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PALYGORSKITE FROM ATLANTIC DEEP SEA SEDIMENTS

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ABSTRACT

A deep sea sediment core collected from the Barracuda Escarpment in the western Atlantic, contains a layer with a large number of nodular aggregates up to a few cm. in size. Palygorskite is the main component of the majority of the aggregates. Other minerals present are clinoptilolite, serpentine, smectites, sepiolite and quartz. In some of the aggregates clinoptilolite rather than palygorskite is the major component. Palygorskite was probably formed by Mg-rich solutions, possibly hydrothermal, acting on sedimentary montmorillonite-group clays.

INTRODUCTION

During a study of the sea floor in the area of the Barracuda Escarpment located in the western tropical Atlantic (Fig. 1), a sediment core (P6409–2) was collected at 16° 46.8′N, 58° 21.1′W, 5015 meters below sea level, by the R/V PILLSBURY of Miami's Institute of Marine Sciences. The core is 410 centimeters in length and for the most part consists of a brown, fine lutite, age undetermined. The mineralogy of samples selected at intervals of about 80 cm through the length of the core was determined by X-ray diffraction. The various samples have a rather similar composition and contain, in order of relative abundance, quartz, smectites, feldspars, kaolinite, muscovite and chlorite. The composition of this sediment is not unusual for this area of the floor of the Atlantic (see Biscaye, 1964), except for a relatively high content of expandable 15 Å clays of the smectite group. These smectites are prevalently dioctahedral, as suggested by the spacing of their (060) planes. Microscopic observations indicate that the smectite minerals are in the form of brown subspherical particles up to 30 μ in size and displaying matted extinction typical of microaggregates.

Our attention was attracted by a 10 cm thick layer located 90 cm below the top of the core. This layer contains within the brown sediment a large number of semi-indurated nodular aggregates of various shapes, mainly subspherical; the diameter of the majority of them is a few mm or less but in some cases reaches 2 or 3 cm. The grains are relatively soft when wet, and when dry can easily be broken or nail scratched. According to their color, grains of two types were distinguished. Type 1 grains are light-brown or yellowish, and when dry have an earthy appearance. They are by far the most abundant type. Type 2 grains are a very light yellow, almost white, and their surface appears smooth when dry. A few grains consist of type 1 material, encrusted by the type 2 material.

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MINERALOGICAL AND CHEMICAL EXAMINATION

Type 1 material was dried at room temperature, ground and press-mounted so as to preserve random orientation. X-ray diffraction patterns of the pressed powder were obtained with a XRD5 General Electric diffractometer (Fig. 2). Patterns of the same material after treatment with ethylene glycol were also obtained. The most intense reflection given by this material is at 10.52 Å and is not affected by glycolation. Comparison of these X-ray patterns with data obtained from samples of palygorskite from Attapulgus (Georgia) (Table 2) indicates that the main mineral of type 1 material is palygorskite. Other minerals present in subordinate amounts are clinoptilolite, a mineral of the serpentine family, quartz and traces of smectites. In some of the samples traces of sepiolite were also detected.

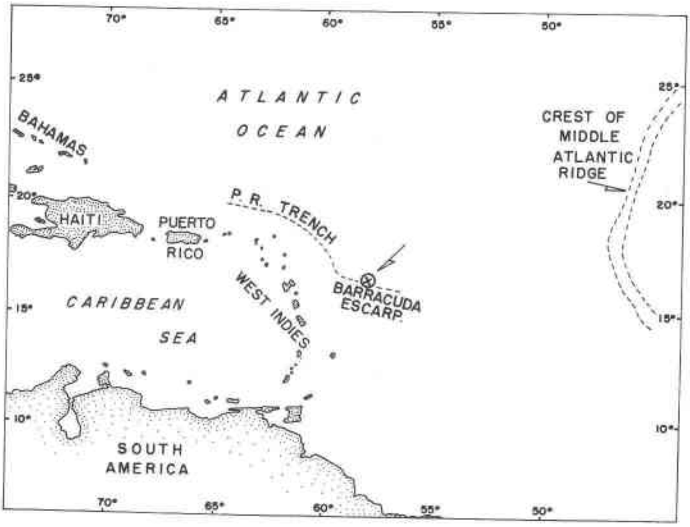

FIG. 1. Location of core P6409-2.

Type 2 material consists mainly of clinoptilolite, as indicated by comparsion of the X-ray pattern with that of clinoptilolite from Hector, California. Ambiguity with heulandite is eliminated because the X-ray reflections of the mineral did not change after keeping the sample at 500°C for 30 minutes (Mumpton, 1960). Other components present in this type of aggregate are palygorskite, montmorillonite, serpentine and quartz.

Examination with a petrographic microscope shows that palygorskite is contained in yellowish particles up to about 30 μ in size (Fig. 3) which display matted extinction typical of microaggregates. Such particles have sizes and shapes similar to those of the smectite particles con-

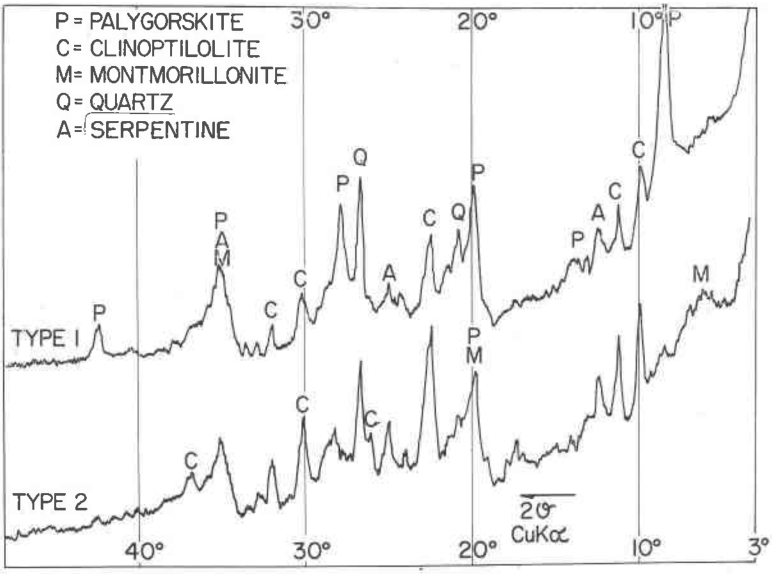

FIG. 2. X-ray diffractometer traces (CuKα radiation) of type 1 and type 2 material from core P6409-2, western Atlantic.

tained in the rest of the sediment core. Clinoptilolite appears at the microscope as colorless laths which occasionally reach up to 25 μ in length (Fig. 4). Serpentine minerals appear as pale-green aggregates reaching up to 30 μ in diameter. Their slightly anomalous, yellow-green interference colors suggest the mineral is antigorite. Occasionally tiny crystals of clinoptilolite and of serpentine were observed enclosed within the palygorskite microaggregates. A few tiny rhombs of dolomite were also observed both in type 1 and 2 aggregates.

Carbon replicas were made of type 1 material, and electron micrographs were obtained with a Norelco electron microscope (Fig. 5). Palygorskite is in the form of fibrous, needle-like crystals reaching 2 or 3 μ in length; the crystals are very similar to those reported by Marshall *et al.*, (1942) and by Bates (in Grim, 1953, p. 122). Platy, micron-size granules are also visible in the electron micrographs; they are probably smectites.

The results of chemical analyses of samples of type 1 and type 2 material are given in Table 2 where they are compared with an analysis of a sample of sediment from the top of the core. The amount of water released by the samples at various temperatures was measured with a moisture analyser (Table 3).

DISCUSSION

Palygorskite has not been previously reported from the deep sea environment. It has been found to form in fresh water and lagunal sedi-

TABLE 1. X-RAY POWDER DATA FOR PALYGORSKITE[a]

	Barracuda Escarpment		Attapulgus, Georgia (Bradley, 1940)	
h k l	*d*(Å)	*I*	*d*(Å)	*I*
110	10.52	100	10.50	ss
200	6.42	22	6.44	ms
130	5.40	20	5.42	m
040	4.48	70	4.49	s
310	4.15	15	4.18	w
240	3.67	20	3.69	m
330; 150	3.52	12	3.50	w
400	3.22	38	3.23	ss
420	3.10	10	3.03	ww
440	2.60	50	2.61	s
510	2.56	50	2.55	w
530	2.37	10	2.38	w
080	2.24	9	—	—
600	2.13	30	2.15	m
550	2.11	18	—	m
480	1.84	9	—	—
390	1.81	9	1.82	ww
800	1.62	8	1.62	ww
680	1.56	14	1.56	w
0120	1.50	24	1.50	m

[a] The data were obtained with a G.E., XRD5 diffractometer. Instrumental factors were as follows: Cukα radiation, $\lambda = 1.54050$. 35KVP; 15 MA; scanning speed 1″/min; time constant 2; scale factor 1000 full scale. Quartz present in the samples served as internal standard. The indices are according to Bradley (1940). *I* = relative intensities of reflection lines.

ments (Kerr 1937; Heystek and Schmidt 1954); or in shallow marine environment as a result of the action of Mg-rich solutions on terrigenous clays (Müller, 1961). In other instances palygorskite has been reported to form by hydrothermal action directly on igneous rocks (Stephen, 1954).

The aggregates reported here appear to be remarkably similar to material dredged from the middle Atlantic Ridge and described by Hathaway and Sachs (1965), with the main difference that sepiolite rather than palygorskite is contained in the Ridge material together with clinoptilolite and serpentine. Due to the similar composition and common paragenesis of palygorskite and sepiolite, much of the discussion contained in Hathaway and Sachs paper is also pertinent to our findings. These authors suggested that silica derived from the devitrification of silicic volcanic ash could have reacted with Mg in solution to form sepiolite, leaving clinoptilolite, quartz and a montmorillonite as residual products.

In our case no volcanic glass was observed, but the presence through-

TABLE 2. CHEMICAL ANALYSES OF SAMPLES FROM CORE P6409-2

	1a	1b	2	3
SiO_2	53.0	49.5	54.0	54.2
Al_2O_3	15.3	15.5	15.8	21.6
Fe_2O_3[a]	5.72	6.01	6.51	8.30
CaO	0.45	0.38	0.75	1.10
MgO	4.40	4.10	2.55	1.92
Na_2O	1.25	1.95	2.65	0.84
K_2O	2.6	2.0	3.0	2.35
TiO_2	0.55	0.60	0.55	*[b]
MnO	0.20	0.16	0.10	0.20
H_2O^-	9.4	13.3	10.5	5.61
H_2O^+	5.4	7.9	6.2	6.10

[a] No separate determination of FeO and Fe_2O_3 was made; Fe was determined as such and is here reported as Fe_2O_3.

[b] Not determined.

1a, 1b = two samples of type 1 material.
2 = sample of type 2 material.
3 = sample from the top of core P6409-2.

out the core of abundant smectites suggests that volcanic glass was originally present in the sediment. In fact, alteration of silicic or basaltic glass in deep sea water and interstitial solutions of normal composition produces commonly clay minerals of the montmorillonite group, as well

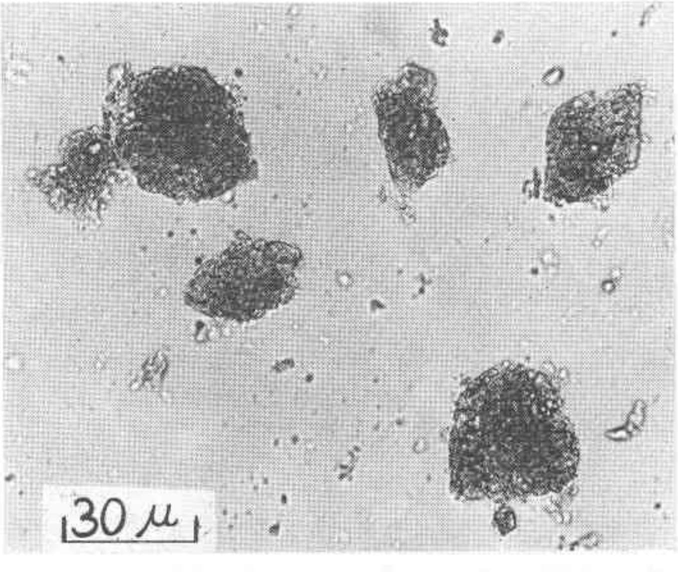

FIG. 3. Palygorskite-containing microaggregates from type 1 material (transmitted light).

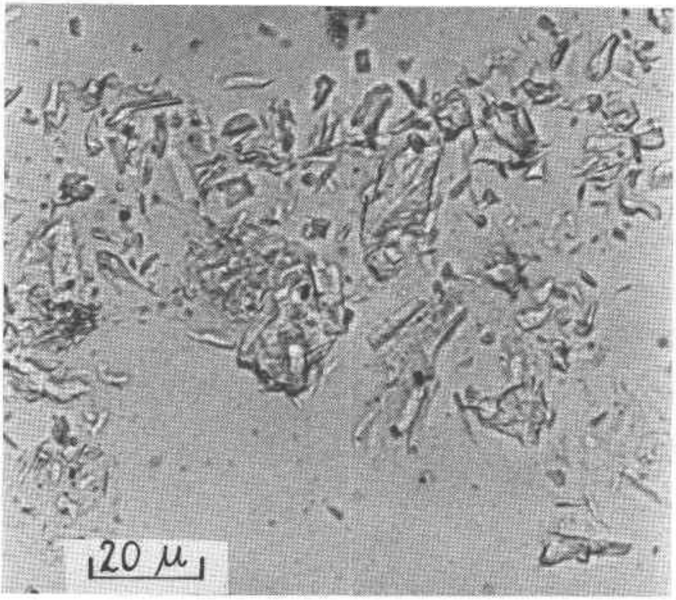

FIG. 4. Crystals of clinoptilolite from type 2 material (transmitted light).

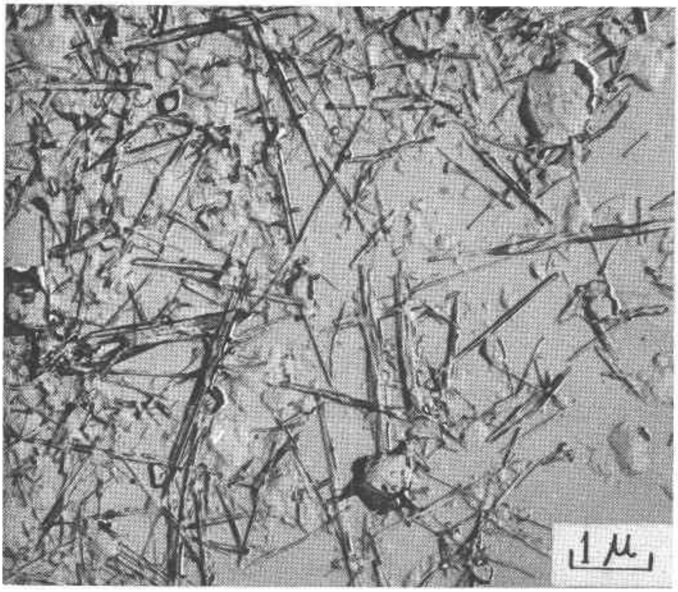

FIG. 5. Electron micrograph of a carbon replica of a palygorskite microaggregate from type 1 material.

TABLE 3. ANALYSES OF H_2O IN SAMPLES FROM CORE P6409-2

Sample	20°C	100°C	200°C	400°C	1000°C
Type 1 (a)	6.9	2.5	1.3	2.5	1.6
Type 1 (b)	11.0	2.3	2.3	4.2	1.4
Type 2	*[a]	10.5	0.78	1.80	4.4
Attapulgus (Georgia)	*[a]	14.0	3.1	4.4	2.5

Percentage (by weight) of water released at increasing temperatures by samples of type 1 and type 2 material and of palygorskite from Attapulgus, Georgia. The analyses were made with a moisture analyser manufactured by the Consolidated Electrodynamics Corp., Model 26-321A-MA. Previous to the analysis the samples were kept at about 20°C in the air with about 60 percent relative humidity. H_2O measured at 20°C was released where the sample was kept in dry nitrogen.

[a] H_2O at 20°C was not measured separately, and is included in that released at 100°C

illustrated by a study of Tertiary ash layers in sediment cores drilled off Florida (E. Bonatti, unpubl. results) and by several other previous works.

It is known from laboratory experiments (Hawkins and Roy, 1963) that reactions of silicate glasses with solutions at pH similar to that of sea water produce smectites only if magnesium is present in the solutions. The concentration of magnesium in sea water is about 1.3 gr/Kg, which is in accordance with the fact that montmorillonite generally forms from volcanic glass on the ocean floor. The MgO/SiO_2 ratio in palygorskite is between 2 and 3 times higher than in common smectites (excluding saponites); in our case, type 1 material has a MgO/SiO_2 ratio about 3 times higher than the sediment from the rest of the core (Table 2). It is therefore probable that the formation of our deep sea palygorskite required solutions with magnesium activities in excess to those which are commonly able to produce smectites on or below the sea floor.

Such Mg-rich solution could have been provided in our case by hydrothermal sources on the sea floor. Evidence of hydrothermal activity was obtained at station P6402–4 (16° 42.3′N, 58° 03.1′W) only a few miles from the location of the palygorskite-containing core. Fragments of basalt were recovered at this station, which had been strongly altered hydrothermally, resulting in the serpentinization of the femic minerals, chloritization and zeolitization of the feldspars, and formation throughout the rock of veins of carbonates (E. Bonatti, unpubl. results). It is indeed probable that hydrothermal activity is quite extensive in this area of the Atlantic Ocean floor, which is strongly disturbed tectonically hosting what is thought to be a major fracture zone.

Thermal liquids associated with basic volcanites could well be high in magnesium derived both from the volcanites themselves and from leeching of the sediments. For instance, serpentinization of femics should release some magnesium and silicon in solution (Thayer, 1966). It is possible that reactions of such Mg-rich liquids with the smectites contained in the sediment resulted in the formation of palygorskite.

This suggestion is supported by the fact that the palygorskite-containing microaggregates appear at the optical microscope very similar to the smectite particles contained throughout the rest of the core. Electron micrographs indicate that an intergrowth of palygorskite and smectites may exist within such microaggregates.

Field evidence in favour of palygorskite being derived from montmorillonite has been provided in the past by Kerr (1937) and Haystek and Schmidt (1954). Synthesis experiment results in the laboratory are not very indicative of the possibility of smectite being a parent material for palygorskite, and of the stability field of the latter, due to the failure of various attempts to synthesize palygorskite (Mumpton and Roy, 1958).

In our case, clinoptilolite is contained in the palygorskite-rich layer and is not present in the rest of the core; probably the processes which formed palygorskite are also responsible for the presence of clinoptilolite. Simple stoichiometric reactions can be written, according to which both palygorskite and clinoptilolite are formed and montmorillonite is one of the parent materials; for instance:

$$\text{montmorillonite} + \text{silica} + (\text{calcium and magnesium in solution}) \\ \rightarrow \text{palygorskite} + \text{clinoptilolite.}$$

A reaction of this type should be possible on the sea floor, since both calcium and silica are known to be present in bottom and interstitial solutions; a possible additional source of silica is quartz, which is present throughout core P6409–2, also within the palygorskite-rich layer. However, other types of reactions are possible as well, and there is no way of knowing with precision what took place in our case.

The type of reaction suggested above for the formation of palygorskite could also explain the presence of serpentine and of traces of sepiolite in the same material. In fact, whether one or the other of these three magnesium silicates is formed must depend on very delicately balanced conditions, involving the activity of Mg^{2+} and other ions and the pH of the solution. For instance, Upite *et al.*, (1963) have synthesized sepiolite and serpentine at 174.5°C and 8 atm pressure; serpentine formed at MgO/Sio_2 ratios of 4 to 1 and 2 to 1; sepiolite formed at ratios 1 to 4 and 1 to 1.

SUMMARY AND CONCLUSIONS

The fact that palygorskite was found more than 5000 meters below sea level in the Western Atlantic suggests that this mineral is stable, or, at least metastable at about 1–2°C and under a pressure of about 500 bars. However, palygorskite is not commonly found in deep sea sediments; rather special conditions must be required for its formation on the ocean floor. It is suggested that an unusually high activity of magnesium is one such condition. There is evidence that the formation of palygorskite in core P6409–2 required smectites as parent material.

NOTE ADDED IN PROOF: In December 1967 an additional number of sediment cores were collected from the Barracuda Fracture Zone. At one station (P6708–13, 16°43′ N., 58°07′ W., 3728 meters below sea level) the sediment was found to consist of palygorskite, clinoptilolite, smectites, serpentine and quartz, that is, the same assemblage found in core P6409-2 and reported in this paper. The two palygorskite-containing samples, even though collected several kms apart from each other, are both from the steep scarp marking the Barracuda Fracture. These findings suggest that the Mg-rich solutions which presumably give rise to the palygorskite-containing assemblages debauch on the sea floor all along the Fracture.

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