11. SPECIAL MINERALOGICAL STUDIES

11.1 CLAY MINERALS IN MESSINIAN SEDIMENTS OF THE MEDITERRANEAN AREA

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ABSTRACT

The clay fraction of Messinian sediments sampled in the Mediterranean area from DSDP Legs 13 and 42A and from land sections in Sicily, Spain, and Algeria characteristically contains great amounts of smectite. Origins for this mineral are discussed. The most probable is the effect of strongly contrasted seasons within a semi-arid Messinian climate on poorly drained soils which would have been periodically eroded. Chlorite, sometimes associated with flexuous attapulgite, frequently is relatively abundant, especially in the eastern basins; both minerals could have formed partly from authigenic agradation.

INTRODUCTION

Upper Miocene Messinian deposits in the Mediterranean area are characterized by a great number of evaporitic salt rocks which include numerous intercalations of shale, marl, and dolomitic marl. The thickness of these intercalations ranges from a few millimeters to 10 meters or more (see Selli, 1960; Cita et al., 1973; Drooger; 1973; Ryan, Hsü, et al., 1973). This study was undertaken to analyze the clay mineralogy of these layers in order to determine whether it is different in the Messinian and the Pliocene as is the case for salt deposits. About 200 samples were analyzed by standard clay mineralogical procedures (X-ray diffraction, DTA, electron microscopy, and chemical analysis) (Figure 1).

SITES 375-376, WEST CYPRUS

The upper Tortonian dolomitic marls with graded sand layers have a clay fraction formed mainly by smectite (50%), lesser amounts of attapulgite, illite, and chlorite (15% each), and a minor amount of kaolinite and irregular chlorite-smectite mixed layers. The clay assemblage in the dolomitic marls is more monomineralic in the Messinian and the Pliocene as is the case for salt deposits. About 200 samples were analyzed by standard clay mineralogical procedures (X-ray diffraction, DTA, electron microscopy, and chemical analysis) (Figure 1).

SITES 125A, EAST MEDITERRANEAN RISE

The dolomitic marls of the upper Messinian are characterized by smectite (85% in Sample 8-1, 141 cm) or by chlorite (30%) associated with dolomite and very long, fine fibers of attapulgite (Sample 9-1, 145 cm), or by an association of smectite-chlorite-illite. Other clay minerals (kaolinite, mixed layers) are rare. In the Pliocene hemipelagic muds, the clay content is more variable: illite and attapulgite dominate (30% each) with kaolinite (20%), smectite (10%), chlorite and irregular mixed layers (5% each). These results agree with the data of Zemmelis and Cook (1973) which show a decrease of chlorite and smectite and an increase of attapulgite from Messinian to Pliocene.

SITE 374, MESSINA ABYSSAL PLAIN

About twenty-five meters of upper Messinian black dolomitic mudstone were drilled at Site 374. The clay composition is of two types: (1) very abundant smectite (70%-75%) with minor amounts of illite and chlorite (10% each), kaolinite and attapulgite (0%-5%), (Cores 12 and 15, Section 2); (2) abundant smectite (50%) and chlorite (25%) with minor amounts of illite (10%-15%) and kaolinite (5%), and traces of attapulgite in very long, fine, transparent fibers. Dolomite is present in the clay fraction of this second type (Cores 13, 14, and 15, Section 1). Attapulgite predominates (up to 60%) in the lower Pliocene. Smectite and chlorite decrease (respectively, 10% and traces) and other clay minerals are variable. These results apply also to the hemipelagic nanofossil
Figure 1. Clay mineralogy of upper Miocene sediments of the Mediterranean basin.
Figure 1. (Continued).
ooze (Core 10 and above) as well as the dolomitic mud and limestone of Core 11.

**CALTA NISSETTA BASIN, ERACLEA MINOA SECTION, SICILY**

The upper and lower parts of this section where evaporitic cycles are well defined were analyzed. The section was sampled by J. C. Fontes, W. D. Nesteroff, and C. Pierre (see Pierre, 1974; Dunoyer de Segonzac and Nesteroff, in press). The Tortonian marls contain illite, chlorite, smectite (40%), and kaolinite. The base of the Messinian is marked by an increase in smectite (up to 65%) and a correlative decrease in kaolinite. Attapulgite is present in only one sample. The upper Messinian is characterized by a large amount of well-crystallized smectite and minor amounts of illite and kaolinite (mean: smectite 57%, illite 18%, kaolinite 23%). No significant variation occurred from the bottom to the top of a cycle. Chlorite appears again in the sandy layers of the uppermost Messinian (“arenazzo” facies). The early Pliocene marine limestone (“trubi” facies) differs from the Messinian sediments and illite-smectite mixed layers generally do not contain clay. In the dolomitic layers, the clay fraction is composed of smectite (mean 60%) associated with illite, some chlorite, and locally traces of attapulgite and kaolinite. These features were not reported by Zemmels and Cook (1973) and Kelts (1973), but the former authors noted the dominance of illite (60%) over chlorite, smectite, and kaolinite in the Pliocene sediments.

**SITE 133, WESTERN SARDINIA SLOPE**

Three lithologic types with distinct mineral assemblages are present in the analyzed samples: (1) Dark red sandy shale (Cores 6 and 7): illite and mixed layers occur in the same proportion with traces of kaolinite, quartz, feldspars, and geothite. The mixed layers are of the illite-smectite, illite-vermiculite, and chlorite-vermiculite types. (2) Light green claystones (Core 5): very abundant smectite (90%) with illite and traces of chlorite and attapulgite. The DTA curves and morphologic aspect (thick and elongated flakes) suggest the presence of a ferric smectite of the beidellite-nontronite type. (3) Red sandy clay (Core 4): well-crystallized illite (50%) and chlorite (45%) with mixed layers and kaolinite.

Such variations within the Messinian were not reported by Zemmels and Cook (1973) and Kelts (1973), but the former authors noted the dominance of illite (60%) over chlorite, smectite, and kaolinite in the Pliocene sediments.

**SITE 134, WESTERN SARDINIA ABYSSAL PLAIN**

There is no clay in the lower and upper layers of Core 10 Section 1, where halite and anhydrite are well developed. The dolomitic marls in the middle of the section (10-1, 110 cm) are rich in smectite (75%), with lesser amounts of other clay minerals. Nesteroff (1973a) has previously pointed out the relative abundance of smectite at the top of the dolomitic marls. The mineral partially shows the same thick and elongated flakes as at Site 133, Core 5.

**SITE 124, SOUTHWEST OF THE BALEARIC RISE**

The Messinian sequence was continuously cored for 65 meters. It is principally nodular anhydrite, locally interrupted by dolomitic mud and to a lesser degree alternating dolomitic marl and gypsum. The evaporite layers generally do not contain clay. In the dolomitic layers, the clay fraction is composed of smectite (mean 60%) associated with illite, some chlorite, and locally traces of attapulgite and kaolinite. These features were not reported by Nesteroff (1973a) and were only suggested by Zemmels and Cook (1973). The latter noted the relative abundance of smectite in the Messinian and illite in the Pliocene-Pleistocene sediments.

**SITE 372, EAST OF THE BALEARIC RISE**

The nannofossil marl and ooze of the Tortonian have a relatively constant clay fraction of illite (35%), chlorite (25%), and smectite (40%). There is no significant change from the middle-upper Miocene (Cores 11 to 9) to the Messinian (Cores 6 to 4), except below Core 11 (Mélières et al., this volume). The Pliocene, however, is marked by the complete disappearance of smectite, the increase of illite (60%), and the appearance of kaolinite (10%) and illite-smectite mixed layers (10%).
Murcia Basin, Spain

The two sections presented in Figure 1 were sampled 35 km east (Section 1) and southwest (Section 3) of Murcia. The stratigraphic boundaries within the basin were established by Bizon et al. (1971). The two main clay minerals in the upper Miocene as well as in the underlying Tortonian are illite and smectite. They both have a high crystallinity, suggesting a high rate of erosion on the bases of illite and environments favorable to the formation of smectite. A minor amount of chlorite occurs in Section 3, and of kaolinite in Section 1. The average chemical composition of the clay fraction is as follows:

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Major elements (%; average values on 7 samples)
SiO₂  Al₂O₃  MgO  CaO  Fe₂O₃  TiO₂
56.21 20.97 2.75 0.71 6.46 1.06
Na₂O  K₂O  Loss at 1000°C
0.29 3.21 8.12
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The composition of the upper Tortonian sediments differs (Sicily, Levantin Basin). The older Tortonian sediments generally have less smectite than do the Messinian sediments. This is illustrated by the mean values of clay mineral percentages in the Mediterranean area:

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Mixed Smectite Chlorite Illite Layers Kaolinite Attapulgite
Pliocene 30 7 33 2 15 13
Messinian 54 10 21 3 8 4
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Chelif Basin, Algeria

The samples were collected by C. Lepvrier in the eastern part of the Chelif Basin (map Oued Fodda 1/50 000°). The upper Miocene is a marly formation interrupted by two evaporitic gypsum layers. The clay fraction in the marl constitutes an association of illite, chlorite, smectite, mixed layers, and kaolinite. The smectite is poorly crystalline. The clay fraction has the following average chemical composition:

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Major elements (%; average values on 7 samples)
SiO₂  Al₂O₃  MgO  CaO  Fe₂O₃  TiO₂
56.0 18.2 3.62 1.1 7.3 0.68
Na₂O  K₂O  Loss at 1000°C
0.24 3.64 7.78
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Trace elements (ppm; average values on 7 samples)
Sr  Ba  V  Ni  Co  Cr  B  Mn  Zn  Ga  Cu  Pb
616 395 178 132 16 138 237 76 151 28 57 17

DISCUSSION

Differences in Clay Mineral Composition Between Messinian and Pliocene Sediments

The Pliocene clay minerals are complex and diversified. They reflect the detrital contribution from different alluvial areas of the Mediterranean periphery: (1) Illite and chlorite in the Balearic Basin (Sites 124, 133, 134, and 372) and in Spain, where they derive from the Alpine series and surrounding crystalline bedrocks; (2) Illite, smectite, attapulgite, kaolinite in the Tyrrhenian Sea (Site 132). These minerals were introduced from Italy, Sicily, Sardinia, and perhaps from North Africa; (3) Illite, smectite and kaolinite from Sicily (Basin of Caltanissetta); (4) African attapulgite, Sicilian smectite, and European illite and chlorite in the Ionian Sea (Sites 374 and 125 A); (5) Smectite and attapulgite in the Levantin Basin. The minerals originated from Asia Minor (Sites 375-376) (see Chamley, 1971, 1975a, b; Mélières et al., this volume).

The Messinian clay minerals are comparatively simple. They are characterized by one or sometimes two primary minerals, the distribution of which is rather constant throughout the whole Mediterranean Basin. Well-crystallized smectite is the most abundant (up to about 100%) and is the ubiquitous mineral. Chlorite is more abundant in the Messinian than in the Pliocene-Pliocene sediments. This is especially the case in the sediments of the eastern Mediterranean where the environment was different from that in the Western basin (Sites 376, 125A, 374; See Cita et al., this volume). The other minerals are sparse, rare, or even absent: they represent the common detrital contribution, whose abundance is diluted by smectite or both smectite and chlorite. There are very few exceptions: argilite from Chelif (Algeria) and red, sandy clay from the Sardinia slope (Site 133) where various minerals reflect strong erosion—perhaps in relation to tectonic events, and argillaceous and ferruginous impurities in some varicolored salt layers (especially gypsiferous beds at Site 132) in which the detrital contribution is very low.

The contrast in Pliocene and Messinian clay contents is illustrated by the mean values of clay mineral percentages in the Mediterranean area:

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Mixed Smectite Chlorite Illite Layers Kaolinite Attapulgite
Pliocene 30 7 33 2 15 13
Messinian 54 10 21 3 8 4
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Detrital Pedogenic Provenance

An arid climate favored the great development of salt evaporites during deposition of Messinian sediments. On the continental areas it resulted in the formation of soils containing abundant and well-crystallized smectites, especially in regions of low relief and little rainfall (Paquet, 1969). Such smectite formation may have prevailed in the Messinian soils existing in the coastal plains and areas exposed as sea-level,
dropped in the subarid climatic environment of the Mediterranean periphery. The continental stream erosion (Clauer, 1976), the depressed water level, and/or periods of tectonic activity resulted in deposition of great amounts of that detrital clay which is interbedded in the typical evaporitic layers (see Nesteroff's [1973] and Heimann and Mascle's [1974] works on sedimentary sequences in the Messinian). This hypothesis is consistent with the mean iron content found in the Messinian clay, as well as with the morphology of some clay particles similar to nontronites or iron-beidellites. It seems to be the most reasonable explanation for the origin of the Messinian smectites.

Other Hypotheses

Differential settling: A preferential settling of the small-size phylite particles of smectite in low-dynamic environments of the Messinian does not agree with the facts. Indeed such a mechanism could not have occurred on a scale so large as the Mediterranean area. Furthermore, the smectites are abundant in coastal basins (i.e., Sicily) as well as in non-coastal basins (i.e., Tyrrenhenian sea). They are abundant in hemipelagic sequences (Ionian Sea) as well as in turbiditic sequences (West Cyprus). Moreover, the other clay minerals, which should have been deposited in relatively great abundance before or after deposition of the smectite are not found. Finally, differential settling of the other small-sized clay minerals (weathered illite, mixed layers) usually occurs with the smectite. These clay minerals, however, are rare or absent in Messinian deposits.

Evolution of volcanic materials: Volcanic activity is known to have occurred in several sectors of the Mediterranean during Messinian (Sicily, North Africa) and Tertiary (Biju-Duval, 1974) time. Some clay minerals, especially smectite, can result from the alteration of volcanic glass and ash provided by such events (Millot, 1964). But the extent of the smectite-rich sediments appears to be out of proportion with the occurrence of volcanic deposits described to date. Moreover, the alteration of volcanic particles into clay does not occur easily in the Mediterranean sediments (Chamley and Giroud d’Argoud, this volume).

Evaporitic clay genesis: The confined ionic conditions which lead to the formation of evaporitic salts (anhydrite, gypsum, halite) could have influenced the formation of evaporitic clays. But this type of smectite is usually rich in magnesium (Triat and Trauth, 1974) which is not the case with the Messinian smectites (MgO = 2.5%-3%). The greatest part of the magnesium could have been utilized for carbonate formation (dolomitic marls) not for silicate formation. In this case, however, the smectite could not have been formed in great amounts and would have a crystal cicatrication or a moderate increase only. Strontium isotopic studies carried out by N. Clauer (Strasbourg) on Sicilian samples show $^{87}\text{Sr}/^{86}\text{Sr}$ values close to 0.717; these values differ from those indicating a marine clay genesis (0.709) and consequently do not support an authigenic formation of smectite.

ORIGIN OF THE MESSINIAN CHLORITES

The origin of chlorite, which occurs in relatively high abundance in some Messinian sediments, is difficult to interpret. The interpretation is more problematical in the sediments of the eastern than in those of the western Mediterranean in which the higher chlorite content, in conjunction with the higher illite content, simply suggests modifications in the detrital contribution. Possibly the chloride was formed, in part, as an evaporite; chloride also occurs in some Triassic series (Lucas, 1962). The following evidence supports an evaporitic genesis for chloride: (1) the upper Tortonian of Site 375 contains subregular mixed layers chlorite-smectite (corrensite) which suggest the initial stages of a chloritization of detrital minerals. (2) Evaporitic chlorites are generally rich in magnesium. Indeed, the Messinian sediments containing high chloride contents, especially the dolomitic marls, nearly always contain automorphic dolomite rhombohedrons, which are similar in size to the clay. (3) The chloritic marl sometimes contains flexuous attapulgite with long, thin, electron-transparent fibers which are quite different from the detrital Pliocene-Pleistocene attapulgites (Chamley and Millot, 1975). Transport of that sort of attapulgite from surrounding land-masses seems unlikely. This suggests that these peculiar fibers, as well as the chlorite, grew, in part, in a magnesian environment.

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REFERENCES


11.2 CLAY MINERALOGY IN VOLCANOGENIC SEDIMENTS

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ABSTRACT

The clay minerals of volcanic glass-rich sediments from Hole 373A and Site 376 are the same as those of their associated sediments. This confirms previous suggestions that submarine evolution of clay minerals from volcanogenic sediments is an unusual occurrence.

Volcanogenic sediments from DSDP Leg 42A were studied by X-ray diffraction in order to determine if any postburial clay modification occurred in this peculiar depositional environment. Clay mineral compositions were determined for sediments from Sites 372 (East Menorca Rise, Cores 34 to 46); 373A (Central Tyrrhenian abyssal plain); and 376 (Florence Rise, west of Cyprus). The investigation of 48 samples from Site 372 did not confirm the presence of volcanic components as expected from initial shipboard descriptions of the lower Miocene clayey muds at the base of this section. Hence, those results will not be discussed here (see Mélières et al., this volume).

The data from the mineralogical study of the less-than-2 micron noncalcareous particles are summarized in Tables 1 and 2 (values in percentages). The average values for “common” sediments, without volcanic components, are from analyses of the Pleistocene from Site 132 (DSDP Leg 12) for the Tyrrhenian Sea (Chamley, 1975a), and of sediments from Site 376 itself for the Levantine Basin.

Layers rich in volcanic glass occur at both sites (e.g., Samples 373A-1-1-111 cm, 376-1-5 90 cm, 376-3-1, 128 cm). They are generally poor in clay minerals, whose relative abundances therefore cannot easily be determined. The horizons chiefly contain sandy glass: