

EXPERIMENTAL PRECIPITATION AND GENESIS OF SEPIOLITE AT EARTH-SURFACE CONDITIONS

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ABSTRACT

Reaction of aqueous silica with sea water produces a hydrated magnesium silicate similar to sepiolite in structure and composition. Our investigations indicate that sepiolite is the only non-aluminous, cation-bearing silicate that can be precipitated directly from sea water. Experiments with magnesium-free sea water and with magnesium chloride solutions show that cations other than Mg^{2+} are not involved in the precipitation of this compound. The equilibrium constant for the reaction: $2Mg^{2+} + 3SiO_{2(aq)} + (n+2)H_2O = Mg_2Si_3O_8(H_2O)_n + 4H^+$ has been determined experimentally at 25°C and one atmosphere total pressure and the ΔG°_f of dehydrated sepiolite calculated to be -903.3 ± 0.5 kcal/mole. Stability relations in the system $MgO-SiO_2-H_2O$ at 25°C and one atmosphere total pressure are examined and models for the genesis of sepiolite in the marine environment, the saline lake environment and by chemical weathering of ultramafic rocks are discussed.

INTRODUCTION

The genesis of clay minerals at earth-surface conditions has aroused the interest of investigators for many years. In particular, much attention has been paid to the origin of the magnesium-bearing clays, sepiolite, attapulgite, palygorskite, and magnesium montmorillonite. Recently the discovery of sepiolite and palygorskite in deep-sea sediments (Bonatti and Joensuu, 1968; Hathaway and Sachs, 1965), the excellent work of Millot (1962a, b) on the occurrence and origin of the magnesium-bearing clays in sedimentary rocks and that of Siffert (1962) and Siffert and Wey (1962) on the laboratory synthesis of these phases have provided us with much insight into the conditions of formation of these minerals. The stability of sepiolite and some other magnesium silicates at 25°C and 1 atmosphere pressure has been discussed by Hostetler (1960); however, little is known about the conditions necessary for equilibrium between these phases and natural waters.

Because of our continued interest in silicate mineral-sea water interactions (see references) as mechanisms for controlling the activities of chemical species in sea water, we decided to study the reactions that occur during the addition of sodium metasilicate to sea water. This addition results in the precipitation of a hydrated magnesium silicate similar

in composition and structure to sepiolite. In this paper, we define the conditions necessary for precipitation of sepiolite from sea water, and determine the equilibrium constant for the precipitation reaction and the free energy of formation of sepiolite. Also, we discuss the experimental results with regard to the formation of sepiolite in sedimentary deposits and to the chemistry of sea water.

PREVIOUS WORK

Recently, Hathaway and Sachs (1965) reviewed the studies pertaining to the occurrence and origin of sepiolite; we will present only a brief summary of the more recent work.

Authigenic sepiolite, as well as other magnesium-bearing clay minerals, is commonly found in Cretaceous and younger sedimentary deposits of marine and lacustrine origin (Bartholomé, 1966). Sepiolite has been found in modern deep-sea sediments associated with clinoptilolite, serpentine, chert, and coccolith ooze (Hathaway and Sachs, 1965). Interestingly, palygorskite has also been discovered in the deep-sea associated with the same minerals (Bonatti and Joensuu, 1968). Millot (1962a, b) reviewed thoroughly the literature concerned with the occurrence and genesis of sepiolite and other magnesium-bearing silicates in sedimentary rocks, particularly those of the African and French Tertiary basins. He concluded that these minerals form during or shortly after deposition of the associated sediments by reactions involving dissolved silica and magnesium. Hathaway and Sachs concluded that sepiolite obtained from samples dredged from the Mid-Atlantic Ridge formed by the reaction of dissolved Mg with silica derived from devitrification of silicic volcanic ash. Bonatti and Joensuu reported that palygorskite in a deep-sea sediment core collected from the Barracuda Escarpment in the western Atlantic formed by the action of hydrothermally-derived, Mg-rich solutions on montmorillonitic clay minerals.

Siffert and Wey (1962) and Siffert (1962) synthesized sepiolite at room temperature by adding NaOH to solutions saturated with amorphous silica and containing various concentrations of $MgCl_2$. Unfortunately, these authors do not report sufficient chemical data to determine the equilibrium conditions between sepiolite and aqueous solution. However, they do report that sepiolite precipitation obtains when the initial pH of their solutions is greater than 10. At these pH values, brucite ($Mg(OH)_2$) precipitates rapidly, and the formation of sepiolite may be promoted initially by precipitation of brucite that later reacted with dissolved silica.

Cole and Hueber (1956) reported the occurrence of a hydrated magnesium silicate of composition $4MgO \cdot SiO_2 \cdot 4H_2O$ formed by the action

of sea water on a concrete sea wall. They were able to synthesize this compound in the laboratory by reacting highly-aluminous cements with magnesium sulfate solutions, but could not form the compound directly from MgCl_2 and sodium silicate aqueous solutions. Both the natural and synthetic magnesium silicate phases were intimately associated with brucite; thus, the composition of the solid phase reported may be incorrect.

Magnesium silicate gels have been extensively studied (*e.g.*, Strese and Hofmann, 1941; Epprecht, 1947; Smirnova, Dushina, and Aleskovskii, 1966), but little data concerning equilibrium relations between the solid phase and aqueous solutions have been obtained from most of these studies. Smirnova, *et al.* reacted H-silica gel with 0.02 and 0.40 M solutions of MgCl_2 buffered at a pH of 9.4 with an ammonia buffer solution, and produced hydrated magnesium silicates compositionally similar to sepiolite. They determined the concentrations of the chemical species in solution after reaction, but did not attempt any equilibrium calculations. In the 0.40 M MgCl_2 solution, the product obtained after 18 days of reaction was $\text{MgO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$, and the final concentrations of Mg^{2+} and dissolved silica were 0.35 mole/liter and 1.3×10^{-4} mole/liter respectively. In the 0.02 M MgCl_2 solution, the product was $\text{MgO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$, and the final concentrations were 1.0×10^{-3} mole/liter and 1.3×10^{-3} mole/liter of Mg^{2+} and dissolved silica respectively. Because of the high pH of these ammonia-buffered solutions, it is possible that brucite was an early precipitate in these experiments.

PROCEDURE AND EXPERIMENTAL RESULTS

Our experiments were carried out by adding SiO_2 spikes to low-silica (~ 0.03 ppm SiO_2) sea water, freshly collected from Ferry Reach, Bermuda, and filtered through a 0.45μ Millipore filter. The solutions were placed in polyethylene containers, and these containers in turn were placed in water-jacketed glass reaction vessels to maintain the temperature of the experimental solutions at $25^\circ\text{C} \pm 0.5^\circ$.

The SiO_2 was added to sea water as a solution of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) adjusted to a pH of about 8.0 by addition of hydrochloric acid. The pH, SiO_2 and magnesium concentrations of the systems were monitored with time. The pH was measured with a glass electrode in conjunction with a saturated calomel reference electrode. Dissolved silica was determined by the method of Mullin and Riley (1955), magnesium by EDTA complexometry using Eriochrome Black T and Calred as indicators.

Addition of SiO_2 in the form of sodium metasilicate solutions to sea water results in the precipitation of a hydrated magnesium silicate. The

precipitates were investigated by means of X-ray diffractometry, electron microscopy, infrared and chemical analyses. In all cases the aqueous solutions were monitored until no further change in composition was observed. At this point we assumed that equilibrium between the solid phase and the solution had been achieved.

Solid Phase

Chemical analysis. The product formed by addition of sodium metasilicate to sea water is compositionally similar to sepiolite. The precipitates were analyzed chemically by the following steps: (1) The precipitate was dried at room temperature, and then heated at 1000°C for one hour to determine water loss, (2) The anhydrous product was treated with hydrofluoric and sulfuric acids, and then heated to 1200°C to determine SiO₂ loss, and (3) The remaining product was dissolved in hydrochloric acid, and magnesium was determined by complexometry.

The precipitates also were analyzed for other constituents besides Mg, SiO₂ and H₂O, such as Cl, Ca, and Na, but no significant amounts of other materials were found; the precipitates are nearly pure MgO-SiO₂-H₂O compounds. A representative chemical analysis of the precipitate is given in Table 1, and compared with analyses of some natural sepiolites. Our product resembles sepiolite in chemical composition; the product is somewhat higher in H₂O than the natural and theoretical mineral compositions but has essentially the same MgO/SiO₂ ratio.

X-ray analysis. Conventional X-ray diffractometer traces of the precipitate were not satisfactory for determining the nature of the precipitate because the product was so poorly crystallized; therefore, trans-

TABLE 1. CHEMICAL ANALYSIS OF COMPOUND PRECIPITATED FROM SEA WATER BY ADDITION OF SODIUM METASILICATE, COMPARED WITH NATURAL SEPIOLITES

	1	2	3	4	5
SiO ₂	45.8	52.50	52.97	55.65	47.61
MgO	23.8	21.31	22.50	24.89	20.04
H ₂ O	30.8	21.27	18.70	19.46	32.38
MgO/SiO ₂	0.64	0.61	0.63	0.67	0.67

1. Sepiolite, Mid-Atlantic Ridge (Hathaway and Sachs, 1965).
2. Sepiolite, Ampandrandava, Madagascar (Caillere, 1936).
3. Sepiolite, Little Cottonwood, Utah, U.S.A. (Nagy and Bradley, 1955).
4. Sepiolite, 8H₂O·(Mg₈(H₂O)₄(OH)₄Si₁₂O₃₀), theoretical composition for structure proposed by Brauner and Preisinger, 1956.
5. Precipitate.

mission Laue camera and Guinier focussing camera patterns of the randomly oriented precipitates were obtained on a standard Phillips-North American x-ray machine using Cu $K\alpha$ radiation. Aluminum metal was used as an internal standard. Table 2 gives the X-ray powder data for the precipitates compared with data for synthetic and natural sepiolites. Comparison of the X-ray data indicates that the structure of our synthetic compound is similar to that of synthetic and natural sepiolite. However, the high background in the region of the 12 Å and 7.5 Å peaks prevented their detection. To confirm the chemical and x-ray data for

TABLE 2. X-RAY POWDER DATA FOR NATURAL AND SYNTHETIC SEPIOLITES

<i>hkl</i> (Brindley, 1959)	Natural Sepiolite		Synthetic Sepiolite		
	Little Cotton- wood, Utah, USA (Nagy & Bradley, 1955)	Mid-Atlantic Ridge (Hathaway and Sachs, 1965)	Siffert (1962)	Epprecht (1947)	This work
110	12.05 (100) ^a	12.13	12.3	—	—
130	7.47 (10)	7.56	7.6	—	—
200, 040	6.73 (5)	6.68	—	—	—
150	5.01 (7)	5.07	4.9	—	—
060	4.498 (25)	4.503	4.5	4.54	4.53
131	4.306 (40)	4.312	4.3	—	—
330	4.022 (7)	4.03	—	4.16	4.15
260	3.750 (30)	3.735	3.75	3.74	3.77
241	3.533 (12)	3.509	3.49	—	—
080	3.366 (30)	3.344	—	3.38	3.32
331	3.196 (35)]	3.184	—	—	3.20
261	3.050 (12)	—	2.98	—	—
370	2.932 (4)	—	—	—	—
081	2.825 (7)	—	—	2.84	—
421	2.771 (4)	—	—	—	—
0·10·0, 510	2.691 (20)	2.684	2.67	—	—
441, 281	2.617 (30)	2.619	—	—	—
530	2.586 (NR)	2.592	—	—	—
112, 371, 191	2.560 (55)	2.561	—	2.52	2.56
2·10·0	—	2.512	2.49	—	—
132	2.479 (5)	—	—	—	—
202, 042	2.449 (25)	2.443	2.43	—	2.46
1·11·0, 222, 461	2.406 (15)	—	2.36	—	2.32
062, 312, 2·10·1	2.263 (30)	2.261	2.24	—	2.22
620, 570, 332	2.206 (3)	—	2.08	—	2.11

* Relative intensities.

NR = not resolved.

the precipitate we also performed infrared and electron microscopic investigations.

Infrared analysis. Infrared absorption spectra of the precipitate and of natural hydrated magnesium silicates were obtained from KBr disks with a double-beam spectrophotometer. The spectra obtained are compared in Figure 1. The absorption peaks of the precipitate are similar to those of sepiolite in agreement with the results of the chemical and x-ray data.

It is important to note the absence of the sharp peak (3720 cm^{-1}) of brucite in the spectrum of our precipitate. Brucite was not precipitated in our experiments because the titrations were carried out at pH values of about 8.0. At higher pH values, brucite and calcium carbonate precipitate from sea water. The broad bands at 3400 cm^{-1} and 1630 cm^{-1} in the precipitate spectrum indicate that the solid contains a large amount of non-structural water.

Electron microscopy. An electron micrograph of the sepiolite precipitate is shown in Figure 2. The precipitate consists of packets of needles approximately $0.2\text{--}0.3\ \mu\text{n}$ in length, and is similar in appearance to the synthetic sepiolite pictured in an electron micrograph by Siffert (1962).

Composition of the aqueous phase in equilibrium with sepiolite

General experiments. Table 3 shows the composition of sea water before and after addition of SiO_2 in the form of solutions of sodium metasilicate. Before addition of silica, the sea water contained about 0.03 ppm SiO_2 and 58.8 mMoles of Mg^{2+} , and had a pH of 8.2 to 8.3. The addition of SiO_2 resulted in the precipitation of sepiolite, and SiO_2 and Mg^{2+} were removed from the sea water solutions. The pH of the solutions decreased slightly during reaction. The reactions were carried out until the pH and concentrations of SiO_2 and Mg^{2+} remained constant. At this point it was assumed that equilibrium between the precipitated solid and solution had been achieved, and the final pH, SiO_2 and Mg^{2+} concentrations were determined (Table 3).

Specific experiments. Several additional experiments were carried out to clarify the sepiolite-sea water reaction. Magnesium and calcium were removed from sea water by addition of NaOH. Enough calcium was then added to the sea water in the form of $\text{Ca}(\text{OH})_2$ to restore the calcium concentration to its original value, and the pH adjusted to 8.2 with hydrochloric acid. The resulting Mg-free sea water was titrated with a sodium metasilicate solution, adjusted to a pH of 8.2 by addition of hydrochloric acid, until 80 ppm of dissolved silica were added to the sea water. No solid precipitated from the sea water immediately, or upon standing for 30 days. The SiO_2 concentration of the solution after

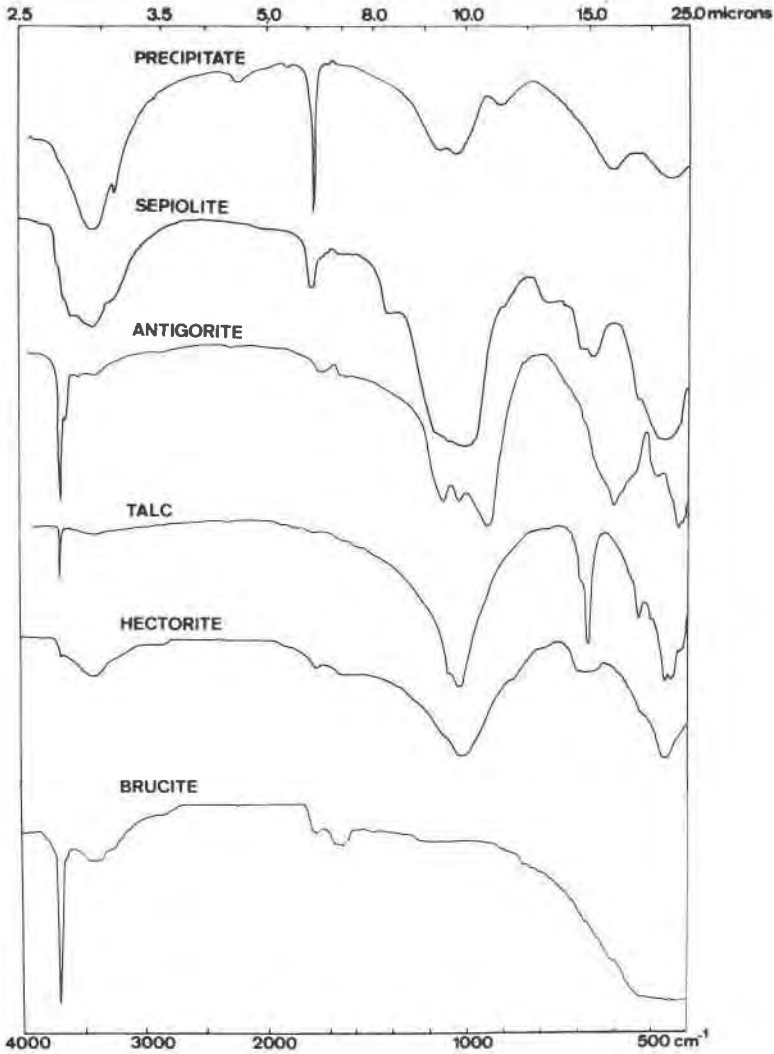


FIG. 1. Infrared absorption spectrum of the product precipitated from sea water by addition of sodium metasilicate compared with the spectra of some natural magnesium silicates and brucite. The spectra were obtained from KBr disks with a double-beam spectrophotometer.

30 days was 80 ppm. We conclude from this experiment that a magnesium silicate is the only non-aluminous, cation-bearing silicate that will precipitate from sea water.

To confirm this conclusion and to determine whether other ions are

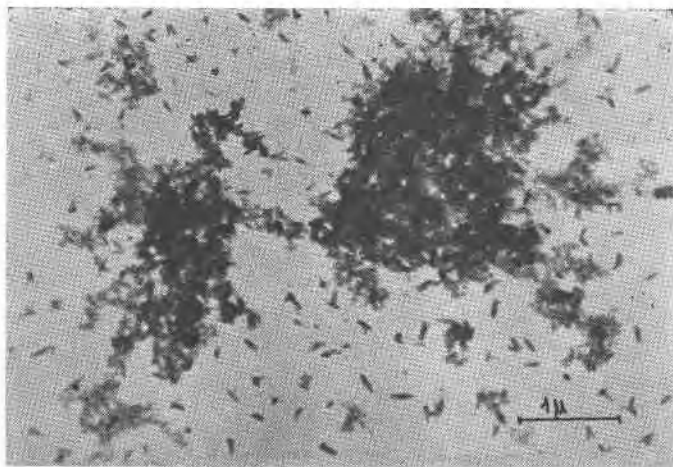


FIG. 2. Electron micrograph of synthetic sepiolite precipitated from sea water by addition of sodium metasilicate. Precipitate consists of packets of needle-shaped crystals about 0.2–0.3 μ in length.

necessary for the precipitation of sepiolite from sea water, a 0.1 M MgCl_2 solution was titrated with sodium metasilicate solution until 100 ppm of SiO_2 were added to the solution. The addition of SiO_2 to the MgCl_2 solution resulted in the precipitation of sepiolite; the same product as obtained from the sea water precipitations. This experiment confirms and expands our previous conclusion that Mg^{2+} is necessary for the precipitation of a nonaluminous, cation-bearing silicate from sea water. However, the titration of MgCl_2 solutions shows that the other ions in sea water are not necessary for the formation of this solid.

To gain insight into the effect of pH on the precipitation of sepiolite from sea water, we added OH^- ion to sea water by (1) titrating sea water with unbuffered sodium metasilicate solutions that had initial pH values greater than 10, (2) adding a small volume of 0.1 N NaOH to sea waters in equilibrium with sepiolite and, (3) adding the same initial amount of SiO_2 to sea waters with pH values ranging from about 7.5 to 9.0.

In the first experiment (1), the titrations resulted in a rapid rise in pH to a value of about 9.4, and precipitation of both brucite and sepiolite. Some previous studies of magnesium silicate synthesis at moderately alkaline pH must be viewed with caution because of the co-precipitation of brucite.

In the second experiment (2), the addition of NaOH to sea water equilibrated with sepiolite resulted in the precipitation of more sepiolite, a lowering of the equilibrium SiO_2 concentration, and a rise in the equi-

TABLE 3. ADDITION OF VARIOUS AMOUNTS OF SODIUM METASILICATE TO SEA WATER.

Composition of the Solution After Reaction. Values of pK for the Reaction $2Mg^{2+} + 3SiO_{2(aq)} + (n+2)H_2O = Mg_2Si_3O_8(H_2O)_n + 4H^+$ are Also Given. Sea Water Initially Contained about 0.03 ppm SiO_2 and 58.8 mMoles Mg^{++} and was Filtered Through a 0.45 μ Millipore Filter. Initial pH was 8.2-8.3. All Experiments were Run at $25^\circ C \pm 0.5^\circ$ and 1 Atmosphere Total Pressure

Amount SiO_2 added to sea water (ppm)	Concentration SiO_2 after reaction		Concentration Mg^{2+} after reaction mmoles	pH after reaction	pK = $-\log \left(\frac{a_{H^+}^4}{a_{Mg^{2+}}^2 a_{SiO_{2(aq)}}^3} \right)$
	ppm	mmoles			
26	21.8	.363	58.4	8.26	19.36
26*	18.8	.314	58.3	8.11	18.58
39	25.1	.419	57.4	7.98	18.36
39*	16.5	.275	57.0	8.19	18.72
40	28.6	.476	58.3	8.07	18.96
50	26.3	.438	54.6	8.09	18.86
52	25.1	.418	57.3	8.02	18.52
52*	17.5	.292	57.1	8.20	18.82
60	28.1	.468	57.4	8.12	19.13
65	29.6	.494	58.3	7.87	18.17
65*	19.0	.316	57.4	8.04	18.30
80	34.2	.570	55.2	8.16	19.49
80	28.5	.475	57.2	8.15	19.28
100	29.7	.495	54.6	8.16	19.29
120	23.7	.395	54.6	8.18	19.07
130	26.7	.445	55.0	7.99	18.51
130*	12.1	.201	55.7	8.11	17.94
140	23.7	.395	53.2	8.15	18.93

* Results after addition of 1 ml of 0.1N NaOH to previous solutions and re-equilibration. Mean value of pK = 18.78. Mean deviation is ± 0.36 . $a_{Mg^{2+}}$ calculated using an activity coefficient ($\gamma_{Mg^{2+}}$) of 0.36 for Mg^{2+} in sea water (Garrels and Thompson, 1962).

brium pH value (Table 3). In the third experiment (3), the sea waters with high pH values contained less SiO_2 after reaction than the waters with low pH.

These experiments show that the sepiolite-sea water equilibrium is definitely pH dependent. Also the rapid precipitation of sepiolite at higher pH values suggests that the rate of reaction depends on the concentration of OH^- ion. Figure 3 illustrates a titration curve as a function of time for a 0.1 M $MgCl_2$ and 140 ppm SiO_2 solution titrated with 0.10 M NaOH. Successive increments of NaOH were added to the solution, and with each increment the pH was monitored until a constant value was achieved. The addition of NaOH resulted in initial slow precipitation of sepiolite at lower pH values, and more rapid precipitation of both sepiolite and brucite at higher pH values. At the end of the titration, all

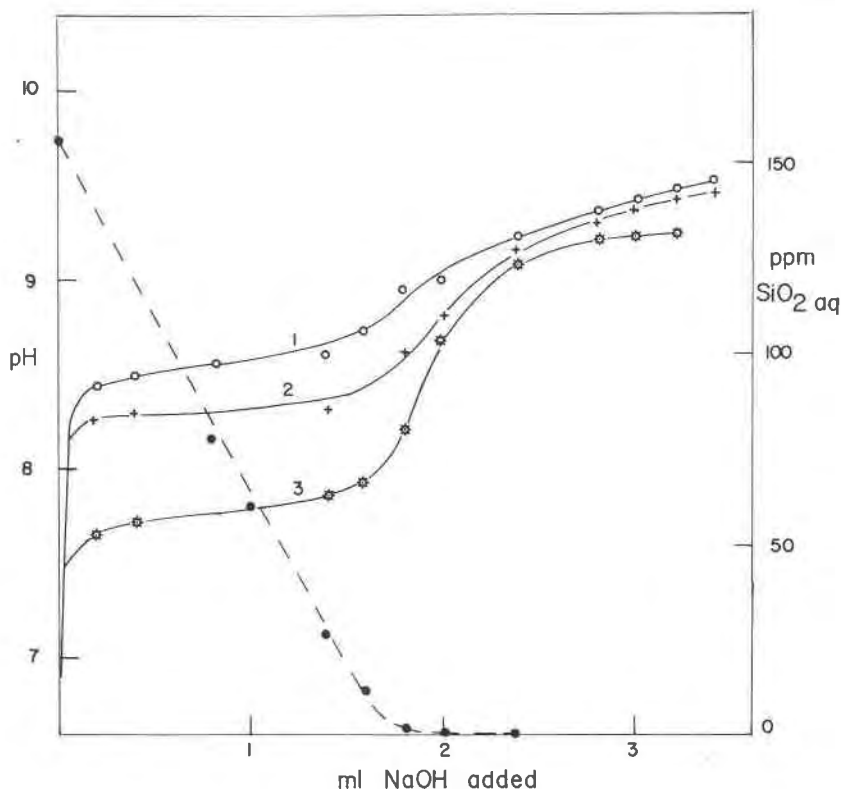


FIG. 3. Titration curve for addition of 0.10 M NaOH to a 0.1 M MgCl₂ solution containing 140 ppm SiO_{2aq} initially. 1, after one hour. 2, after 26 hours. 3, after 15 days. Dashed curve shows ppm SiO_{2aq} after 15 days.

the SiO₂ was consumed. From Figure 3, it can be seen that the rate of reaction depends on the concentration of OH⁻ ion.

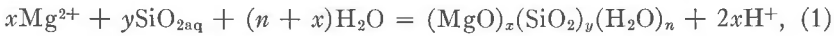
Several other NaOH titrations of MgCl₂-SiO₂ solutions of various concentrations were carried out. However, the mechanism of precipitation of hydrated magnesium silicates by addition of NaOH to MgCl₂-SiO₂ solutions is complicated, and the initial solids are commonly richer in Mg than the sepiolite precipitate obtained from sea water. These initial Mg-rich precipitates may be metastable.

EQUILIBRIUM CONSTANT CALCULATION AND ΔG°_f SEPIOLITE

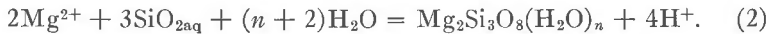
The chemical and mineralogical data show that the precipitate is sepiolite containing SiO₂ and MgO in the ratio of 3 to 2. Because we know the composition of the solid and the composition of the sea water in

equilibrium with the solid, we are able to calculate an equilibrium constant for the sepiolite precipitation reaction at 25°C and 1 atmosphere total pressure.

The general reaction may be written



and in terms of a solid with a SiO₂/MgO ratio of 3/2



The equilibrium constant for this reaction is

$$\frac{a_{\text{H}^+}^4}{a_{\text{Mg}^{2+}} a_{\text{SiO}_{2\text{aq}}}^3} = K_{(2)}, \quad (3)$$

assuming both the solid and H₂O have an activity of one. The values of the equilibrium constant for reaction (2) as calculated from the data in Table 3 and an activity coefficient for Mg²⁺γ_{Mg²⁺} of 0.36 (Garrels and Thompson, 1962) are given in Table 3. The mean value of K₍₂₎ is 10^{-18.78}.

The free energy of formation of sepiolite containing no water (ΔG^o_{f sepiolite}) may be calculated from the relationship

$$\Delta G^\circ_{\text{reaction}} = \Delta G^\circ_{\text{f products}} - \Delta G^\circ_{\text{f reactants}}, \quad (4)$$

where ΔG^o_{reaction} at 25°C and 1 atmosphere total pressure is

$$\Delta G^\circ_{\text{r}} = -1.364 \log K. \quad (5a)$$

The ΔG^o_r for the sepiolite precipitation reaction is

$$\Delta G^\circ_{\text{r}} = -1.364 (-18.78) = 25.62 \text{ kcal.} \quad (5b)$$

From equations (2) and (4), neglecting the free energy contribution of H₂O, except that necessary to balance the reaction, we may write

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{f sepiolite}} + 4\Delta G^\circ_{\text{f H}^+} - 2\Delta G^\circ_{\text{f Mg}^{2+}} \\ &\quad - 3\Delta G^\circ_{\text{f SiO}_{2\text{aq}}} - 2\Delta G^\circ_{\text{f H}_2\text{O}}, \end{aligned}$$

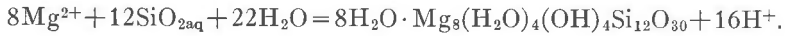
and from 5b and free energy values of Rossini, *et al.* (1952)

$$25.62 = \Delta G^\circ_{\text{f sepiolite}} + 4(0) - 2(-108.99) - 3(-199.2) - 2(-56.69)$$

$$\Delta G^\circ_{\text{f sepiolite}} = -903.3 \pm 0.5 \text{ kcal/mole.}$$

This value is for dehydrated sepiolite; the amount of H₂O in the sepiolite structure is variable and thus the free energy of formation of natural sepiolites varies somewhat. However, we may calculate ΔG^o_{f sepiolite} for the theoretical composition of the structure of sepiolite proposed by

Brauner and Preisinger (1956) to provide an estimate of the ΔG°_f of natural sepiolites. The theoretical composition is $8\text{H}_2\text{O} \cdot \text{Mg}_8(\text{H}_2\text{O})_4(\text{OH})_4 \text{Si}_{12}\text{O}_{30}$. According to the general reaction (1), the reaction for precipitation of this solid from sea water is written



The equilibrium constant is

$$K^1 = \frac{a_{\text{H}^+}^{16}}{a_{\text{Mg}^{2+}}^8 a_{\text{SiO}_{2\text{aq}}}^{12}} = K_{(2)}^4 = 10^{-76.12},$$

and the free energy of formation for the theoretical composition of sepiolite is

$$\begin{aligned} \Delta G^\circ_{f \text{ sepiolite}} &= \Delta G_r^\circ + 8\Delta G^\circ_{f \text{ Mg}^{2+}} + 12\Delta G^\circ_{f \text{ SiO}_{2\text{aq}}} + 22\Delta G^\circ_{f \text{ H}_2\text{O}} \\ &\quad - 16\Delta G^\circ_{f \text{ H}^+} = 4(25.62) + 8(-108.99) + 12(-199.2) \\ &\quad + 22(-56.69) = -4,407.0 \text{ kcal/mole.} \end{aligned}$$

DISCUSSION

The results of the experiments and calculations reported above provide us with the information necessary to draw some conclusions concerning the genesis of sepiolite at earth-surface conditions. Figure 4 shows an activity diagram for the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ at 25°C , unit activity of H_2O and one atmosphere total pressure. The diagram was constructed according to the techniques given in Garrels and Christ (1966) using the ΔG°_f sepiolite calculated in this paper, the ΔG°_f brucite (Hostetler, 1963), and a ΔG°_f of amorphous silica consistent with a solubility of 115 ppm dissolved silica (Morey, Fournier, and Rowe, 1964). The diagram illustrates well the influence of pH on the sepiolite-sea water equilibrium. Less silica is required to precipitate sepiolite from moderately alkaline sea waters than from moderately acid waters. If silica is added to sea water and the pH maintained at a relatively low value, sepiolite does not form, even metastably; instead the sea water becomes saturated with respect to amorphous silica.

We also have plotted in Figure 4 the compositions of some natural waters that are of interest to the problem of sepiolite genesis as functions of the concentrations of Mg^{2+} , H^+ , and SiO_2 . Surface sea waters and most fresh waters (average chemical compositions of streams and of the Great Lakes are given as examples) are undersaturated with respect to sepiolite; however, some saline waters are saturated or oversaturated.

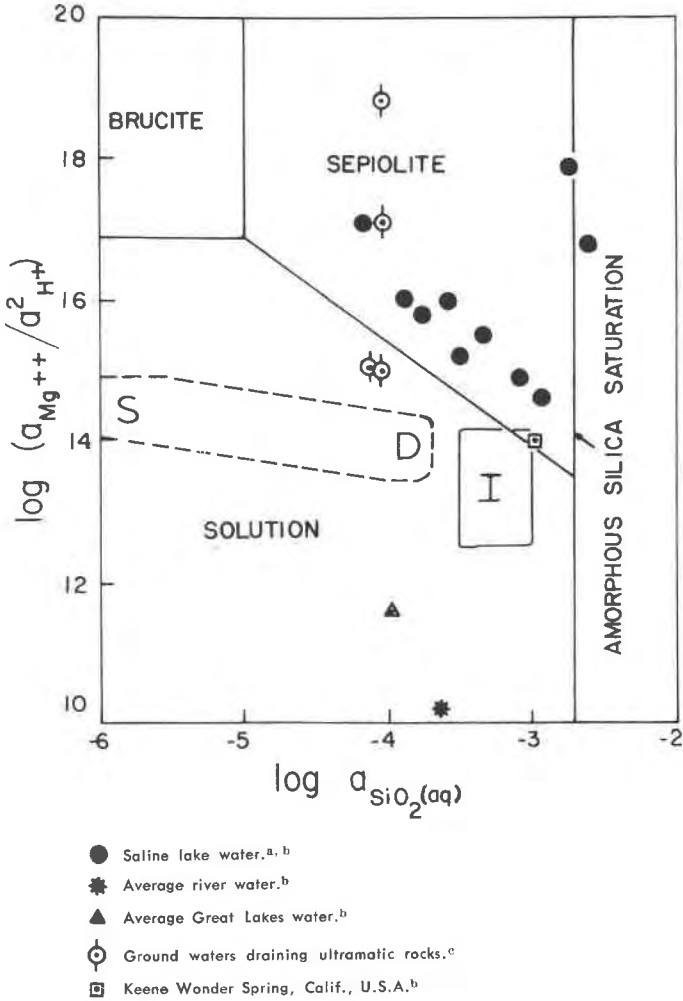


FIG. 4. Activity diagram for a portion of the system MgO-SiO₂-H₂O at 25°C, unit activity of H₂O, and one atmosphere total pressure. The positions of the stability field boundaries were calculated from thermodynamic data (Hostetler, 1963; Rossini, *et al.*, 1952), the free energy of formation of sepiolite obtained in this paper, and are consistent with an amorphous silica solubility of 115 ppm (Morey, Fournier, and Rowe, 1964). The various symbols represent water analyses plotted as functions of $\log m_{Mg^{2+}}/a_{H^+}^2$ and $\log a_{SiO_{2(aq)}}$ from: (a) Saline lake water pH values calculated from total HCO₃⁻ and assumed equilibrium with atmospheric P_{CO₂} = 10^{-3.6} atmospheres. (b) River, Great Lakes and Keene Spring data from Livingstone, D. A., 1963. (c) Ground water data from Barnes, I., La-Marche, Jr., V. C. and Himmelberg, G., 1967. The areas labeled S, D, and I represent the composition of surface, deep, and interstitial sea water respectively.

Genesis of sepiolite in the saline or alkaline lake environment. Sepiolite commonly is found in recent and ancient sedimentary deposits formed in saline or alkaline lacustrine environments (see Rateev, Pokidin, and Kheirov, 1963; and Millot, 1960 a, b). This occurrence is consistent with the saline water analyses shown in Figure 4. Notice that a group of saline waters exhibit a trend that closely parallels the saturation boundary of sepiolite; these waters may actually be in equilibrium with sepiolite, or a similar hydrated magnesium silicate phase. In fact, if $a_{\text{Mg}^{2+}}/a_{\text{H}^+}^2$ could be plotted instead of $m_{\text{Mg}^{2+}}/a_{\text{H}^+}^2$, these saline water analyses would fall even closer to the sepiolite-solution boundary.

Saline and alkaline lakes are found in areas where annual evaporation exceeds precipitation. Stream waters entering the lake basins are concentrated by evaporation. Garrels and Mackenzie (1967) showed that the theoretical evaporation in equilibrium with atmospheric P_{CO_2} and at 25°C of waters derived from springs draining feldspathic igneous rocks in the Sierra Nevada and separated from their weathering residues should lead to a water of saline lake composition. They showed that a direct result of this evaporation would be the precipitation of sepiolite. A reasonable model for the formation of sepiolite in saline or alkaline lake environments based on the above discussion would be:

1. Dilute waters derived from rock weathering enter a lake basin in which evaporation exceeds precipitation, and the waters are concentrated at earth-surface temperatures with concomitant rise in pH.
2. If dissolved silica is not abstracted by biochemical processes, *e.g.*, uptake of silica by diatoms, sepiolite may precipitate directly from the water (see Figure 4).
3. If silica is abstracted by organisms to the extent that the activity of silica in the lake water is lowered below sepiolite saturation, Mg will precipitate in another phase, *e.g.*, hydromagnesite or brucite. However, in the interstitial waters of low-silica saline and alkaline lakes, diatoms will redissolve and sepiolite may form as an authigenic mineral in the lake sediment, probably by reaction between an earlier formed Mg-bearing phase and dissolved silica.

Genesis of sepiolite in the marine environment. Surface and deep sea water at 25°C and one atmosphere total pressure is undersaturated with respect to sepiolite (Figure 4). The recent discovery of sepiolite in a modern deep-sea environment (Hathaway and Sachs, 1965) shows that sepiolite does form in the marine environment, but it is certainly not as common a product of this environment as the Mg-aluminosilicate chlorite. It can be seen from Figure 4 that the sepiolite saturation boundary cuts through

the area representing marine interstitial water compositions. Some of these waters are saturated with respect to sepiolite. However, cold bottom waters are not saturated; their silica concentrations are too low. In cold marine interstitial waters containing moderately high dissolved silica concentrations due to the dissolution of diatoms or the devitrification of volcanic glass, sepiolite may precipitate directly from aqueous solution by the reaction presented previously. The solubility of sepiolite probably decreases with decreasing temperature; thus, the increased thermodynamic stability of sepiolite with decreasing temperature could promote the formation of sepiolite in the cold, interstitial waters of deep-sea sediments. However, if aluminum is available in reactive aluminous phases in the sediment a Mg-aluminosilicate (chlorite-like clay minerals) will form instead of sepiolite. Experimental and theoretical work (*e.g.* Sillén, 1961; Holland, 1965; Mackenzie, *et al.*, 1965, 1966, 1967) suggests that cation-aluminosilicates instead of nonaluminous silicates are stable in the marine environment under most conditions. The scarcity of sepiolite in modern and ancient marine deposits and the relative abundance of chlorite in these same types of deposits substantiate this conclusion.

The mechanism proposed above for the formation of sepiolite in marine sediments should not be overgeneralized. Sepiolite commonly is found in limestones and calcite marls of presumed marine origin, particularly from the Cretaceous and Tertiary periods. Some of these carbonate sediments probably formed in small, shallow-water, marine basins sufficiently isolated from communication with open-ocean water so that the waters in these basins became highly saline. In this case, if silica were not removed from solution by organisms, sepiolite could precipitate from the concentrated sea water. Shallow marine waters often have higher pH values during the day because of the photosynthetic activity of marine plants; such diurnal increases in pH could initiate the precipitation of sepiolite. Alternatively, some of these carbonate sediments were probably deposited in normal salinity sea waters, and the sepiolite in them may have formed as described above for deep-sea sediments. Interestingly, the common association of sepiolite with carbonate sediments that are low in aluminum, but not with shales that are high in aluminum and commonly contain chlorite, suggests that sepiolite forms in the carbonate-depositing environment because of the lack of aluminum.

Genesis of sepiolite by the chemical weathering of ultramafic rocks. Sepiolite is found associated with serpentine (*e.g.* Caillère and Henin, 1949), and is believed to be an alteration product of mafic minerals. Chemical analyses of several ground waters derived from the chemical weathering of ultramafic rocks containing primarily olivine, pyroxene, and serpentine are

shown in Figure 4. The ultrabasic waters with pH values greater than 11 are oversaturated with respect to sepiolite; the slightly alkaline magnesium bicarbonate waters are only slightly undersaturated. The origin of these waters is discussed in detail by Barnes, *et al.* (1967). The chemical weathering of ultramafic rocks may lead to the formation of brucite and magnesium carbonates, as well as a spectrum of magnesium silicates. The specific weathering reactions and the compositional changes involving mafic minerals and weathering solutions are not well known. However, it is obvious from Figure 4 that sepiolite could form by reactions involving mafic minerals, such as olivine, and weathering solutions. These reactions could conceivably result in the production of ground waters saturated with respect to sepiolite.

SUMMARY

The behavior of magnesium in the geochemical cycle has been of increasing interest to geologists, particularly with respect to sea water-sediment equilibria. We investigated the conditions under which the magnesium silicate sepiolite precipitates from sea water, determined the equilibrium constant for the reaction at 25°C and one atmosphere total pressure and calculated a free energy of formation for sepiolite. Additional experimental work in magnesium-free sea water and in magnesium chloride solutions indicate that: (1) sepiolite is the only nonaluminous, cation-bearing silicate that will precipitate directly from sea water as the dissolved silica concentration is increased, (2) other ions present in sea water (aside from Mg^{2+} , $SiO_{2(aq)}$, and OH^-) are not necessary for the formation of sepiolite, and (3) depression of the pH of sea water prevents the precipitation of sepiolite and allows the concentration of silica (in the absence of other regulatory mechanisms) to increase to saturation with respect to amorphous silica.

The genesis of sepiolite under some common environmental conditions and its significance as an environmental indicator have been discussed. Sepiolite occurs in saline and/or alkaline lakes, as a weathering product of ultramafic rocks, and in the marine environment. The most important factors in the genesis of sepiolite are: (1) absence of aqueous aluminum species and of reactive aluminous solid phases, and activities of Mg^{2+} , OH^- , and SiO_2 consistent with the equilibrium constant for sepiolite (*e.g.* moderately high silica concentrations and low $a_{Mg^{2+}}/a_{H^+}^2$; moderately low silica concentrations and high $a_{Mg^{2+}}/a_{H^+}^2$). In the presence of aluminum, magnesium will be incorporated into aluminosilicate structures such as chlorite instead of precipitating as sepiolite. If there is biologic (*e.g.* diatoms) or mineralogic (*e.g.* clay minerals) control that keeps silica concentration low, sepiolite will not precipitate. If the pH of the en-

vironment is maintained in the slightly acidic to acidic range, sepiolite will not precipitate and silica (in the absence of another regulatory mechanism) will increase to saturation with respect to amorphous silica.

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