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SEPIOLITE ASSOCIATED WITH MIOCENE DIATOMITE, SANTA CRUZ BASIN, CALIFORNIA

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ABSTRACT

Sepiolite has been found as veinlets in Middle Miocene diatomite recovered in a dredge haul made on the southeast wall of Santa Cruz Basin, California Continental Borderland. The sepiolite is moderately well crystallized and of normal chemical composition, but has unusual dehydration characteristics and a fibrous to membrane-like habit. The precipitation of sepiolite under these previously unrecorded conditions is caused by reaction of magnesium-rich ground water or sea water with silica-rich connate water of the diatomite. Thermodynamic considerations indicate that sepiolite is probably in equilibrium with sea water in contact with diatomite.

INTRODUCTION

The formation of sepiolite in marine sediments has been reported several times (Hathaway and Sachs, 1965; Rex, 1970); and the mineral is found with altered volcanic ash or clinoptilolite, presumably derived from volcanic ash. The sepiolite reported here, although formed in marine sediments, is not associated with volcanic ash or its alteration products, but with diatomite. The material was collected in a dredge haul made by the research vessel Velero IV of the University of Southern California during an investigation of the walls of Santa Cruz Basin. This basin occupies a central position in the northern California Continental Borderland, and is flanked by banks of predominantly Miocene sediments (summarized by Emery, 1960; Moore, 1969). The dredge haul was made on a scarp along the southeastern side of the basin, at about 33° 32′ N, 119° 17′ W, from 1590 to 605 m (Fig. 1). When brought on board, the dredge was filled with olive-gray surficial mud, which upon closer examination was found to contain several freshly fractured, cobble-size pieces of soft, friable gray lutite that appeared to be broken from an outcrop. A pale yellow, pearly, jelly-like substance, later identified as sepiolite partly coated exposed fractures of the lutite and penetrated it along veinlets. A sample of the sepiolite was scraped off and stored in a sealed container for subsequent examination, and the remainder was dried at room conditions. No significant differences were later observed between the wet and dry samples.

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Closer study of the lutite revealed it as a laminated, calcareous, radiolarian-rich diatomite of Middle Miocene age (Luisian) (Barnes, 1969). Carbonate content by gasometric analysis was found to be 10 percent, and consists mostly of foraminiferal tests and coccolithopore fragments. The sepiolite, which assumed a light yellowish-gray, scaley appearance upon drying, is confined to fractures oriented perpendicular to the laminae (Fig. 2). The scales are faintly striated at right angles to the laminae, suggesting fault-type movement along the fractures. The fractures formed after the diatomite attained its present semiconsolidated state, possibly during uplift of the basin wall. The sepiolite was emplaced after this event, and perhaps after re-exposure on the sea floor.

The sepiolite was identified from X-ray diffraction scans, which were made of the material in its original wet state, of air-dried material at room conditions and in dry air, of glycerol-saturated material, and after heat treatment to 325° C. The dry-air scan produced the most detailed pattern (Table 1). Agreement with the calculated pattern and with other sepiolites (Brindley, 1959) is fair. A slight contraction of the 110 spacing accompanied the progressive drying. This spacing measured 12.6, 12.4, and 12.2 Å for samples run wet, at room conditions (about 50 percent relative humidity), and in dry

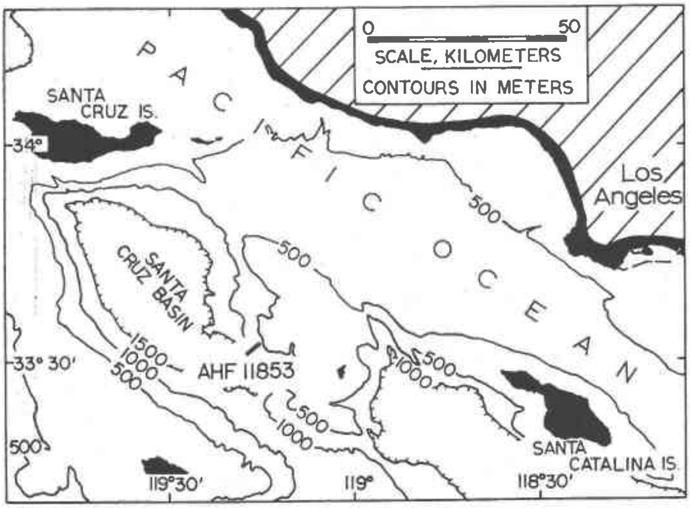

FIG. 1. Map showing location where sepiolite was recovered on California Continental Borderland.

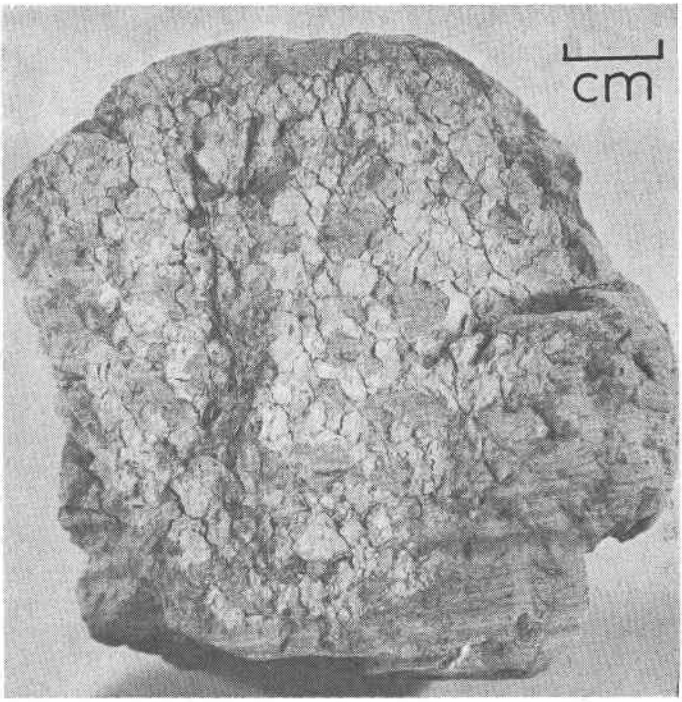

FIG. 2. Laminated diatomite with scaley sepiolite covering fracture surface.

air, respectively; and increases in 12.7 Å upon saturation with glycerol. Heating to 325° C resulted in contraction to 11.9 Å, but did not alter the pattern appreciably. This temperature is at the threshold of irreversible dehydration of sepiolite (Martin-Vivaldi and Cano-Ruiz, 1956) and explains the observed contraction. A weak, but sharp and persistent pattern of dolomite was recorded with sepiolite. An X-ray diffraction pattern of the diatomite revealed a low, broad band at 4.0 Å, such as is characteristic of the disordered cristobalite structure of opaline substances. Other minerals recorded were calcite, small quantities of quartz, illite, and apatite, and traces of halite, kaolinite, feldspar, and sepiolite.

Differential thermal analysis of the sepiolite produced three highly reproducible endotherms at 144°, 168°, and 195° C, but the sharp endotherm followed by an exotherm between 700–800° C characteristic of sepiolite (Grim, 1968) is either missing or considerably weakened and shifted to 800–900° C (Fig. 3). The DTA curve for the diatomite corresponds well to those of opaline materials (Flörke, 1955; Franks and Swineford, 1959).

The sepiolite fibers are in part rather large, and can easily be observed with a petrographic microscope. Examination with a scanning electron microscope reveals a felted, fibrous morphology, with fiber widths as large as 3μ. The fibers are intimately intergrown, and terminations are rare. In places the sepiolite is not fibrous at all, but assumes a membrane-like habit (Fig. 4a). Solution of siliceous tests was noted in a few instances, and replacement of a rod-like object by sepiolite was observed in one case (Fig. 4b) The free-standing fibers and membrane-like habit, however, imply that direct crystallization predominated.

Spectrographic analyses of carefully picked but unavoidably impure sepiolite and of diatomite from which carbonates had been removed with a pH 5 sodium acetate solution (Jackson, 1956), show the presence of a large number of minor elements in addition to Si and Mg (Table 2). The observed clay minerals, apatite, and feldspar suffice to explain the more abundant minor-element concentrations, and the siliceous tests undoubtedly contribute to the trace elements. The sepiolite contains, with a few exceptions, of which Fe is most notable, a smaller number and lesser quantities of minor elements. By a direct comparison it is apparent that these elements come from the contaminating diatomite rather than from the sepiolite. The minor-element proportions of the two analyses indicate that the sepiolite is

TABLE 1. X-RAY DIFFRACTION DATA FOR SEPIOLITE FROM SANTA CRUZ BASIN

hkl[1]	d(Å)[2]	I[3]	hkl[1]	d(Å)[2]	I[3]
110	12.2	300	$0^{o}10^{o}$,510, 441,281 }	2.67	10NR
130	7.60	10			
200, 040	6.53	20B	530,022,112, 371,191 }	2.58	10NR
150	5.07	6			
060	4.53	12	202,042	2.442	3
131	4.31	10	550,$1^{o}11^{o}0$, 222,461 }	2.39	4NR
041	4.12	6			
260	3.79	10	062,312,$2^{o}10^{o}1$	2.26	5NR } B
170	3.70	12	620,570,332	2.225	9NR
080,420,331	3.30	30NR	402,082	2.89 }	5B,NR
261	3.02	4	601	2.047	
081	2.823	2	571	2.029	4
421	2.771	3			

[1] Indices of calculated pattern for sepiolite (Brindley, 1959).

[2] X-ray diffractometer, Cu $K\alpha$ radiation, 1 20 / min scanning speed, ½ in / min chart speed, time constant, 2 sec. Partially oriented mount, 1% relative humidity.

[3] Relative intensities, B - broad; NR - not resolved.

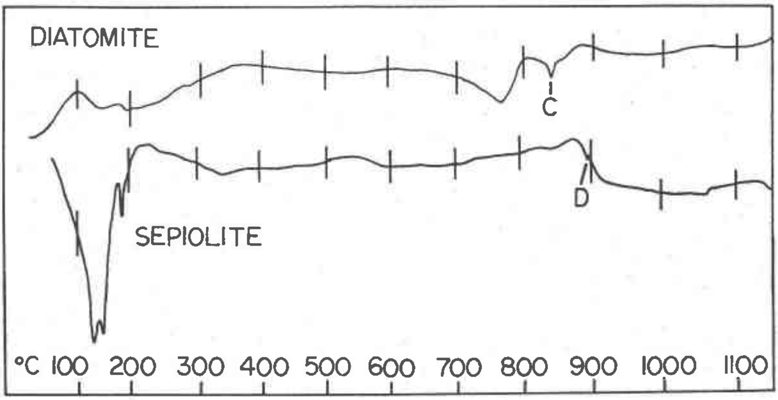

Fig. 3. Differential thermal analysis curves for Santa Cruz Basin sepiolite and diatomite. C—calcite endotherm; D—dolomite endotherm.

contaminated with 10–20 percent diatomite, an estimate that is confirmed by visual inspection of the material. Calculated chemical analyses from the spectrographic analyses and from water determinations are given in Table 3. Compared to the theoretical composition of sepiolite based on the structure of Brauner and Preisinger (1956), the Santa Cruz Basin sepiolite appears to contain less MgO and more Fe_2O_3 and CaO. Taking the diatomite contamination of 10–20 percent into account, the SiO_2:MgO ratio is very close to that of the theo-

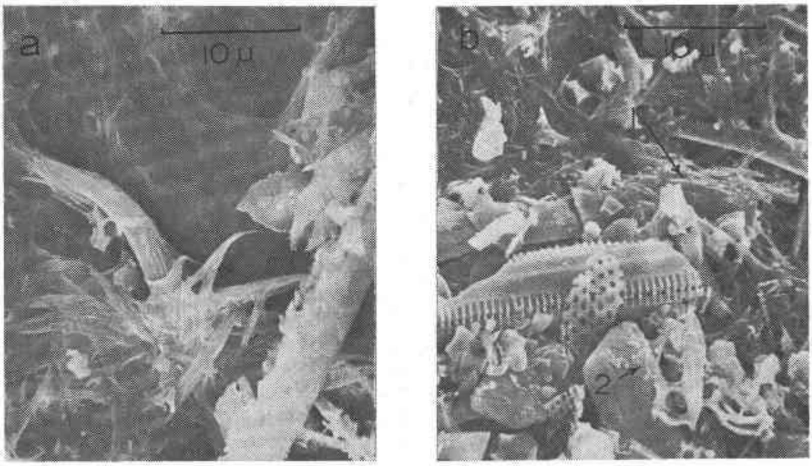

Fig. 4. Scanning-electron photomicrographs of sepiolite, a) coarsely fibrous and membrane-like sepiolite; b) sepiolite replacing a rod-shaped object (1), and fragment of radiolarian test showing solution (2).

retical composition. The CaO is attributed in part to the diatomite also, but some of it could be from dolomite which may not have been removed completely by the mild leaching. The Fe_2O_3 appears to be bound with the diatomite, as no evidence of other iron phases was observed, making it a slightly ferriferous sepiolite. The water content of the sepiolite is close to that of the theoretical composition (Table 3), but a much greater proportion than expected is lost above 110° C. This anomaly is reflected by the DTA curve (Fig. 3), which displays a large multiple endotherm between 140–200° C. Water loss below 110° C is attributed to that which is adsorbed in the channels of the sepiolite structure (Nagy and Bradley, 1955). In the Santa Cruz Basin sepiolite, this water appears to be retained into the 140–200° C range.

DISCUSSION

Reviews on the origin of sepiolite (Hathaway and Sachs, 1965; Heron and Johnson, 1966) show that this mineral can form in diverse sedimentary environments, from alteration of serpentine, and under hydrothermal conditions. Experimental work suggests that a high pH (Siffert and Wey, 1962) or a Ca-rich environment (Mumpton and Roy, 1958) is necessary to form sepiolite. Sedimentary sepiolite has been reported in ancient saline or alkaline lakes or embayments (Bradley, 1929; Millot, 1962a, b; Buie and Gremillion, 1963), on the sea floor (Hathaway and Sachs, 1965), and in desert soils (Vanden

TABLE 2. SPECTOGRAPHIC ANALYSES OF SEPIOLITE AND DIATOMITE FROM SANTA CRUZ BASIN[1]

MAJOR ELEMENTS			MINOR ELEMENTS		
	Sepiolite	Diatomite		Sepiolite	Diatomite
Si	32. %	37. %	Ag	<.0001%	.00081%
Al	.33	2.3	B	<.002	.0070
Ti	.020	.10	Cr	.0092	.037
Fe	1.4	1.0	Cu	.0061	.014
Mg	14.	1.0	Ni	.0030	.034
Ca	.99	4.7	Mn	.036	.023
Na	.66	1.4	Mo	0.0	.013
K	0.0	<.020	Sn	.050	.028
P	0.0	.94	Sr	.0056	.054
			V	.0016	.020
			Zr	0.0	.011
			Other elements		
				0.0	0.0

[1] Carbonates and NaCl removed prior to analysis. Relative accuracy of analysis is ± 15%. H. W. Johnson, analyst.

TABLE 3. CHEMICAL COMPOSITION OF SEPIOLITES AND DIATOMITE

	1	2	3	4
SiO_2	55.65	52.50	53.22	47.19
Al_2O_3		0.60	0.48	2.59
TiO_2			0.03	0.10
Fe_2O_3		2.90	1.56	0.85
FeO		0.70		
MnO			0.04	0.02
MgO	24.89	21.31	18.05	0.99
CaO		0.47	1.08	9.64
Na_2O			0.69	1.13
K_2O			0.00	0.14
P_2O_5			0.00	1.28
CO_2				4.48
H_2O^-	11.12	12.06	6.67	3.46
H_2O^+	8.34	9.21	15.58	26.72
Total	100.00	99.75	97.40	98.59

1. Sepiolite, theoretical composition, $8H_2O^{o}\left[Mg_8(H_2O)_4(OH)_4(Si_{12}O_{30})\right]$, Brauner and Preisinger (1956).

2. Sepiolite, Ampandrandava, Madagascar (Caillere, 1936).

3. Sepiolite, California Borderland. Oxides SiO_2 through P_2O_5 recalculated from spectrographic analysis.

4. Diatomite, California Borderland. Oxides SiO_2 through P_2O_5 recalculated from spectrographic analysis.

Heuvel, 1966; Grim, 1968, p. 516). Within these environments, the chemical conditions and the constituents required to form sepiolite have been supplied by concentration of weathering products in basins or soil zones, volcanic ash, dolomite, marl, or a combination of these.

The conditions favorable to the formation of the Santa Cruz Basin sepiolite have been met by a combination of parameters that is somewhat different than those listed above. However, as is evident from its habit and its restricted occurrence along fractures in the essentially unaltered diatomite, the sepiolite has formed predominately by direct crystallization at low temperature. Silica from diatom and radiolarian tests is a potential source that is readily available due to the large surface area and high permeability of the diatomite, and a small amount of solution has been confirmed by observation. The presence of calcareous tests may also have contributed to the conditions required for sepiolite formation by providing the Ca as suggested by Mumption and Roy (1958).

The low MgO content of the diatomite and the restriction of sepiolite to fractures indicates that Mg was derived from an external source and moved in solution through the fractures to react with connate water of the diatomite. The source of Mg may have been (1) sea water which entered the fractures after the diatomite was deformed and re-exposed on the sea floor, (2) Mg-rich ground water from elsewhere in the bank, or (3) a combination of these two sources. Direct entry of sea water as a source of Mg cannot be ruled out entirely, but is less likely than a ground water source because special circumstances are needed to allow sea water to enter the fractures, and a considerable quantity would be needed to form the sepiolite. A mixing of sea water and ground water is even less likely because the conditions for such an event to occur within the fractures are further limited. Movement of ground water through Tertiary strata of the eastern margin of Santa Cruz Basin is the least restrictive source from spatial considerations, and would be facilitated by deformation and uplift of this area. From evidence of petrologic studies, it is highly probable that such ground water would be Mg-rich. Miocene strata in southern California are dolomitic in places on the mainland (Spotts and Silverman, 1966) and on the borderland (Pierce and Melson, 1967). Extensive dolomitization, dolomite veins several inches thick, and magnesium sulfate deposits in the vicinity of andesitic intrusions within Miocene strata have been observed by the author in the Palos Verdes Hills, 100 km east of Santa Cruz Basin.

An estimate of the stability of sepiolite in sea water has been made by Wollast, Mackenzie, and Bricker (1968) from an experimental study in which they determined the conditions of pH, $a_{Mg^{2+}}$, and $a_{SiO_2(aq)}$ under which this mineral will precipitate from sea water. Their calculations indicate that sepiolite is unstable in sea water at 25°C., but that deep sea water approaches the stability field of sepiolite, and that some interstitial sea waters are within it. Using the theoretical composition of sepiolite obtained by Brauner and Preisinger (1956), they assume sepiolite forms by the reaction

$$8Mg^{2+} + 12SiO_{2aq} + 22H_2O = 8H_2O \cdot Mg_8(H_2O_4)(OH)_4Si_{12}O_{30} + 16H^+,$$

for which the equilibrium constant is given by

$$K = a_H{}^{16}/(a^8{}_{Mg^{2+}} + a^{12}{}_{SiO_2(aq)})$$

The equilibrium constant indicates that the stability of sepiolite in sea water is strongly dependent on pH, and by calculating the stability field of sepiolite, they show that it is necessary to raise the pH of sea water, in addition to increasing the dissolved silica concentration, to precipitate sepiolite from sea water. Wollast, Mackenzie, and Bricker

(1968) also suggest that the stability of sepiolite probably increases at lower temperatures, thus promoting formation of sepiolite in cold, interstitial waters. This effect, however, may be counteracted by a solubility decrease of amorphous silica at lower temperatures, from 115 ppm at 25°C to about 60 ppm at 0–5°C (Morey, Fournier, and Rowe, 1964; Krauskopf, 1956).

These equilibrium relations of sepiolite determined by Wollast, Mackenzie, and Bricker (1968) support the conclusions on the origin of the Santa Cruz Basin sepiolite as inferred by its occurrence. They discredit the possibility that the sepiolite formed by a simple mixing of sea water with silica-rich connate water of the diatomite; and instead indicate an origin by mixing of magnesium-rich, possibly high-pH ground water with connate water of the diatomite.

The association of sepiolite with diatomite is one that might be expected to occur more frequently than the absence of reports indicates. Diatomite is a ubiquitous constituent in the Upper Tertiary of southern California and occurs in several large commercial deposits (Woodring, Bramlette, and Kew, 1946; Diblee, 1950). A large and potentially favorable environment not previously investigated may thus be available to the formation of sepiolite.

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