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MAGADIITE FROM TRINITY COUNTY, CALIFORNIA

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Abstract

Magadiite occurs in altered volcanic rocks in Trinity County, California, with chemical composition equivalent to magadiite from Kenya. X-ray powder diffraction of both California and Kenya magadiite shows a monoclinic cell with $a=7.22$, $b=15.70$, $c=6.91$, all ± 0.05 Å, $\beta=95°16' \pm 5'$. Kenyaite is also probably monoclinic, $a=7.79$, $b=19.72$, $c=6.91$, all ± 0.05 Å, $\beta=95°54' \pm 5'$. Electron micrography and diffraction confirm that the symmetry is less than tetragonal. DTA analysis gave for both minerals several strong exothermic dehydration peaks between 100 and 200°C, and an exothermic peak near 700°C due to breakdown of the structure.

Introduction

Magadiite and kenyaite, unusual sodium silicates with layered structures, were first described from the Lake Magadi basin in Kenya (Eugster, 1967) and later encountered in Oregon and California (magadiite, Eugster *et al.* 1967) and in the High Natron beds south of Lake Magadi (magadiite and kenyaite, R. L. Hay, pers. comm). Mineralogical data on the California magadiite and revisions of the magadiite and kenyaite cell parameters are reported in this paper with a discussion of phases in the system Na_2O-SiO_2-H_2O.

The California deposit of magadiite is located 1/4 mile east of the east fork of the Trinity River about 3 miles north of Trinity Lake (see Weed Sheet Geological Map, Sec. 30, T 37 N, R 6 W). Unlike the Kenya and Oregon occurrences, it is not associated with an alkaline lake, but with altered volcanic rocks. Perhaps its genesis is more closely related to waters of the Aqua de Ney type (Feth *et al.*, 1961; Barnes *et al.*, 1967). Details of the geologic setting are being studied by R. A. Sheppard and A. J. Gude (pers. comm.).

Chemical Data

Chemical data on natural and synthetic magadiites are assembled in Table 1. The agreement for all major constituents, even including H_2O^-, is excellent, both between samples from the same locality and for samples from different localities. There is little doubt that magadiite was first synthesized by McCulloch (1952) from solutions with molar SiO_2:Na_2O ratios of 13:1. These solutions were kept at 100°C, 1 atm for up to 3 years. Iler (1964) repeated the synthesis with somewhat less siliceous solutions.

TABLE 1. CHEMICAL COMPOSITION OF NATURAL AND SYNTHETIC MAGADIITES

	1	2	3	4	5	6
Weight %	Magadiite Lake Magadi	Magadiite Oregon	Magadiite California	Magadiite California	Magadiite synthetic	Magadiite reconstituted
SiO_2	77.62	77.78	76.73	77.36	78.0	78.79
TiO_2	.06	trace	.01	n.d.	n.d.	.03
Al_2O_3	.79	.20	.18	.15	n.d.	.50
Fe_2O_3	.55	.12	.06	.02	n.d.	.12
MnO	.01	<0.01	n.d.	n.d.	n.d.	<.01
MgO	.26	.44	1.55	.51	n.d.	.05
CaO	.14	.12	.31	.06	n.d.	.14
Na_2O	5.55	5.74	5.82	5.61	5.9	5.55
K_2O	.35	.10	.12	n.d.	n.d.	.16
H_2O^+	5.28	5.96	4.59	15.17	16.1	5.20
H_2O^-	9.32	9.46	9.39			9.65
			Atomic Ratios			
Na	1.000	1.000	1.000	1.000	1.000	1.000
Si	7.216	6.982	6.799	7.112	6.818	7.350
OH	3.275	3.572	2.714	4.651	4.694	3.225
H_2O	2.890	2.832	2.775			2.992

1. 6: from Eugster (1967), O. von Knorring, analyst.
2. Alkali Valley, Oregon; collected by B. F. Jones, O. von Knorring, analyst.
3. Trinity County, California; collected by R. A. Sheppard, V. C. Smith, analyst.
4. Trinity County, California; collected by E. J. Dohman, B. J. Jahnke, analyst.
5. from McCulloch (1952).

We have obtained well crystallized magadiite under similar conditions in 3 weeks. X-ray properties are identical with those of natural magadiite.

Figure 1 shows the silica-rich portion of the system Na_2O-SiO_2-H_2O and some of the phases reported in this system. The ternary phases are kenyaite, magadiite, $Na_2O \cdot 8SiO_2 \cdot 9H_2O$ (or $Na_2O \cdot 8SiO_2 \cdot 2H_2O$ at 110°C) made by McCulloch (1952) and Iler (1964), $3Na_2O \cdot 13SiO_2 \cdot 11H_2O$ reported by Baker et al (1950) and the three hydrates $Na_2O \cdot 3SiO_2 \cdot 5H_2O$, $Na_2O \cdot 3SiO_2 \cdot 6H_2O$, and $Na_2O \cdot 3SiO_2 \cdot 11H_2O$ postulated by Rowe *et al.* (1967). The literature on the anhydrous sodium silicates is voluminous, but recent data on $Na_2Si_3O_7$ were given by Jamieson (1967).

The crystalline silica hydrates seem to have been discovered and rediscovered a number of times. Most of them were made from alkali silicates by cation exchange. $2SiO_2 \cdot H_2O$ was described first by Lottermoser (1908). Schwarz and Menner (1924) found that they could make it by

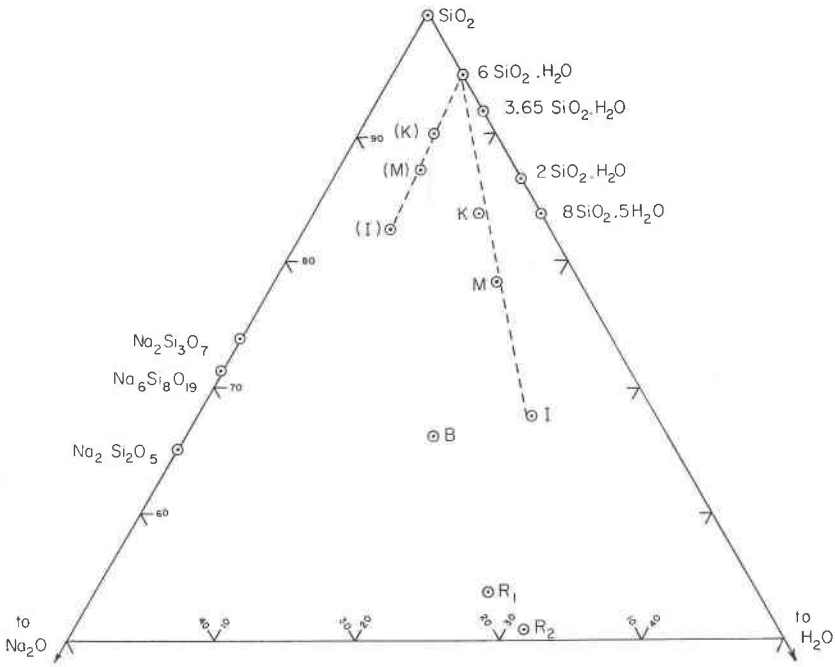

FIG. 1. Silica-rich portion of the system Na_2O-SiO_2-H_2O, in weight percent. K: kenyaite, M: magadiite, 25°C, (K), (M): same minerals at 110°C. I: $Na_2O \cdot 8SiO_2 \cdot 9H_2O$, (I): $Na_2O \cdot 8SiO_2 \cdot 2H_2O$ (both from Iler, 1964). B: $3Na_2O \cdot 13SiO_2 \cdot 13SiO_2 \cdot 11H_2O$ (Baker *et al*, 1950). R_1: $Na_2O \cdot 3SiO_2 \cdot 5H_2O$, R_2: $Na_2O \cdot 3SiO_2 \cdot 6H_2O$ (from Rowe et al, 1967).

acidifying $Na_2O \cdot 2SiO_2$. Detailed studies on $2SiO_2 \cdot H_2O$ were published by Liebau (1964) and Wodtcke and Liebau (1965). Pabst (1958) obtained a compound of the composition $8SiO_2 \cdot 5H_2O$ by acidifying gillespite, $BaFeSi_4O_{10}$. Iler (1964) produced a phase of the approximate composition $3.65SiO_2 \cdot H_2O$ from $Na_2O \cdot 8SiO_2 \cdot 9H_2O$, while Eugster (1967) obtained $6SiO_2 \cdot H_2O$ by acidifying magadiite. Wey and Kalt (1967), by making $2SiO_2 \cdot H_2O$ from $KHSi_2O_5$, demonstrated that potassium silicates behave in a similar manner. Field observations on the Lake Magadi magadiite indicate that alkalis can also be lost by prolonged exposure to dilute ground waters. Eugster (1967) postulated the sequence magadiite→kenyaite→chert.

Morphological and Crystallographic Data for Magadiite and Kenyaite

Figure 2a shows an electron micrograph and Figure 2b an electron diffraction pattern of the California magadiite. The very thin platy na-

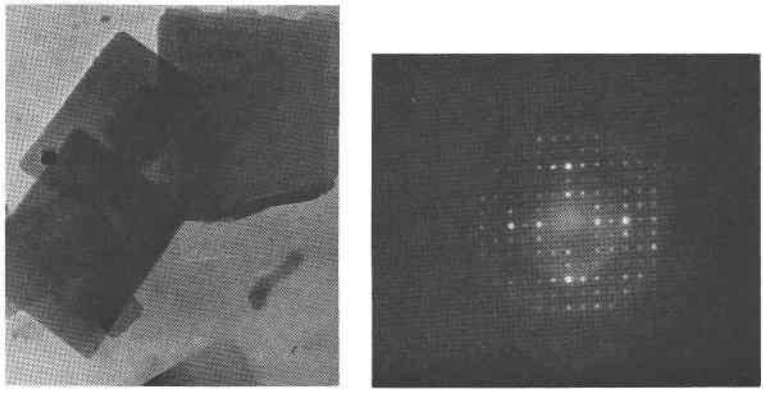

FIG. 2. (a) Electron micrograph, 90,000×. (b) Electron diffraction pattern of magadiite from Trinity County, California.

ture and the near-orthogonal outline is apparent in Figure 2a. The angle between the two sets of parallel diffraction rows is 84°40′ and the angle between the diagonals formed by these rows is 89°20′. Therefore, magadiite cannot be tetragonal, as postulated by Eugster (1967). Similarly, Figure 3a and 3b show an electron micrograph and a diffraction pattern for Lake Magadi kenyaite. Again, the angle between diffraction rows is near 84°. During exposure to the electron beam, magadiite and kenyaite single crystals rapidly disintegrate and the diffraction pattern is replaced by broad rings.

X-ray diffraction data for California and Kenya magadiites are shown in Table 2. Agreement between the two localities is excellent and all re-

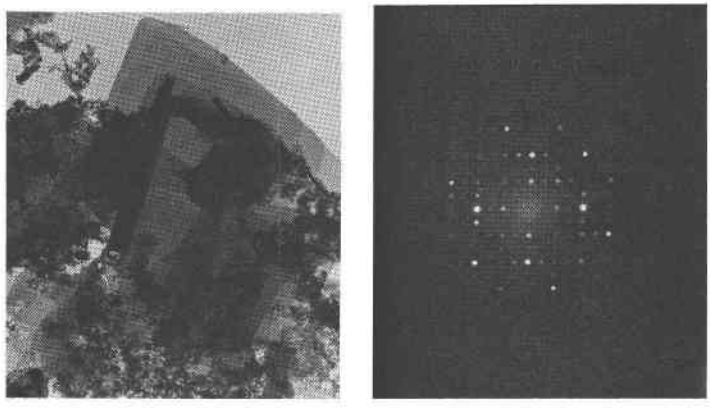

FIG. 3. (a) Electron micrograph, 90,000×. (b) Electron diffraction pattern of kenyaite from Lake Magadi, Kenya.

TABLE 2. X-RAY DIFFRACTION DATA FOR MAGADIITE FROM TRINITY COUNTY, CALIFORNIA, AND LAKE MAGADI, KENYA

hkl	*d*(calc), Å	California	Magadi*	
		d(meas), Å	*d*(meas), Å	*I**
010	15.72	15.77	15.41	100
020	7.84	7.79	7.755	9
100	7.19	7.19	7.213	3
001	6.87	6.88	6.860	3
120	5.30	5.62	5.612	4
030	5.23	5.18	5.181	19
021	5.17	5.01	5.007	16
101	4.75	4.69	4.699	3
130	4.23	4.46	4.464	18
031	4.16	4.00	4.008	9
040	3.92	3.93	3.909	4
200	3.59	3.62	3.632	10
131, 210	3.52, 3.50	3.54	3.543	12
002, 140, 041	3.44, 3.44, 3.40	3.43	3.435	80
220	3.26	3.30	3.296	35
022	3.15	3.20	3.200	10
050	3.14	3.14	3.146	50
141, 102, 230, 211	3.02, 2.99, 2.96 3.01	2.99	2.994	3
051, 032	2.85, 2.87	2.855	2.864	3.5
122	2.80	2.812	2.818	2.5
240	2.65	2.736	2.721	3.5
231	2.64	2.635	2.642	5
042, 132	2.58, 2.60	2.590	2.592	4.5
160	2.45	2.527	2.520	3.5
241, 300	2.41, 2.39	2.405	2.396	2
250, 212	2.36, 2.35	2.348	2.352	4.5
013	2.26	2.263	2.259	2.5
232	2.160		2.161	1
123	2.05	2.061	2.060	2.5
261	1.991		1.992	4
162	1.971	1.940	1.940	1
312	1.873	1.868	1.869	1
181, 271	1.814, 1.811	1.819		1
360	1.779		1.777	1
280	1.722	1.735	1.737	1
421	1.662	1.665	1.667	1
034, 191, 104, 272	1.633, 1.637, 1.639, 1.631	1.635	1.638	1.5
092, 323, 450	1.555, 1.554, 1.560	1.557	1.562	1.5
292, 390	1.406, 1.410	1.409		
1011	1.400	1.392		
015, 391	1.370, 1.367	1.369		
174, 105	1.323, 1.329	1.327		

$a=7.22$, $b=15.70$, $c=6.91$ Å, all ± 0.05 Å; $\beta=95°16' \pm 5'$.

* Eugster (1967).

TABLE 3. X-RAY DIFFRACTION DATA FOR KENYAITE FROM LAKE MAGADI, KENYA

hkl	*d*(calc), Å	*d*(obs), Å[a]	*I*[a]
010	19.73	19.68	100
020	9.86	9.925	50
100	7.74	7.775	2
001, 110	7.26, 7.21	7.272	5
030	6.57	6.620	5
021	5.84	5.637	7
101	5.04	5.142	12
130	5.01	4.965	35
031	4.87	4.689	28
121	4.49	4.471	5
131	4.00	3.945	10
210	3.80	3.754	5
002	3.63	2.638	20
012, 141	3.57, 3.52	3.525	22
051	3.46	3.428	85
230	3.33	3.320	45
032	3.17	3.198	55
231, 042	2.93, 2.92	2.934	14
132	2.85	2.827	12
052, 142	2.67, 2.66	2.652	3
202, 251, 320	2.52, 2.52, 2.49	2.520	3
152, 212	2.46, 2.50	2.480	3
003, 222, 330	2.42, 2.44, 2.40	2.416	5
023, 232	2.35, 2.35	2.343	7
233	1.88	1.880	3

$a=7.79$, $b=19.72$, $c=7.30$ Å, all ± 0.05 Å; $\beta=95°54' \pm 5'$.
* From Eugster (1967)

flections can be indexed on a monoclinic cell. This includes even those reflections which were originally assigned to impurities (Eugster, 1967). Corresponding data for kenyaite are given in Table 3. The fit is not as good as that for magadiite, but again, kenyaite cannot be tetragonal, but must be monoclinic, or perhaps even triclinic.

THERMAL DATA

A DTA pattern for California magadiite is shown in Figure 4. Several strong endothermic peaks between 100° and 200°C are probably connected with dehydration reactions while the exotherm at 740° indicates complete breakdown formation of a new phase of the structure. Kenyaite gives similar results, with endotherms at 155°, 185° and 220°C and an exotherm at 680°C. Patterns taken with a differential scanning calorim-

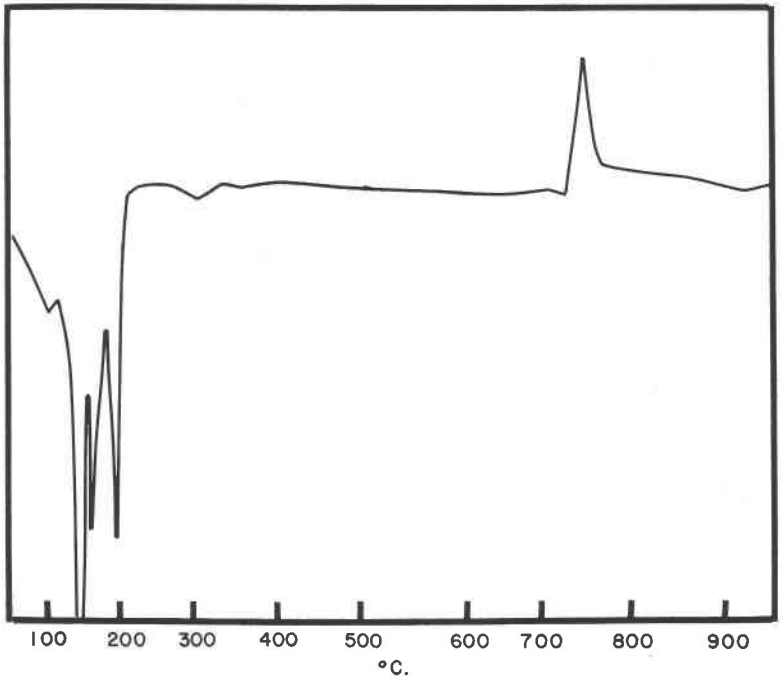

FIG. 4. DTA pattern of Trinity County, California, magadiite. Heating rate: 12°C/minute. The first endotherm at 140°C may be due to H_2O^-, that is H_2O molecules occupying fixed structural positions (see table 1). The other endotherms below 200°C are probably caused by the release of (OH) groups from the structure. The exotherm at about 750°C is probably due to the formation of a new phase.

eter give endotherms for magadiite at 139°, 167° and 205°C. Curves can be repeated with the same sample, if it is cooled in air.

To check for structural changes during dehydration, we heated oriented slides of California magadiite for 24 hours to 250° and 300°C. Diffraction data for treated samples are given in Table 4. If the sample is heated to 250°C and allowed to cool in air for 10 minutes, rehydration seems to occur readily and the original X-ray pattern is restored, if somewhat less well defined. However, when the heated sample is cooled over silica gel, the structure remains collapsed. The X-ray pattern shows basal reflections only, with a repeat distance of 13.8 Å. This is very close to the *c* dimension of the phase $6SiO_2 \cdot H_2O$ obtained by acidifying magadiite (Eugster, 1967). Heating to 300°C leads to further collapse and the sample does not rehydrate readily to magadiite.

Magadiite expands upon treatment with ethylene glycol to a basal

TABLE 4. X-RAY DIFFRACTION DATA FROM ORIENTED SLIDES OF HEAT-TREATED CALIFORNIA MAGADIITE

Oriented untreated	Heated 250°C, cooled in air	Heated 250°C, cooled over silica gel.	Heated 300°C cooled over silica gel.	Heated 300°C, cooled in 50% R.H.
15.78 vvs	15.78 vs	13.60 s	12.45 m, b	14.98 m
7.900 s	7.830 m	6.916 ms	6.511 vw, b	7.628 vw
5.246 vs	5.215 s		5.574 w, b	5.246 m
4.484 w	4.462 vvw, b	4.611 m	4.439 vvw, b	
4.022 vw				
3.900 wm	3.900 vw			
3.619 vvw				3.534 vvw
3.453 vw	3.440 vvw	3.453 w	3.427 vvw, b	3.506 vvw
3.290 w				3.232 vvw
3.132 s	3.116 wm			
2.998 vvw				
2.831 wm	2.822 ww	2.814 vvw	2.822 vvw	2.822 w
2.755 vw				
2.603 s	2.592 wm			
2.542 vw				
2.362 vw				
2.227 vvw, b				
1.949 m	1.945 w			
1.731 vw				
1.637 vvw				
1.561 vw				
1.492 vvw, b				
1.415 vvw				

spacing of about 18.0 Å. Infiltration is gradual with the 15.8 Å peak persisting for some time. Large ionic amines (see Jordan, 1949) do not cause an increase in basal spacings. The cation exchange capacity was found to be 60 meq/100g dry sample.

CONCLUSIONS

Magadiite from Trinity County, California, has chemical and X-ray properties which are very similar to those of the Lake Magadi, Kenya, magadiite. Both kenyaite and magadiite are probably monoclinic, as shown by electron diffraction patterns and a more complete indexing of the X-ray diffraction data. Both minerals have considerable similarities with clay minerals in spite of the unusual chemistry. A more complete crystallographic analysis is necessary before we can understand some of the complexities in their behavior, such as rehydration, fixed content of H_2O^- and the $Na^+ \rightleftharpoons H_3O^+$ exchange.

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