# SEPIOLITE AND CLINOPTILOLITE FROM THE MID-ATLANTIC RIDGE<sup>1</sup>

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#### Abstract

Sepiolite has been found in samples dredged from the Mid-Atlantic Ridge. The mineral is intimately associated with laminated clay and coccolith ooze, both containing clinoptilolite; one sample contained chert. Serpentine was recovered in the same dredge, but the sepiolite seems to have formed by the reaction of Mg in solution with  $SiO_2$  liberated during alteration of silicic volcanic ash, rather than by direct alteration of the serpentine.

### INTRODUCTION

Early in 1963, about 15 rock dredge hauls were made in equatorial Atlantic waters from the Woods Hole Oceanographic Institution's research vessel CHAIN. These hauls were concentrated near Saint Paul's Rocks, a region where the Mid-Atlantic Ridge is displaced laterally by a number of large faults. One of the hauls, CH 35 Dr. 11 was made near 01°23'S, 29°49'W, (Fig. 1). About 11.5 kilograms of rock were brought to the surface in dredging a slope from a depth of 4,200 to 3,600 meters. Most of this rock probably had been encountered near a depth of 3,600 meters. There the dredge snagged, the ship became anchored by the trawl wire, and it was necessary to back over the dredge to break it loose from the bottom.

The dredge haul was composed of the material listed in Table 1.

Figures 2 and 3 show two views of a representative piece of the white waxy material (type III) as it was found in the dredge. Most pieces of the type illustrated consist of nearly white or very light tan, generally tabular masses ranging up to  $17 \times 19 \times 6$  centimeters. When wet the pieces were very soft, had a greasy talclike feel and a pearly luster. Upon drying they became harder and more earthy. Many of the pieces are foliated, and some are intimately associated with lenses or layers of finely laminated brown clay. In places, veins of the white material cut through the clay and form boxwork structures. These veins can be seen cutting laminated clay in the bottom part of the piece after removal of the brown clay by handpicking. Light-brown clay also coats the surfaces of the pieces. At least one and usually both flat surfaces of the tabular white material are coated with a thin manganiferous crust, and one of the pieces contained intercalated bands of hard white cherty material.

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.



FIG. 1. Chart of the equatorial Atlantic Ocean showing the location of dredge haul Ch 35 Dr. 11.

Much of the material is traversed by burrows up to 7 mm in diameter (Fig. 3); this is some indication of the hardness in situ. The interiors of many of the burrows are entirely coated with a thin manganiferous crust of nearly uniform thickness.

At the depth where the material was found, hydrostatic pressure is about 350 bars and water temperature is between 2° and 3° C.

# MINERALOGIC EXAMINATION

A sample of the white waxy mineral from the type III material was dried, ground, and packed as a randomly oriented powder for x-ray

| Туре | Description   | % by Weight |
|------|---|-------------|
| I    | Rounded weathered brownish cobbles and pebbles of serpentine                            | 37          |
| Π    | One angular, slickensided cobble of granular magnetite with minor amounts of serpentine | 31          |
| III  | Masses of white waxy material with pearly luster, and light-brown clay                  | 21          |
| IV   | Cobbles and pebbles of friable chalky material containing numerous burrows              | 3<br>11     |

| THE | TABLE | 1. | DREDGE | HAUL | MATERIA |
|---|-------|----|--------|------|---------|
|---|-------|----|--------|------|---------|

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FIG. 2. Piece of type III material showing sepiolite (top) with veins cutting through laminated brown clay (lower right). Each small division of scale is 1 mm.

examination. Additional samples of the white mineral were not dried but dispersed in distilled water and mounted on porous tiles by drawing the water of the suspension through the tiles by vacuum. A thin layer of the mineral thus remains on the surface of the tile. One tile mount was left untreated, one was treated with ethylene gycol, and a third was heated



FtG. 3. Back of piece shown in Fig. 2 showing borings lined with manganiferous material. One large boring appears above 2.4 on the scale. Each small division of scale is 1 mm.

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FIG. 4. A piece of type III material showing boxwork of sepiolite veins remaining after removal of the laminated brown clay. Each small division of scale is 1 mm.

to 40 ° C. X-ray diffractometer patterns were made of the randomly oriented powder and of the tile mounted material. Another x-ray diffractometer pattern was made of the heated tile after further heating to 550° C. These patterns indicate that the white mineral in the type III material is sepiolite. Figure 7A shows the pattern for the randomly oriented powder; a comparison of the x-ray powder diffraction data of this sample with data for sepiolite from Utah (Brindley, 1959) is given in Table 2. An electron micrograph showing the fibrous shape of our sepiolite particles is shown in Figure 5. One of the pieces contained quartz in the form of intercalated white chert bands. The brown clay associated with the type III material, shown as laminated masses and coatings of the pieces in Figs. 2, 3 and 4, was found on similar x-ray examination to be composed of montmorillonite, a zeolite, and a small amount of sepiolite (Fig. 7C). The zeolite was identified as clinoptiloite, rather than heulandite, on the basis of the resistance of its structure to thermal attack. The clinoptilolite in the brown clay persisted after heat treatment at 800° C. for 20 minutes. Mumpton (1960), and Shepard (1961) showed that heulandite first undergoes a phase change by heating at temperatures of 250°-300° C. and then is destroyed at about 500° C. Previous unpublished work on heulandite and clinoptilolite by Hathaway confirmed these results. A comparison of the x-ray powder data for clinoptilolite from Hector, California, with the  $>8\mu$  fraction from the

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brown clay described above is shown in Table 3. Removal of the clav and very fine silt-sized particles concentrated the clinoptilolite in nearly pure form. Examination of the  $>8\mu$  fraction under the petrographic microscope showed a large number of stubby laths and irregular aggregates of clinoptilolite, a small amount of quartz, a few unidentified isotropic grains with medium index of refraction, and rare dolomite rhombs. The x-ray diffraction pattern for the  $> 8\mu$  fraction is shown in Fig. 7D.

A sample of the white chalky material from the type IV pieces (Fig.

|  |                                | d(Å)                                    |                    |                    |                    |  |  |  |
|--|--------------------------------|---|--------------------|--------------------|--------------------|--|--|--|
|  | h k l <sup>1</sup>             | Little Cottonwood,<br>Utah <sup>1</sup> |                    | Mid-Atlantic Ridge |                    |  |  |  |
|  | 110                            | 12.05                                   | (100) <sup>2</sup> | 12.233             | (100) <sup>2</sup> |  |  |  |
|  | 130                            | 7.47                                    | (10)               | 7.56               | (5)                |  |  |  |
|  | 200, 040                       | 6.73                                    | (5)                | 6.68               | (4)                |  |  |  |
|  | 150                            | 5.01                                    | (7)                | 5.07               | (3)                |  |  |  |
|  | 060                            | 4.498                                   | (25)               | 4.503              | (11)               |  |  |  |
|  | 131                            | 4.306                                   | (40)               | 4.312              | (10)               |  |  |  |
|  | 330                            | 4.022                                   | (7)                | 4.033              | (2)                |  |  |  |
|  | 260                            | 3.750                                   | (30)               | 3.735              | (7)                |  |  |  |
|  | 241                            | 3.533                                   | (12)               | 3.509              | (4B)               |  |  |  |
|  | 080                            | 3.366                                   | (30)               | 3.344              | (14)               |  |  |  |
|  | 331                            | 3.196                                   | (35)               | 3.184              | (8)                |  |  |  |
|  | 261                            | 3.050                                   | (12)               |                    |                    |  |  |  |
|  | 370                            | 2.932                                   | (4)                |                    |                    |  |  |  |
|  | 081                            | 2.825                                   | (7)                |                    |                    |  |  |  |
|  | 421                            | 2.771                                   | (4)                |                    |                    |  |  |  |
|  | 0.10.0, 510                    | 2.691                                   | (20)               | 2.684              | (7B)               |  |  |  |
|  | 441, 281                       | 2.617                                   | (30)               | 2.619              | (6B)               |  |  |  |
|  | 530                            | 2.586                                   | (NR)               | 2.592              | (8B)               |  |  |  |
|  | 112, 371, 191                  | 2.560                                   | (55)               | 2.561              | (12)               |  |  |  |
|  | $2 \cdot 10 \cdot 0$           |   |                    | 2.512              | (4B)               |  |  |  |
|  | 132                            | 2.479                                   | (5)                |                    | ,                  |  |  |  |
|  | 202, 042                       | 2.449                                   | (25)               | 2.443              | (2)                |  |  |  |
|  | $1 \cdot 11 \cdot 0, 222, 461$ | 2.406                                   | (15)               |                    |                    |  |  |  |
|  | 062, 312, 2 · 10 · 1           | 2.263                                   | (30)               | 2.261              | (6)                |  |  |  |
|  | 620, 570, 332                  | 2.206                                   | (3)                |                    |                    |  |  |  |

TABLE 2. X-RAY POWDER DATA FOR SEPIOLITE

<sup>1</sup> Brindley (1959).

<sup>2</sup> Numbers in parentheses are relative intensities. B—broad, NR—not resolved.

<sup>3</sup> X-ray pattern was made using the following instrumental factors: Cu K $\alpha$  radiation,  $\lambda = 1.54050$ ; 40 KVP; 40 MA; scanning speed 1/4°/min.; chart scale 1/4°/in.; time constant 0.5 sec.; scale factor 2,000 cps full scale; low angle cut-off 2° 20; NaCl present in sample served as internal standard.

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FIG. 5. Electron micrograph of a Pt preshadowed replica of the sepiolite showing its fibrous structure.

6) was also prepared as a randomly oriented powder, and an x-ray diffractometer pattern was made. A strong diffraction pattern for calcite was produced by this material, but a considerable insoluble residue was obtained by solution of the calcite in dilute acetic acid. Gasometric determination of  $CO_2$  in the sample gave about 40% CaCO<sub>3</sub>. An x-ray diffractometer pattern (Fig. 7B) of this insoluble residue showed sepiolite and clinoptilolite. Petrographic and electron microscopic examination of the type IV material showed that the calcite fraction is mostly coccolith ooze with some discoasters. Attempts to observe the relationship of the coccolith material to the sepiolite and clinoptilolite by electron microscope replication techniques were not successful. Some pieces of the type III material showed intercalations of sepiolite and white chalky coccolith ooze like that of the type IV material.

A sample of the sepiolite from the type III material was selected for chemical analysis. Care was taken to avoid contamination by the brown clay associated with the sepiolite. In Table 4 the chemical composition of this sepiolite is compared with four relatively pure sepiolite samples reported in the literature and with the theoretical composition based on the structure proposed by Brauner and Preisinger (1956).

As the sample was preserved in water-tight containers prior to analysis,

|                                 | d(Å)                   |
|---------------------------------|------------------------|
| Hector, California <sup>1</sup> | Mid-Atlantic Ridge     |
| 9.00 (100) <sup>2</sup>         | 9.0 (100) <sup>2</sup> |
| 7.94 (40)                       | 7.96 (61)              |
| 6.77 (30)                       | 6.78 (14)              |
| 6.64 (20)                       |                        |
| 5.91 (10)                       | 5.92 (14)              |
| 5.24 (30)                       | 5.25 (12)              |
| 5.11 (10)                       | 5.12 (31)              |
| 4.69 (20)                       | 4.65 (18)              |
| 4.48 (20)                       | 4.49 (10)              |
| 4.34 (20)                       | 4.35 (6)               |
| 3.96 (100)                      | 3.96 (71)              |
| 3.90 (80)                       | 3.91 (34)              |
| 3.83 (10)                       | 3.83 (4)               |
| 3.73 (10)                       | 3.70 (9)               |
| 3.55 (20)                       | 3.55 (11)              |
| 3.46 (20)                       | 3.50 (9)               |
| 3.42 (60)                       | 3.42 (25)              |
|                                 | 3.16 (21)              |
| 3.12 (30)                       | 3.12 (10)              |
| 3.07 (20)                       | 3.07 (10)              |
| 3.04 (20)                       | 3.035 (18)             |
| 2.97 (50)                       | 2.965 (31)             |
| 2.87 (10)                       | 2.900 (4)              |
| 2.82 (30)                       | 2 705 (22)             |
| 2.80 (10)                       | 2.195 (22)             |
| 2.73 (10)                       | 2.730 (9)              |
| 2.72 (10)                       |                        |
| 2.68 (10)                       |                        |
| 2.44 (10)                       | 2.430 (6)              |

TABLE 3. X-RAY POWDER DATA FOR CLINOPTILOLITE

<sup>1</sup> Mumpton (1960).

<sup>2</sup> Numbers in parentheses are relative intensities.

the high value for  $H_2O$ -shown in analysis 1 probably results from the retention of interstitial sea water. Samples left exposed to room air soon lost their waxy luster and became chalky in appearance through loss of retained water. If it is assumed that most of the low temperature water is interstitial, a recalculation of the analysis to allow about 10%  $H_2O$ -(An amount in agreement with previous analyses and with the theoretical composition) shows good agreement with other analyses of relatively pure sepiolites. The low value for  $H_2O$ + may indicate that some of the low-temperature water actually is zeolitic water which should have been

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FIG. 6. A piece of type IV material (coccolith ooze and associated sepiolite) showing numerous burrows with manganiferous linings. Piece is about 6 cm. in diameter.

assigned to  $H_2O+$ . Sodium is an expected impurity, as the sample was originally in contact with sea water, and weak halite lines were observed on the x-ray diffraction pattern. Less than one per cent CaCO<sub>3</sub> is present. Aluminum and iron probably are due to small amounts of the associated brown clay that were not removed in hand picking of the samples. A semiquantitative spectrographic analysis (Table 5) shows that, with the above exceptions, this sepiolite is quite pure.

## DISCUSSION

The deposits of sepiolite which are documented in the literature may each be assigned to one of four general kinds of field association:

1. With deposits formed in highly saline or alkaline lacustrine environments. Examples of recent deposits of this kind are reported by Yarzhemskiĭ (1949) and Rateev and others (1963). Examples in ancient deposits are described by De Serres (1818), Bradley (1930), Rateev and Osipova (1958), Millot (1960a), and Regis (1961).

2. With dolomite and marl. Examples are reported by Brougniart (1822), Longchambon and Mourgues (1927), Rateev (1954), Rogers *et al.* (1954), Keeling (1956), Rateev and Kotel'nikov (1956), Kaveev (1960) and Mueller (1961). Some of these dolomites and marls probably formed under conditions covered by category (1) but it is not always clear



FIG. 7. X-ray diffractometer traces of material from the Mid-Atlantic Ridge. Instrumental settings were as follows: Cu K $\alpha$  radiation; 40 KVP; 40 MA; 2°/min. scanning speed; scale factor, 1000 counts/sec full scale; time constant, 1.0 second, traces A and D are from randomly oriented powders; B and C are from oriented aggregates.

whether the sepiolite formed in the lacustrine environment or during diagenesis of the sediment. Sepiolite has also been observed by Hathaway in dolomite and dolomitic sediment from Florida.

3. With serpentine, and believed to be an alteration product from the serpentine. Examples are reported by Smith (1849), Bonatti (1932), Caillère and Hénin (1949), Zhuĭkova (1953), Yusupova (1955), Muraoka *et al.* (1958) and Maksimovic and Radukic (1961).

4. Directly crystallized from hydrothermal solutions or as products of hydrothermal alteration. Examples are described by Serdyuchenko (1949), Aurola (1956) and Midgley (1959).

The boundary between categories (3) and (4) is not sharp. In some cases alteration of serpentine may have taken place under either hydrothermal or weathering conditions; in other cases sepiolite in association with serpentine may not have resulted from the alteration of the serpentine but may have been deposited directly by hydrothermal solutions as proposed by Aurola (1956).

|                   | 1    | 2    | 3     | 4     | 5      | 6      |
|-------------------|------|------|-------|-------|--------|--------|
| $SiO_2$           | 45.8 | 56.1 | 52.50 | 52.97 | 54.97  | 55.65  |
| $Al_2O_3$         | 0.35 | 0.42 | 0.60  | 0.86  | 0.26   |        |
| $Fe_2O_3$         | 0.16 | 0.20 | 2.90  | 0.70  | 0.21   |        |
| FeO               | 0.04 | 0.05 | 0.70  |       |        |        |
| Mn O              | 0.00 | 0.00 |       | 3.14* |        |        |
| CaO               | 0.28 | 0.34 | 0.47  |       |        |        |
| MgO               | 19.8 | 24.3 | 21.31 | 22.50 | 25.35  | 24.89  |
| CuO               | **   | **   |       | 0.87  |        |        |
| Na <sub>2</sub> O | 0.92 | 1.13 |       |       | 0.09   |        |
| $K_2O$            | 0.09 | 0.11 |       |       | 0.02   |        |
| $H_2O-$           | 25.6 | 10.0 | 12.06 | 8.80  | 9.25   | 11.12  |
| $H_2O+$           | 5.2  | 6.4  | 9.21  | 9.90  | 10.04  | 8.34   |
| $TiO_2$           | 0.00 | 0.00 |       |       |        |        |
| $P_2O_5$          | 0.10 | 0.12 |       |       |        |        |
| $\mathrm{CO}_2$   | 0.22 | 0.27 |       |       | 0.76   |        |
| Cl                | ***  | ***  |       |       |        |        |
| Total             | 99   | 99   | 99.75 | 99.74 | 100.25 | 100.00 |

TABLE 4. CHEMICAL ANALYSES OF SEPIOLITE

1. Sepiolite, Mid-Atlantic Ridge (analysts: Paul Elmore, Sam Botts, Gillison Chloe, Lowell Artis and H. Smith).

2. Analysis 1, above, recalculated to 10% H<sub>2</sub>O- (see text).

3. Sepiolite, Ampandrandava, Madagascar (Caillère, 1936).

4. Sepiolite, Little Cottonwood, Utah (Nagy and Bradley, 1955).

5. Sepiolite, Goles, South Serbia (Maksimovic and Radukic, 1961).

6. Sepiolite, theoretical composition for structure proposed by Brauner and Preisinger (1956),  $8H_2O \cdot [Mg_8(H_2O)_4 (OH)_4 (Si_{12}O_{30})]$ .

\* Mn reported as Mn<sub>2</sub>O<sub>3</sub>.

\*\* See Table 5.

\*\*\* A qualitative test shows Cl to be present.

There does seem to be a clear-cut separation between the first two categories, the sedimentary occurrences, and categories (3) and (4), the nonsedimentary occurrences. None of the reports of sedimentary materials indicate that either the alteration of serpentine or the introduction of hydrothermal material was involved in the formation of the sepiolite.

The occurrence of sepiolite in a deep-sea environment has not been reported previously. At first the serpentine recovered in the same dredge haul (type 1 material) seemed to be a possible source for the sepiolite. This serpentine is brown and weathered, and contains veins of white material. Thin-sections and x-ray diffraction patterns of these materials showed no sepiolite, only calcite, various pyroxenes and amphiboles,

| Major elements,   | not look | ed for: (See T | able 4). |      |    |    |    |
|-------------------|----------|----------------|----------|------|----|----|----|
| •                 | Si       |                | Ca       |      |    | Р  |    |
|                   | Al       |                | Na       |      |    | Mn |    |
|                   | Fe       |                | K        |      |    |    |    |
|                   | Mg       |                | Ti       |      |    |    |    |
| Elements found:   |          |                |          |      |    |    |    |
|                   | В        | 0.0007         | Cu       | 0.01 |    |    |    |
|                   | Ba       | 0.0007         | Ni       | 0.01 |    |    |    |
| Looked for, not f | ound:    |                |          |      |    |    |    |
| Ag                |          | Cr             | Mo       |      | Sn |    | W  |
| As                |          | Ga             | Nb       |      | Sr |    | Y  |
| Au                |          | Ge             | Pb       |      | Та |    | Ye |
| Be                |          | Hf             | Pd       |      | Te |    | Zn |
| Bi                |          | Hg             | Pt       |      | Th |    | Zr |
| Cd                |          | In             | Re       |      | Tl |    |    |
| Ce                |          | La             | Sb       |      | U  |    |    |
| Co                |          | Li             | Sc       |      | V  |    |    |
| Not looked for:   |          |                |          |      |    |    |    |
| Pr                |          | Tb             | Lu       |      | Cs |    |    |
| Nd                |          | Dy             | In       |      | Rb |    |    |
| Sm                |          | Ho             | Os       |      | F  |    |    |
| Eu                |          | Er             | Rh       |      |    |    |    |
| Gd                |          | Tm             | Ru       |      |    |    |    |
|                   |          |                |          |      |    |    |    |

TABLE 5. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS<sup>1</sup> OF SEPIOLITE FROM MID-ATLANTIC RIDGE

(J. L. Harris, Analyst)

<sup>1</sup> Results are reported in per cent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc. which represent approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results will include the quantitative value about 30% of the time.

and minerals of the serpentine group; the brown color seems to be iron oxide staining of the serpentine. Sepiolite is associated only with light brown laminated clay, friable coccolith ooze, and hard white chert. No serpentine-group minerals were observed in the sepiolite. In many pieces the sepiolite fills cracks in the clay to form boxwork structures. This relationship indicates that deposition of material as laminae preceded formation of the sepiolite. Intercalation of sepiolite and coccolith ooze in some of the pieces establishes that the sepiolite was in contact with pelagic sedimentary material at the time of formation. The lack of direct association of sepiolite with the serpentine suggests that the serpentine did not alter in place to form sepiolite.

Lapparent (1936) proposed that sepiolite was produced in a manner analogous to montmorillonite, but that it was not necessary to have volcanic glass as a starting material. He suggested that the mineral is formed by the direct action of Mg salts in solution on SiO<sub>2</sub> gels in the presence of Ca. Rateev (1954) proposed a similar origin for sepiolite from Krasanaya Polyana. He suggested that Mg in the form of colloidal minerals such as Mg(OH)<sub>2</sub> has reacted with authigenic SiO<sub>2</sub> hydrogels in a lacustrine environment. Aurola (1956) suggested that, in addition to direct crystallization of sepiolite from hydrothermal solutions, impure opal with high Mg content also may alter to form sepiolite. Hast (1956) reported the formation of sepiolite at room temperature by the reaction of SiO<sub>2</sub> with MgO, Mg(OH)<sub>2</sub> and MgCO<sub>3</sub>, but Mumpton and Roy (1958) were unable to produce sepiolite in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O, and P. B. Hostetler (pers. comm.) has not been able to duplicate Hast's results. Mumpton and Rov (1958) suggested that the absence of CaO might be responsible for the failure of sepiolite to form, or that structural control must be exercised by a parent mineral to form sepiolite as a metastable phase. Millot (1960a, b) reported, however, that in authigenic lacustrine sediment of Eocene age in Africa, near-shore sediment is higher in Al than deposits farther from shore, and that the dominant clay mineral is kaolinite. As the distance from shore increases, the sediment becomes lower in Al and higher in Mg; kaolinite gives way to montmorillonite, which in turn gives way to attapulgite. The sediment farthest from shore contains sepiolite. It seems unlikely that structural control by a single parent mineral would produce this diversity of minerals.

Siffert and Wey (1962) report the formation of sepiolite at ordinary temperatures from saturated solutions of  $Si(OH)_4$  to which various volumes of 0.1M MgCl<sub>2</sub> were added. At pH 10.0 or above (adjusted by addition of NaOH), sepiolite formed in three weeks from mixtures ranging from 1:1.67 to 1.43:1 MgO:SiO<sub>2</sub>. Upite *et al.* (1963), have synthesized sepiolite from mixtures of MgO and SiO<sub>2</sub> in water at 174.5° C. and at 8 atmospheres pressure. Serpentine formed at MgO:SiO<sub>2</sub> ratios of 4:1 and 2:1 whereas sepiolite formed at ratios of 1:4 and 1:1.

The sepiolite reported by Siffert and Wey (1962) contained 36.9 per cent  $H_2O$  (+and-) even after drying at 70° C. This, together with the high water content (30.8 per cent  $H_2O$ +and-) of the Mid-Atlantic ridge material, suggests that sepiolite that has formed in, and remained in an aqueous environment may contain somewhat more water than previously supposed from analyses of terrestrial material.

The high pH found by Siffert and Wey to be necessary for the formation of sepiolite at lower temperatures may have been provided in the case of the Mid-Atlantic Ridge material by the clinoptilolite-bearing brown clay. Values of pH as high as 10.1 have been observed in clinoptilolite-bearing tuffs from the Mojave Desert (R. G. Schmidt, pers. comm.).

The high concentration of clinoptilolite points toward volcanic ash as the most probable origin for the brown clay. Several authors have reported the occurrence of clinoptilolite as an alteration product of volcanic glass (Deffeyes, 1959; Wilmarth and others, 1960; Suzuki, 1961; Nemecz and Varju, 1962; Hay, 1963; Sudo, 1963). In all of these occurrences the volcanic ash was reported to be rhyolitic or high in SiO2. Volcanic materials such as rhyolite are not common near the Mid-Atlantic Ridge, but Daly (1925) reported rhyolite and obsidian with as much as 71-72 per cent SiO<sub>2</sub> on Ascension Island. Peterson and Goldberg (1962) reported a province of silicic volcanism on the East Pacific rise, a dominantly low-silica area; Murata and Erd (1964) reported small amounts of clinoptilolite in sediment from the eperimental Mohole; and Biscave (1964) tentatively identified clinoptilolite in a large number of samples from the South Atlantic Ocean, and concluded that this mineral might possibly have formed from the alteration of volcanic ash in situ. The occurrence of clinoptilolite in deep-sea sediment thus suggests that silicic volcanic material has been contributed to the ocean regions.

Several of the authors cited in the preceding paragraph have proposed that clinoptilolite forms from rhyolite glass by loss of SiO<sub>2</sub> from the glass, the SiO<sub>2</sub> usually appearing as opaline material in association with the clinoptilolite. No opal was observed in the Mid-Atlantic Ridge samples, but quartz occurs as thin bands of chert intercalated with bands of sepiolite. SiO<sub>2</sub> released during alteration of the ash may have reacted with Mg in solution in sea water, to form sepiolite by a process similar to that postulated by Lapparent (1936), and excess SiO<sub>2</sub> may have formed the bands of chert. Decomposition of serpentine also may have provided Mg-rich solutions, and possibly some of the SiO<sub>2</sub>. If the presence of Ca is necessary as suggested by Mumpton and Roy (1958), the close association of calcite in the form of coccolith ooze fulfills this requirement. Alternatively, the molar ratio of Ca: Mg in sea water is 1:5.3; thus normal sea water may provide the necessary Ca. The experiments of Siffert and Wey (1962), however, suggest that high pH rather than Ca can promote the formation of sepiolite. In this occurrence the clinoptilolitebearing clay may have provided a high pH environment.

Donald Langmuir, in work still in progress (pers. comm.), has studied the theoretical considerations concerning the formation of sepiolite and has tentatively concluded that sepiolite is either a stable or very nearly stable phase in sea water. The lack of previous reports of sepiolite in the marine environment suggests that sepiolite does not readily form in sea water, but the occurrence reported here indicates that once formed it may exist as at least a metastable phase if not a stable phase.

### CONCLUSION

The occurrence of sepiolite with the field relationships observed, experimental data and theoretical considerations all indicate that sepiolite can form in a deep-sea environment. We infer that silica derived from the devitrification of silicic volcanic ash could have reacted with Mg in solution to form sepiolite. Clinoptilolite, quartz, and a montmorillonite remain as residual products.

The absence of contacts between serpentine and the sepiolite suggests that the sepiolite did not form by direct alteration of the serpentine. Mg-rich solutions also could have been contributed by decomposition of serpentine, although normal sea water contains relatively high concentrations of Mg and could readily provide the necessary ions.

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