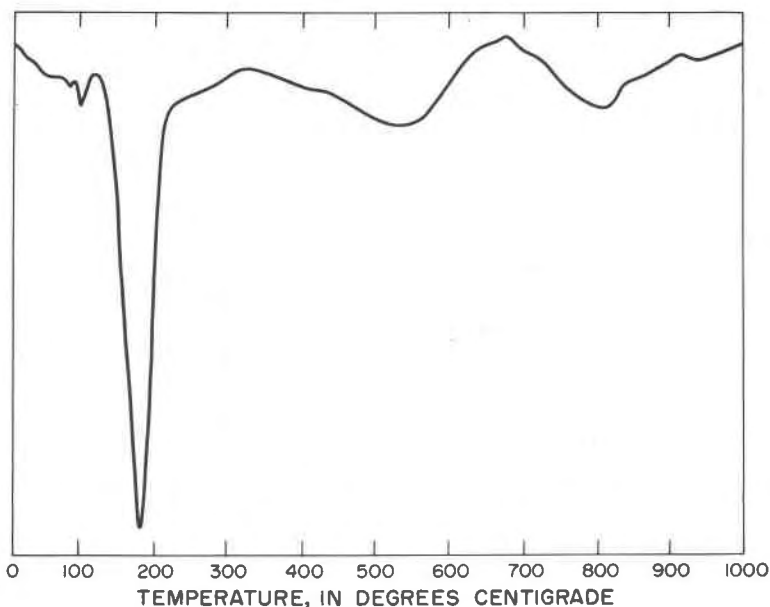


Fig. 3. Differential thermal analysis curve for makatite, by Erwin L. Dosch.

of makatite, measured by a sink-float technique in a mixture of bromoform and acetone, is 2.072 ± 0.005 .

DIFFERENTIAL THERMAL ANALYSIS

A differential thermal analysis of makatite is shown in Figure 3. The sample was heated in a static nitrogen atmosphere at 10° per minute using a platinel thermocouple. Sharp endothermic peaks are at 80° , 100° , and 185°C ; the peak at 185°C is particularly large. Broad endothermic peaks are at 530° and 810°C , and a possible broad exothermic peak is at 675°C . The endothermic peaks between 80° and 185°C probably result from the loss of water and suggest that the water is lost in three stages.

X-RAY DATA

X-ray diffractometer powder data and cell dimensions for makatite are given in Table 2. The powder data were indexed by computer from preliminary cell dimensions derived by Akira Kato using Ito's (1950) method. Final cell dimensions were obtained by a least-squares refinement through use of the U.S. Geological Survey's FORTRAN IV Program W9214. The orthorhombic cell parameters are: $a = 16.840 \pm 8 \text{ \AA}$, $b = 10.256 \pm 4 \text{ \AA}$, $c = 19.146 \pm 7 \text{ \AA}$, and $V = 3,306.9 \pm 1.5 \text{ \AA}^3$. Agreement between the observed and calculated d values is generally good. How-

TABLE 2. X-RAY DIFFRACTOMETER DATA FOR MAKATITE^a

<i>hkl</i>	<i>d</i> (calc.) (Å)	<i>d</i> (obs.) (Å)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc.) (Å)	<i>d</i> (obs.) (Å)	<i>I</i>
011	9.04	9.04	53	611	2.680	2.680	6
200	8.41	8.42	29	035	2.550	2.550	14
203	5.09	5.09	100	334, 613	2.496	2.493	17
121	4.759	4.786	7	622	2.383	2.384	10
022	4.516	4.520	5	614	2.362	2.356	19
303, 400	4.217	4.215	29	342	2.266	2.266	5
105	3.737	3.734	10	606	2.107	2.108	7
321	3.694	3.714	12	436	2.042	2.040	2
322	3.532	3.521	8	640	1.893	1.893	6
030	3.419	3.419	36	805	1.846	1.845	6
500	3.381	3.368	29	717	1.779	1.779	7
215	3.279	3.300	10				
231	3.127	3.125	35				
033	3.015	3.014	21				
116	2.996	2.998	57				
225	2.882	2.883	42				
520	2.816	2.815	2				
332	2.793	2.793	11				

Orthorhombic							
<i>a</i> (Å)=16.840±8							
<i>b</i> (Å)=10.256±4							
<i>c</i> (Å)=19.146±7							
<i>V</i> (Å ³)=3,306.9±1.5							

^a Diffractometer, nickel-filtered CuK α_1 radiation, 1° divergence slit, 0.01-inch receiving slit, scanning speed of $\frac{1}{2}^\circ 2\theta$ per minute, fluorite internal standard.

ever, significant differences between the observed and calculated values for the (321), (322), (500), and (215) reflections suggest that makatite may have lower symmetry than orthorhombic. Attempts to derive cell parameters by electron diffraction and X-ray single crystal techniques were unsuccessful.

CHEMICAL ANALYSIS

Material for chemical analysis was obtained by first removing the trona by repeated washings in an ultrasonic bath of distilled water. The relatively large pyrogenic or epiclastic anorthoclase crystals that remained after this treatment were removed by hand picking under a binocular microscope. The remaining material weighed 1.2 grams—all nearly pure makatite. The results of a chemical analysis of this material by Vertie C. Smith are given in Table 3. Minor organic material accompanied the analyzed makatite, and its loss accounts for the low total of 97.44 percent in column 1 of Table 3. By simplifying the mole ratios, the formula of makatite can be expressed as Na₂Si₄O₉·5H₂O, or as NaSi₂O₃(OH)₃·H₂O if H₂O⁺ is arbitrarily assigned to (OH) groups and H₂O⁻ is assigned to (H₂O).

Using the measured cell volume, the calculated density is 2.068 g/cm³

TABLE 3. CHEMICAL ANALYSIS OF MAKATITE

	1	2	Mole ratios
SiO ₂	61.04	63.17	4.26
Al ₂ O ₃	.15	—	
Fe ₂ O ₃	.11	—	
MgO	.04	—	
CaO	.28	—	
Na ₂ O	14.76	15.28	1.00
K ₂ O	.09	—	
H ₂ O ⁺	12.71	13.15	2.96
H ₂ O ⁻	8.12	8.40	1.89
TiO ₂	.14	—	
Total	97.44	100.00	

1. Sample B-94, Lake Magadi, Kenya, Serial No. D 102127; analyst: Vertie C. Smith. Al₂O₃ includes P₂O₅, and total iron is reported as Fe₂O₃. Low total probably due to loss of organic material.

2. Analysis in column 1 recalculated to 100 percent disregarding Al₂O₃, Fe₂O₃, MgO, CaO, K₂O, and TiO₂.

for 21[NaSi₂O₃(OH)₃·H₂O]. The measured specific gravity (2.072) and calculated density are in good agreement, but $Z=21$ is probably inconsistent with orthorhombic symmetry.

The composition of makatite is compared to that of magadiite and kenyaite in Figure 4. Makatite contains more Na₂O and H₂O but less SiO₂ than either magadiite or kenyaite. The composition of makatite is very close to that of two crystalline sodium tetrasilicates, one synthesized by Baker *et al.* (1950) and the other by McCulloch (1952). McCulloch (p. 2455) showed that the two synthetic compounds had distinctly different X-ray diffraction powder patterns. The X-ray data of makatite do not match either synthetic material, which suggests the existence of at least three polymorphs of a hydrous silicate with a mole SiO₂/Na₂O ratio of about 4.

GENESIS

The solubility of silica in sodium carbonate-bicarbonate brines is a major factor in the precipitation of sodium silicate minerals (Eugster, 1967; Jones *et al.*, 1967). Sodium carbonate-bicarbonate brines that are exposed to the atmosphere commonly have a pH of 9.5–11. These alkaline brines can store substantial amounts of silica in solution. Jones *et al.* (1967) found that the Lake Magadi brines contain silica in concentrations as high as 1,450 parts per million.

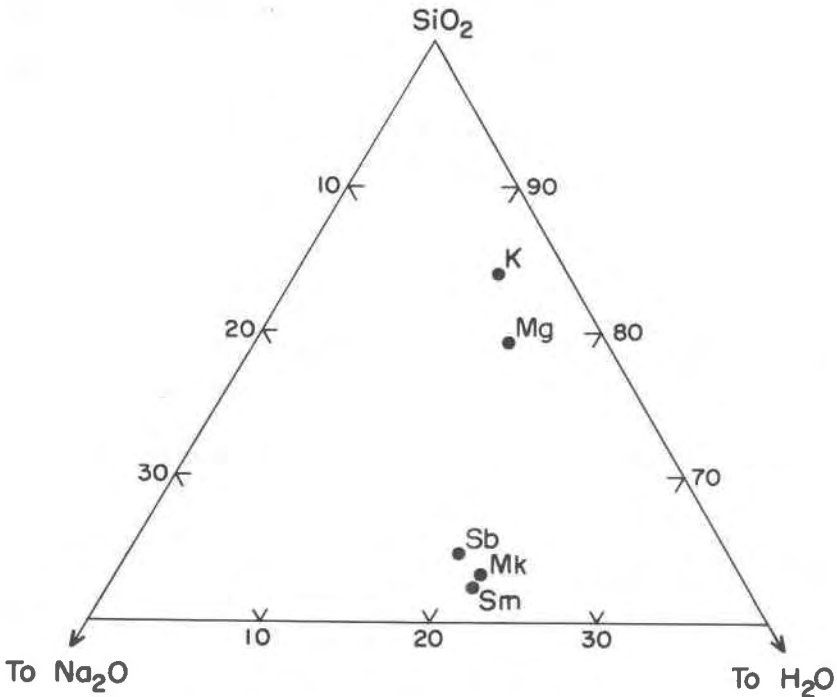


FIG. 4. Silica-rich part of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$, in weight percent. Abbreviations: K, kenyaite; Mg, magadiite; Mk, makatite; Sb, synthetic tetrasilicate by Baker *et al.* (1950); Sm, synthetic sodium tetrasilicate by McCulloch (1952).

Direct precipitation of a sodium silicate mineral from waters of a sodium carbonate-bicarbonate lake that contains a high concentration of dissolved silica can be effected by lowering the pH or by evaporation. The precipitation of magadiite in the High Magadi Beds was attributed by Eugster (1967; 1969) to a lowering of pH by dilution. The High Magadi Beds were probably deposited in a stratified lake in which fresh water lay over sodium carbonate-bicarbonate brine. Magadiite precipitated at the interface where the pH was lowered. Thus, precipitation in stratified lakes probably explains the bedded deposits of magadiite. Evaporation of the brine probably would not result in bedded deposits of sodium silicate minerals, but instead would result in a deposit of trona containing disseminated sodium silicates.

Makatite and magadiite in the trona of drill hole B seem to be of diagenetic origin because both replace trona. Direct precipitation from the brine seems unlikely unless the present silicates have simply recrystallized from primary deposits of the same mineralogy. Probably the

makatite and magadiite crystallized from saline and alkaline fluid that was trapped in the trona during deposition. Reaction of the fluid with a precursor silicate gel or mineral may have been necessary for the ultimate crystallization of makatite and magadiite.

The conditions that lead to the formation of makatite rather than magadiite are not understood. The two hydrous sodium silicates differ in chemical composition; therefore, chemical parameters such as the activities of sodium, silica, or water may have controlled their crystallization. Inasmuch as both minerals occur in trona, the activities of sodium and water probably were not the chief controlling factors. The distribution of the two silicates in the closely sampled 70- to 96-foot interval of drill hole B suggests that the activity of silica was the principal control. Makatite occurs alone in trona from the 88.5- to 95.5-foot interval. Magadiite occurs in trona or in trona with clay in zones both above and below the interval containing only makatite. The magadiite zones also locally contain kenyaite or makatite. The magadiite zones either contain interstitial clay with the trona or adjoin claystone beds. Actually, the clay and the claystone consist chiefly of zeolites that probably formed diagenetically. The occurrence of magadiite with or near clay or claystone suggests that the availability of silica from glass, zeolites, or diatoms favored the formation of the more siliceous magadiite rather than makatite.

ACKNOWLEDGMENTS

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REFERENCES

- BAKER, B. H. (1958) Geology of the Magadi area. *Kenya Geol. Surv. Rep.* **42**, 81 p.
- BAKER, C. L., L. R. JUE, AND J. H. WILLS (1950) The system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ at 50, 70, and 90°. *J. Amer. Chem. Soc.* **72**, 5369-5382.
- EUGSTER, H. P. (1967) Hydrous sodium silicates from Lake Magadi, Kenya: precursors of bedded chert. *Science*, **157**, 1177-1180.
- (1969) Inorganic bedded cherts from the Magadi area, Kenya. *Contrib. Mineral. Petrology*, **22**, 1-31.
- HAY, R. L. (1968) Chert and its sodium-silicate precursors in sodium-carbonate lakes of east Africa. *Contrib. Mineral. Petrology*, **17**, 255-274.
- ITO, TEI-ICHI (1950) *X-ray Studies on Polymorphism*. Maruzen Company, Tokyo, 231 p.
- JONES, B. F., S. L. RETTIG, AND H. P. EUGSTER (1967) Silica in alkaline brines. *Science*, **158**, 1310-1314.
- MCCULLOCH, LEON (1952) A new highly siliceous soda-silica compound. *J. Amer. Chem. Soc.* **74**, 2453-2456.

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