A SEPIOLITE FROM MULLION, CORNWALL

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ABSTRACT

Sepiolites are rare minerals in Great Britain, there being hitherto only two recorded occurrences. The identity of the present sample has been established by means of X-ray diffraction, differential thermal analysis, thermogravimetry, chemical analysis, and infra-red absorption analysis, and some speculations on its genesis are offered.

INTRODUCTION

Sepiolites are rare minerals in Great Britain, the first recorded occurrence being from Kynance Cove, Cornwall (Caillère and Hénin, 1949) and the second from the Keuper Marl of the Midlands (Keeling, 1956). The new occurrence of sepiolite now described is in a locality not far from the first at Kynance Cove, but the material differs from that of Kynance in general appearance and in its mode of occurrence. It was found as a thin vein about 7 mm thick, cutting the massive serpentine rock on the south-east side of the harbour at Mullion; no associated calcite was seen.

DESCRIPTION OF THE MINERAL

The sample is markedly fibrous, the outside is hard and of a buff colour. The vein when broken open shows a mixture of felted fibres and granules; on keeping in the laboratory atmosphere the sample becomes remarkably hard. In thin section the mineral is seen to be a mixture of two types of material: the first is fibrous with a high birefringence and a moderate refractive index \( n = 1.51-1.52 \), the fibres having straight extinction and positive elongation; the second is interstitial and appears to be microcrystalline or amorphous. Some of the fibres surround the isotropic material to form grains of approximately 0.02 mm diameter.

A chemical analysis* of the bulk material gave: SiO\(_2\) 50.06, Fe\(_2\)O\(_3\) 3.49, TiO\(_2\) 0.16, Al\(_2\)O\(_3\) 1.27, CaO 0.04, MgO 22.24, Mn\(_2\)O\(_3\) 0.06, Na\(_2\)O 0.08, K\(_2\)O 0.10, H\(_2\)O \((-110^\circ C)\) 12.02, H\(_2\)O \((+110^\circ C)\) 10.40, total 99.92. This analysis is equivalent to 2MgO.3SiO\(_2\).2H\(_2\)O, the usually accepted formula for sepiolite, and is very close to that given for Bou Azzer sepiolite by Caillère (1952).

*Analyst, L. J. Larner.
An X-ray powder diffraction examination was made using both filtered CuKα and CoKα radiation with a camera of 10 cm radius; the data are given in Table 1. These are typical for sepiolite and compare with those given by Keeling (1956) and by the A.S.T.M. X-ray Powder Data File, card No. 2-0032; they do not, however, agree with the results of Longchambon quoted by Caillére (1951). The main difference is the absence of a strong reflection at 4.28 Å in the data of Longchambon. As there appeared to be two types of material in the Mullion sepiolite, an attempt was made to identify the extra line with the isotropic phase, but subsequent examination of other sepiolites using the same X-ray diffraction cameras always showed the line at about 4.28 Å. Two of these sepiolites were of the sedimentary type, one a meerschaum from Kenya, East Africa, and the other from Salinelles, Gard, France. It seems likely that the line at 4.28 Å is not due to an impurity, and that the pattern quoted by Caillére (1951) is incorrect. In the data for the Mullion sepiolite there is an extra line at 3.03 Å, which may be due to a small amount of calcite impurity.

A differential thermal curve was obtained for 0.2 g of the sample diluted with 0.4 g of α-Al₂O₃ (corundum) in a ceramic crucible, using α-Al₂O₃ as the reference material; the temperatures were measured with chromel-alumel thermocouples and the heating rate was 10°C/min. This curve (Fig. 1) shows two endotherms, one at 122°C and a second at approximately 815°C; superimposed on the latter is a sharp exotherm with a peak temperature of 837°C. To discover the significance of the peaks, samples of the sepiolite were heated in a thermostatically controlled oven and furnace, at 180°C for five days, and at 1000°C for five and for twenty-four hours. The sample heated at 180°C showed no change, the X-ray diffraction

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pattern being identical with the unheated material, indicating that the first endotherm is due to the removal of water not essential to the structure. The shape of the endotherm is typical of loosely-held water which may be regarded as zeolitic in nature. The second endotherm at 815°C is due to dehydroxylation; superimposed on this is the exotherm at 837°C which is caused by the chemical heat of formation of anhydrous silicates. X-ray diffraction of the samples heated at 1000°C indicates the presence of enstatite, MgSiO₃, and a trace of cristobalite.

A thermogravimetric analysis was made on a 155 mg sample of the sepiolite, using a recording thermobalance with a sensitivity of 0.1 mg; the sample was heated from room temperature to 1000°C in 3 hours, at approximately 5.5°C/min. The thermogram (Fig. 2)
is similar to those published by Caillère and Hénin (1957), resembling most the curve for the compact material from Ampandrandava. There is some discrepancy between the results obtained by dynamic thermogravimetry and by static loss on ignition (quoted in the analysis). This is probably mainly due to the drying out of the sample on storage in the laboratory, since the static weighing was made soon after collecting the sample, while the thermogram was made some six years later.

On the thermobalance there is a rapid loss in weight of 10.4 per cent. between 80°C and 140°C, followed by a less steep loss of 3.1 per cent. between 250°C and 600°C; at 600°C there is an inflection and a further loss in weight of 1.1 per cent. between that temperature and 800°C, where there is a change in the rate of loss; finally 1.5 per cent. is lost between 800°C and 900°C.

An infra-red absorption spectrogram of the Mullion sepiolite is shown in Fig. 3. The sample for the analysis was made by milling about 5 mg in iso-propyl alcohol in a vibrating ball mill of the type described by Ford, Wilkinson, and Price (1954); when it had been milled for about 15 minutes a drop of the suspension was removed by pipette and spread on a sodium chloride plate, the iso-propyl alcohol was allowed to evaporate, and the plate was ready for the spectrometer. The sample used weighed 2 mg on a disc of 25 mm diameter, or 0.004 mg/mm². The method of deposition from iso-propyl alcohol was preferred to the KBr disc method, since sepiolite contains both free water and hydroxyl groups, and experience has shown that there may be some reaction with the hygroscopic KBr.

![Infra-red absorption spectrum of sepiolite from Mullion, Cornwall.](image)
Sepiolite being of a fibrous nature, there is no great likelihood of the deposited sample showing much preferred orientation.

The absorption spectrum was obtained on a double-beam Perkin-Elmer Infracord spectrometer, the record being between 2.5 and 15 μ. The spectrum shows peaks at about 2.9, 3.1, 6.1, 6.25, 8.35, 9.33, 9.9, and 10.3 μ, and there are also minor peaks at 12.7 and 14.5 μ. There is a general resemblance with the spectrum for sepiolite published by Launer (1952); however, there is some disagreement in the absorption peak values for the Si—O vibrations in the 9—12 μ region. The peaks at 6.1 and 6.25 μ are not very sharp, and may only represent the spreading out of the peak at 6.2 μ due to the broad H—O—H angle deformation vibrations. This peak can be assigned to the "free water," and is probably associated with the zeolitic water mentioned earlier. The double peak at 2.9 and 3.1 μ is due to H—O stretching, and may be influenced by sorbed water. Illites and montmorillonites also show this double peak, but, unlike sepiolite, the peaks are of unequal size; kaolinites and micas have only a single peak in this region.

**ORIGIN OF SEPIOLITE**

There must be some speculation as to the origin of the sepiolite from Mullion. Caillère (1951) notes that sepiolite may occur as an alteration product of serpentine, although it is usually described as being formed under lacustrine conditions of high basicity (Millot, 1949). At Mullion the sepiolite is associated with serpentine rock; the serpentine may be represented as 6MgO.4SiO₂.4H₂O, while sepiolite is 2MgO.3SiO₂.2H₂O. This indicates that the sepiolite was formed either by the removal of magnesia or by the addition of silica. If magnesia had been removed, it is likely that some trace of it would be found in the area either as dolomite or as magnesite. There are numerous calcite veins in the area, and chemical tests on a large number have failed to show any significant amount of magnesium; it is therefore unlikely that the sepiolite was formed by the removal of magnesium. This leads to the conclusion that the sepiolite owes its origin to the addition of silica, which in the Lizard area is readily available, for in many of the areas, Mullion and Kynance Cove included, an acid igneous rock has invaded the serpentine. Reaction with the siliceous emanations from this material presumably led to the formation of the sepiolite. The invading acid "magma," Kennack gneiss, was not seen in the Mullion sepiolite locality, but a saponite was formed by reaction between serpentine rock and in-
vading Kennack gneiss at Church Cove (Midgley and Gross, 1956); by analogy, it seems likely that the Mullion sepiolite originated under similar conditions.

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REFERENCES


LAUNER, P. J., 1952, Amer. Min., 37, 764.
