

## STABILITY CONSTANTS AND GIBBS FREE ENERGIES OF FORMATION OF MAGADIITE AND KENYAITE

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### ABSTRACT

Thermodynamic data for magadiite and kenyaite determined from solubility measurements at 25°C indicate that these minerals are stable in alkaline waters rich in sodium and silica. Waters with these characteristics are reasonably common in nature, ranging from alkaline bicarbonate-carbonate lakes and springs on one hand to sodium chloride rich brines, springs and interstitial marine and continental waters on the other. The sodium silicate minerals provide a mechanism for moderating dissolved silica, sodium ion and pH in such environments. Magadiite has been reported from four localities (Lake Magadi, Kenya; Alkali Lake, Oregon; Lac Tchad, Africa; Trinity County, Calif.) where it is associated with either sodium bicarbonate or sodium chloride waters. Kenyaite has thus far been observed only as an alteration product of magadiite in the High Magadi Beds in Kenya.

### INTRODUCTION

Two new hydrous sodium silicate minerals, magadiite and kenyaite, have been described by Eugster (1967). A third mineral of this type, makaite ( $\text{NaSi}_2\text{O}_3(\text{OH})_3 \cdot \text{H}_2\text{O}$ ), has been described by Sheppard, Gude and Hay (1969) (pers. comm.). These minerals occur in Pleistocene saline lake deposits in the Lake Magadi area, Kenya. Magadiite appears to be a direct precipitate from alkaline brines; kenyaite, is an intermediate product in the transformation of magadiite to chert by the action of fresher waters percolating through the lake beds. Plates and layers of chert, that still preserve the laminations of the original deposit, have been found in some of the magadiite beds (Eugster 1967). Kenyaite nodules have been observed in magadiite beds where these beds are exposed on the slopes of hills. The chemical transition magadiite→kenyaite→chert involves only the removal of  $\text{Na}^+$  ion and partial dehydration. The widespread nature of the magadiite deposits and the formation of laminated chert from magadiite by non-biologic mechanism, have far-reaching geologic implications. This paper reports the experimentally determined stability constants and free energies of formation of magadiite and kenyaite.

### EXPERIMENTAL

Samples of magadiite and kenyaite were equilibrated in distilled water at 25°C and one atmosphere total pressure. The samples are portions of the same purified samples used in the analyses reported by Eugster (1967). The purification procedures are described in that paper. Two samples of each mineral were weighed and placed in 100 ml of distilled water in polyethylene bottles. A one-gram sample and a one-half-gram sample of each mineral were used to eliminate total surface area as a variable in the final solution composition. It was also thought that the different sample sizes would disclose the presence of amorphous silica

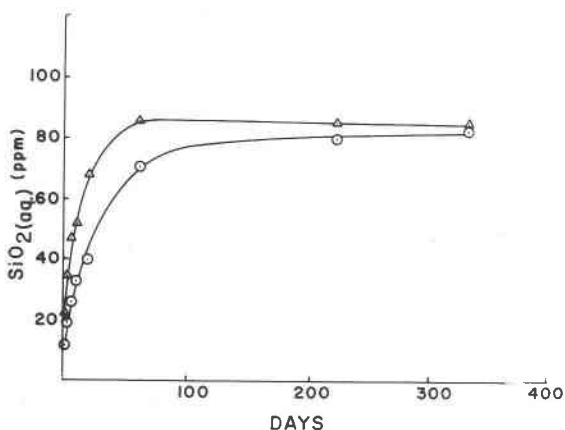


FIG. 1. Release of silica from magadiite in distilled water.  $\Delta$ One gram solid/100 ml water.  $\circ$ One-half gram solid/100 ml water.

should any be present. The final silica concentrations of the different weight suspensions should vary if siliceous impurities are present in the samples (provided, of course, that the amorphous silica was present in insufficient amount to reach saturation; if not, all of the solutions would become saturated with respect to amorphous silica). The bottles were placed on a shaker table to promote more rapid equilibration. Aliquots were periodically removed from the bottles and analyzed for silica (Figs. 1 and 2) using the reduced silicomolybdate method described by Mullen & Riley (1955). When the silica concentration of the samples reached a constant value, the activity of  $\text{Na}^+$  in solution was determined using a sodium sensitive glass electrode and pH was measured using a hydrogen ion sensitive glass electrode.

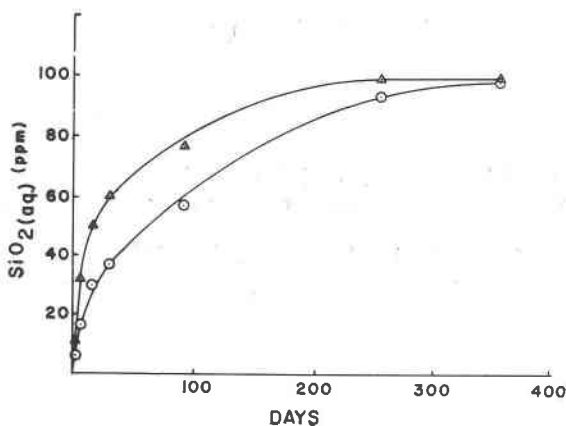


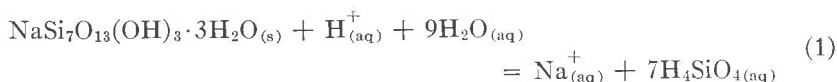
FIG. 2. Release of silica from kenyaite in distilled water.  $\Delta$ One gram solid/100 ml water.  $\circ$ One-half gram solid/100 ml water.

	pH	$a_{\text{Na}^+}$	$a_{\text{H}_4\text{SiO}_4}$
Magadiite	8.16	$10^{-2.58}$	$10^{-2.84}$
Kenyaite	8.18	$10^{-2.55}$	$10^{-2.78}$

The samples were examined by X-ray diffraction methods before and after the experiment. On the basis of the X-ray data no observable changes were found in the solid phases.

#### STABILITY CONSTANTS AND FREE ENERGIES OF FORMATION

From the experimental data it is possible to calculate the stability constants and free energies of formation of magadiite and kenyaite. Reaction (1) describes the solution of magadiite:



The stability constant for this reaction is:

$$K_{\text{magadiite}} = \frac{(\text{Na}^+)(\text{H}_4\text{SiO}_4)^7}{(\text{H}^+)(\text{H}_2\text{O})^9} \quad (2)$$

The experimental data provides the activity of sodium ion and the activity of hydrogen ion directly. The activity of silicic acid should not be significantly different from its concentration in relatively dilute solutions because it is an uncharged molecular species. The activity of water in these dilute solutions does not deviate significantly from unity. In concentrated brines, however, this term is not unity and must be considered. Substituting the experimental data into equation (2):

$$K_{\text{magadiite}} = 10^{-14.3} \quad (3)$$

The free energy of reaction (1) is given by:

$$\Delta G_{\text{R}}^{\circ} = \Delta G_{\text{Na}^+}^{\circ} + 7\Delta G_{\text{H}_4\text{SiO}_4}^{\circ} - \Delta G_{\text{H}^+}^{\circ} - 9\Delta G_{\text{H}_2\text{O}}^{\circ} - \Delta G_{\text{magadiite}}^{\circ} \quad (4)$$

Where

$\Delta G_{\text{R}}^{\circ}$  = Gibbs free energy of the reaction

$\Delta G_{\text{subscript}}^{\circ}$  = Gibbs free energy of formation of the subscripted species

The  $\Delta G_{\text{R}}^{\circ}$  in kilocalories is related to the log of the stability constant at 25°C and one atmosphere total pressure by:

$$\Delta G_{\text{R}}^{\circ} = -1.364 \log K \quad (5)$$

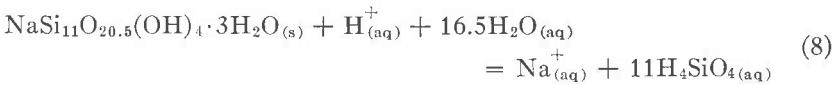
Therefore:

$$\Delta G_{\text{R}}^{\circ} = 19.5 \text{ kcal} \quad (6)$$

Free energy values for all of the other species in equation (4) except magadiite are tabulated in standard references (for example, Robie and Waldbaum, 1969) and the free energy of formation of magadiite can be calculated:

$$\Delta G_{\text{magadiite}}^{\circ} = -1762.2 \text{ kcal} \quad (7)$$

For the solution of kenyaite:



then

$$K_{\text{kenyaite}} = \frac{(\text{Na}^+)(\text{H}_4\text{SiO}_4)^{11}}{(\text{H}^+)(\text{H}_2\text{O})^{16.5}} \quad (9)$$

Substituting the experimental values:

$$K_{\text{kenyaite}} = 10^{-25.0} \quad (10)$$

For reaction (8)

$$\Delta G_{\text{R}}^{\circ} = \Delta G_{\text{Na}^+}^{\circ} + 11\Delta G_{\text{H}_4\text{SiO}_4}^{\circ} - 16.5\Delta G_{\text{H}_2\text{O}}^{\circ} - \Delta G_{\text{H}^+}^{\circ} - \Delta G_{\text{Kenyaite}}^{\circ} \quad (11)$$

The Gibbs free energy of the reaction at 25°C and one atmosphere total pressure is:

$$\Delta G_{\text{R}}^{\circ} = -1.364 \log K = 34.0 \text{ kcal} \quad (12)$$

Substituting in equation (10) the Gibbs free energy for Kenyaite is:

$$\Delta G_{\text{kenyaite}}^{\circ} = -2603.5 \text{ kcal} \quad (13)$$

#### DISCUSSION

The minerals magadiite and kenyaite were first observed in alkaline lake deposits in Kenya (Eugster, 1967). Magadiite has also been found at Alkali Lake, Oregon (Eugster, Jones and Sheppard, 1967; Rooney, Jones and Neal, 1969), Lac Tchad, Africa (Maglioni, pers. comm.) and will probably be recognized as a constituent of other alkaline lake sediments. An occurrence of magadiite associated, not with alkaline lake deposits, but with altered volcanics has been reported from Trinity County, California (McAtee, House, Eugster, 1968). These investigators suggest that its genesis is related to waters of the Aqua de Ney type rather than alkaline brines.

Figure 3, constructed from the thermodynamic data, shows the stabilities of magadiite and kenyaite as a function of  $(\text{Na}^+)/(\text{H}^+)$  vs  $(\text{H}_4\text{SiO}_4)$ . Magadiite and kenyaite are stable in solutions undersaturated with respect to amorphous silica. Kenyaite, however, has been observed only as an intermediate product in the magadiite  $\rightarrow$  chert transformation (H. P. Eugster, 1969) and does not appear to precipitate directly from solution. In silica saturated systems kenyaite is stable at  $(\text{Na}^+)/(\text{H}^+)$  ratios higher than 5. At lower  $(\text{Na}^+)/(\text{H}^+)$  ratios amorphous silica is the stable phase. Magadiite has no field of stability with respect to kenyaite in systems saturated with amorphous silica (Fig. 3). The composition of average sea water is plotted on Figure 3. It can be seen that magadiite is not stable in sea water. However, an increase in the activity of silica to  $\sim 10^{-3.2}$  at the  $(\text{Na}^+)/(\text{H}^+)$  ratio of sea water will provide environment in which magadiite is stable. This magnitude of silica activity is not uncommon in interstitial waters in many deep sea sediments (Goldberg and

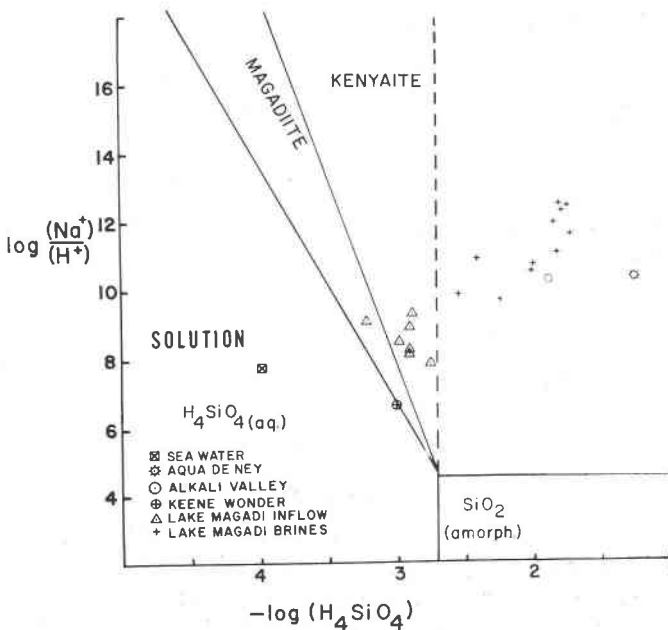


FIG. 3. Stability relations among some phases in the system  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  at  $25^\circ\text{C}$  and one atm total pressure. The amorphous silica boundary is consistent with an  $\text{SiO}_2$  (amorph) solubility of 115 ppm (Morey, Fournier, and Rowe, 1964). Analyses of a number of natural waters are plotted as functions of  $\log(m_{\text{Na}^+}/m_{\text{H}^+})$  and  $\log m_{\text{H}_4\text{SiO}_4}$ . Analyses of Lake Magadi inflow waters and brines from Eugster (pers. comm.); Alkali Lake analysis from Jones (pers. comm.); analyses of Aqua de Ney and Keene Wonder Springs from White, Hem and Waring (1963); average sea water composition from Harvey (1955).

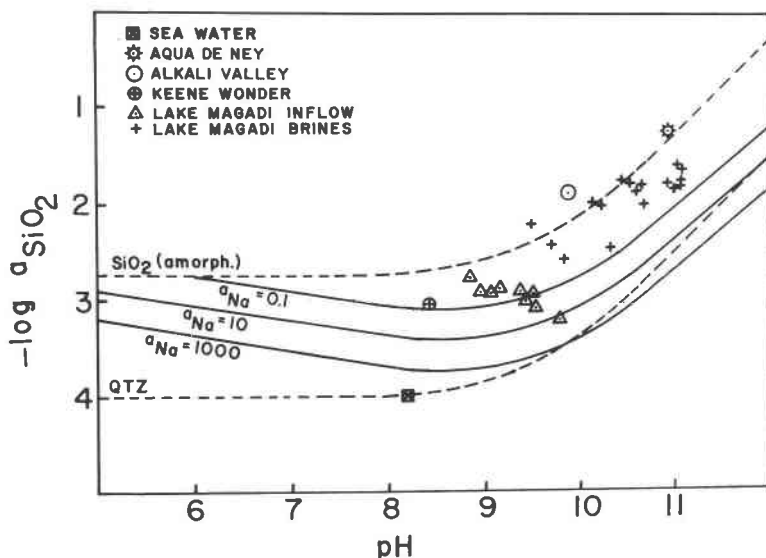


FIG. 4. Solubility curves for magadiite (this work) amorphous silica (Morey, Fournier, and Rowe, 1964) and quartz (Morey, Fournier, and Rowe, 1962) as functions of  $\log a_{\text{H}_4\text{SiO}_4}$  and pH at 25°C and one atm total pressure. Natural water compositions are the same as those plotted on Figure 3.

Arrhenius, 1958) and one would predict that magadiite should be observed in this environment in the absence of reactive aluminous phases. The chert horizons encountered by the JOIDES drilling project in the Atlantic may have been derived from a magadiite precursor. These cores should be examined for the presence of magadiite and other sodium silicate minerals. If reactive aluminum species are available, an aluminosilicate will form rather than a non-aluminous component, analogous to the reaction between sepiolite and aluminum rich phases described by Wollast, Mackenzie and Bricker (1968). The formation of sodium silicate minerals and of chert derived from these minerals would thus be restricted to interstitial waters of non-aluminous sediments in the marine environment. Figure 4 shows solubility curves of magadiite at various activities of sodium ion, relative to the solubility curves of quartz and amorphous silica. It can be seen that for all values of sodium ion activity the minimum in the solubility curve for magadiite occurs at about pH 9. At higher pH values the solubility of magadiite increases in response to the increasing solubility of silica. At lower pH values, the solubility of magadiite increases as a function of decreasing  $(\text{Na}^+)/(\text{H}^+)$  ratio. This second relation can be seen more clearly in Figure 3. Over the entire pH range an increase in the activity of  $\text{Na}^+$  increases the field of stability of

magadiite. Increasing the pH of systems with pH values below 9 or decreasing the pH of systems with pH values above 9 in which  $\text{Na}^+$  is fixed, decreases the solubility of magadiite. This provides a simple mechanism involving only the hydrogen ion activity for the precipitation of magadiite in natural systems. The decrease in pH of silica-rich alkaline brines in response to periodic influxes of fresh water could lead to the precipitation of magadiite. Likewise, the increase in pH of waters in closed basins in response to progressive evaporation might lead to the precipitation of magadiite.

When sediments containing magadiite are exposed to silica saturated soda-poor waters, the magadiite loses sodium ion and is converted to kenyaite. If the leaching process is continued, the kenyaite is depleted of sodium and inverts to chert. In this manner chert can be formed by an abiotic process.

The compositions of a number of natural waters have been plotted on Figures 3 and 4. The inflow waters feeding Lake Magadi are all undersaturated with amorphous silica but super-saturated with respect to magadiite and, with one exception, to kenyaite. The Lake Magadi brines are undersaturated, or in some cases saturated, with amorphous silica and all are saturated with respect to kenyaite. The Alkali Valley brine is supersaturated with both silica and kenyaite. Keene Wonder, an alkaline spring in Inyo Co., California, is undersaturated with silica but saturated with respect to magadiite while Aqua de Ney, a sodium chloride spring in Siskiyou Co., California, is saturated with amorphous silica and supersaturated with respect to kenyaite. No siliceous solids are precipitating from Lake Magadi inflow waters at the present time, except when these waters locally are evaporated to dryness during the dry season. Under these conditions silicate gel of albite composition precipitates (Eugster, pers. comm.). Siliceous solids have not been observed as precipitates from the Magadi brines, although these waters appear to be supersaturated with respect to kenyaite. The temperature of both the brines and the inflow waters is considerably above  $25^\circ\text{C}$ , in some cases reaching  $85^\circ\text{C}$ – $90^\circ\text{C}$ , but the equilibrium data available at this time are for  $25^\circ\text{C}$ . The elevated temperature and perhaps kinetics of the precipitation reaction could explain the apparent supersaturation. These data suggest that the solubility of magadiite and kenyaite probably increase very rapidly with increasing temperature. Magadiite has been observed precipitating from the Alkali Valley waters although, in composition, these waters plot the kenyaite field. The water temperature at the time of sampling was  $30^\circ\text{C}$ . The temperatures of waters from Keene Wonder and Aqua de Ney are close to  $25^\circ\text{C}$ . Keene Wonder is saturated with respect to magadiite and Aqua de Ney is supersaturated with respect to

kenyaite. Deposits from these springs have not yet been examined for magadiite and kenyaite but would be logical environments for the occurrence of these minerals.

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