

MAGADIITE FROM ALKALI LAKE, OREGON

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ABSTRACT

Magadiite ($\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) has been identified in veins cutting playa sediments and in muds associated with alkali salts and brines at Alkali Lake playa, Oregon. Magadiite has apparently precipitated directly from solution, perhaps as a result of pH changes on dilution by runoff. The magadiite veins may be related to syneresis cracking in very fine-grained playa sediments derived from acid volcanics.

INTRODUCTION

Recently, Eugster (1967) described two new hydrous sodium silicates, magadiite ($\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) and kenyaite ($\text{NaSi}_{11}\text{O}_{20,5}[(\text{OH})_4 \cdot 3\text{H}_2\text{O}]$), from Lake Magadi, Kenya. The magadiite apparently precipitated from alkaline lacustrine brines; subsequently percolating water converted magadiite to kenyaite and finally to chert. According to Eugster, this simple inorganic mechanism might explain the formation of many bedded cherts.

During the course of independent field studies, white chert-like veins of magadiite were observed in playa sediments of Alkali Lake, Oregon, and in muds associated with alkali salts and brines. The origin of the magadiite is closely related to the hydrochemistry of the playa and its saline deposits.

LOCATION AND GEOLOGIC SETTING

Alkali Lake basin is crossed by U. S. Highway 395 in the northeastern part of Lake County, south-central Oregon, about 100 km north of Lakeview. The basin, which covers approximately 800 km², is a graben formed by post-Miocene block faulting (Mundorff, 1947). Elevations range from 1200 to 1800 m. The climate is semi-arid with precipitation averaging about 25 cm per year. There are no permanent streams, although heavy rainfall in the drainage basin is carried into the playa as flood runoff. Most of the area is covered by abundant sagebrush and greasewood, but the playa itself is essentially barren. Relict shorelines in the basin indicate a Pleistocene high-water stand 84 m above the basin floor.

The rocks which crop out within the Alkali Lake basin are Tertiary age or younger. The principal unit is the Clarno Formation (Eocene and early Oligocene), which consists of rhyolite and related rocks. This unit is overlain by basalt flows of Miocene age that are probably equivalent

to the Columbia River basalts. The basin floor is layered by Pleistocene lake beds of clay, silt, and volcanic ash or pumice, with recent surficial deposits of alluvium and soda.

Alkali Lake playa, covering an area of 15 km², occupies a large deflation hollow in the unconsolidated lake beds of the basin floor. A large part of the playa is covered by numerous circular depressions, called "potholes"; some are as much as 12 m across and 1 to 2 meters deep (Allison and Mason, 1947). Most of these depressions contain lenses of crystalline sodium salts. These lenses are thickest toward the center, and are either exposed or submerged beneath shallow brines. The edges of the soda lenses are concealed beneath wet green mud, but correspond roughly with the rims of the depressions; holes dug between potholes did not encounter salt layers. On the basis of crystal morphology, optics, and chemical analysis, Allison and Mason identified the bulk of the crystalline material as natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and also noted the possibility of small amounts of trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). Their chemical analysis of surface efflorescence outside the potholes indicates that trona and thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), readily derived from the dehydration of natron, were the principal salts. Our X-ray diffraction data on preserved samples indicate that natron, trona, and small amounts of halite are associated with pothole brines and that trona and thermonatrite are indeed the principal components of surficial crusts. However, the salines found within the muds at the edges or between the potholes are trona and gaylussite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$). Comparison of the saline mineral assemblages suggests diagenetic reaction of sodium carbonate brines with organic matter and calcium carbonate of the lacustrine muds (Eugster and Smith, 1965; Jones, 1966).

Although the entire playa surface may be desiccated in dry years, the potholes normally contain variable and concentrated brines (Rettig and Jones, 1964, Jones, 1966) that apparently result from evaporation of artesian waters at a rate roughly equivalent to discharge. An artesian well near the southern margin of the playa discharges representative inflow to the potholes; the water is clear and dilute (500 ppm), but highly alkaline (pH = 9.7 to 9.8). At times of above average precipitation, a large shallow pond occupies the southeast part of the Alkali Lake playa. Sodium is by far the dominant cation in all these waters, and the carbonate content is also directly related to total dissolved solids. The pH of the brines may be as high as 11.0, and silica contents can exceed 2500 ppm (Jones, Rettig, and Eugster, 1968). In 15 analyses, the mole ratio of sulfate to chloride ranges from 0.33 in the well water to 0.44 for the most highly concentrated brine, but there is no systematic relation to total solutes.



FIG. 1. Magadiite ridges on the west side of Alkali Lake playa.
View to the northeast.

Occurrences. At Alkali Lake, magadiite has been identified in veins that cut lacustrine muds on the west and south sides of the playa, including the areas of the large playa pond. It has also been tentatively identified as a precipitate from a pothole brine pond. In addition, X-ray diffraction data on bulk samples suggest that magadiite is a component of the very fine-grained montmorillonitic muds bordering the potholes.

The magadiite veins form low ridges 10 to 30 cm wide which project several cms above the lake bed sediments. At the surface the vein material is a hard, white, porcelaneous substance which readily crumbles into small blocks. The veins are found in a belt about 1 km long and 50 m wide between a slight rise forming the western edge of the playa and a higher terrace of younger lacustrine sediments. The veins form a pattern of rectangles 1 to 3 m across (Fig. 1).

In order to sample material at depth, a shallow trench was dug transversely through several ridges. Each vein extends at least 1 m deep and has sharp contacts with the enclosing sediment. Similar veins, which are farther apart and form a very crude polygonal pattern, were noted in the area of the large pond on the southern part of the playa. These veins fracture conchoidally to reveal a massive, smooth substance resembling hardened meerschaum. At the contact with enclosing muds,

the material is marked by minute fractures perpendicular to the attitude of the vein.

Although our work has been confined to small areas on the south and west sides of the playa, aerial photographs of the Alkali Lake playa reveal several separate areas of patterned ground which may be related to the formation of magadiite veins.

Magadiite-bearing material was also found in a well-developed pothole, which had recently received some diverted discharge from the artesian well mentioned previously. Apparently this material formed by direct surface precipitation from alkaline brines. The precipitate was floating in very shallow brine and consisted of delicate, ball-like aggregates of white semi-crystalline material with patchy opalescence. A sample of this precipitate was preserved in mother liquor for later examination in the laboratory.

Physical properties. The magadiite veins are composed predominantly of a fine-grained matrix of faintly birefringent material. In thin sections from the veins on the west side of the playa, the matrix includes rounded to subrounded grains which are clearly outlined but could not be separately identified (Fig. 2a). Inasmuch as X-ray data give little indication of impurities, these may be relict grains which have completely altered to magadiite. Veinlets of spherulitic magadiite with low-order interference and a mean refractive index of 1.48 were prominent (Fig. 2b). Veins from the playa pond area seem somewhat more uniform in this section. Some ragged masses of homogeneously birefringent material suggest outlines of relict grains, but spherulitic extinction and low refractive index indicate that this is also magadiite. X-ray data for all samples suggest only clay as a possible additional mineral component.

X-ray diffraction patterns (Fig. 3) of magadiite are characterized by a large spacing of 15.8 Å that initially suggested a clay mineral. If the substance is saturated with ethylene glycol, the 15.8 Å peak gradually expands to 18.8 Å, indicating a layer lattice structure of the montmorillonite type. On heating, crystallinity appears to be essentially destroyed above 550°C; samples heated at 950°C for 5 hours duration produce well-defined X-ray diffraction patterns of tridymite. Tabulation of d and intensities for the Alkali Lake magadiite (Table 1) compares favorably with the detailed data given by McAtee, House, and Eugster (1968). Additional confirmation is provided by the X-ray diffraction data for acid-treated specimens showing several broad peaks near those of the hydrated silica phase (SH) described by Eugster (1967).

The precipitate from the Alkali Lake pothole brine was washed clean of sodium carbonate (mostly trona) by continuous flow centrifugation

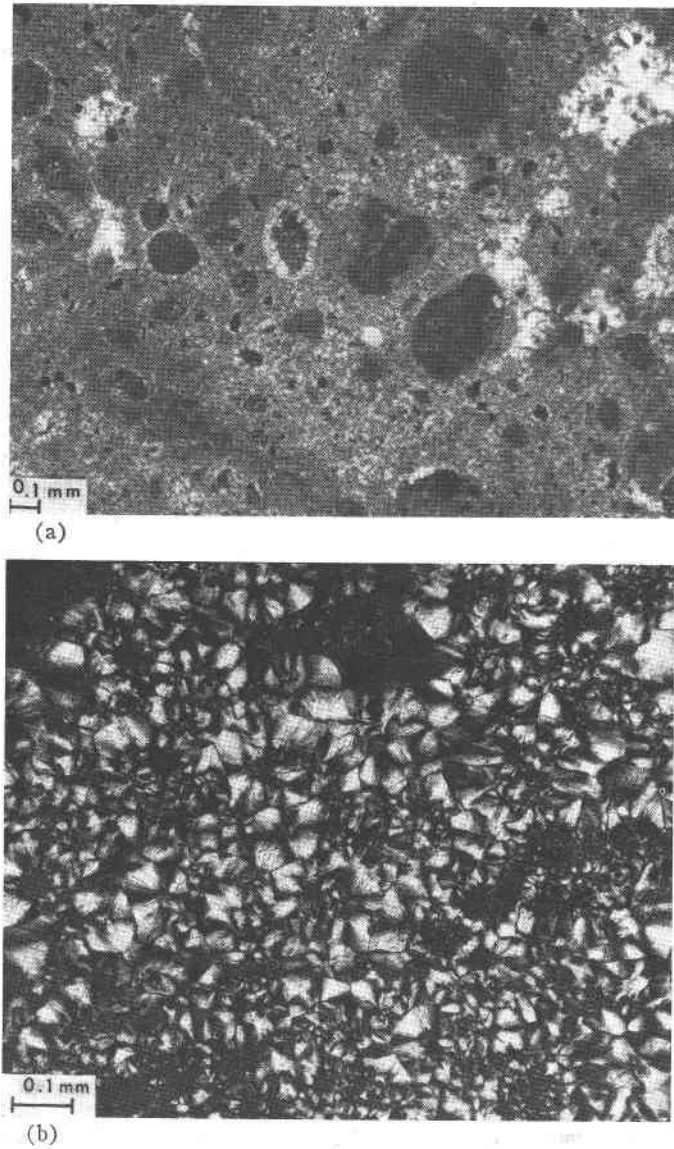


FIG. 2. Photomicrographs of (a) apparent relict grains within magadiite veins; and (b) microscopic veinlets of spherulitic magadiite in massive fine-grained magadiite matrix.

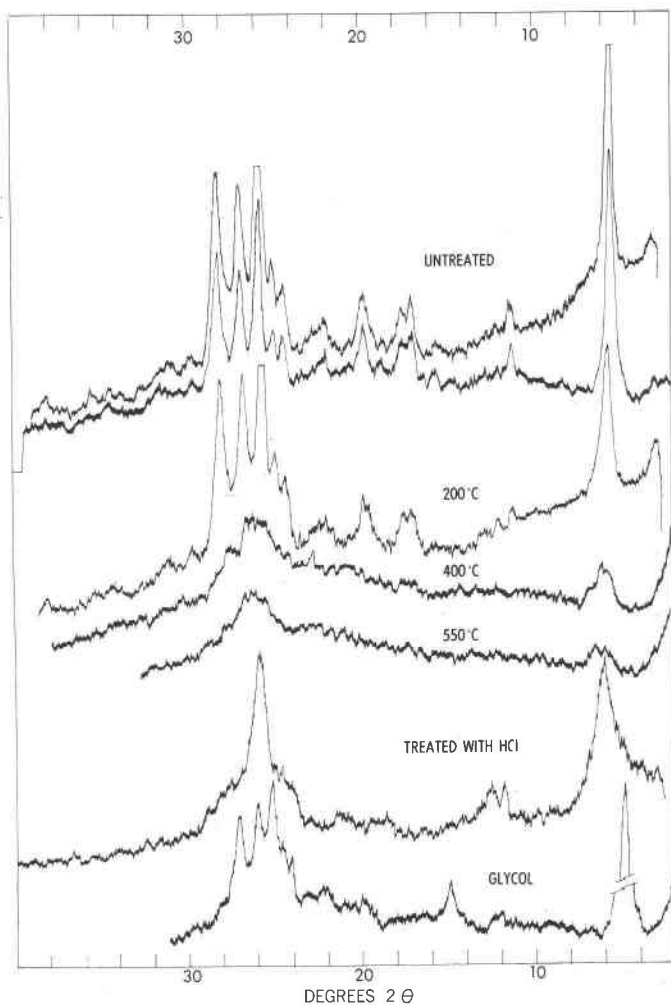


FIG. 3. X-ray patterns of magadiite from veins in Alkali Lake playa. The patterns of untreated material represent veins from the western side of the playa and the playa pond, respectively.

leaving a small amount of residue. With high-power magnification, minute magadiite spherules are readily distinguished scattered through a heterogenous, fine-grained matrix, which appears to be a mixture of irregular masses of magadiite and clay minerals. This was confirmed by somewhat poorly defined diffraction patterns which suggests the precipitate has incorporated detrital material held in suspension in the brine.

TABLE 1. COMPARISON OF X-RAY DIFFRACTION DATA FOR MAGADIITE FROM ALKALI LAKE; FROM LAKE MAGADI, KENYA (EUGSTER, 1967); AND FROM TRINITY COUNTY, CALIFORNIA (MCATEE, HOUSE, AND EUGSTER, 1968). NI-FILTERED COPPER $K\alpha$ RADIATION

Alkali Lake		Lake Magadi		Trinity Co.
$d(\text{\AA})_{\text{obs.}}$	<i>I</i>	$d(\text{\AA})_{\text{obs.}}$	<i>I</i>	$d(\text{\AA})_{\text{obs.}}$
15.80	100	15.41	100	15.77
7.82	26	7.755	9	7.79
7.25	10	7.213	3	7.19
—	—	6.860	3	6.88
5.68	10	5.612	4	5.62
5.21	26	5.181	19	5.18
5.03	21	5.007	16	5.01
—	—	4.699	3	4.69
4.48	24	4.464	18	4.46
4.00	17	4.008	9	4.00
—	—	3.909	4	3.93
3.62	26	3.632	10	3.62
3.53	25	3.543	12	3.54
3.44	74	3.435	80	3.43
3.30	53	3.296	35	3.30
—	—	3.200	10	3.20
3.14	57	3.146	50	3.14
—	—	2.994	3	2.99
2.90	12	2.864	3.5	2.855

Because of the impurities and small quantity of the pothole material, all detailed study of the magadiite was done on vein samples.

Table 2 presents chemical analyses of Alkali Lake magadiite and compares it with data for magadiite from Kenya. Small amounts of CO_2 and Cl can be attributed to pore water impurities.

Differential thermal-analysis curves record several reactions on heating to 1100°C . The most prominent peaks are endotherms at 150°C and 200°C , undoubtedly resulting from dehydration or dehydroxylation. An exothermic reaction between 250°C and 350°C is probably related to breakdown of bicarbonate from trona impurity. The exotherm at 700°C results from crystallization of tridymite. Heating in air for several hours duration followed by X-ray diffraction examination showed no change in the pattern at 105°C ; some decrease in line intensity at 200°C and only a small 15 \AA peak and a broad 3.4 \AA mound remaining at 400°C . Above 500°C , all diffraction maxima have essentially disappeared (Fig. 3).

Figure 4 displays the magadiite infrared transmission spectra from 2.5 to $40 \mu\text{m}$. The principal features of the spectra are a broad, weak

TABLE 2. COMPARISON OF CHEMICAL ANALYSES OF MAGADIITE AND ASSOCIATED SEDIMENT, ALKALI LAKE, OREGON, WITH MAGADIITE FROM KENYA

Oxide wt %	1 Magadiite 3AK3	2 Magadiite #JN 67-1	3 Sediment #JN 67-2	4 Magadiite Lake Magadi
SiO ₂	77.78	77.5	52.3	77.62
TiO ₂	trace	.02	.43	.06
Al ₂ O ₃	.20	.44	8.0	.79
Fe ₂ O ₃	}.12	.00	1.1	—
FeO		.24	1.9	—
MnO	.00	.00	.06	.01
MgO	.44	.50	8.4	.26
CaO	.12	.12	3.1	.14
Na ₂ O	5.74	5.0	5.8	5.55
K ₂ O	.10	.26	2.3	.35
P ₂ O ₅	—	.00	.11	—
CO ₂	—	.05	2.2	—
H ₂ O ⁺	5.96	4.4	6.7	5.28
H ₂ O ⁻	9.46	10.1	2.4	9.32
Cl	—	.015	.015	—
F	—	.0007	.001	—
Other volatiles	—	.50	4.9	—
Sum	99.92	99.14	99.72	99.93

1. Collected by B. F. Jones and A. H. Truesdell; O. von Knorring, analyst (also see McAtee, House, and Eugster, 1968).

2, 3. Collected by J. T. Neal; L. N. Shapiro, analyst.

4. From Eugster (1967).

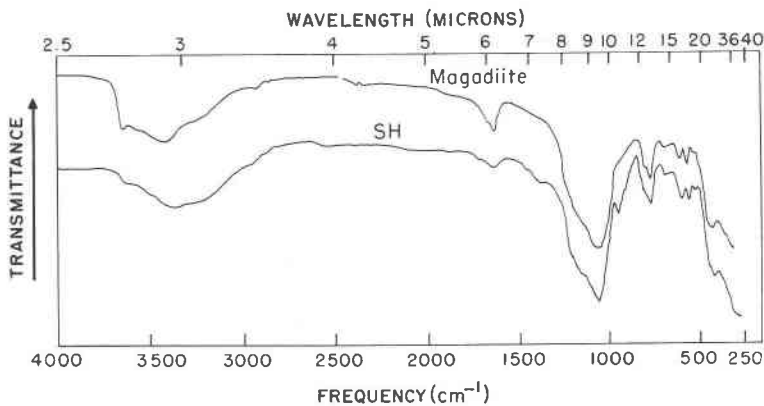


FIG. 4. Infrared transmission spectra of Alkali Lake magadiite and SH derived by acid leach.

absorption area near $5\ \mu\text{m}$ and a strong, sharp peak in the 8- to $10\text{-}\mu\text{m}$ range. For layer-lattice silicates, absorption bands in the $3\ \mu\text{m}$ area are generally caused by hydroxyl vibrational modes. Absorption events in the 8- to $10\text{-}\mu\text{m}$ range may be attributed to Si-O vibration, where Si is in the tetrahedral configuration (Stubican, 1963).

Origin. Up to 2700 ppm of dissolved silica has been determined in brines from Alkali Lake playa (Jones, Rettig, and Eugster, 1968). Such values represent substantial supersaturation with respect to amorphous silica, even at pH's near 10.5, and result from evaporative concentration of surface waters. This suggests that magadiite may well precipitate directly from solution just as sodium carbonate minerals do.

Eugster, Jones, and Sheppard (1967) proposed that magadiite could precipitate from silica-rich, sodium carbonate brines as a result of mixing with fresh water which lowers the pH. This would have been the principal effect of discharge from the artesian well on brine in the pothole where incipient magadiite was found. Although the pH change may have been as little as 0.5 unit, a decrease in pH from 10.3 to 9.8 lowers amorphous silica saturation more than 500 ppm. By the mixing of well water, decrease in temperature of the pothole brine would also tend to reduce silica held in solution. The highly alkaline sodium carbonate waters containing abundant SiO_2 can be attributed to weathering and rapid subsurface hydrolysis of acid volcanic materials in the Alkali Valley drainage basin (Jones, 1966).

The fillings or veins of magadiite from distinct but varied patterns in the Alkali Lake sediments. In other localities, sediment contraction and the associated development of polygons have been attributed to desiccation or syneresis. The regular form and boundaries of the magadiite fillings, coupled with the fact that contraction cracks are highly ephemeral features (whether formed subaerially or under water), seem to indicate that the formation of the cracks and the precipitation of magadiite were relatively synchronous.

Although the cracks containing magadiite at Alkali Lake were most certainly formed by contraction of very fine-grained sediments, it is problematic whether they result solely from desiccation or whether syneresis is involved. The orthogonal pattern of the magadiite ridges at the western playa edge suggests mud-cracking, but it does not preclude origin by syneresis. Bulk X-ray diffraction data identifying minor magadiite in the very wet muds bordering the potholes suggest that colloidal magadiite could be extruded into syneresis cracks formed on aging of the gel-like clay in the finest playa sediments. Perhaps the syneretic process concurrently causes contraction, release of water from the clay-gel, and precipitation of magadiite. Any mechanism lowering tempera-

ture or pH could also precipitate magadiite from interstitial brine *after* its syneretic extrusion.

The irregular magadiite veins of the playa pond area suggest that the flooding of Alkali Lake could be related to both magadiite precipitation and the formation of cracks in the playa sediments. In an investigation of syneresis and subaqueous cracking, White (1964) notes that chemical precipitates are the dominant filling of cracks formed under water, whereas subaerial cracks are usually filled by silt and clay. He describes syneresis cracks formed by Ca and Mg-rich fresh water flooding ditches lined with sodium montmorillonite. Van Straaten (1954) has also described subaqueous cracks which he related to changing salinity after partial compaction. At Alkali Lake, such mechanisms may have participated in the formation of magadiite as well.

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