

## 20.2. DISTRIBUTION OF THE FINE-GRAINED SEDIMENT COMPONENT IN THE MEDITERRANEAN

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### INTRODUCTION

Two series of X-ray determinations of the mineral compositions of Leg 13 samples were run independently at Riverside, California and Paris, France. This paper is an attempt to place the results in the general geologic framework of the Mediterranean Basins.

The first series of X-rays was run by H. E. Cook and I. Zemmels at the Riverside DSDP facilities (see Chapter 20.1) and I wish to thank them for kindly permitting me the use of their data. The second series was run at the "UER Sciences de la Terre," University of Paris VI, France. A small difficulty arose in the process of integrating the two series. Palygorskite was frequently reported in the Riverside analyses while it was not identified in the second series. In the Mediterranean deep-sea piston core samples, this is generally absent, a single occurrence having been reported near Greece (Chamley, 1971). It is thus possible that interstratified clay minerals were often misidentified as palygorskite due to the routine identification techniques. Because of this possibility, and to facilitate discussion, I refer to this and associated minerals under the general term "interstratified clays" when discussing the tables of Chapter 20.1.

With the exception of the single Atlantic site (120), all holes were drilled in the Mediterranean Sea. The geography of this land-circled sea explains the high proportions of terrigenous clastics in the sediments. Quartz and feldspars are common components, while detrital dolomite occurs in some areas of the Alboran Sea and the Valencia Trough.

The biological contribution is mainly a debris of calcareous nannoplankton and foraminifera. Carbonates reach high proportions in pelagic deposits and decrease near the shores or in turbidites of terrigenous origin, such as the Nile muds.

Clay mineral assemblages reflect a more complex mode of emplacement. They are due not only to local terrigenous input, but also to the complex hydrological structure of the different basins of the Mediterranean Sea and are generally distributed by surface or bottom currents.

### GORRINGE BANK

At Site 120, drilling recovered Lower Miocene nanno oozes (Unit 3) overlying Lower Cretaceous marls (Unit 4).

The Miocene oozes are highly calcareous (70%) and consist of quartz, plagioclase, and clay minerals. The latter comprise abundant mica (40%) and montmorillonite (40%) together with small amounts of chlorite and kaolinite.

The Cretaceous marls consist of medium amounts of calcite (30-40%), quartz, plagioclase, and clays. The clay mineral assemblage is slightly different from that of the Miocene sequence. It consists of abundant mica (60%),

lesser amounts of montmorillonite (15-20%), chlorite (5%) and traces of kaolinite. Core 2 is exceptional in that it has a higher percentage of kaolinite (10%), and that K-feldspar is present.

Noteworthy are isolated occurrences of clinoptilolite, a secondary mineral encountered in calcareous oozes (Hekinian *et al.*, 1970), and hematite in the last core (7) recovered above basement. The iron oxide, staining the sediment green and red, suggests enrichment in iron by hydrothermal solutions rising through fractures in the basement (von der Borch *et al.*, 1971).

Analysis shows that during the time span Lower Cretaceous-Lower Miocene, bulk composition of the marls remained constant. However, during this time a definite trend is noticeable in the fine fraction. Mica decreases from 60 to 40 per cent and the quartz from 20 to 10 per cent, while montmorillonite increases from 15 to 40 per cent, that is, finer particles (montmorillonite) become more abundant. This suggests quieter settling conditions over the site towards the Lower Miocene.

On the other hand, the clay mineral assemblage is quantitatively different from that of modern sea-floor samples which are composed approximately as follows: illite (70%), montmorillonite (15%), kaolinite (10%), and chlorite (5%) (Heezen *et al.*, 1960; Biscaye, 1965; Griffin *et al.*, 1968). This modern assemblage consists of coarser particles, but, as it is distributed over large geographic areas of the Atlantic Ocean, this difference can not be related to the recent uplifting of the Goringe Bank.

Thus the difference between modern samples and those of Miocene age is more likely to be the result of a change in the world wide distribution of clay minerals due to climatic evolution.

### ALBORAN SEA

At Site 121, Quaternary hemipelagic marl oozes were found overlying Calabrian and Pliocene turbidites and unconformably above Tortonian pelagic marls. Metamorphic basement was reached under the Tortonian.

The pelagic deposits and the fine-grained sections of the turbidites are marl oozes. They consist of quartz, moderate amounts of calcite (25 to 40%), plagioclase, and clays. Small amounts of dolomite, probably of continental origin, are present in all the bulk samples. The clay mineral assemblages contain mainly mica and montmorillonite together with small amounts of kaolinite (10%) and chlorite (5-10%). While the percentages of the last two minerals is constant in all samples, the proportions of mica and montmorillonite vary inversely. From the sea floor to the bottom, mica decreases (50 to 20%) while montmorillonite increases (10 to 50%). This suggests diagenetic transformations which are discussed in detail in Chapter 24.2. Unusual

mineralization, such as the cristobalite in Core 21, is related to lithification of turbidite sand layers, probably during the Messinian desiccation of the Mediterranean.

The associations of Site 121 belong to the mineralogical group of the western Mediterranean Basin (Nesteroff *et al.*, 1963; Rateev *et al.*, 1966). However, they reflect local continental input such as the relatively high amounts of montmorillonite, which is characteristic of the whole fringe of northern Africa. This montmorillonite could originate from the alteration of volcanic rocks of the Atlas Range and Andalusia.

In conclusion, it is remarkable that the terrigenous contribution to the Alboran Sea deposits has not noticeably changed since the Tortonian, suggesting the permanence of the sources.

### WESTERN BASIN

Five sites were positioned in the western basin; two in the Valencia Trough (122 and 123) and three in the Balearic Basin (124, 133 and 134). The drilling penetrated thick accumulations of turbidites and contourites of Pliocene and Quaternary age before reaching the Messinian evaporitic series. In Site 133, pelagic marl oozes of Quaternary age directly overlie continental deposits (Hole 133, Cores 2 to 7). Situated due west of this last site, the six holes of Site 134 penetrated Quaternary-Pliocene pelagic nanno oozes before reaching Messinian evaporites (Hole 134, Core 10).

The fine grained sections of the turbidites and contourites are moderately calcareous marl oozes while the pelagics grade from marl oozes near Sardinia to nanno oozes seaward on the abyssal plain. The sediments are comprised of quartz, plagioclase, K-feldspar, clays, and so forth. Dolomite, probably a terrigenous input, is present in the Valencia Trough (Sites 122 and 123). The clay mineral assemblages consist mainly of mica (70-85%) together with chlorite and kaolinite (1 to 10% of each). Local, but secondary, variations are of note. Kaolinite is rare in the Valencia Trough (Sites 122 and 123) and on the Balearic margin (Site 124). Also the montmorillonite is often absent, and it occurs only in the less than two microns fraction on the Sardinian margin (Hole 133).

Previous investigators pointed out the great mineralogical homogeneity of the surface sediments in the deep parts of the western Mediterranean Basin (Nesteroff *et al.*, 1963; Biscaye, 1965; Rateev, *et al.*, 1966; Chamely, 1971). The present study confirms that sedimentation in the deep parts of the western basin is dominated by the detrital input of the Rhône river (Chamley, 1971), and that this has been true at least since the Pliocene flooding of the Mediterranean.

The petrographic units, underlying the rather homogeneous Pliocene-Quaternary sections, are varied. On the Valencia basement ridge, a thick accumulation of ash (Site 123, Unit 4, Core 6) is characterized by montmorillonite, K-feldspar, and phillipsite. On the Balearic Rise, the Messinian evaporitic series exhibits a special mineralogy, with dolomite and montmorillonite but no kaolinite (Site 124, Unit 3, Cores 6 to 10). Thus, at Site 124, the fine terrigenous input of Messinian times, which was probably of local origin, differed from that which followed the

Pliocene flooding, when Rhone river sediments were distributed throughout the Western Basin.

### TYRRHENIAN BASIN

At Site 132, a continuous section of Pliocene and Quaternary marl oozes overlie Messinian evaporites. The marl oozes, mainly pelagic, consist of calcareous biogenic clastics (60%) together with quartz and clays. The small amounts of dolomite present suggests it to be of detrital origin.

Clay minerals in the bulk samples and 2-20 $\mu$  fractions are dominated by mica (75 to 80%) together with moderate amounts of chlorite and kaolinite (5-10% each). Montmorillonite is absent in the coarser fractions, but appears in the less than two micron fraction, where it makes up 20 per cent of the clays at the expense of mica. These analyses confirm previous investigations of surface sediments (Nesteroff *et al.*, 1963; Rateev, *et al.*, 1966) and show that detrital terrigenous clays dominated the sedimentation.

A portion of the montmorillonite could be transported by the rivers of central Italy, where it is relatively abundant (Quakernaat, 1968). However, its main origin is explained by the alteration of volcanic minerals, as suggested by numerous investigators (Grim and Vernet, 1961; Hekinian *et al.*, 1970; Thomadin, 1970; Chamely, 1971). The fine particle size and consequent transportability resulted in deposition in the deeper parts of the basins, such as occurs at Site 132 (see Rateev *et al.*, 1966). In the same general area off Naples, Norin (1953), and later Muller (1961), showed, however, that in some cases the first stages of marine alteration of volcanic glass produce illite, analcime, kaolinite, quartz, and so forth.

Thus, our first conclusion concerning the pelagic marl oozes is that the terrigenous input in the Tyrrhenian Sea has not changed since the beginning of the Pliocene.

Trace minerals are noted in some cores. Hematite occurs at the base of the Pliocene, in the horizons directly overlying the evaporites. This iron oxide, which stains the sediments reddish, was probably derived from weathered subaerial outcrops just after the Pliocene flooding. Isolated occurrences of phillipsite should be considered with thought to the secondary development of this mineral in highly calcareous pelagic sediments (Hekinian *et al.*, 1970).

The Messinian evaporitic series (Unit 3, Cores 21 to 27) are comprised of dolomitic marls interbedded with gypsum. It is noteworthy that the clay mineral suite is very similar to the Pliocene Quaternary assemblage. This suggests that the weathering of subaerial outcrops surrounding the Tyrrhenian sea, and the consequent terrigenous contribution to marine marl oozes, was the same during the Messinian episode and the Pliocene-Quaternary.

### IONIAN BASIN

Two sites are situated on the Mediterranean ridge in the Ionian Basin. The first, Site 125, is located in a cobblestone zone characteristic of the ridge and the second, Site 126, in a deep cleft in the ridge.

At Site 125, the drilling penetrated pelagic marl oozes and nanno oozes of Quaternary and Pliocene age and bottomed in dolomitic oozes (Cores 6A to 9A) belonging to the evaporitic suite of Messinian age.

The Pliocene and Quaternary pelagic oozes are highly calcareous (60-70%) and include quartz, plagioclase, K-feldspar, and clays. The clay mineral assemblage consists mainly of interstratified clays (60%), small amounts of montmorillonite (10%) and moderate amounts of mica (20-30%) and kaolinite (20-25%). Chlorite is rare (2-3%). The isolated high pyrite value in Core 2A corresponds to a layer of sapropel.

The Messinian dolomitic oozes include a slightly different clay mineral assemblage. Compared with the Pliocene-Quaternary suite, montmorillonite is more abundant (30%) at the cost of interstratified clays (18%) and kaolinite (5%), while mica (30%) and chlorite remain constant.

At Site 126, drilling penetrated an accumulation of Quaternary turbidites and contourites, which filled the cleft, before bottoming in Serravallian marls (Core 5) exposed in the thalweg of the cleft. The turbidites and contourites consist of sequences of bioclastic and terrigenous sands grading to marl oozes. The sediments are highly calcareous and are comprised of quartz, plagioclase, K-feldspar, clays, and dolomite. The latter mineral is supposedly eroded from the walls of the cleft, which cut through the Messinian evaporitic series. The clay mineral assemblage contains approximately equal amounts (30%) of mica, interstratified clays, and montmorillonite, with small amounts of kaolinite (10) and chlorite (5%).

The Serravallian marls are low in calcium carbonate (5-13%) and display a different clay mineral suite from the overlying turbidites. The clays contain large amounts of montmorillonite (50%) and kaolinite (20%) at the expense of illite and interstratified clays. In addition, these marls are rich in pyrite and contain apatite.

The clay mineral suites of the Pliocene and Quaternary pelagic oozes of Site 125, and those of the fine grained sediments of the Quaternary turbidites of Site 126, belong to the western ridge assemblage of Rathnam and Ryan (1969). In addition, the clays from the top of the Messinian evaporite series are of roughly the same composition. This assemblage is characterized by dominant amounts (60%) of interstratified clays and montmorillonite (*complexe gonflant* of Chamley (1971) in which the latter mineral is poorly crystallized and the interstratified clays are more abundant). The remaining constituents are mica and a larger amount of kaolinite (20%) than is normally present in the adjacent areas.

The persistence of the same clay mineral assemblage from the Messinian to the present indicates the same source and the same mode of emplacement during this period. Rathnam and Ryan (1969) suggest that this assemblage results from the fallout of wind-transported particles on topographic highs, as opposed to bottom current transported minerals. As the seismic profiles and the presence of evaporites indicate, this part of the Mediterranean ridge was not a topographic high during the Messinian. A different interpretation is needed. One alternative is that this area was not reached by bottom currents before the formation of the ridge, and consequently received only sediments from surface currents and aerial outfall.

On the other hand, the Serravallian clay mineral assemblage is drastically different. The montmorillonite-kaolinite association could suggest a Nile origin, or a closer local

source such as Libya. In any event, the provenance, or mode of distribution, changed between the Serravallian and the Messinian.

## HELLENIC TROUGH

Drilling in the Hellenic Trough (Sites 127 and 128) penetrated a thick accumulation of Quaternary turbidites and contourites. Below this (Hole 127) was Cretaceous rock (Cores 16 and 17), underlain by Pliocene marl ooze (Core 18), in turn underlain by dolomite of Cretaceous age. This succession is interpreted as due to slumping, or as a tectonic *mélange* (Chapter 9).

The Quaternary turbidites and contourites consist of sequences grading upward from terrigenous and bioclastic sands to marl oozes. The terrigenous fraction consists of quartz, plagioclase, K-feldspar, clays, and small amounts of dolomite. The clay mineral assemblage contains large amounts of mica (60%), relatively high amounts of chlorite (5-10%), and lesser amounts of kaolinite (2-8%). Montmorillonite is noticeable only in the fine fraction, of where it reaches 10 to 20 per cent. Occasional high percentages of pyrite are related to sapropelitic horizons.

The Pliocene marl ooze at the bottom of Hole 127 (Core 18) contains a clay-mineral assemblage which differs from that of the Quaternary. Here, interstratified clays are dominant (50%) at the expense of mica (20%) and montmorillonite (10%), with kaolinite and chlorite forming the remainder of the clay fraction.

Compositions of the fine fraction and clay mineral suites of the Quaternary turbidites in the Hellenic Trough resemble the Kithia assemblage of Rathnam and Ryan (1969). These authors have suggested that this assemblage was brought in from the Aegean Sea by bottom currents. However, the dominance of mica indicates a more local continental origin, such as Greece, for the clays. Thus it seems probable that the fine terrigenous constituent was eroded locally by turbidity currents and deposited in the deeper parts of the Hellenic trough. The uniformity of the assemblage throughout the hole indicates that this input remained constant during the Quaternary.

On the other hand, the clay minerals of the pelagic Pliocene horizon at the bottom of Hole 127 (Core 18) are significantly different from those of the Quaternary suite. They, along with dominant interstratified clays and montmorillonite (*complexe gonflant* of Chamley, 1971), belong instead to the western ridge assemblage of Rathnam and Ryan, which is believed to be emplaced largely by current or aeolian transport. Thus during the Pliocene, at this particular spot in the Hellenic trough, the pelagic marl ooze received the same fine-grained terrigenous contribution as the central Ionian basin.

## Levantine Basin

Two sites are situated in the Levantine Basin, one on the Mediterranean Ridge (130) and one on the Nile Cone (131). At both locations thick accumulations of dark turbidites, with occasional intercalations of light colored pelagic oozes, were penetrated.

The fine grained sections of the turbidites sequences are dark gray clays which are poor in calcium carbonate (1 to 5%) and are comprised of quartz, feldspar, and clay

minerals. Pyrite is common (2 to 10%). Dolomite (1 to 10%) occurs in the coarser fractions, suggesting a terrigenous detrital origin. Gypsum is associated with sapropelitic episodes (Chapter 23). Siderite occurs in two samples. The clay minerals are dominated by montmorillonite. It occurs in moderate amounts in the coarser fractions (20% in the 2-20 $\mu$  fraction) and reaches 50 to 80 per cent in the less than 2 micron fraction. Interstratified clays are present in relatively low amounts (10%) and were computed with the montmorillonite content. The remainder is comprised of kaolinite (20%) and moderate amounts of mica (10%) and chlorite (2%).

The interbedded pelagic marl oozes display a higher percentage of calcium carbonate (50 to 70%) and a subtly different assemblage of clay minerals. Montmorillonite is still the dominant mineral, but interstratified clays are more abundant (20%) at the expense of the montmorillonite. The amount of kaolinite remains unchanged, but the proportions of mica and chlorite are higher. A good example of pelagic deposits is Unit 3 (Core 6) of Site 130 in which the proportion is 75 per cent interstratified clays versus 5 per cent montmorillonite.

The composition of Nile sediments is well known. Sands are characterized by hornblende and epidote (Sukri, 1950), while clays are dominated by montmorillonite together with considerable amounts of kaolinite (Elgabaly and Khadar, 1962); Hamdi, 1967; Fayed, 1970). Thus, the mineralogy of the turbidites indicates a fluvial origin from the Nile. In addition, the surprisingly low percentage of calcium carbonate in the clayey layers at the top of the sequences point to a turbidity current mechanism of deposition for the entire sequence, as hypothesized by Nesteroff (1962).

In contrast, the interbedded pelagic horizons contain fine terrigenous particles of a different origin. The partial replacement of montmorillonite by interstratified clays suggest sources in the north. Consequently the emplacement of the pelagic oozes can be related to the general hydraulic regime of the eastern basin. Today, the currents entering this basin from the north are fed with suspended particles by the Aegean Sea and the Asian continent, while the Nile waters are mainly deflected to the east. This confirms the previous observations that the fine Nile clastics do not pass directly northward across the ridge (Emery *et al.*, 1965; Rateev *et al.*, 1966; Rathnam and Ryan, 1969).

The results confirm that the Nile Cone was built up from Nile River sediments which accumulated as turbidites, while the interbedded pelagic horizons were fed by north-eastern currents. Thus presently extant conditions have been maintained since the lower Quaternary.

### STRABO MOUNTAINS

The sediments recovered from Site 129 were difficult to interpret. A reasonable hypothesis is that they represent tectonically disturbed (*mélange*) dolomitic marl oozes. All sediments analyzed are Miocene in age. Cores 1, 2, and 3 are pelagic dolomitic marl oozes of Serravalian age, with Core 3 being contaminated by Messinian fauna. The last core, 3A, is a brackish-water dolomitic marl ooze of Messinian age. CB1 is a composite washed Core-Bit sample.

The oozes are comprised of quartz, feldspar, clay minerals, and a mixture of calcite and dolomite or dolomite only. The high proportions of dolomite suggest a secondary replacement of calcite.

The clay mineral suites are rather diversified. One assemblage is comprised of interstratified clays in greater amounts (40-60%) than montmorillonite (30%), lesser amounts of mica (10-20%) and some chlorite (2-5%). A second assemblage consists of abundant montmorillonite (30-40%) with small amounts of interstratified clays (5%), abundant mica (30-45%), and chlorite (5-10%). Kaolinite is absent or rare in both assemblages. A unique assemblage was observed in CB1, with high amounts of montmorillonite and kaolinite together with low amounts of mica.

The first two assemblages are very different from the Nile suite and indicate influences from the Aegean Sea and Turkish continent. This suggests that during the Miocene pelagic deposits in Site 129 were derived from sources similar to those of modern times. While the assemblage in CB1 is similar to that of the Nile suite further speculation must depend upon more careful analysis.

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### 20.3. A PRELIMINARY INVESTIGATION OF THE CLAY MINERALS IN THE WESTERN ALBORAN BASIN, SITE 121

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#### INTRODUCTION

Site 121 of the Deep Sea Drilling Project is located above the floor of the Western Alboran Basin of the Mediterranean Sea, a few kilometers north of the central flat-floored plain, at a water depth of 1163 meters. The drill hole penetrated sediments of Pleistocene, Pliocene, and late Miocene age and terminated at 868 meters below bottom in a basement of quartz-biotite schist and granodiorite. Twenty-four cores were taken, and from the recovered sequence 28 samples were analyzed for the present study.

The small size ( $\approx 5$  grams) of the shipboard samples precluded determination of the mineral assemblages other than those of the fine silicate fraction ( $< 2\mu$ ).

The distribution of clay minerals in the sequence penetrated is remarkably homogeneous (Figure 1). However, a careful examination of the individual diffractograms and of computations of the abundances and relative proportions of the various clay minerals does allow a subdivision of the clay variations into two types.

#### Techniques

The greater-than- $63\mu$  sand fraction of each sample was removed by sieving, and the carbonate material was destroyed by treating with 0.1N HCl. The less-than- $2\mu$  clay fraction was separated first by decanting and then with a centrifuge. After  $Mg^{++}$  saturation, the sediment was smeared as a mud slurry onto a glass slide. The X-ray diffraction patterns were obtained with a Phillips instrument and were presented graphically on a Hewlett-Packard X-Y Plotter.

#### DIAGENETIC ALTERATION IN RELATION TO THE DEPTH OF BURIAL

##### Formation of Montmorillonite

The montmorillonite becomes more abundant relative to illite (18Å/10Å ratio in Figure 1) toward the bottom of the drillhole. Furthermore, the illite shows no qualitative systematic variation in the samples analyzed (as indicated in the width of the 10Å peak at its 1/2 peak height and by the comparison of the intensity of the 5Å and 10Å peaks).

In contrast, there is a sympathetic relationship between the relative increase in the abundance of montmorillonite down hole and a simultaneous perfection in its crystallinity. This observation is deduced from the parameters developed by Chamley (1971) and Biscaye (1965) concerning the geometry of the 17Å peak after glycolization, and is particularly evident in the interval between 520 and 860 meters below bottom.

A preliminary interpretation of the diffractograms suggests that the clay assemblage contained a three layered mineral composed of illite, interstratified illite-montmorillonite, and montmorillonite, which after hydration, has evolved into montmorillonite. This original component, known as the "complexe gonflant" after Chamley (1971), is reorganized to montmorillonite with two interlayers of water. Such a re-ordering occurs in an endothermic reaction aided by the increase in temperature and burial depth. If this interpretation can be confirmed, it will provide insight into the diagenetic evolution of clays upon burial after deposition. Up to the present time, we have only observed the dehydration of montmorillonite under the effect of increased lithostatic pressure (first stage of Burst, (1969)