24. STUDIES OF DIAGENESIS AND LITHIFICATION

24.1. DIAGENESIS IN MEDITERRANEAN SEA CORE SAMPLES FROM SITE 124 – BALEARIC RISE AND SITE 125A – IONIAN BASIN

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ABSTRACT

Uppermost Miocene and lower Pliocene sediments from two sites in the western and eastern basins of the Mediterranean Sea were studied mineralogically to determine the extent of diagenesis in relatively young pelagic carbonates associated with evaporites. Authigenic albite and pyrite, recrystallized and partially silicified fossil tests, partially dolomitized calcite ooze, and chloritized glass shards were observed. Many more samples should be studied to verify diagenesis of the clay minerals.

INTRODUCTION

The youngest reported authigenic albites are from Eocene carbonate rocks (Von Foullon, 1891; Grandjean, 1909, 1910; Kastner, 1971). However, on the basis of suggested models for authigenesis of feldspars (Kastner and Siever, in preparation) and taking for granted the availability of the required chemical components in most marine carbonates, we predicted the presence of authigenic albite in younger carbonate rocks as well. Accordingly, we chose carbonate sediments associated with evaporites and diatomite beds as follows: (1) uppermost Miocene (Messinian Stage), western basin, Mediterranean Sea: Site 124–Balearic Rise, Cores: 6, 7, 11, and 13, at 38° 52.4′N, 4°59.7′E; water depth 2726 m, 362-418 m below sea water/sediment interface; (2) uppermost Miocene and Lower Pliocene, eastern basin, Mediterranean Sea; Site 125A–Mediterranean Ridge, Core 6, at 34°37.5′N, 20°25.8′E; water depth 2782 m, 71-80 m below sea water/sediment interface. The lithology of the above cores and the location of the samples that we studied in detail are shown in Table 1.

As predicted, authigenic albite overgrowths around detrital albite cores were identified in two of the samples as shown in Table 1 and Figure 1. Notwithstanding the thin sedimentary cover and young age, diagenetic effects are noticeable in these sediments. Most of the foraminiferal tests are at least partially recrystallized and a few slightly silicified. Most of the tests are filled with Fe-Mg-rich clays and pyrite. The calcareous ooze is partially dolomitized, and glass shards are slightly chloritized. The most abundant authigenic product is pyrite which, though scattered throughout the samples, is concentrated mainly in thin layers and associated with iron oxide (and/or hydroxide) and Fe-Mg clays (montmorillonite or chlorite), as shown in Figure 2.

A combination of petrographic microscope, X-ray diffractometer, and electron microprobe techniques enabled us to study the details of mineralogy and petrography of these fine grained sediments. The identity and relative proportions of clay minerals, as given in Table 1, were determined by the method described by Biscaye (1965) and Siever and Kastner (1967). An Applied Research Laboratories EMX electron microprobe X-ray analyzer was used for the mineralogical analysis of carbon-coated polished thin sections as described by Kastner (1971).

SITE 124 SAMPLES

Core 6, Section 1, 93-95 cm

Fine-grained, ordered dolomite rhombs with several thin diatomite layers. Detrital quartz and K-feldspar grains are poorly sorted, grain size ranging from 20 to 120 μm. All are angular but there is a slight increase in roundness of the larger grains. On the basis of their varied cathodoluminescence properties (different intensities of blue, orange, or no luminescence) they are of polygenetic origin; that is, they come from a variety of source rocks. The albites are much smaller, about 30 μm. The lower half of the sample contains less dolomite and more chlorite than the upper half. Pyrite is scattered throughout the sample and is highly concentrated in thin layers which form almost monomineralic beds (Figure 2). These pyrite layers occur more frequently adjacent to the diatomite layers and are associated with a higher concentration of iron oxide (or hydroxide) than in the rest of the sample.

Core 7, Section 1, 100-101 cm

Massive, coarse-grained gypsum with large dolomite rhombs. This sample has the largest diversity of detrital components as described in Table 1. Detrital quartz, K-feldspar, glauconite, and glass shards up to 150 μm long, as well as smaller albite, muscovite, pyrite, and foraminiferal tests, occur almost exclusively in thin layers parallel to bedding with only a few detrital grains between the layers. Such a distribution of detritals may result from occasional flooding of the evaporite basin or from intermittent strong eolian transport.

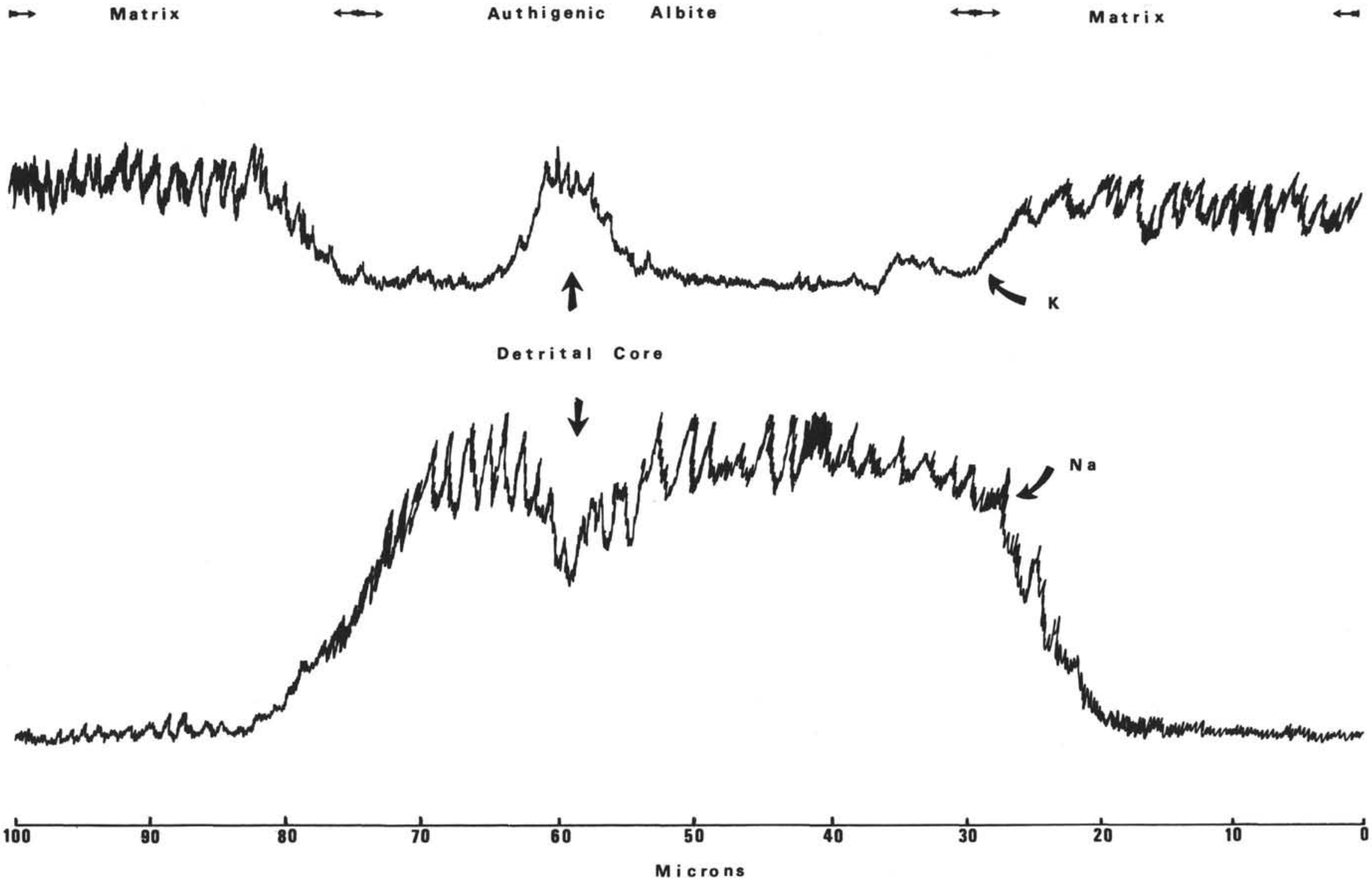

Figure 1. *Continuous electron beam scans for Na and K across dolomite matrix with some illite and authigenic albite with a potassium rich albite detrital core. Site 124, Core 13, Section 2, 72-73 cm.*

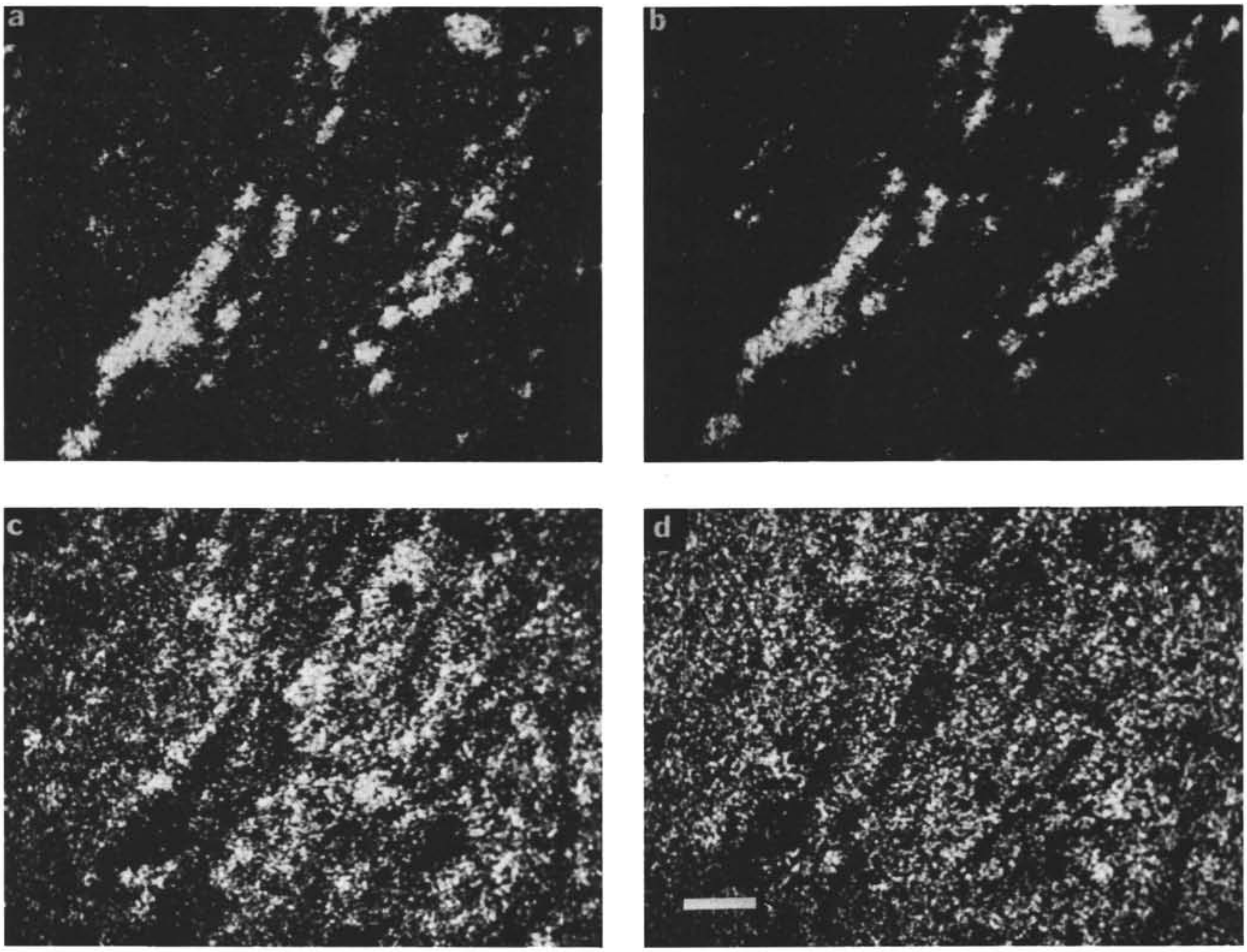

Figure 2. *Electron beam scanning photographs of pyrite layers in a dolomite matrix with chlorite and illite, in thin section of Site 124, Core 6, Section 1, 93-95 cm.*
a) $Fe_{k\alpha}$ X-ray image
b) $S_{k\alpha}$ X-ray image
c) $Mg_{k\alpha}$ X-ray image
d) $Al_{k\alpha}$ X-ray image
Scale bar represents 50 microns for all the photographs.

Authigenic albite, as overgrowths around detrital albite cores, is present but not abundant. The foraminiferal tests are recrystallized; a few are filled with clay and pyrite, a few with gypsum, and a few are partially silicified. The glass shards are partially altered to chlorite. The glauconite pellets are intact; they are not oxidized and do not have desiccation cracks.

Core 11, Section 2, 93-95 cm

Homogeneous, fine-grained, ordered dolomite rhombs. Relatively few detrital grains of quartz and K-feldspar of polygenetic origin are present. They are angular and small, the largest quartz grains being only 70 μm long. A few pyrite cubes are disseminated in the dolomite ooze.

Core 13, Section 2, 72-73 cm

Fine-grained, ordered dolomite rhombs. The detrital quartz and albite grains are angular, very small (not larger than 40μm) and are of polygenetic origin. Only a few detrital albite grains have authigenic albite overgrowths.

Core 13, Section 2, 101-102 cm

Fine-grained, ordered dolomite rhombs with several thin diatomite layers. The dolomite rhombs do not luminesce in the center, but their outer rims do luminesce, apparently indicating a change in the chemistry of the surrounding water during precipitation. The sorting index of the angular detritals is very low. The quartz grains range from 20 to 150 μm, the K-feldspars from 20 to 80 μm, and the albites from 10 to 40 μm. Iron oxide (or hydroxide) is concentrated adjacent to the diatomite layers.

SITE 125A SAMPLES

Core 6, Section 1, 98-99 cm

Foraminiferal tests floating in very fine grained calcite matrix. Large scattered dolomite rhombs constitute about 5

TABLE 1
Minearalogy of Seven Samples from Sites 124 and 125 Based on Petrographic Microscope, X-ray Analysis of Bulk Samples, and Electron Microprobe

Site	Core	Section	Interval Sampled (cm)	Sediment Description	Clay Minerals	Coarse Minerals (>10 μm)	Authigenic Silicates
124	6	1	93-95	Dolomite with thin diatomite beds.	$\frac{\text{Kaolinite}}{\text{Chlorite}} = 0.2$; $\frac{\text{Chlorite}}{\text{Illite}} = 1$; and traces of a mixed-layer clay.	Quartz, albite, K-feldspar, muscovite, pyrite	
	7	1	100-101	Gypsum.	$\frac{\text{Montmorillonite}}{\text{Illite}} = 2.1$ traces of chlorite.	Quartz, albite, K-feldspar, muscovite, glauconite, glass shards, pyrite.	Albite
	11	2	93-95	Dolomite.	Traces of illite.	Quartz, K-feldspar, pyrite.	
	13	2	72-73	Dolomite.	$\frac{\text{Chlorite}}{\text{Illite}} = 1.5$; and traces of a mixed-layered clay.	Quartz, albite, muscovite.	Albite
	13	2	101-102	Dolomite with thin diatomite beds.	Traces of a mixed-layered clay.	Quartz, albite, K-feldspar, muscovite.	
125A	6	1	98-99	Foraminiferal ooze.	Traces of a mixed-layered clay.	Quartz, albite, K-feldspar, pyrite.	
	6	1	128-129	Dolomite.	No traceable clay minerals.	Quartz, K-feldspar, pyrite.	

per cent of the total carbonate. Only a few medium-grained, angular detrital quartz, K-feldspar, and albite grains are present.

The foraminiferal tests are partially or completely recrystallized. All the chambers of the small tests are completely filled with an Fe-Mg-rich clay and pyrite. The larger chambers of the large tests show a higher degree of filling than the smaller chambers, as shown in Figure 3. The correlation between test size and amount of clay filling might be helpful for an evaluation of the current density. This is discussed by Siever and Kastner (1967).

Core 6, Section 1, 128-129 cm

Fine grained ordered dolomite rhombs. Large, angular, detrital quartz (up to 150 μm), K-feldspar, and pyrite and recrystallized foraminiferal tests are scattered throughout the sample.

All the dolomite and gypsum samples are from the evaporitic sequence. The calcite sample of Site 125A, Core 6, Section 1, 98-99 cm overlies the evaporite sequence of the eastern basin.

DISCUSSION

Despite the young age of the sampıes studied (uppermost Miocene and lower Pliocene), and the thin sedimentary overburden (Site 124: 362-418 m; Site 125A: 71-80 m below sea water/sediment interface), the samples show that a large variety of diagenetic processes of different kinds and intensities took place. The short depth interval of these samples does not allow interpretations about progressive changes that can be linked to depth of burial.

Quantitatively, the major constituent of five samples is fine-grained (a few microns), and ordered, rhombs of dolomite. The association of these dolomite oozes with evaporites, their homogeneity, the small dimensions of the rhombs, and the fact that such young dolomites are ordered, suggest to us that they probably are primary or penecontemporaneous dolomites. Isotopic studies, which may corroborate this interpretation, are discussed in Chapter 30.

On the other hand, petrographic observations show that the large dolomite rhombs of some samples (Site 124, Core 7, Section 1, 100-101 cm; and Site 125A, Core 6, Section 1, 98-99 cm) grew at the expense of the matrix components and penetrate crystallographic faces of the components. We conclude that they are diagenetic dolomites.

All foraminiferal tests are at least partially recrystallized, and the slight silicification of several tests is not surprising in an environment where diatomites are abundant.

As noted above, the foraminiferal tests, large and small, are partially or completely filled with clay. We suggest this represents mechanical filling of tests by sediment, rather than diagenetic formation of minerals within them. A direct correlation of test size and the amount of clay filling has been suggested as a possible indicator of current density. Yet an opposite correlation between test size and filling amount has been found by Siever and Kastner (1967) in foraminiferal tests from the vicinity of the Mid-Atlantic Ridge, where the smaller tests are empty and the larger ones filled. The tests in both mid-Atlantic and Mediterranean are intact. A satisfactory explanation for the difference of test filling in the two regions will have to await more systematic observations of this effect.

Fine-grained pyrite is also present inside the foraminiferal tests, suggesting that the organic matter of the foraminifera was not completely decayed prior to filling

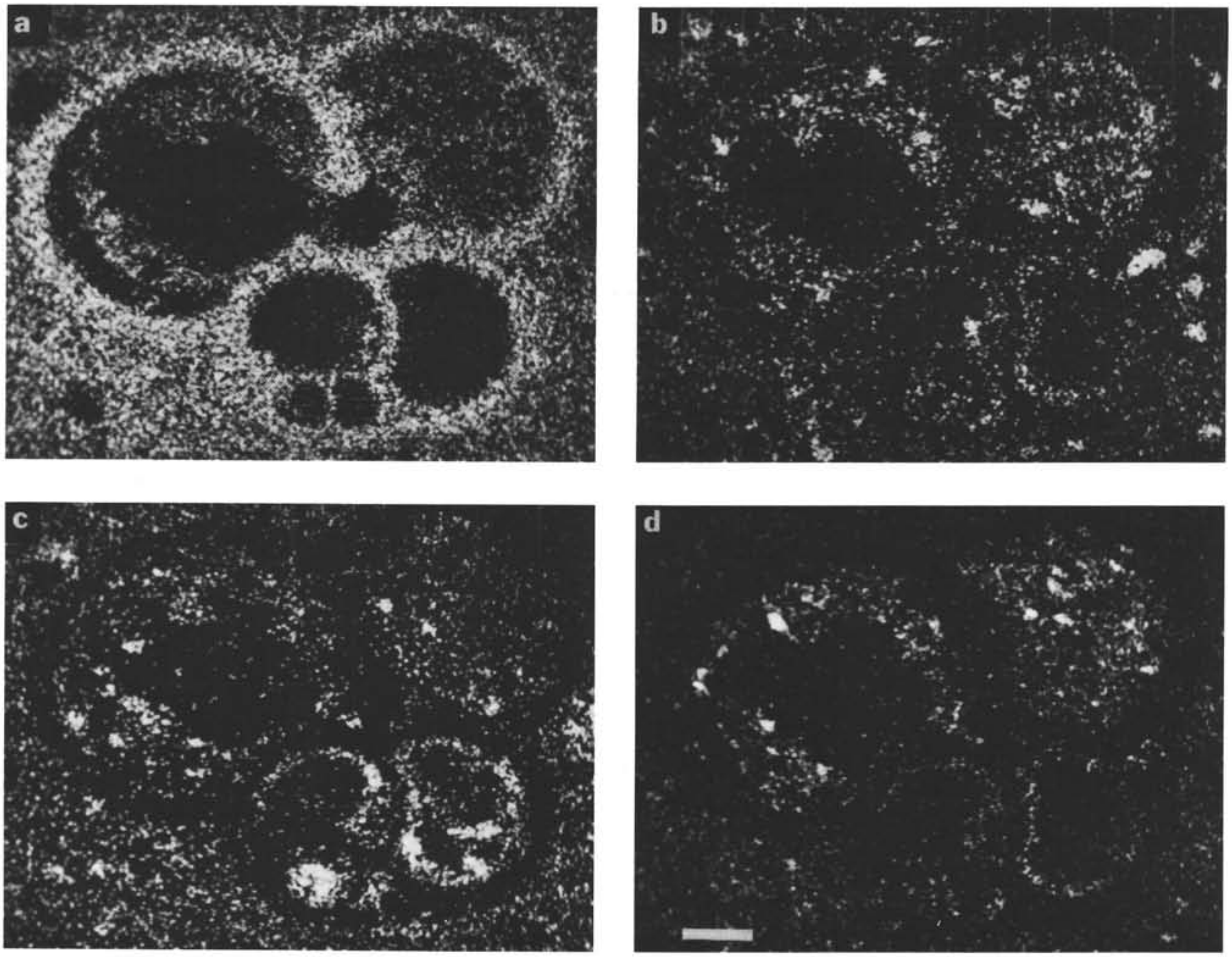

Figure 3. *Electron beam scanning photographs of a large Foraminiferal test partially filled with Fe-Mg rich clay and small pyrite crystals, in thin section of Site 125A, Core 6, Section 1, 98-99 cm.*
a) $Ca_{k\alpha}$ X-ray image
b) $Mg_{k\alpha}$ X-ray image
c) $Al_{k\alpha}$ X-ray image
d) $Fe_{k\alpha}$ X-ray image
Scale bar represents 50 microns for all the photographs.

with Fe-Mg rich clays. The close relation between Fe-Mg rich clay minerals and pyrite formation has been discussed by Siever and Kastner (1971) and Drever (1971). They suggested that the diagenetic pair, Fe-Mg clay and pyrite, is related to Fe-Mg exchange in clays associated with sulfate reduction. The pyrite rich layers formed probably in a similar manner.

On the basis of the argument that authigenic feldspars will form readily in diagenetic environments provided that the essential constituents are available in abundance (Kastner, 1971; Kastner and Siever, in preparation), we have predicted that there is a high probability of finding authigenic feldspars in the samples such as those studied, which are associated with (1) evaporites–which indicate high alkali concentration, (2) diatomite–a major source of silica, and (3) clay minerals and detrital feldspars. The fact that we found authigenic albite overgrowths around detrital albite grains in two of the samples supports our view of the chemical controls on authigenic feldspar formation. The scarcity of authigenic feldspars in these samples probably indicates that the kinetics of feldspar formation at low temperatures and pressures is very slow. Consequently, presumably the older the rocks the higher the abundance of authigenic feldspars expected to be found in them.

ACKNOWLEDGEMENTS

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24.2. EXAMINATION OF SELECTED LITHIFIED ROCKS FROM SITES 121 – ALBORAN BASIN, 125 – IONIAN BASIN, 129 – STRABO TRENCH AND MOUNTAINS, AND 131 – NILE CONE

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INTRODUCTION

Deep-sea cores containing a variety of lithified carbonate and carbonate-clastic sediments were recovered from the Mediterranean Sea during Leg 13 of the Deep Sea Drilling Project.

The purpose of this report is to describe these lithified sediments and to attempt to draw some preliminary generalizations relative to the problem of cementation.

PROCEDURE

Lithified materials were sampled and subjected to textural and mineralogical analysis, using both optical and X-ray diffraction techniques. CuK α radiation was used in all diffraction mineral analyses.

To aid in the optical identification of carbonate phases, staining methods were employed. Where the exact location of a particular phase was desired, acetate peels were made and compared with standard thin sections.

RESULTS

Detailed descriptions of the rocks follow:

Sample 13-121-14-1, 144-148 cm – Alboran Basin.

The sample was taken from a section of core four centimeters long, consisting of a dark gray, well-lithified quartz sandstone. The grains are cemented by anhedral low-magnesian calcite (see also Chapter 30.1), with little pore space left between the grains. Some dolomite rhombs have formed at the expense of the calcite cement, as confirmed by diffraction analysis. Detrital grains consist predominantly of quartz with subordinate amounts of muscovite and biotite micas (see Figure 9 of Chapter 3). Some micritic rock fragments of detrital origin are present. Material resembling rock gypsum was observed, but the mineral was not confirmed by diffraction. The quartz grains range in size from coarse silt to medium sand, and in roundness from subangular to round. All of the genetic quartz types were identified. Organic particles include tests of foraminifera, filled partially or completely with pyrite. Some of these tests exhibit geopetal structure, indicating that they were free of lithic material at the time of deposition. The mica flakes exhibit some coarse form of alignment subparallel to the bedding surfaces. Numerous dark fragments of possible organic origin are present, and these too are aligned subparallel to the bedding.

Sample 13-121-15-1, 131-133 cm – Alboran Basin

The sample was taken from a rather thick unit of dark gray, fairly well-lithified quartz sandstone. This material is similar in appearance and in composition to that described above, although less well lithified. The boundary with the underlying unconsolidated sediment is sharp but irregular. Some of the underlying khaki-colored fine sediment is included in this unit as part of an elliptical structure which may represent a burrow of organic origin (see Figure 16 of Chapter 3).

Low-magnesian calcite, undergoing replacement by dolomite, was confirmed by optical as well as diffraction methods as the grain-cementing material. It occurs as isolated rhombs in the calcite cement. The edges of these rhombs are sharp, precluding the possibility of transportation.

Sample 13-125A-6-1, 137 cm – Ionian Basin

This sample consists of a light gray fragment from a crushed, partly-indurated crust at the contact between Lower Pliocene pelagic oozes (above) and dolomitic and pyritic marls (below) of the Messinian evaporite layer (see Figure 12 of Chapter 7). The piece is roughly cylindrical in shape and somewhat rounded, measuring 1.2 cm long by 0.8 cm in diameter. The mineralogy of the sample is stoichiometric dolomite, having a $\bar{1}\bar{1}0$ reflection peak at 2.98Å.

This fragment is fine-grained and is made up entirely of subhedral and euhedral dolomite rhombs. The subhedral rhombs are rounded at the edges. There is some suggestion of stratification in the fragment. Some of the layers appear to be less well-cemented than the remainder of the rock. No