9. BURIAL DIAGENESIS OF PELITIC AND CARBONATE DEEP-SEA SEDIMENTS FROM THE ARABIAN SEA

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ABSTRACT

The holes completed during Leg 23A were drilled into largely pelagic carbonate sequences ranging in age from Recent to Paleocene as well as into the siliciclastic turbidites of the Indus Cone. They presented the opportunity to study carbonate and clay mineral diagenesis of sedimentary sequences that accumulated in the same basin.

The clay minerals observed in the 1300-meter-deep Indus Cone borehole (Site 222) are illite, chlorite, kaolinite, 17Å and 11Å mixed-layer illite/montmorillonite, and palygorskite. The first three of these clay minerals were brought into the basin by the Indus River, whereas the 17Å mixed layer was stripped from the continental shelf of India and redeposited by density currents into the deep sea. Palygorskite is either of eolian or authigenic origin.

Under increasing overburden pressure progressive lithification of the clays takes place by compaction and expulsion of pore waters. Moreover, from 300 to 1300 meters a slight decrease of illite and a concomitant increase of 17Å mixed layers is also observed. Over the same depth range the peak width at half height of air-dried illite narrows. These changes are interpreted to indicate a breakdown of illite, a reduction of expandable layers in "open" illites, and a neoformation of 17Å mixed-layer illite/ montmorillonite. Hence, clay mineral diagenesis starts at much shallower depths than previously believed.

Investigation of the nannofossil carbonates recovered at Sites 220 and 223 demonstrates that compaction only accounts for the transformation of soft to stiff ooze. Further lithification and reduction of porosity takes place by cementation which increases with depth. The top of the semilithified chalk marks the limit where the grain framework is stabilized by cementation at point contacts. It is at this stage that the fossils begin to exhibit progressive changes with depth.

First, precipitation of overgrowth cement on discoasters is observed. Below about 100 meters the individual segments of coccoliths also start accreting secondary calcite. With increasing depth, accretionary growth on these segments bridges the space between placolith shields, finally filling it completely. Moreover, precipitation of calcite overgrowths also fuses micarb particles causing further induration of the sediment. At even greater depths the central fields of coccoliths are clogged, and calcite crystals have grown into foraminiferal chambers.

Lithification of nanno oozes in the deep-sea environment is largely accomplished by dissolution of supersoluble particles, pressure solution and reprecipitation of syntaxial low magnesian calcite overgrowths on discoasters, coccoliths, and micarb grains (autolithification). It is not related to age of the sediment and is less controlled by depth than by primary carbonate content. A sudden rise of the original carbonate content subsequently causes a lithification front which also appears on the seismogram.

Early silicification affected some Eocene chalks. The silica is derived from organic opal and is reprecipitated as low-cristobalite spherules. Silicification postdates precipitation of overgrowth cements in these intervals.

It is concluded that lithification of clays and of pelagic carbonates is achieved through entirely different processes which operate at different rates. Generally, pelagic carbonates become lithified at much shallower depths.

INTRODUCTION

During Leg 23A the *Glomar Challenger* drilled six holes in the Arabian Basin recovering various types of deep-sea sediments ranging from siliciclastic turbidites to almost pure nannoplankton oozes. At Site 222, a 1300-meter terrigenous hole containing mostly pelitic sediments was drilled into the Indus Cone which represents the present penetration record of the vessel. Sites 220 and 223 encountered 329 and 717 meters, respectively, of dominantly carbonate oozes and chalks.

Therefore a unique opportunity was available to study the diagenetic changes following burial of pelitic sediments and of carbonate oozes deposited within the same basin and to compare the nature and rapidity of these processes. Of the six sites drilled during Leg 23A the three sites mentioned above were selected for this study.

The first part of this report discusses diagenesis of pelitic sediments, next progressive lithification or diagenesis of deep-sea carbonates is discussed and, finally, an attempt is made to compare both diagenetic realms.

Because of the dissimilar mineralogical composition of the two sediment types, namely, clay minerals versus calcitic nannofossil tests, entirely different methods of study had to be employed. X-ray techniques were used to study the clay minerals and their changes during early diagenesis, whereas the carbonate oozes were primarily studied with the scanning electron microscope (SEM).

DIAGENESIS OF PELITIC SEDIMENTS

Site 222 is particularly suitable for the study of burial diagenesis of pelitic sediments because of the deep penetration and the monotonous lithological and geochemical facies of its sediments (Chapter 6, this volume). The sequence consists of structureless mudstones, laminated and graded silts, and sands with many thin intervals of green nanno detrital clays. The samples from this site were compared with several clay fraction samples from Site 223. A total of 38 samples from Site 222 (see Table 1) and 13 samples from Site 223 (see Table 2) were analyzed by the author.

Previous Studies

Clay minerals form the bulk of the nonbiogenous fraction of marine sediments. Therefore, our understanding of their origin, dispersal patterns, and diagenetic modification after burial is important for any interpretation of ancient sediments.

Until a few years ago it was generally believed that clay minerals carried to the sea by streams or wind were modified considerably upon contact with the marine environment; for instance, Grim and Johns (1954) assumed that detrital montmorillonite was progressively transformed to illite and chlorite. However, more recent studies (Weaver, 1958; Griffin et al., 1968; Hathaway, personal communication 1973; and others) have shown that except for the neoformation of montmorillonite devitrification of volcanic glass, virtually all other clay minerals are of detrital origin and remain almost unaffected on the sea floor. But, once buried, distinct compositional changes affect the clay minerals with increasing overburden. A number of detailed studies on deep borehole sections, which are summarized in Dunoyer de Segonzac (1970), revealed that montmorillonite is first transformed to irregular mixed-layered illite/ montmorillonite which alters with progressively deeper burial to a regular mixed-layered illite/montmorillonite and then finally to illite. Thus the amount of expandable layers decreases continuously downhole. This progressive illitization which results from a structural rearrangement of the lattice is accompanied by adsorption of sodium, potassium, and magnesium ions; this was noted by Powers (1959) and has since been confirmed by various authors (e.g., Long and Neglia, 1968; Dunoyer de Segnozac, 1969; Perry and Hower, 1970; Weaver and Beck, 1971).

During deeper diagenesis and early metamorphism (anchimetamorphism), kaolinite is destroyed and a number of new mineral phases appears such as chlorite, paragonite, pumpellyite, etc. (Dunoyer de Segnozac, 1970; Frey, 1970).

At present the transformations affecting clay mineral assemblages during deep burial and early metamorphism are well documented. However, there is still considerable uncertainty about the depth at which the progressive transformation of montmorillonite begins. Of course, there will be no fixed depth, but rather a depth range because this transformation is primarily temperature dependent and, to a lesser degree, is dependent on pressure, age of the formation, and composition of interstitial waters. Therefore, in areas with a high geothermal gradient, such as the Rhinegraben or the Salton Sea, the transformation will occur at shallower depths than in stable areas with normal geothermal gradients.

According to published data the transformation of montmorillonite into irregular mixed-layer illite/montmorillonite takes place at depths ranging from 1200 to 2500 meters (see also Dunoyer de Segonzac, 1970, Fig. 5). However, Heling (1970) observed that the amount of montmorillonite layers in mixed-layer illite/montmorillonite was already reduced at 700-900 meters in the Rhinegraben. To the present writer's knowledge this is the only published case history that reports and attributes montmorillonite contraction to burial in sediments with less than a 1000-meter overburden.

The progressive contraction of the smectitic layers to illite is reflected by the "sharpness" of the 10Å peak, which is measured as the peak width at half height, a technique introduced by Weaver (1960). As pointed out by Dunoyer de Segonzac (1970), this method was not adopted in the U.S., but has been widely used in Europe to determine the diagenetic grade of sediments.

The illite peak width at half height measured in millimeters in somewhat misleadingly called "illite crystallinity" in European literature. The students using "illite crystallinity" have always been aware that peak width is not a direct measure of crystal perfection in the crystallographical sense, because peak width depends on several factors such as crystal size, occurrence of expandable layers, number of water layers absorbed in each one of them, and randomness of their occurrence as pointed out by J.C. Hathaway (personal communication, 1973). However, if the clay samples are always of the same restricted grain size ($<2\mu$) and if a large number of samples are

	Depth		7Å Kaolinite	10Å Illite	14Å Chlorite	11Å Mixed-laver	17Å Mixed-laver	Palvgorskite	III (1-1 Peak V Hei	ite Vidth at Half ght)
Sample	(m)	Age	(%)	(%)	(%)	(%)	(%)	(%)	Air-Dried	Glycolated
1-2, 24	1.7	Pleistocene	11	53	19		7	10	26	24
2-1,60	53.6	Pleistocene	7	40	11		24	18	22	17
3-3, 4	104.4	Late Pliocene	14	46	21		13	6	22	16
6-3, 20	140.2	Late Pliocene	14	54	21		11	-	10	7.5
6-4, 110	142.6	Late Pliocene	9	39	10		28	14	-	23
8-3, 54	187.5	Late Pliocene	11	59	18		12	<u></u>	10	8.7
9-2, 34	214.8	Late Pliocene	9	58	19		14	-	12	9.5
9-2, 105	215.5	Late Pliocene	10	56	19		15	-	14	8
11-2, 120	309.7	Late Pliocene	9	61	15	<5	10	-	13.5	12
12-2, 115	355.6	Late Pliocene	12	49	22	Antice	17		18	9
13-2, 128	401.7	Early Pliocene	14	51	22		13	-		9.5
16-1,58	445.5	Early Pliocene	12	55	18		15			13.5
16-1, 138	446.3	Early Pliocene	12	54	20		14	-	17	9
18-1, 138	493.3	Early Pliocene	12	53	19		9	7	17	9
19-3, 41	543.4	Early Pliocene	9	62	18	. 8	11	-	17	11
19-3, 94	543.9	Early Pliocene	11	48	13		18	10	25	20
20-2, 85	589.3	Early Pliocene	8	53	16	12	11		18	8
20, CC	591.0	Early Pliocene	10	47	17	8	18	TT 2	24	10.5
21-2, 118	636.6	Early Pliocene	15	51	20		14		14	9
22-2, 85	692.3	Early Pliocene	11	57	20	<5	8	-	14	9.5
23-4, 53	752.0	Late Miocene	8	51	13	5	22	<u></u>	13	-
24-2,97	806.4	Late Miocene	16	49	23	-	12	Т	14	8.5
25-2, 16	862.6	Late Miocene	14	45	20	<5	17	=	-	11
25-2, 67	863.1	Late Miocene	10	49	16		12	13	29	28
27-2, 133	927.8	Late Miocene	13	54	18	1.55	15		9	9
28-4, 52	993.0	Late Miocene	11	41	17	7	24		12	9
28-5, 21	994.2	Late Miocene	12	50	18	5	15		15	10
30-1, 123	1098.2	Late Miocene	13	46	23	5	13		14	8.7
31-6, 82	1136.3	Late Miocene	13	51	19		17	221	13	9.5
32-2, 48	1171.9	Late Miocene	6	48	11	9	19	Т	—	17
32-6, 31	1176.8	Late Miocene	12	53	17	<5	14		17	11
33-2, 87	1213.3	Late Miocene	9	66	14		11		14	9
33-6, 91	1219.4	Late Miocene	14	51	21		14		13	8
34-1, 107	1259.0	Late Miocene	9	51	13	< 5	23		8 — 1	12
34-5, 24	1264.2	Late Miocene	12	45	18	< 5	23	1000	-	11.5
35-1, 71	1286.7	Late Miocene	11	47	14	-	16	12	37	17
35-3, 87	1289.8	Late Miocene	13	47	18	-	21		10	7
36-2, 31	1296.8	Late Miocene	10	54	17	7	12		13.5	10.5

 TABLE 1

 Relative Abundance of Clay Minerals and Illite Peak Width of Half Height Crystallinity

 $< 2\mu$ (Fraction) at Site 222

Note: Sum of clay minerals equals 100 percent. T indicates a trace was found.

analyzed, illite peak width becomes a reliable parameter of diagenesis and early metamorphism of sediments, as has already been successfully demonstrated (see review paper by Dunoyer de Segonzac, 1970).

Whereas distinct trends towards improved "illite crystallinity" below approximately 1000 meters of overburden have been noted by many authors in stratigraphic sections from various parts of the world, the rather irregular variations observed at shallower depths are considered to reflect the inherited detrital crystallinity. It is one of the purposes of this paper to document the progressive burial diagenesis of pelitic sediments starting from unconsolidated mud at the sea floor and to document an example of very shallow onset of clay mineral (montmorillonite) transformation.

Analytical Techniques

The shipboard samples were disaggregated in the shorebased laboratory, and then the $<2\mu$ fraction was separated using Atterberg sedimentation cylinders. After ethyleneglycol solvation and heating for 1 hour at 550° Celsius, oriented specimens were air-dried and analyzed by standard X-ray diffraction techniques.

Eight samples were boiled in 2N HC1 which dissolved the chlorite. Afterwards, they were X-rayed following the method described by Maxwell and Hower (1967) to determine the mica polytypes. Two of these samples were subsequently analyzed as oriented specimens to identify the nature of the 11Å mixed-layer mineral. Some random powder film patterns were made using a Guinier camera and

Sample	Depth (m)	Age	7Å Kaolinite (%)	10Å Illite (%)	14Å Chlorite (%)	17Å Mixed-layer (%)	Palygorskite (%)
1-2,60	2.1	Late Pleistocene	9	39	14	28	10
3-1, 123	86.2	Early Pleistocene	7	37	23	21	12
5-5,63	156.6	Early Pliocene	10	44	11	22	13
7-3,8	227.0	Late Miocene	10	30	13	28	19
9-2,87	273.3	Late Miocene	8	33	10	32	17
11-6,80	317.3	Late Miocene	8	33	13	36	10
13-2,50	349.0	Late Miocene	7	30	21	37	15
16-2,60	386.1	Late Miocene	7	45	11	17	20
20-4, 102	425.5	Middle Miocene	5	31	9	42	13
26-4,56	483.5	Middle Miocene	17	35	22	20	6
32-4, 118	568.7	Middle Eocene	11	3	-	86	5 <u>11</u>
36-1, 141	629.4	Early Eocene		24	-	68	8
37-1, 133	657.3	Late Paleocene	26	8	-	66	-

 TABLE 2

 Relative Abundance of Clay Minerals (<2µ Fraction) at Site 223</td>

Note: Sum of clay minerals equals 100 percent.

FeK_{α} radiation to detect small amounts of palygorskite and to determine the chlorite polytypes. In addition, the potassium and aluminum contents of a few samples ($< 2\mu$ size fraction) were measured by X-ray fluorescence.

The water content and porosity data used in this report were determined at sea by the chemist using the method described in Chapter 2.

Identification of Clay Minerals

The clay minerals found at Site 222 are illite, irregular mixed-layer illite/montmorillonite, kaolinite, chlorite, and palygorskite.

Illite is identified by a strong 001 peak at 10.0Å, a weak 002 peak at 5.0Å, and again a strong 003 peak a 3.33Å. Ethylene-glycol solvation leaves these peaks unaffected. The micas are of the dioctehedral 2M and disordered 1Md polytypes.

Chlorite is recognized by strong, sharp 002 and 004 peaks at 7.1Å and 3.55Å, respectively, and weak, broad 001 and 003 peaks at 14.2Å and 4.72Å, respectively. These peaks are not affected by ehtylene-glycol solvation; upon heating, however, the intensity of the 001 peak increases and the peak shifts to 13.8Å, while the other basal reflections almost completely disappear. The 060 reflection could not be resolved on powder film patterns either because it coincides with a quartz line or because the amount of chlorite in the samples is too small. Therefore, the chlorite variety cannot be determined, but the abovementioned peak intensities before and after heating suggest an Fe-rich variety.

Kaolinite's 001 peak coincides with the 002 peak of chlorite at 7.1Å. The presence of kaolinite in addition to chlorite is identified by a peak at 3.60Å (002). If necessary, this peak can frequently be resolved by using a low goniometer speed of $1/4^{\circ} 2\theta$.

Mixed-layer illite/montmorillonite and montmorillonite; most diffractograms of the air-dried samples from Site 222 display a low-angle shoulder on both the 001 illite and the 001 chlorite peak and a platform in-between these peaks. However, the samples from Site 223 have the shoulder on the high angle side of the chlorite peak. After ethylene-glycol solvation a broad peak centered between 16.0Å and 17.0Å is formed, while the low-angle illite shoulder and the platform usually disappear.

Reynolds and Hower (1970) have shown that pure montmorillonite as well as irregular mixed-layer illite/ montmorillonite containing as much as 60 percent illite layers have a 17Å peak. Although DSDP X-ray data sheets list the mineral with this behavior as montmorillonite, it should be called 17Å irregular mixed-layer illite/montmorillonite as suggested by Hayes (1973). The amount of expandable layers is determined by the spacing of the 002 illite/003 montmorillonite peak (Reynolds and Hower, 1970). However, as this peak is never sufficiently individualized on our diffractogram, the amount of expandable layers cannot be determined. Nevertheless, the behavior of the mixed-layer peaks suggests that a more or less continuous series of mixed-layer illite/montmorillonite minerals is present ranging from montmorillonite-poor to montmorilloniterich types, with those containing 40-60 percent expandable layers being the most frequent. They also contain a few chlorite layers, but these were disregarded in the quantitative analysis.

In some samples a low-angle shoulder on the illite 001 peak is observed between 11.7Å and 10.4Å after glycolation. This shoulder might be caused either by an irregular mixed-layer mineral such as illite/montmorillonite with few expandable layers or illite/chlorite, or by small amounts of palygorskite. Hot 2N HC1 which destroys chlorite did not affect this low-angle shoulder, but after heating to 550° Celsius it disappeared. Hence, it represents either a mixed-layer illite/montmorillonite or palygorskite. Because the shoulder tails off to 11.7Å, we favor the former. This scarcely expandable illite/montmorillonite which is labelled 11Å mixed layer in Table 1 occurs only in minor amounts.

Fully expandable, pure montmorillonite which is absent in Site 222 was found in large amounts in the lower stratigraphic intervals at Site 223 (as well as at Site 224 by P. Stoffer, personal communication).

Palygorskite, which is present in almost every sample at Site 223, was rarely observed at Site 222 (see Table 1). Its major peak (110) occurs at 10.5Å where it may coincide with mixed-layer illite/montmorillonite. If present in larger amounts, it is readily identified by a series of other peaks (Christ et al., 1968), especially by the 200 peak at 6.4Å. Although palygorskite in small quantities and in the presence of illite/montmorillonite mixed-layers is difficult to recognize by X-ray methods only, it is easily identified with the electron microscope by its typical needle-like shape (Figure 1).





Figure 1. SEM micrographs of palygorskite fibers (a) 224-11-1, 80 cm, (b) associated with illite flakes.

In the $<2\mu$ size fraction other minerals such as quartz and feldspar are always present and occasionally clinoptilolite was also noted.

Much discussion regarding the merits of various techniques for determining the relative abundance of clay minerals occurs in the literature. However, no method, no matter how sophisticated, exists which is universally acceptable. I have, therefore, chosen a' simple method which is as good as any other, especially if the clay mineral suite remains the same.

We measured the areas under the 17Å illite/montmorillonite, 10Å illite, 10.5Å palygorskite, and 7Å chlorite + kaolinite peaks. The area of the 7Å peak was divided between chlorite and kaolinite according to their peak height ratio at 3.55Å and 3.60Å, respectively. The relative abundances of these clay minerals was then calculated by adding 1/3 illite/montmorillonite, 1/1 illite, 1/2 kaolinite, 1/2 chlorite, 1/2 palygorskite, and normalizing to 100 percent. Palygorskite, because of its needle-like shape, has no preferred orientation as do micaceous minerals, and it is therefore difficult to estimate its proportion from oriented samples.

Provenance of Clay Minerals

The clay mineralogy of the surface sediments in the northern Arabian Sea has been investigated by Stewart et al. (1965), Gorbunova (1966), and Eckhardt et al. (1970). Goldberg and Griffin (1970), in an extensive study of the clay minerals from sediments and airborne dust, depict the general aspects of clay mineral distribution and origin in the northern Indian Ocean.

As mentioned earlier in this paper, the clay mineral suite of some Leg 23A sites consists of illite, kaolinite, chlorite, 17Å irregular mixed-layer illite/montmorillonite (montmorillonite of many authors), 11Å irregular mixed-layer illite/ montmorillonite. and palygorskite.

On the basis of the clay mineral distribution of the surface sediments (Goldberg and Griffin, 1970) and the vast amount of information gathered during Leg 23A, it is possible to better understand the lateral and vertical distribution of the clay minerals in the northern Arabian Sea and to infer their transport paths and source areas.

Illite is the dominant clay mineral on the Indus Cone (>50 percent of clay fraction) whereas 17Å mixed-layer illite/montmorillonite shows highest values (>50 percent) on the shelves bordering the Indian peninsula. The concentration pattern (Goldberg and Griffin, 1970, fig. 3) suggests that the Indus drainage is the main source of illite. At Sites 222 and 221, illite is found in large amounts, not only in the clays of the fine grained Cone sediments, but also in the coarser graded beds. It is concluded, therefore, that illite is distributed from the Indus mouth as far as the foot of Carlsberg Ridge by density currents which at least partly follow the distributive deep-sea fan channels. Composition and structure of the graded beds (Jipa and Kidd, this volume) as well as the occurrence of coarse grained mica and plant fragments in the Indus Cone's surface sediments Stackelberg, 1972) further substantiate this (von interpretation.

Highest chlorite concentrations are observed in the Gulf of Oman and in a tongue-like protrusion into the Arabian

Basin south of the Indus mouth. From this distribution Goldberg and Griffin (1970) concluded that the source area of chlorite must be located in the Persian Gulf or its surroundings. If true, it is conceivable that chlorite is brought to the Arabian Basin by the overflowing saline high-density Persian Gulf bottom waters which were reported by various authors (Emery, 1956; Hartmann et al., 1971). Recently Hartmann et al. (1971) have documented an input of fine-grained particles, which occur in and originate from the Persian Gulf, into the Gulf of Oman; e.g., aragonite and palygorskite (also see subsequent text discussions). These particles are also present in the northern part of the Oman Gulf but are absent in its southwestern part. Therefore, it is unlikely that chlorite found on the Indus Cone would have its source in the Persian Gulf. Moreover, as no difference in chlorite abundance is observed between the turbidite beds and structureless mudstones at Site 222, it is more likely that most of the chlorite is also derived from the Indus.

According to Eckhardt et al. (1970) and Goldberg and Griffin (1970), 17Å irregular mixed-layer illite/montmorillonite shows a strong decrease from the Indian coast towards the deep sea where it is found only in small amounts (<30 percent). However, detrital 17Å (mixed layer) in amountsgreater than 50 percent(Riverside laboratory together with redeposited shallow water organisms and aragonitic pellets (Jipa and Kidd, this volume) occurs in some graded beds from Site 221, which is situated on the Arabian Abyssal Plain.

These high amounts of detrital "montmorillonite" in the deep sea at Site 221 are obviously turbidity current deposits and probably originate on the Indian shelf or upper slope. High amounts (>80 percent of $<2\mu$ fraction) of true montmorillonite with 100 percent expandable layers occur at Sites 223 and 224 in a thick sequence over basalt. This montmorillonite is an alteration product of volcanic particles (Chapters 7 and 8, this volume). Today, similar high concentrations of montmorillonite are located over parts of the Carlsberg Ridge (Goldberg and Griffin, 1970, fig. 4).

According to these authors kaolinite shows no distinct pattern which would reflect the source area. Because of lack of control points, it is presently not possible to decide which is the most important source and transport mechanism (wind, water) for kaolinite. However, chlorite and kaolinite have a strong postive correlation at Site 222 (see next paragraph) which is indicative of a common source. Hence, kaolinite is probably also largely derived from the Indus River.

Palygorskite is identified for the first time with certainty and in larger amounts than previously observed in the northern Arabian Basin, although Goldberg and Griffin (1970) observed a low-angle shoulder at 10.5Å on the illite 001 peak which suggested to them that palygorskite might be present. Heezen et al. (1965) observed high palygorskite concentrations in the Gulf of Aden, and Goldberg and Griffin (1970) noted an eastward decrease towards the tip of India. It is probable that palygorskite is picked up.in the arid parts of Africa and southern Arabia (Müller, 1961) by the southwest monsoons which distribute it across the Arabian Sea. The ratio palygorskite/illite corresponds exactly to the bathymetric profile (Goldberg and Griffin, 1970, fig. 8) with lowest values on the distal Indus cone. It is therefore just as likely that palygorskite is of authigenic origin resulting from the alteration of volcanic glass and that the low values merely indicate dilution by detrital illite.

Indeed, in the westernmost drill sites, 223 and 224, which are protected by the Owen Ridge from the influence of turbidity currents of the Indus, the highest palygorskite values are recorded (Table 2 and X-ray data, Chapters 7 and 8, this volume). However, in most of the Indus Cone sediments of Site 222, palygorskite is undetectable, probably because it is diluted by the enormous detrital sediment input from the Indus as reflected by the extremely high sedimentation rate (Chapter 6, this volume). In the Pleistocene samples palygorskite shows up regularly because of a much lower sedimentation rate, i.e., less river borne deposition. (Chapter 6, this volume). It is interesting to note that below the Pleistocene sequence there is no difference in palygorskite abundance between the green and gray facies which are thought to represent slower and faster rates of deposition (Chapter 6). It is conceivable that the rates for both facies are high and do not differ markedly.

Analyses of dust samples show that montmorillonite, illite, chlorite, kaolinite, and possibly also palygorskite are transported by wind. The question, therefore, is which medium, air or water, is the more important transporting agent of the clay minerals that are being deposited in the Arabian Sea. The data indicate that the rivers of eastern India definitely contribute most of the clay minerals which are deposited on the Indian shelf, the Arabian Abyssal Plain, and the Indus Cone, whereas the clay mineral sedimentation from off the South Arabian coast to the Owen Ridge (the latter acting as a barrier to the density currents of the Indus Cone) appears to have a greater eolian and authigenic component.

Depth-Dependent Clay Mineral Variations

For reasons mentioned earlier, it was assumed that Site 222 might be suitable to demonstrate early diagenesis of pelitic sediments by studying clay minerals as an indicator. Therefore, the clay minerals of the $<2\mu$ fraction from 38 samples were investigated in detail looking for depth-dependent changes which could be attributed to burial diagenesis. The results are shown in Table 1 and are plotted against depth in Figures 2 and 3. Although the sediment interval measures 1300 meters, because of extremely rapid deposition, it only encompasses a 6-m.y. period spanning Pleistocene to part of Late Miocene time.

From Figure 2, which shows the amount of kaolinite and chlorite versus depth, it is obvious that neither mineral displays a consistent trend of variation through time. The mean relative abundance of kaolinite is 11 percent versus 17 percent chlorite. Moreover, it was found that these minerals are positively correlated. This, plus the fact that the sum of the clay minerals equals 100 percent, strongly affects the illite, 11Å mixed layer, and 17Å illite/ montmorillonite content. In order to eliminate the influence of the positive correlation between kaolinite and chlorite, the abundances of 17Å illite/montmorillonite,



Figure 2. Kaolinite and chlorite abundance in percent total of all clay minerals (17Å and 11Å illite/montmorillonite, illite, kaolinite, chlorite, and palygorskite) versus depth of Site 222. Based on <2µ fraction.

illite, and 11Å mixed layer listed in Table 1 were recalculated to 100 percent. These values are plotted on

Figure 3. From this plot, illite. 17Å illite/montmorillonite, as well as illite peak width at half-height, seem to be directly related to depth.

From about 300 meters to 1300 meters, illite decreases slightly accompanied by a simultaneous slight increase of 17Å illite/montmorillonite. However, it is rather difficult to judge precisely at which depth these trends start. Lacking more data, the trend lines shown in Figure 3 could as well be extended to a shallower depth of about 200 meters. Despite the rather high variability the calculated slopes of the trend lines are significant on the 95 percent level. The values from 0 to 300 meters scatter widely, and the number of samples is too small to allow construction of trend lines there; nevertheless, they indicate an illite increase and perhaps also a decrease of 17Å illite/montmorillonite down to about 300 meters. This together with the behavior of the illite peak width data (which are discussed below) suggest that the trend lines in Figure 3 are valid.

As indicated in Figure 3 the width at half height of the illite 001 peak is expressed in millimeters. Therefore, lower values signify a higher degree of illite crystallization. This measure, however, depends on the experimental conditions, particularly on the goniometer and paper speeds. I measured illite "crystallinity" of each sample on air-dried and glycolated specimens which were recorded at 40 kv, 22 ma, and 1° 2θ /min using a paper speed of 1600 mm/hr.

Kübler (1966; 1968) used illite peak width at half-height to define an intermediate zone between diagenesis and epimetamorphism which he called zone of anchimetamorphism (anchizone). Using the experimental conditions mentioned above, a peak width of 15 would mark the boundary between the diagenetic realm and the anchizone.

Illite peak width is also an independent measure of the amount of randomly interstratified illite/montmorillonite of low expandability (i.e., so-called "open" illite which contains less than 20 percent expandable layers), especially if it is compared with the peak width of glycolated illites (Figure 3).

Palygorskite strongly interferes with the illite 001 reflection causing a broadening of this peak. Therefore, illite peak width should not be measured if palygorskite is present. In Figure 3, which shows illite peac width versus depth, the illite peak width values of palygorskite-bearing samples are also plotted, but these values are disregarded for calculation of the trend line. Moreover, in the diffractograms of some air-dried samples, the platform between 8° and $6.5^{\circ} 2\theta$ which is caused by the illite/montmorillonite mixed-layer minerals was just above the half-height of the illite peak. If the peak width of such samples were measured the values would be meaningless and moreover lead to erroneous conclusions. Therefore, they too were disregarded.

The illite peak width of air-dried specimens matches the behavior of illite abundance. At 150 meters a value of 10 is observed which locates this illite within the anchizone. The peak width then increases slightly in a downhole direction, but from about 350 meters onwards, it shows a continual decrease while the peak width of glycolated illite remains constant over the entire depth range. The negative slope of the trend line shown in Figure 3 is significant on the 95 percent confidence level.



Figure 3. Ratio of 17Å mixed-layer illite/montmorillonite and of illite to total of 17Å and 11Å illite/montmorillonite and illite versus depth of Site 222. Also shown is peak width at half height (illite crystallinity) of glycolated and of air-dried illites. Full symbols indicate palygorskite-bearing samples which were disregarded in calculating the trend lines. All measurements made on $<2\mu$ fraction. Water content in weight percent and degree of consolidation as well as percent 2M and 1Md mica are also plotted.

The trends observed at Site 222 were not seen at Site 223 (Table 2). This is mainly due to the fact that the borehole is shallower (740 meters), and that below 570 meters mostly neoformed montmorillonite is present. Moreover, the illite peak width could not be measured because of the presence of large amounts of palygorskite.

Discussion of Results

The question arises as to the reasons for the changes of clay mineral abundance and illite peak width with depth. Do they reflect different source rocks being eroded, different climatic conditions in the source area or are they caused by burial diagenesis?

Of course, changes in abundance of various clay minerals at depths shallower than 1000 meters are known from many boreholes, even from those drilled in the open ocean, but so far such changes were frequently attributed to nondiagenetic causes. For example, Lancelot et al. (1972) observed in Leg 11 boreholes a marked increase of kaolinite and a decrease of illite and chlorite which they interpreted as reflecting changing climatic conditions in the source area. This is probably correct, but only the determination of the amount of expandable layers in the illite/montmorillonite mixed-layer minerals and of the illite peak width would allow excluding diagenetic changes as a cause. Again changes in source rocks being eroded through time would also have to be evaluated.

Several lines of evidence indicate that in the source area hinterland of the Site 222 sediments, i.e., in the catchment area of the Indus River, neither different source rocks were being eroded nor weathering conditions had changed significantly since Late Miocene. This evidence is in the constancy of the chlorite and kaolinite content, the almost constant ratio of 2M/1Md mica polymorphs in the clay sized fraction, and insignificant changes in the distribution of trace metals (Chapter 6, this volume) and of mineralogic composition of whole rock samples (Jipa and Kidd, this volume).

The illites in the uppermost part of the hole show peak widths which are characteristic of illites from the anchizone, whereas below 300 meters "open" illites with broader peaks appear. This change as well as the concomitant changes of 17Å mixed layer and illite abundance at about the same depth are judged to be detrital and not diagenetic in nature and therefore is indicative of changes within the source area.

The gradual decrease of the illite peak width of air-dried specimens compared with constant peak width of glycolated specimens below 300 meters means that the amount of expandable layers in the "open" illite are decreasing. Increasing overburden and higher temperatures are the most logical explanation for this.

On the basis of the water content of the sediments (Figure 3) the most rapid compaction due to expulsion of pore waters takes place in the uppermost 100 meters where the water content is reduced by nearly half. From 100 meters to about 450 meters it remains almost constant, but below this depth the decrease is exponential, so that the water content is only 10 percent at the bottom of the hole.

By determining the presumed crustal age at Site 222 from magnetic anomalies (Sclater, 1972), the bottom water temperature (Wyrtki, 1971) and the water content of the sediments, a calculation of the sediment thermal conductivity can be made (Bullard, 1963). These calculations allow one to derive inhole temperature for any depth. Thus, temperature values of 23.5° at 500 meters, 41.5° at 1000 meters, and 51.5° at 1300 meters (Whitmarsh, personal communication, 1973) can be derived if there is no thermal influence from the Owen Fracture Zone.

The diagenetic evolution at Site 222 clays begins on a population of detrital "open" illites which already have rather narrow peaks to begin with, and therefore a peak width of 13 at the bottom of the hole does not mean that the sediments are now anchimetamorphic. Kübler (1964) has shown that illite peak width becomes independent of lithology only for deep burial. Hence, at shallower depths and uniform lithology the change of illite peak width rather than its absolute value reflects diagenetic evolution (Figure 3).

Perry and Hower (1970) showed that the diagenetic reaction by which highly expandable illite/montmorillonite is transformed into illite/montmorillonite of lower expandability takes place by adsorption of postassium rather than by expulsion of interlayer water as suggested by Burst (1969). They assume that the potassium is gained from breakdown of coarse-grained detrital illite, and they were able to show that although the potassium content of the clay fraction increases with depth it remains constant in the whole rock. The authors predicted that the alumina and silica which are also released by the breakdown of illite would lead to the formation of additional amounts of illite/montmorillonite, an aspect, however, which they did not observe. In contrast to their observation, we did not note any statistically significant change in the potassium and aluminum content of the clay fraction (Table 3). However, no change would be noted if the ions are mainly distributed among clay-size particles, i.e., by breakdown of degraded clay-sized illite and neoformation of clay-sized illite/montmorillonite. This is likely at Site 222 because our sediments consist largely of clay-sized particles.

The depth-dependent variations observed at Site 222 (Figure 3), such as decreasing amounts of illite with concomitant increase of illite/montmorillonite and narrower illite peak width, are best explained by the diagenetic reactions proposed by Perry and Hower (1970),

TABLE 3 K₂O and A1₂O₃ Content of the Clay Fraction of Some Samples From Site 222

Sample	K ₂ O (%)	A12O3(%)
22-2, 85	3.5	17.3
25-2, 16	3.3	18.1
27-2, 133	3.4	19.2
30-1, 125	3.2	16.9
31-6, 82	3.4	15.2
36-2, 31	3.6	19.7

although a point critical for the final proof, namely, the decrease of the amount of expandable layers in 17Å illite/montmorillonite, is lacking. However, from the decrease of expandable layers in the illite, as shown by its peak width, we infer that a similar change takes place in 17Å illite/montmorillonite (see also Heling, 1970).

DIAGENESIS OF DEEP MARINE CARBONATE SEDIMENTS

In the deep sea the majority of carbonate sediments consists of nannofossil and foraminiferal tests. However, the pure end members are rarely observed, as the two fossil types almost always occur as mixtures.

In the cores from the Arabian Basin, nannofossils are the dominant calcareous component, although in some intervals foraminifera are abundant enough to form foraminiferal oozes. Siliceous organisms, glass shards, and noncarbonate minerals are recorded as minor constituents.

At Sites 219, 220, 221, and 223 thick sequences of pelagic carbonates were recovered (see Chapters 3, 4, 5, and 7, this volume). Aboard ship, progressive lithification with increasing depth was noted, leading from soft ooze to chalk and finally to limestone. These changes in consolidation of the sediments are accompanied by changes in water content, porosity, density, and sonic velocity.

Previous Studies

The diagenetic phenomena and processes through which a soft ooze becomes progressively lithified to limestone were investigated in the laboratory. We noted (as have previous workers) that the state of preservation of nannofossils varies greatly even within the same sample. Not only do coccoliths dissolve selectively (Bukry, 1971; McIntyre and McIntyre, 1971), they also selectively lose identity by accretive diagenetic processes; calcite overgrowths mask more delicate features rather early rendering identification of species difficult to impossible (P.H. Roth in Berger and von Rad, 1972). Only detailed and statistical studies of the flora will, therefore, lead to a full understanding of the diagenesis of nannofossil oozes. Rather than going into such an involved study, in this chapter an attempt is made to understand the broad aspects of diagenesis and lithification of deep-sea carbonates.

Until a few years ago it was generally held among carbonate sedimentologists that lithification of carbonates which involves cementation and conversion of metastable carbonate phases to stable low-Mg calcite is accomplished in the vadose and phreatic meteoric environments. Although this hypothesis plausibly explained the data gained mainly on shallow water carbonates, it did not convincingly explain lithification of deep marine carbonates.

However, since the mid-sixties increasing examples of both shallow-water submarine cementation (Alexandersson, 1960; Ginsburg et al., 1967; and others) and cementation in the deep sea were gained from crusts dredged from the sea floor. The Deep Sea Drilling Project's boreholes, however, offer for the first time an opportunity to study in long intervals the progressive lithification of a deep-sea lime mud to a micrite.

Analytical Techniques

Because of the extremely fine-grained nature of these sediments their submicroscopic texture, facies, and fossil preservation had to be studied mainly by the scanning electron microscope. This work was carried out with a Cambridge Steroscan Mark IIA instrument at the Geology Department of Berne University. The samples were first dried after which broken fragments were mounted on specimen holders. Early runs showed that carbon- and gold-coated samples were charged at high voltages resulting in poor resolution. Therefore, all mounted samples were first placed in a desiccator and left in contact with vapor of osmic acid for about 2 days. This treatment very successfully prevented later excess charging. Afterwards, the samples were carbon and gold-plated in high vacuum.

Some silicified samples were analyzed for Si, Ca, and A1 using an EDAX setup on the Stereoscan. These measurements were made at the electron microscope laboratory of Basel University.

Critical samples were studied in thin section. Where necessary, they were hardened with epoxy resin prior to sectioning.

Lithology of Studied Sections

Sites 220 and 223, both of which display thick organic carbonate sequences, were selected for this study. Additional samples from Sites 221 and 219 were studied for comparison.

The diagenetic history of a sediment is assumed to be strongly dependent on its primary composition and texture. Therefore, the lithology of the intervals studied is briefly summarized; more detailed descriptions and interpretations are given in the site chapters (this volume).

Site 220 is situated in the southeastern part of the Arabian Basin at a water depth of 4036 meters, while Site 223 drilled in 3636 meters of water on the continental rise of Oman is close to the western margin of the basin.

At Site 220 a 329-meter Pleistocene to Lower Eocene sedimentary section overlies basalt. The lithologic and physical properties pertinent to the diagenesis of these sediments are summarized in Table 4. The Late Neogene is represented by about 70 meters of soft to stiff nanno detrital clays with abundant foraminifera (Plate 1, Figure 1). They are underlain by 150 meters of pelagic carbonates of middle Miocene to late Eocene age consisting mainly of nanno oozes and chalks (Plate 1, Figure 3), with some foram ooze and chalk intervals (Plate 1, Figure 2). It is within this unit that the change from unconsolidated to semi-lithified sediments takes place. In the Eocene, Radiolaria become abundant and about 70 meters of radiolarian and sponge spicule-rich nanno oozes and chalks (Plate 1, Figures 4 and 5) overlie 40 meters of nanno chalk containing interbedded brown chert layers. Two thin lithified limestone layers were recovered between flows of the underlying basalts. With the exception of the uppermost unit the carbonate content exceeds 70 percent throughout the sequence, including Oligocene strata which are almost pure carbonate.

The 717-meter-thick sedimentary sequence of Site 223 consists of silty and clayey nannofossil oozes and chalks, diatomaceous nanno chalks and diatomites, and a brown claystone immediately over basalt (Table 5 and Plate 2). The sediments above 450 meters are moderately bioturbated in places and show many well preserved and only slightly flattened burrows filled with fecal pellets (Plate 1. Figure 6). Although nearly the same time-stratigraphic interval as at Site 220 was penetrated, the differences between these sites are striking: the sequence at Site 223 is twice as thick, the carbonate content is much lower, and chert horizons are missing. Moreover diatomites and carbonate-free claystones only occur at Site 223. Therefore, it is to be expected that the diagenetic history of these two sections will differ. Comparison of the diagenetic evolution of both sequences might also tell us whether the clay content influences cementation of carbonates too, just as it hinders their late diagenetic recrystallization (Bausch, 1968).

Origin and Evolution of the Diagenetic Fabrics

Site 220

Although the sediment thickness at this site only measures 329 meters, it displays all the changes from soft nannofossil ooze to semilithified chalk and finally to lithified limestone and chert. These changes were noted on the shipboard megascopic core descriptions, but unfortunately no penetrometer readings were made which would have allowed a more precise definition of consolidation than that given in Table 4.

Holocene sediments were not recovered at this site, but the uppermost sediments of Pleistocene age are still very soft, containing about 50 percent interstitial water. Within the upper 100 meters the sediment changes in consolidation from a soft to a stiff ooze. This change is accomplished by the expulsion of pore water (Table 4) which is most pronounced in the upper 10 to 30 meters. At 100 meters the water content is reduced to 40 percent.

Below this upper zone of soft to stiff ooze a 60-meterthick sequence of alternating stiff ooze and weakly semilithified chalk layers was observed (Table 4). Initially only thin 1 to 5-cm-thick weakly semilithified chalk bands comprising about 30 to 50 percent of a core are interbedded with stiff ooze. However, the difference in consolidation between these alternating layers is small. The thickness of the chalk layers and their total length per core increases with depth until at 160 meters the entire sediment is semilithified. This indicates that the alternation is not a drilling artifact, an explanation which was discussed onboard ship. Further, the water content at 160 meters is reduced to 35 percent.

From 160 to 220 meters a zone of semilithified white chalk was recovered which oddly enough is underlain by another zone of alternating stiff and semilithified layers. Moreover, the water content and the porosity increases slightly within these two zones. The lowermost part of the sedimentary sequence consists of semilithified chalk with thin lithified chert beds. In the basalt at the base of the hole, thin lithified limestone layers were found.

This nearly progressive lithification with depth is accomplished by diagenetic processes, the nature of which can be inferred from the resulting diagenetic textures. The evolution of the diagenetic fabrics of Site 220 carbonates is shown in Plates 3 to 5. In the zone of soft and stiff oozes the original depositional fabric remains unchanged, i.e., no visible diagenetic textures have yet evolved. Probably little dissolution took place after burial and the preservation status of the fossils is largely inherited: foraminifera show solution features, while the coccoliths are generally well preserved (Plate 3, Figure 1) although some show solution features or are fragmented (Plate 3 Figure 2). The increasing consolidation within this zone, therefore, is attributed to the expulsion of pore water with increasing overburden.

Unquestionable diagenetic textures are first observed in the zone of alternating stiff and weakly semilithified layers. In a stiff ooze from Core 7 (102.6 m) the rays of discoasters show well-defined crystal faces resulting from calcite cement precipitated as overgrowths (Plate 3, Figure 3). Many of the coccoliths are partly or entirely fragmented, while others have acquired thin secondary calcite overgrowths on individual segments (Plate 3, Figures 3 and 4). However, one has to be careful with relating degree of overgrowth of coccoliths to burial depth, because some of them might be reworked such as the one shown in Plate 3, Figure 4. Small equant to prismatic calcite crystals 0.3 to 1.0 μ in size form a large part of this sediment. They were called microcrystalline carbonate particles or simply micarb during shipboard investigations. This term is now used in the DSDP sediment classification. The origin of these particles is discussed later.

The aspect of a 5-cm-thick chalk layer from the lowermost part of the zone with alternating stiff and weakly semilithified layers is shown in Plate 3, Figures 5 and 6. The coccoliths are well preserved; their individual segments have crystal face terminations (arrow Plate 3, Figure 6), but the central areas are still unclogged. Euhedral calcite crystals fill some of the pore space (arrow Plate 3, Figure 5).

The chalks from the semilithified zone (160-220 m) show a more advanced diagenetic fabric. In a sample from the upper part of this zone the individual segments on the proximal and distal sides of placolith shields are abnormally and irregularly thickened and show crystal face terminations along the rim as well (arrows Plate 4, Figures 1 and 2) which undoubtedly resulted from secondary calcite accretion. In addition, detailed examination indicates that fracture surfaces of coccoliths have healed and terminate with crystal faces. Hence, dissolution and fragmentation preceded precipitation of calcite overgrowths.

In the lower part of the semilithified chalk individual coccolith segments have grown considerably bridging the space between proximal and distal shield (arrows, Plate 4, Figures 4 and 5). Moreover, the central areas of some coccoliths are almost filled, and micarb particles have developed crystal faces. Wise and Kelts (1972) noted that these crystals are fused through calcite overgrowths. The rays of discoasters terminate with crystal faces and are greatly thickened rendering identification very difficult (Burns, 1972; Wise and Kelts, 1972; and others).

Below the semilithified chalks is a less-lithified zone consisting of alternating stiff and semilithified layers. This is difficult to explain because the diagenetic fabric of these radiolarian and foraminifera-bearing nannofossil sediments is further advanced than the overlying chalk. The central areas of some coccoliths are clogged, growing segments have almost completely filled the space between proximal and distal shield (arrow Plate 5, Figures 1 and 3) and, in addition, micarb particles have developed. Also, the walls of foraminifera are recrystallized (Plate 4, Figure 6). In this zone which is characterized by a greater abundance of siliceous fossils, more coccoliths display evidence of dissolution prior to cementation (Plate 5, Figures 2 and 4). The diagenetic differences between stiff and semilithified samples is small, cementation by overgrowths being slightly stronger in the latter. The reason for the observed inversion in lithification might therefore be compositional.

The lowermost semilithified sediments above the basalt contain well-preserved coccoliths, but the pore space is reduced considerably by the overgrowths on coccoliths and the micarb particles. Some coccoliths are completely overgrown and the resulting crystal growth entirely fills the irregularly shaped pore. Lithification and reduction of pore space is further accentuated by pressure solution (Plate 5, Figure 6).

Thin limestone layers were encountered between basalt flows at this site as well as at Site 221. Diagenetic fabric marks the end stage of the pelagic carbonates in the Arabian Sea. Most of the coccoliths' central areas are filled, their segments have accreted thick calcite overgrowths and the pore space is largely filled with subhedral calcite crystals. The limestone from the Site 221 basalt sequence is almost completely cemented, and most of the coccoliths are recrystallized and are unrecognizable in the SEM (Plate 11, Figures 5 and 6). Radiolaria have been dissolved and the molds later filled with a calcite mosaic (Plate 10, Figure 4).

Site 223

The sediment sequence at this site is more than twice as thick as that of Site 220 although only slightly more geologic time is spanned. Moreover, coring was fairly continuous and Site 223, therefore, provides an even more complete case history of progressive lithification of pelagic carbonates.

Zoning according to degree of consolidation is similar at both sites (Tables 4 and 5). The shallow zone of soft to stiff sediments at this site, however, comprises only the upper 35 meters. It is underlain by a 195-meter thick zone of alternating stiff and weakly semilithified layers which is followed by a 200-meter-thick semilithified chalk interval. The boundary between these two zones lies 70 meters

TABLE 4 Site 220 Lithologic Units, Their Ages, Total Carbonate, Water Content, and Degree of Consolidation Versus Depth

DEPTH m	GE	OCHRONO- OGICAL AGE	ABSOLUTE AGE m.y.	GRAPHIC LITHOLOGY	CORES	LITHOLOGICAL UNITS	10	30	CaCO ₃	(Wt %) 70	90
-	PLIO. PLEIS.	Late Early Late Early	1.80		1 2 3	I Orange to brown NANNO DETRITAL CLAY	1	1 Ť
- - -50 -	MIOCENE	Late Late or Middle			5	Scattered beds of FORAM SAND.					
		Early				2					
- -100 - - - - - - -	OLI GOCENE	Late			6 7 8	II White NANNO OOZE/CHALK.					• •
150 - - - -		Middle- Early Undiff.			9						•
- - -200		Late			11						۲
-250	EOCENE	Middle		b b	12 13 14 15	III Light orange RAD SPICULE RICH NANNO OOZE/CHALK with thin ASH beds.					ŕ
N. N. N. N. N.					16					÷	
-300		Early			17	IV Light orange MICARB RICH NANNO CHALK and thin CHERT bands.					
-250		UNDATED	51.0		19 20 21	V BASALT flows with thin interbedded sediments.				•	

Water	Content (Wt %)	Consolidation
10	30	
		Soft to stiff
	÷	Alternation of stiff and weakly semi lithified layers
		Semilithified
	•	Alternation of stiff and semilithified layers
		Semilithified
		Lithified

TABLE 4 – Continued

	Site	223 Litholo	ogic	Units, Their	Ages	, Total Ca	rbonate,	Wa	ter Content, and Deg	ree of (consolid	lation	Versus	Depth
DEPTH m	GE	OCHRONO- DGICAL AGE	ABSOLUTE AGE m.y.	GRAPHIC LITHOLOGY	CORES		LITHOLO	GIC	AL UNITS	10	C 30	aCO3 () 50	/t %) 70	90
- - - - - - - - - - - - - - - - - - -	PLEI STOCENE	Late Early			2		a)	01i SIL and SAM	ive DETRITAL SANDY T RICH NANNO OOZE I CARBONATE DETRITAL D,					
		-						-						
-150		Late			4									
-150 - - - - - - - - - - 200	PLIOCENE	Early			6	TTAL SILT RICH NNNO DETRITAL D DIATOMITE.		b)	Yellow green NANNO DETRITAL CLAYEY SILTSTONE,					
	IOCENE	Late			7	I Olive to green DETR NANNO ODZE/CHALK, N SILTSTONE, and NANN							i.	
300	W				10 11 12 13		_	c)	Yellow green DIATOM RICH DETRITAL SILT NANNO CHALK, NANNO DIATOMITE and CHALK BRECCIA.		•		·	

 TABLE 5

 Site 223 Lithologic Units, Their Ages, Total Carbonate, Water Content, and Degree of Consolidation Versus Depth

Water Content (Wt %)	Consolidation
· ·	Soft to stiff
	Alternation of stiff and weakly semi- lithified layers
	Semilithified





TABLE 5 - Continued

Water Content (Wt %)	Consolidation
<u>10 30</u>	
· · ·	Semilithified
•	
	Semilithified with few semilithified to lithified layers
•	
	~
* •	
	Semilithified to lithified
	lithified

TABLE 5 - Continued

deeper than at Site 220. Semilithified sediments with intercalated harder layers occur from 430 to 600 meters, and below 600 meters only semilithified to lithified montmorillonite claystones are found which are not considered further in this study.

The diagenetic fabric of Site 223 carbonates and its evolution with depth is shown in Plates 6 to 10. The soft to stiff clayey nanno oozes at the top of the sequence show whole and fragmented radiolaria, very well preserved nannofossils, and tiny carbonate particles (Plate 6, Figure 1). Graded beds and the presence of shallow-water organisms in this interval suggest that much of the sediment material has been redeposited and consequently has suffered mechanical fragmentation. Post-depositional changes except of consolidation were not observed, and the sediments still show the original depositional fabric.

Weakly semilithified samples from the next lower zone of alternating stiff and weakly semilithified sediments contain coccoliths, the most delicate features of which are preserved, while parts of the same coccoliths are replaced by euhedral carbonate crystals (Plate 6, Figure 2) or dissolved by pressure solution (Plate 6, Figure 3). Moreover, these samples as many others from this site and Site 220 show well-preserved coccoliths such as Pseudoemiliania lacunosa together with other species (e.g., Umbilicosphaera mirabilis) showing strong solution features (Plate 6, Figures 5 and 6). Most of these differences are attributed to the different resistivity to solution of various coccolith species (McIntyre and McIntyre, 1971). Note that some of these coccoliths which are fragmented have subsequently developed euhedral crystal faces on the segments. Discoasters with thickened rays having a euhedral form were first observed at an inhole depth of 90 meters. At 150 meters some of the delicate foraminiferal tests are crushed (Plate 10, Figure 2), whereas the more robust globigerinids are left intact (Plate 10, Figure 1).

In the lowermost sample from the semilithified zone a slightly compressed coccolith is seen as well as large calcite crystals (Plate 8, Figure 2). The latter formed through precipitation of calcite overgrowths on smaller particles which welded them into larger grains, a process described by Wise and Kelts (1972).

The white silty clay-rich nanno chalks recovered from 430 to 600 meters, although mostly semilithified, contain some lithified layers. Comparison of the samples from this zone (e.g., Plate 8, Figures 4 to 6) with the lowest samples of the zone above (Plate 7) clearly demonstrates the presence of a "lithification jump" between these two units. which is accompanied by a drastic drop in water content (Table 5) and porosity.

The samples shown in Plate 8, Figures 4 to 6 are from lithified carbonate layers mentioned above. The segments of the coccoliths are abnormally and irregularly thickened (arrow; Plate 8, Figure 4) which undoubtedly indicates secondary calcite accretion rather than primary secretion within the living organism.

The central areas of some coccoliths are clogged and the pore space between proximal and distal shield is bridged by some segments. The pores of echinoid spines are partly filled with cement which has grown in optical continuity with its host, and euhedral calcite crystals also fill some of the interparticle pores. This extensive cementation by secondary calcite overgrowths on different kinds of particles leads to a dense rock where the coccoliths representing most of the framework "grains" appear tightly packed (Plate 8, Figure 5). This process, however, is not due to compaction but mainly to growth of the particles by secondary calcite accretion.

In deeper samples the coccolith elements have accreted more calcite and almost all of them have filled central areas (Plate 9, Figures 1 to 3). Moreover, calcite crystals are growing in the empty space of foraminifera chambers filling them partly or completely (Plate 9, Figures 5 and 6, and Plate 10, Figure 3). Where the filling is incomplete, the regular shape of the crystals suggests that they originated as free-growing crystals and not as overgrowths on detrital particles.

The foraminiferal walls are recrystallized to a coarser mosaic which is locally even digested by large crystals of the cement. Fractured surfaces of isolated globigerinids from this zone were studied under the SEM. The granular structure of the inner lamellae has recrystallized to a mosaic of larger equigranular crystals, the prismatic crystals of the outer lamellae have merged into larger ones and have grown into the void created by the decomposition of the organic membranes (Plate 10, Figures 5 and 6).

Coccoliths were also found in some layers within the claystone near the bottom of the hole. They are masked by clay minerals, but nevertheless it is evident from the presence of delicate morphological features and absence of overgrowths (Plate 9, Figure 4) that clay inhibits lithification by cementation when present in larger amounts.

In order to provide another example of the transition from stiff to semilithified chalk for comparison with Sites 220 and 223, a brief discussion of Site 221 follows. At that site the change takes place within a pure Oligocene nannofossil ooze and an inhole depth of 170 to 215 meters (Chapter 5, this volume) i.e., at about the same depth as at Site 220.

The sediments of Core 16 (170 m) are stiff and contain discoasters with thickened rays and coccoliths with slightly thickened segments; coccoliths also show evidence of pressure solution (Plate 11, Figure 1).

In the semilithified chalk from Core 17 (215 m) the calcite overgrowths are thicker as shown by *Sphenolithus moriformis* on Plate 11, Figure 2. The sediments of the lowermost core above the basalt (260 m) contain abundant euhedral calcite crystals (Plate 11, Figure 4) similar to those observed in chambers of a foraminifera at Site 223 (Plate 9, Figure 6). Some of the crystals shown in Plate 11, Figure 4 are enlarged coccolith segments still in place (arrow), others are micarb particles with calcite overgrowths, while still others might be true pore-filling cement. Again, as at Sites 220 and 223, precipitation of large amounts of overgrowth cement has converted the original nanno ooze into a hard limestone.

Microcrystalline Carbonate Particles (Micarb)

During shipboard smear slide examinations tiny carbonate particles, a fraction of a micromillimeter to a few micromillimeters in size, were noted in varying amounts. Their origin was unknown although it was suspected that they might be isolated elements or fragments. These particles are seen in most of the samples illustrated in Plates 1 to 11; however, they are particularly abundant in the more pure nanno chalks.

A typical example with many micarb particles is the Oligocene chalk from Site 221 is shown in Plate 11, Figure 4. Wise and Kelts (1972) most convincingly demonstrated that these particles form when coccoliths are partly dissolved and then disintegrate. This explains the positive correlation of micarb and coccoliths abundance which is generally observed.

As there is a wide variation in the size and shape of the structural elements of coccoliths as well as of the coccoliths themselves, one could anticipate this to be reflected in the particles resulting from their disintegration. That is exactly what is observed in the SEM micrographs. Of course, other disintegrating calcareous tests (e.g., foraminifera) could also contribute some of the larger micarb grains.

Since the proportion of micarb grains is not related to the percentage of detrital minerals, but increases with the abundance of coccoliths in the sediment, it is concluded that in the Arabian Sea the micarb particles originate in the basin from disintegrating coccolith plates, the shape of which may later be modified through the accretion of secondary calcite. An extrabasinal source (eolian, river) is at best insignificant.

It was demonstrated that micarb particles can experience later growth by the accretion of secondary calcite and that they may develop euhedral crystal faces which sometimes renders them difficult to distinguish from true pore filling cement.

Precipitation of calcite overgrowths also fuses micarb particles which therefore plays an important role in the lithification process of pelagic carbonates.

Silicification of Chalks

Thin chert layers interbedded with nannofossil chalk were observed in the Eocene at Arabian Sea Sites 219, 220, and 221. Detailed examination with the SEM of chalk samples from these chert-bearing sequences as well as from the Early Eocene of Site 223 and from the Late Miocene evaporite sequence of Site 227 (Red Sea) revealed the presence of many spherules about 3 to 9μ in diameter.

Identical spherules have been reported from various DSDP drill sites in the Atlantic and Pacific and are also known from onshore chert-bearing sequences. The mineralogic nature of the spherules was identified as disordered cristobalite-tridymite (low-cristobalite, "lussatite"). Recently Berger and von Rad (1972), von Rad and Rösch (1972), and Wise and Kelts (1972) described these spherules in great detail and also summarized the older literature. Therefore, only a brief account on the cristobalite-bearing samples from the Arabian Sea is given.

The low-cristobalite-bearing spherules were most frequently observed in empty foraminifera chambers, interparticle pores, radiolarian molds, or any other voids (Plate 12, Figures 1, 2, 4). The spherules consist of segmented vermiform crystal elements and of radiating blades. The blades are 0.15 to 0.30μ thick, up to 2 to 3μ wide, and range in length from a fraction of a micron to the size of the spherule (see also Wise and Kelts, 1972, p. 184). These blades appear segmented in a manner similar to illitic clay minerals (Plate 12, Figures 3, 6). They are not always organized in well-developed spheres but often form irregular clusters on coccoliths or other particles which they partly or completely envelope. It is possible that the small vermiform segmented structures represent the early phase of cristobalite crystal growth; however, more information is needed to judge this hypothesis. The cristobalite spherules are almost always associated with euhedral clinoptilolite crystals (Plate 12, Figures 1 to 3).

In the low-cristobalite-bearing foram nanno chalk of Site 220, Core 17, Section 1 the lumina of the foraminifera and of the few Radiolaria present are partly filled with spherules. Some radiolarian tests were dissolved and their voids subsequently filled with low-cristobalite spherules. Thin sections show that the nannofossils and the tests of the foraminifera are still entirely calcitic. However, more detailed spectrographic analyses on the SEM reveal that some nannofossils have already been completely replaced by silica while most of them remain unaffected (Plate 13, Figures 5 to 8).

The contacts of low-cristobalite-bearing chalk with the adjoining chert layers are clear-cut. In the chert layer the original foraminiferal nanno chalk is completely silicified; however, the calcareous fossils have retained their shape, while some of the radiolarian tests have been completely dissolved. Even the ultrastructure of the foraminifera test which has been replaced by chalcedony is still preserved. The lumina of foraminifera, Radiolaria, or their molds are filled with chalcedony fibers which are rooted on the wall and coalesce towards the center of the voids as shown in Berger and von Rad, 1972, Pl. 33, Fig. 3. In the same sample, therefore, opaline silica of unaltered Radiolaria coexists with chalcedony. According to Berger and von Rad's (1972) classification, these immature cherts belong to their type II.

Interpretation

The processes causing lithification of lime muds are far from being understood, and the literature on this subject is still scant. The problem inherent to lithification of carbonate oozes both shallow water and deep marine is clearly posed by Bathurst (1971, p. 504): "how to cement a carbonate ooze, while it is largely uncompacted with initially a primary porosity of 50 percent or more." The new data reported above may further our understanding of the complex processes of diagenesis and lithification of deep marine carbonates.

Lithification of a limestone is caused by compaction, dissolution-cementation, and recrystallization. Since in both of the stratigraphic intervals studied the first obvious signs of cementation were noted in the zone of alternating stiff and weakly semilithified layers, the loss of water content and hence also porosity reduction above this zone must result from compaction. The further decrease in water content to the top of the semilithified chalk is less at Site 220 than at Site 223 (Tables 4, 5). This is simply due to the fact that this boundary is at a greater depth at the latter site. It appears that the decrease of water content is mainly a function of depth until the semilithified chalk is reached.

The reduction in porosity from the uppermost core to the top of the semilithified chalk is 11 percent (from 75 to 64 percent) at Site 220, and 20 percent (from 83 to 63 percent) at Site 223. Clearly, such porosity reductions would not be large enough to cause obvious compaction features in sediments. Thus the crushing of only a few thin-walled forminifera was observed at Site 223. Our data thus confirm the well-known fact that calcilutites suffer only minor compaction compared with terrigenous mudstones (Pray, 1960). However, an interesting example of a Cretaceous chalk showing distinct compaction features was reported by Wolfe (1968).

From the diagenetic textures it appears that early lithification of nannofossil oozes which consist exclusively of low-Mg calcite is accomplished by deposition of syntaxial overgrowth cements on discoasters, coccoliths, and fragments thereof (micarb grains). The thickening of the discoasters probably began while they were close to the sediment-water interface according to the findings of Burns (1972).

The thick euhedral rays of discoasters are certainly a secondary feature. Many examples were seen where tiny micarb particles were enveloped and incorporated into a discoaster ray by overgrowth cement. Moreover, paleon-tologic evidence leads to the same conclusion (Wise and Kelts, 1972; Burns, 1972; and others).

Whereas according to the literature, deposition of overgrowth cement onto discoasters starts soon after burial, calcite overgrowths on coccoliths were first found at about 100 meters, and it is only in the semilithified chalks that their segments start bridging the intershield space of individual placoliths and that micarb grains develop euhedral crystal faces. An explanation for this differential in time for the precipitation of overgrowth cement was stated by Wise and Kelts (1972). Discoasters are single crystals with all their rays in optical continuity, and they therefore behave as large seed crystals similar to echinoderm particles, whereas the coccoliths consist of many tiny segments with varying optical orientation. The syntaxial rims on echinodermal grains in calcarenites generally fill the entire pore space while neighboring multicrystalline particles have hardly attracted any cement. Pray (1969; in Bathurst, 1971) has called this behavior "competitive cementation."

A state of identical advanced overgrowth cementation where the placolith shields are completely fused by projecting segments is observed at an inhole depth of 260 meters at Site 220, whereas at Site 223 it occurs at 430 meters. The degree of lithification by precipitation of overgrowth cement therefore is not related to age, and less to depth of burial than to the original carbonate content of the sediment (Tables 4 and 5). However, if the original carbonate content of a nanno ooze were the same, lithostatic pressure would become the controlling factor. This was clearly demonstrated by Bernoulli (1972) who noted that the Scaglia Formation (an Upper Cretaceous foraminiferal nannoagorite in Italy) had retained a chalky aspect in areas of little overburden, whereas it is fully cemented where it has been affected by strong tectonism or deep burial.

The upper level of the semilithified chalk marks the limit where the framework of the rock has gained rigidity resulting from the point contacts of the overgrowth cement. Below this level lithification by cementation shows a gradual increase at Site 220 with only a minor "jump," whereas at Site 223 a distinct diagenetic "jump" is observed at 425 meters. It appears that this "lithification front" (Lancelot et al., 1972), at least at Site 223, is related to a marked increase in the carbonate content of the sediment. Such lithification fronts also appear as acoustic markers on the seismograms.

Cementation has completely occluded the pore space only in the limestones which were recovered from the basalt flows. The chalks, even the lowermost ones, have retained a fairly large porosity as shown by the SEM micrographs. However, the micrographs also show that increasing amounts of cement were deposited with depth. This then raises such questions as, the source of the calcite cement, the transport paths of the ions in solution, and the chemical conditions of the diagenetic environment (composition and concentration of ions, pH, eH).

It was shown that the nanno oozes in the upper part of the stratigraphic column are not lithified. Hence, early lithification of the chalk on the sea floor is excluded. At Sites 220 and 221 the chalks lie over basalt and the large amount of CaCO3 required for cementation cannot be derived from older sediments. Autolithification therefore appears to be the only alternative. Dissolved CaCO3 is gained from the dissolution of the more readily soluble fine-grained carbonate particles and by pressure solution at contact points. It is deposited in void spaces as overgrowth cement on more stable nuclei. Discoasters, coccolith segments, and micarb grains can act as such nuclei. Because of the great abundance of micarb grains in nanno oozes, they can therefore play an important role in the lithification process. Manheim and Sayles (1971) analyzed the interstitial waters of nanno ooze/chalk sequences drilled during Leg 8 in the Pacific. They noted increasing calcium and strontium concentrations with depth. It has been shown by Kinsman (1969) that strontium-rich aragonitic shallow water sediments are progressively altered to strontium-poor limestones by dissolution-reprecipitation processes.

The strontium increase noted by Manheim and Sayles (1971) therefore suggests that calcite particles are dissolved and reprecipitated as a strontium poorer phase. The increasing calcium concentration with depth which they found suggests that calcite is being dissolved and that the rate of dissolution exceeds the rate of precipitation. This could explain why nonovergrowth pore filling cement in foraminiferal chambers was observed only in the lowest samples where the concentration of calcium, on the basis of the above data, would be expected to be greatest. During late diagenesis the dissolved CaCO₃ is gained largely from pressure solution. The importance of solution welding for ultimate lithification of a chalk to a highly consolidated rock is indeed apparent from many electron micrographs of ancient nannoagorites (Fischer et al., 1967; Honjo, 1969; and others).

The study of silicified samples reveals that the formation of low cristobalite spherules and the simultaneous growth of clinoptilolite postdate early cementation in the chertbearing sequences, and it also shows that the formation of chert "beds" takes place rather early during the diagenetic history of pelagic carbonates. Most of the silica was obviously derived from opaline skeletal matter. It is interesting to note that in the Arabian Sea all the bedded cherts and low cristobalite spherules occur in Radiolaria and sponge spicule-bearing chalks of Eocene age, whereas in the diatomites of Site 223 (Table 5) no silicification is observed.

Unfortunately, the interstitial water geochemical data from the Arabian Sea sites was not available at the time of writing, and therefore many questions regarding the mechanisms of lithification of pelagic carbonates remain open.

CONCLUSIONS

The results of this study show that lithification of pelitic and of carbonate deep-sea sediments deposited in the same basin occurs through different mechanisms operating at different rates.

The lithification of pelitic muds is largely a function of compaction under increasing overburden pressure which simultaneously causes the expulsion of pore water and the mechanical reorientation of clay mineral flakes. The observations made at Site 222 show that the clay minerals which are mainly river borne (Indus) with a lesser eolian component are not altered in the marine environment until after burial. However, the mineralogic observations suggest that diagenetic reactions start affecting clay minerals at a much shallower depth than hitherto assumed. Although the observed changes are small, they indicate a breakdown of illite, a reduction of expandable layers in "open" illites and probably also in 17Å mixed-layer illite/montmorillonite, together with the formation of additional amounts of 17Å illite/montmorillonite at depths greater than about 350 meters. By these processes the originally soft clayey mud is gradually consolidated into a semilithified clay at 450 meters and to a lithified claystone at 1000 meters.

Calcareous nannofossils and foraminiferal tests which comprise most pelagic carbonates originate in the euphotic zone. While settling through the water column and accumulating on the sea floor, they are differentially dissolved according to their resistivity to solution. This accounts for the observation that in pelagic carbonates well-preserved and corroded species occur together with the most solution-prone forms being completely absent. Dissolution causes disintegration of coccoliths into isolated shields and further into individual segments or elements which are found as microcrystalline particles, called micarb, in the sediment.

Contrary to the early diagenesis of pelites where compressive stress is the most important factor, compaction plays a minor role in the diagenesis of pelagic carbonates. It only accounts for the consolidation of soupy ooze found at the sediment/water interface into the stiff oozes occurring at depths from 10 to about 200 meters.

However, as soon as the framework grains get fused at contact point by cement, the further lithification will depend solely on cementation and recrystallization.

Nannofossil oozes are cemented by deposition of calcite overgrowths on discoasters, coccoliths, and fragments thereof. Hence, these constituents of microscopic size grow by accretion.

Lithification by cementation increases with depth. It is primarily dependent on the carbonate content of the sediment and also on depth of burial. The higher the carbonate content, the more nuclei the sediment contains and the more thoroughly it will get cemented. Moreover, it may absorb dissolved $CaCO_3$ from less carbonate-rich layers next to it. This explains the onset of semilithified chalks at different depths at Sites 220 and 223 and it might also be the reason for the occurrence of slightly less-lithified diatomites within the chalk sequence at Site 223. Whereas the lithification of terrigenous muds is a gradational process, "lithification fronts" at which the degree of cementation rises sharply are observed in pelagic carbonates. At Site 223 it can be shown that such a lithification front is caused by a rapid rise of the primary carbonate content of the sediments.

The great amounts of dissolved carbonate needed to cement the nanno oozes are gained from dissolution of supersoluble grains and from pressure solution at grain contacts. Cementation therefore takes place by a dissolution-reprecipitation process (autolithification). There is no need to introduce carbonate from an outside source.

With an initial porosity of 65 percent at the top of the semilithified chalk, an enormous amount of $CaCO_3$ is needed until such rocks ever become tightly cemented. Comparison with nannoagorites which had been deeply buried (Fischer et al., 1967; Honjo, 1969; Bernoulli, 1972) shows that this is accomplished through most intense pressure solution and aggrading neomorphism.

A comparison of Figure 3 with Figure 5 illustrates that carbonates are lithified at much shallower depths than terrigenous clays. Even the lithified claystones at the bottom of Hole 222 never attained the degree of induration which required the diamond saw for their splitting. However, some ringing hard terrigenous sandstone beds were observed in the claystone sequence. Close inspection revealed that they contain a recrystallized nanno ooze matrix (Plate 13-4) which caused the high degree of induration. Hence, a primary carbonate component also accelerates lithification of terrigenous sediments. However, the driving mechanisms of carbonate and opaline silica mobilization and nucleation-reprecipitation are not well known, and more geochemical and experimental data are needed to fully understand the evolution of diagenetic fabrics.

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Sites 220 and 223 Microfacies, Scanning Electron Microscope Micrographs

Figure 1	220-1-1, 60 cm (0.60 m); foram nanno detrital silty clay, soft; total carbonate 32%; Pleistocene.
Figure 2	220-7-1, 60-61 cm (102.6 m); foram ooze, stiff; note euhedral clinoptilolite crystals in foraminifera cham- bers; thin-layer; compare with Plate 3-3, Early Miocene.
Figure 3	220-9-2, 60 cm (152.1 m); nanno chalk with micarb particles, weakly semilithified; total carbonate 90%; Middle Oligocene.
Figure 4	220-14-1, 95 cm (250.95 m); nanno ooze with sponge spicules, Radiolaria, and foraminifera, stiff; total carbonate 86%; Middle Eocene.
Figure 5	220-16-2, 60 cm (290.1 m); rad sponge spicule-rich nanno chalk, semilithified; Middle Eocene.
Figure 6	223-13-2, 50 cm; slightly flattened, horizontal burrow filled with fecal pellets which consist of nanno ooze; light layers are silty clay; thin section; Late Miocene.



Site 223 Microfacies, Scanning Electron Microscope Micrographs

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Figure 1	1-2, 60 cm (2.1 m); detrital silty clay nanno ooze with rare Radiolaria and diatoms, soft; least resistant coccoliths partly dissolved; total carbonate 50%; Late Pleistocene.
Figure 2	5-5, 63 cm (156.63 m); rad diatom-bearing nanno detrital silty clay, weakly semilithified; many of the siliceous fossils are fragmented; total carbonate 39%; Early Pliocene.
Figure 3	10-2, 77 cm (292.27 m); detrital silty clay-rich nanno chalk with rare diatoms and Radiolaria, semilithified, total carbonate 69%; Late Miocene.
Figure 4	17-2, 50 cm (395.0 m); nanno-rich diatomite, semi- lithified; total carbonate 16%; early Late Miocene.
Figure 5	18-2, 87 cm (402.37 m); diatomite with Radiolaria and sponge spicules, semilithified; total carbonate 9%; early Late Miocene.
Figure 6	26-4, 56 cm (483.06 m); detrital silty clay micarb- rich nanno chalk, semilithified; total carbonate 88%; early Middle Miocene.



Progressive Stages of Diagenetic Change of Site 220 Pelagic Carbonate 1, Scanning Electron Microscope Micrographs

Figure 1	1-1, 60 cm (0.60 m); Soft foram nanno detrital silty clay (see also Plate 1-1); total carbonate 32%, well-preserved coccoliths (upper left) occur together with others showing incipient dissolution (upper right); Pleistocene.
Figure 2	Same as above; distal view of broken and slightly

etched Cyclolithella? annula (Cohen).

- Figure 3 7-1, 60 cm (102.6 m); stiff detrital clay-rich nanno ooze from zone of alternating stiff and weakly semilithified layers; carbonate content 76%; many isolated shields of coccoliths exhibiting various stages of disintegration and also micarb particles; wellpreserved coccolith (upper left) and *Sphenolithus* sp. (arrow) display thin calcite overgrowths and euhedral crystal faces; Early Miocene.
- Figure 4 Same as above; reworked *Cruciplacolithus delus* (Bramlette and Sullivan) with calcite overgrowths around central area; segments of partly fragmented coccolith (arrow) are identical in shape and size to the micarb grains visible in Figure 3.
- Figure 5 9-2, 60 cm (152.1 m); nanno chalk from weakly semilithified layer with different well preserved coccolith species. Note euhedral pore-filling calcite crystals (arrow points to euhedral face); total carbonate 90%; Middle Oligocene.
- Figure 6 Same as above; coccoliths with unclogged central areas and *Sphenolithus moriformis* (Brönniman and Stradner) Bramlette and Wilcoxon; euhedral crystal faces on individual elements (arrows) are signs of secondary calcite overgrowths.



Progressive Stages of Diagenetic Change of Site 220 Pelagic Carbonate 2, Scanning Electron Microscope Micrographs

Figures 1,2 10-2, 58 cm (161 m); semilithified nanno chalk; secondary calcite overgrowths on distal and proximal parts of placoliths cause irregular growth of individual segments (arrows); total carbonate 96%; Middle Oligocene.

Figures 3-5 11-1, 60 cm (198.6 m); semilithified rad-bearing nanno chalk; unbroken placoliths mixed with heavily corroded shields; crystal faces on partly dissolved forms indicate that precipitation of overgrowth cement postdates dissolution. Discoasters with greatly thickened rays and euhedral crystal faces; central areas of coccoliths partly filled with secondary calcite cement; Individual segments of coccoliths bridge space between placolith shields (arrow); total carbonate 92%; Late Eocene.

Figure 6 14-1, 48 cm (250.48 m); semilithified foram nanno chalk with sponge spicules and Radiolaria; many foraminifera are fragmented and their walls are recrystallized (arrow); Middle Eocene.



Progressive Stages of Diagenetic Change of Site 220 Pelagic Carbonate 3, Scanning Electron Microscope Micrographs

Figure 1	14-1, 95 cm (250.95 m); stiff nanno ooze with sponge spicules, Radiolaria, and foraminifera, lower zone of alternating stiff and semilithified layers central areas of coccoliths and space between distal and proximal shield of placolith almost completely filled with calcite overgrowth; micarb grains show crystal faces and occlude some of the pore space; total carbonate 86%; Middle Eocene.
Figure 2	Same as above; remnant of corroded coccolith, the segments of which have developed crystal faces by accretion of calcite overgrowth.
Figure 3	15-2, 135 cm (262.85 m); semilithified rad sponge spicule-rich nanno chalk from lower zone of alter- nating stiff and semilithified layers; distal and proxi- mal shields of placolith are completely fused by large crystals which obliterate its ultrastructure; total carbonate 74%; Middle Eocene.
Figure 4	16-2, 60 cm (290.1 m); <i>Reticulofenestra bisecta</i> (Hay, Mohler, and Wade) with segments and central field corroded; arrow denotes corroded segments which were later overgrown by calcite; Early Eocene.
Figure 5	18-3, 90 cm (329.9 m); detrital clay-rich nanno chalk; well-preserved <i>Chiasmolithus consuetus</i> (Bramlette and Sullivan) (arrow) and <i>Chiasmolithus</i> sp. together with many fragmented shields, micarb particles, and clay mineral flakes; total carbonate 72%; Early Eocene.
Figure 6	Same as above; <i>Cruciplacolithus delus</i> (Bramlette and Sullivan) and <i>Coccolithus</i> sp., the carbonate particle of organic origin (center) is completely enveloped by calcite overgrowth which has also filled the interparticle pore (arrow); note solution welding with <i>Cruciplacolithus</i> .



Progressive Stages of Diagenetic Change of Site 223 Pelagic Carbonates 1, Scanning Electron Microscope Micrographs

Figure 1	1-2, 60 cm (2.1 m); well-preserved placoliths together with broken Radiolaria and probably detrital car- bonate particles; Soft; total carbonate 39%; Late Pleistocene.
Figure 2	3-1, 145 cm (86.45 m); Euhedral carbonate crystal peripherally replacing otherwise unetched coccolith shield; sediment weakly semilithified; Early Pleistocene.
Figure 3	3-1, 123 cm (86.23 m); Gephyrocapsa with missing bar and solution welding in weakly semilithified sediment; total carbonate 53%; Early Pleistocene.
Figure 4	Umbilicosphaera micrabilis Lohman, very well pre- served; same sample as above.
Figure 5	5-5, 63 cm (156.63 m). Umbilicosphaera mirabilis Lohman; complete as well as stubby segments show euhedral crystal faces; Early Pliocene.
Figure 6	Same sample as above. Arrow denotes well-preserved <i>Pseudoemiliania lacunosa</i> (Kamptner) which occurs together with badly corroded coccoliths. Note that short segments of coccoliths (lower right) also show euhedral crystal faces; total carbonate 39%.



Progressive Stages of Diagenetic Change of Site 223 Pelagic Carbonates 2, Scanning Electron Microscope Micrographs (All samples are from semilithified chalk zone, Table 5)

Figure 1	8-1, 127 cm (249.27 m); whole coccoliths with moderate solution features and well-developed crystal faces on rim; total carbonate 57%; Late Miocene.
Figure 2	11-6, 80 cm (317.3 m); Cyclococcolithina leptopora (Murray and Blackman) denoting fragmentation after dissolution total carbonate 29%; Late Miocene.
Figure 3	15-2, 73 cm (377.23 m); Cyclococcolithina leptopora (Murray and Blackman) in lower left and perfectly preserved <i>Reticulofenestra pseudoumbilica</i> (Gartner) in upper right corner of micrograph; total carbonate 14%; Late Miocene.
Figure 4	Same as above; Cyclococcolithina? leptopora (Murray and Blackman) with corroded segments.
Figures 5,6	16-2, 60 cm (386.1 m); nanno detrital silty clay with fragmented placoliths and euhedral carbonate crystals (5); the coccoliths in 6 display partly clogged central

areas and stubby segments with euhedral crystal faces (arrows), telltale signs of dissolution and reprecipita-

tion; total carbonate 28%; Late Miocene.

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Progressive Stages of Diagenetic Change of Site 223 Pelagic Carbonates 3, Scanning Electron Microscope Micrographs

Figure 1 17-2, 50 cm (295.0 m); proximal view of *Reticulofenestra pseudoumbilica* (Gartner). Peripheral part of central area cemented; early Late Miocene.
Figure 2 20-4, 102 cm (425.52 m); corroded and slightly compressed *Coccolithus* sp.; tiny calcite crystals enveloped by overgrowth cement which binds them

into larger crystals in clayey matrix; total carbonate

- Figures 3,4
 Figures 3,4
 21-1, 105 cm (430.05 m); hard layer in lower semilithified chalk zone (Table 5). Individual coccolith segments thickened bridging between placolith shields and terminating with euhedral crystal faces (arrow, 4); euhedral pore filling crystals are seen in 3, (arrow); total carbonate 80%; Middle Miocene.
- Figures 5,6 23-2, 100 cm (453.5 m); hard layer in lower semilithified chalk zone; segments of coccoliths with thick calcite overgrowths having euhedral crystal faces; central areas of coccoliths filled with calcite cement; note tight fabric of rock resulting from precipitation of overgrowth cement; total carbonate 91%; Middle Miocene.



Progressive Stages of Diagenetic Change of Site 223 Pelagic Carbonates 4, Scanning Electron Microscope Micrographs

Figure 1 26-4, 56 cm (484.06); advanced state of calcite deposition on coccoliths; some unidentifiable carbonate particles are completely overgrown by cement and occlude some of the interparticle pore space; total carbonate 88%; Middle Miocene.

Figure 2,3 28-5, 108 cm (503.08 m); coccoliths exhibiting advanced growth of segments and occlusion of central areas; total carbonate 85%; Late Oligocene.

Figure 4 34-2, 105 cm (592.55 m); *Reticulofenestra bisecta* (Hay, Mohler, and Wade) in a clayey matrix; although smeared by clay minerals, the preservation of delicate structure in central field is recognizable; total carbonate 21%; Middle Eocene.

Figures 5,6 32-4, 118 cm (568.68 m); true pore filling euhedral calcite crystals partly or completely filling foraminiferal chambers (cf. Plate 10, Figure 3); wall of foraminifer recrystallized and partly replaced by larger crystals of the calcite cement (5); Upper middle Eocene.



Preservation of Fossils

Figure 1	223-3-1, 123 cm (86.23 m); well-preserved thick- walled <i>Spaeroidinella</i> sp.; thin-section; Early Pleisto- cene.
Figure 2	223-5-5, 63 cm (165.63 m); thin-walled foraminifer crushed by compaction; thin section; Early Pliocene.
Figure 3	223-32-4, 118 cm (568.68 m); chambers of globi- gerinid foraminifera filled with calcite cement; thin section (cf. Plate 9, Figures 5,6); Middle Eocene.
Figure 4	221-19, 3 cm (265 m); calcite cement cast of Radiolaria embedded in nannoagorite from between basalt flows; thin section; Middle Eocene.
Figures 5,6	223-28-5, 104 cm (503.04 m); fractured surfaces of <i>Globigerina</i> cf. <i>angustiumbilicata</i> ; euhedral calcite crystals grow into molds formed by decomposition of organic membranes (arrow, 5); some of the originally smaller crystals have also recrystallized to larger ones; Late Oligocene.



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Diagenesis of Site 221 Pelagic Carbonates, Scanning Electron Microscope Micrographs

Figure 1	16-5, 29 cm (173.29 m); well-preserved coccoliths showing thickened segments with crystal faces and pressure solution; stiff sediment; Late Oligocene.
Figure 2	17-2, 40 cm (216.9 m); Sphenolithus moriformis (Brönnimann and Stradner) Bramlette and Wilcoxon with perfect euhedral element; Middle Oligocene.
Figure 3	Same as above; nanno chalk with many coccoliths more or less fragmented and with many microcrystal- line carbonate particles.
Figure 4	18-6, 39 cm (259.89 m); nanno chalk cemented by small euhedral calcite crystals that formed by precipitation of overgrowth cement on micarb grains and on coccoliths (arrow) which become unrecognizable.
Figures 5,6	19-3 (265 m); thin limestone layer between basalt flows; tightly cemented coccoliths enveloped and recrystallized; few coccoliths recognizable in SEM; Middle Eocene.



Incipient Silicification of Chalks, Scanning Electron Microscope Micrographs

Figures 1,2	223-36-1, 141 cm (629.41 m); well-developed spher- ules of low cristobalite (disordered cristobalite- tridymite) and prismatic clinoptilolite crystals grow- ing in voids of chertified chalk, total carbonate 10%; Early Eocene.
Figure 3	Same as above: spherule showing radial arrangement

Figure 3 Same as above; spherule showing radial arrangement of low-cristobalite blades which also cluster on clinoptilolite crystal (left).

Figure 4 219-24, CC (246 m); spherulitic growth of low cristobalite in foraminifera chambers and interparticle pores; silicified foram ooze; total carbonate 53%; Middle Eocene.

Figures 5,6 223-36-1, 141 cm; detail of spherules' surfaces showing size and segmentation of vermiform and blade-like low-cristobalite crystals.



Figure 1	223-36-1, 141 cm (629. 41 m); clinoptilolite crystal enveloping isolated shield of coccolith; Early Eocene.
Figure 2	Same as above; spherule showing blade-like shape of low-cristobalite crystals.
Figure 3	220-17-1, 43 cm (197.43 m); low-cristobalite spherule with trapped tiny coccolith; filaments are from fungi which contaminated sample; Early Eocene.
Figure 4	222-28-5, 60 cm (988.60 m); detail of calcite cement from lithified terrigenous sandstone; cement results from overgrowth cementation of nannofossils and subsequent recrystallization of nanno ooze matrix; Late Miocene.
Figures 5-9	220-17-1, 43 cm (197.43 m); Nanno chalk showing selective silicification of fossils (8 and 9) and low- cristobalite spherules (7). Results of spectrographic point measurements are shown (7 to 9). Spherule (7) and nannofossil (8) consist entirely of silica (7 and 8). The coccolith (9) shows a strong calcium double peak at 3.69 and 4.01 keV and a weak silica peak (Fig. 9) which is probably due to background scatter. (Photos and analysis courtesy of M. Guggenheim and L. Henning, Basel University.)



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