

19. MINERALOGY OF FIRM MUDS AND MUDSTONES ASSOCIATED WITH VOLCANOSEDIMENTARY LAYERS FROM THE TYRRHENIAN SEA, HOLES 650A AND 651A, O.D.P. LEG 107¹

J. Allouc² and Y. Champetier²

ABSTRACT

At Holes 650A and 651A, set respectively in the Marsili Basin and the Vavilov Basin, Pleistocene sediments (turbiditic inputs interbedded with essentially hemipelagic sediments) may show layers of mudrocks with moderate to strong induration. Except in the two samples from Hole 651A, it seems that zeolite crystallization does not play a role in the induration phenomenon. This latter appears to result from *in situ* clay authigenesis. Secondary K-Fe beidellite or Fe-Mg beidellite form diagenetic growths and bridges between sedimented particles. Turbidites are rich in volcanoclastics (glass, pumices and other volcanogenic elements) but the induration phenomenon appears to be associated essentially with the occurrence of basaltic detritus. It is proposed that clay authigenesis results from low temperature alteration of basaltic fragments issued from Vavilov and probably Marsili seamounts in sediments isolated from seawater by overlying deposits.

INTRODUCTION

The early submarine lithification of pelagic or hemipelagic carbonate muds is a common process in the Mediterranean Sea (Allouc, 1986, and references therein). Diagenetic processes affecting oceanic carbonate sediments during their burial were analyzed in detail in DSDP cores from many sites (synthesis in Garrison, 1981). In the western Mediterranean Sea, the carbonate cementation and recrystallization which starts at about 400 m below the seafloor was studied by McKenzie et al. (1976) in Site 372 of Leg 42.

By contrast, the diagenetic hardening of essentially silico-aluminous materials buried to no more than a few hundred meters is a process which, until now, has been observed less frequently in marine sediments. Some layers of this nature, interbedded with brownish pelagic clays, were noted in several areas of the Pacific Ocean (Hoffert et al., 1978; Hoffert, 1980, and references therein). In these areas, the hardening results from crystallization of clay minerals and authigenic zeolites derived by alteration of Eocene volcanogenic particles.

In the Mediterranean Sea (Tyrrhenian Sea, Hole 373A, Leg 42), Bernoulli et al. (1978) refer to the occurrence of a foraminiferal sandstone cemented by authigenic phillipsite at a sub-bottom depth of about 269 m. The neoformation of zeolite was explained by the proximity of an altered basaltic flow (Bernoulli et al., 1978).

But, in this area, evidence of pervasive silicate authigenesis and subsequent hardening of volcanogenic sediments deposited far above the volcanic basement seems not to have been reported until now.

The *in situ* transformation of pyroclastic sands or volcanic ashes and glasses to zeolites or clays have been described or supported in Quaternary volcanogenic sediments of the Mediterranean Sea (cf., for instance, Müller, 1961; Shumenko and Shimkus, 1979, for zeolites; Norin, 1953; Grim and Vernet, 1961, for clays), but it was later established that these kinds of transformation were not common in this area (Chamley and Giroud

d'Argoud, 1978). Thus, indurated sediments from Holes 650A and 651A appear as a rather unusual occurrence in the Mediterranean Sea sedimentary environment. Their study yields complementary information concerning the susceptibility of volcanoclastic grains to alteration and to the process of early diagenesis leading to induration in mostly noncarbonated deposits.

SEDIMENTARY ENVIRONMENT AND MATERIAL

In the intervals where samples from Holes 650A and 651A were taken, sediments consist mostly of turbidites rich in coarse or medium volcanogenic detritus (gravel to silt) interbedded with volumetrically subordinate muds (often calcareous muds) interpreted as hemipelagic deposits.

Ten samples were taken from Core 18X (Sections 1 and 2) and Core 43X (Section 1) of Hole 650A situated approximately in the center of the Marsili Basin, about 45 km northeast of the Marsili seamount. According to Shipboard Studies (Kastens, Mascle, et al., 1987), the samples are Pleistocene (Nannozone NN19 and NN20).

Lithologic descriptions (Kastens, Mascle, et al., 1987) give the following information:

1. Sediments of Core 18X belong to an interval showing alternations of graded sand and silt containing variable fine-grained volcanoclastic particles (volcanic glass and pumices, composition not given) and homogeneous calcareous muds (10%–20% CaCO₃); calcareous muds are dominant. Indurated sediments consist only of some calcareous mudstone layers, which are some centimeters thick;

2. Sediments of Core 43X are made up mainly of calcareous muds (mean CaCO₃ 15%–20%). They belong to an interval where clastic layers are less frequent than in the previous one. However, percentages of fine-grained vitric particles remain approximately the same (about 5% after smear slide observations). Indurated material occurs as small pieces of drilling biscuit.

One sample was taken from Core 11R (Section 3) and another from Core 12R (Section 1) of Hole 651A set above a basement ridge marking the axis of the Vavilov Basin at about 35 km north of the Vavilov seamount. According to shipboard studies (Kastens, Mascle, et al., 1987), layers of indurated clay and mudstone from Cores 11R and 12R are Pleistocene (Nannozone NN21) but a piece of indurated clay from the Core 12R was

¹ Kastens, K. A., Mascle, J., et al., 1990. *Proc. ODP, Sci. Results*, 107: College Station, TX (Ocean Drilling Program).

² Laboratoire Sédimentologie-Substances utiles et énergétiques E.N.S.G., B.P. 452, 54001 NANCY Cedex (France).

dated as late Pliocene on the basis of its nannofossil content; it was not sampled for this study.

The drilling results (Kastens, Mascle, et al., 1987) indicate that:

1. Sediments of Core 11R consist mostly of nearly homogeneous sand of pyroclastic origin, together with coarser volcanogenic detritus (composition not given). There is only some occurrence of mudrocks: small pieces of mud or mudstone and a 3-cm-thick mudstone layer, from which a sample was taken;

2. Sediments of Core 12R show a succession of three graded units composed of coarse siliciclastic facies (indurated breccia and sand with gravel). These coarse-grained facies, components of which indicate an essentially extrusive igneous origin, pass upward into clays and mudstones containing some scattered volcanogenic fragments (see "Bulk Composition and S.E.M. Observations" below).

Figure 1 gives the bulk mineralogy of the samples. Samples from Cores 18X and 43X of Hole 650A correspond essentially to grey muds or grey calcareous muds. However, Sample 650A-18X-1, 95–96 cm, contains about 25% sand and about 60% silt; it is classified as a sandy silt. Dried up Samples 650A-18X-1, 96–97 cm, and 650A-18X-2, 149–150 cm, show a weak cohesion, they are easily crumbled with the fingers and disintegrate in water. Only Samples 650A-18X-1, 9–10 cm, and 650A-43X-1, 3–5 cm, are really indurated and keep their cohesion in water. According to Rabinowitz et al. (1985), they are classified as firm muds.

Sample 651A-11R-3, 132–135 cm, shows two parts separated by a sharp contact:

1. The lower part consists of a very indurated olive grey mudstone noted 651A-11R-3, 132–135 cm;

2. The upper part consists of a cohesive grey sandstone mainly composed of variable volcanogenic fragments (see "Results, Site 651A" below). It is noted 651A-11R-3, 132–135 cm. Sample 651A-12R-1, 16–19 cm, is a very indurated olive-grey to greyish-green mudstone.

METHODS

In order to eliminate seawater salts before the mineralogical and chemical analyses, the samples were washed in demineralized water. After which, they were crushed in an agate mortar and a portion of each was decarbonated at a constant pH 3 with HCl R.P., 1.5 N. For the very indurated mudstone from Hole 651A, an ultrasonic disaggregation was also necessary. Then, Ca, Fe, Al, and K were measured in the centrifuged supernatant by atomic absorption spectrometry, in order to estimate the calcium carbonate percentage and to control the effect of the HCl etching on insoluble residue.

After washing and setting in a stable suspension by resin Na⁺ (cf. Rouiller et al., 1984 and references therein), the clay fraction < 2 μm was separated by successive siphoning. For special mineralogical investigations, a separation at 1 μm or 0.5 μm was carried out on the same samples by ultracentrifugation (Rouiller et al., 1984).

The mineralogical composition of bulk sediments, carbonate-free sediments, and clay minerals was determined by X.R.D. (Co or Cu target, 1° θ/mn or 1°2 θ/mn). A special investigation at 1°2 θ/4 mn was operated in the calcite peak (104) field for Mg-calcite detection.

For the bulk mineralogy we have adopted the method discussed by Mann and Müller (1979). The height of typical peaks (at 4.26 Å for the quartz, 3.15–3.21 Å for the feldspars, 3.03 Å for the calcite, and 4.07 or 2.71 Å for the phillipsite) is multiplied by 4, 2, 1.5, and 2, respectively, and then added to 100%. Moreover, calcite percentage (deduced from chemical analyses), served as a rough internal standard. Semiquantitative estimation of the relative amounts of plagioclase and K-feldspar was performed by comparing the peak height at 3.20 Å (pl) with the one at 3.24–3.25 Å (Kf).

After removing free iron by a buffered dithionite-citrate system (cf. below: selective extraction), mineralogical characteristics of the clay frac-

tion were determined by various treatments using the oriented paste method (normal, glycol, or ethylene glycol, heating, hydrazine). The relative abundance of illite, kaolinite, smectites, and mixed-layers was calculated according to the method given by Chamley (1969). The chlorite/kaolinite weight ratio was deduced from Elverhøi and Rønningsland's graph (1975). Smectites have been characterized according to their d(060) lattice dimension (Brown, 1963; Desprairies, 1951; Chamley et al., 1955) and the test proposed by Greene-Kelly (1953).

The infrared absorption spectrometry was performed with a double beam system on a BECKMAN 42.50 spectrometer over the 4000–200 cm⁻¹. Samples were dehydrated at ambient temperature (depression of 76 mm Hg) or dried at 110°C over a period of 24 hr. Pressed discs at 10 metric tons with 1 mg or 0.5 mg sample/300 mg KBr were used.

Chemical analyses of bulk samples and of carbonate-free < 1 μm or 0.5 μm fractions were carried out by atomic absorption spectrometry titration, after fusion with strontium metaborate (Jeanroy, 1972).

Selective chemical extractions were made on the bulk insoluble residue or on the clay fraction of carbonate-free samples:

1. By the citrate-bicarbonate Na + dithionite Na reagent at pH 7 (Mehra and Jackson, 1960) in order to estimate the proportion of free Fe (not engaged in a silica lattice).

2. By the oxalic acid + ammonium oxalate reagent at pH 3 (Tamm in Schwertmann, 1964) in order to extract amorphous or weakly crystallized forms of Fe (Jeanroy, 1953). Moreover, amorphous silicates and aluminosilicates are sensitive to this reagent. For instance, it extracts large amounts of amorphous silica and alumina from volcanic ash soils (Fey and Leroux, 1975).

Si, Al, Fe, and K obtained by this method were analyzed by atomic absorption spectrometry.

Semiquantitative microchemical analyses were performed by energy-dispersive spectrometry (E.D.S.). The microprobe PGT system 3 (Si, Li) was coupled with the S.E.M. (CAMBRIDGE S 250), and the microprobe TRACOR TN 2000 with the T.E.M. (JEOL 200 CX). The accelerating voltage was 10–15 Kv for the first case and 200 Kv for the second case.

Quantitative microchemical analyses were carried out on wavelength dispersive spectrometers (W.D.S.):

1. CAMECA MBX (15 Kv): Analyses on thin section, for data on silt or arenite-sized elements.

2. CAMECA SX 50 (15 Kv): Analyses on particles scattered on a carbon stand, for data on clay-sized particles.

C_{or} and N were analyzed by a "Total Analyzer CHN" CARLO ERBA. In this system, the combustion with O₂ was followed by a moderate reduction in order to obtain N₂ without reduction of CO₂. The gases produced were separated by chromatography and quantified by a Wheatstone microbridge.

RESULTS

Site 650A

Bulk Composition and S.E.M. Observations

The bulk mineralogy of samples is given in Figure 1. Samples (650A-15X-1, 95–96 cm, excepted) contain about 40%–55% clay minerals, 10%–25% quartz, 10%–20% feldspars (mainly plagioclases) and 10%–20% calcite. The remainder, representing at most about 10% of the bulk sediment, consists of dolomite, micas, various ferromagnesian minerals (amphiboles and some pyroxenes), variable silt-sized or barely sand-sized volcanogenic fragments and, in some cases, unidentified zeolites. Volcaniclastics consist mainly of ash and glass with a fresh appearance (with few or without dissolution pits) but there are also some more or less altered unidentifiable lava detritus and scarce yellow glassy silt-sized particles resembling palagonite.

Like the feldspar/quartz ratio, the clay content in firm muds (Samples 650A-15X-1, 95–96 cm; 650A-43X-1, 3–5 cm) appears slightly higher than in the soft muds. These results are in agreement with their respective SiO₂, Al₂O₃, CaO, and K₂O contents

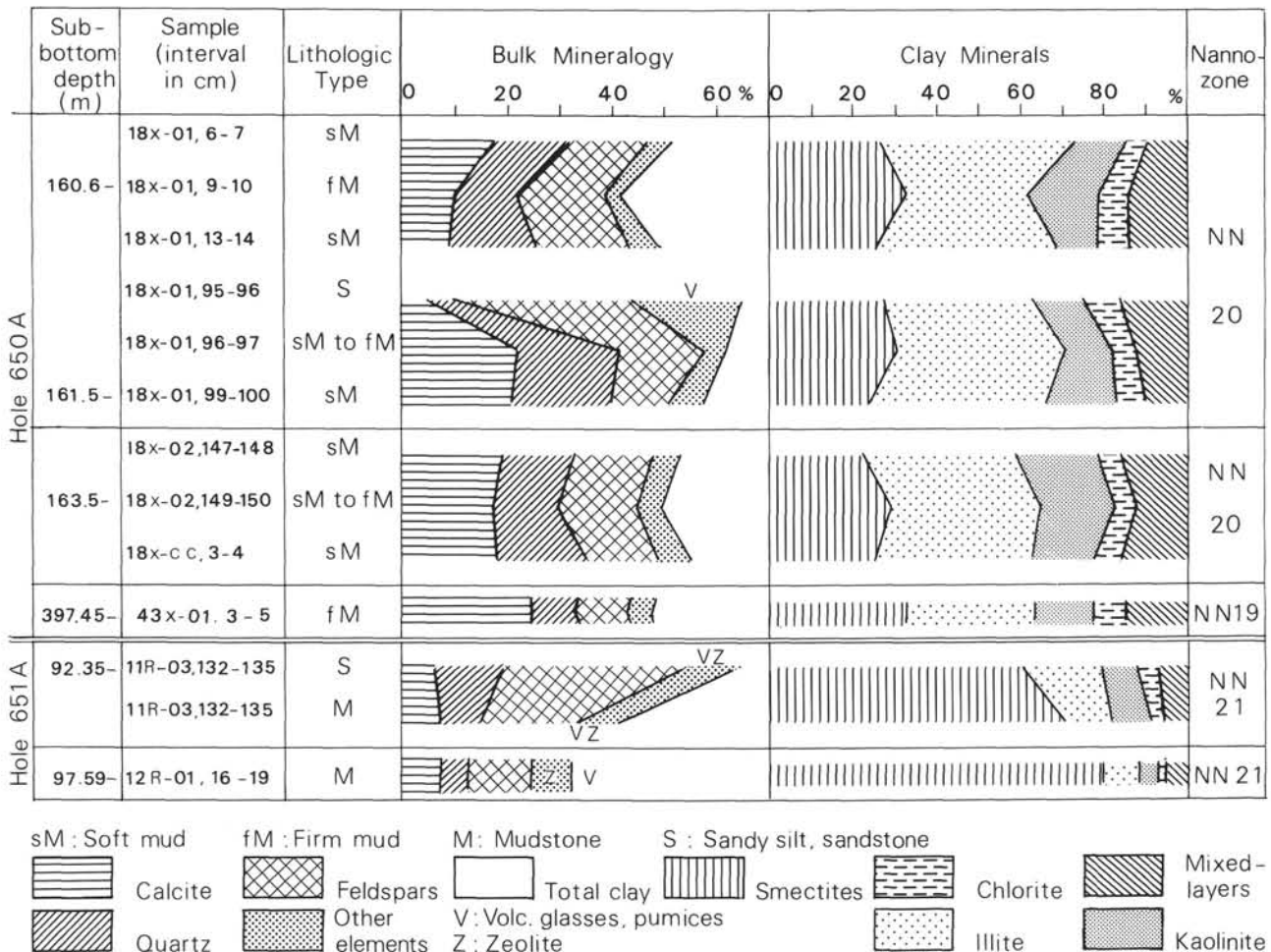


Figure 1. Bulk mineralogical composition of sediments at Holes 650A and 651A.

(Table 1). As indicated by selective extractions, the contents of amorphous silicate or aluminosilicates is very low or nil. The free iron is generally less than 1% and C_{org} less than 0.4% of the carbonate-free sediment (Tables 1 and 2).

Observations on thin sections show that there is no mineral pore-filling in the chambers of foraminifera. SEM investigations show that the clay assemblage of firm muds contains numerous gently folded layers, with secondary growths that resemble tiny bulges, papilla, or "bacteria" (Figs. 2-3, Plate 1). According to the semiquantitative E.D.S. analyses on the biggest secondary growths (Fig. 2) and also to the very low percentages of organic carbon and amorphous aluminosilicates in these sediments (Tables 1 and 2), these shapes, very probably, correspond to a clay mineral. This type of clay particle is less frequent in the soft muds and, in particular, the secondary growths are much less abundant (Fig. 1, Plate 1).

Sample 650A-15X-1, 95-96 cm, is clearly different from other samples from Hole 650A. The content of carbonates (3%) and of clay minerals (about 35%) are lower, but the feldspar content is high (35%-40%) with a predominance of unzoned plagioclase with a composition close to andesine. Furthermore, this sample contains about 20% pyroclastic material. There are numerous glass fragments with both splintered and fibrous forms containing gas tubes suggesting an airborne cooling (Fig. 4, Plate 1). There is no evidence of a diagenetic alteration to clays. Some electron microprobe runs of these volcanic glasses yield the following results (Table 3). According to the SiO_2 and Al_2O_3 contents (McBirney, 1984) or the $SiO_2\%$, $(K_2O + Na_2O)\%$ in

Zanettin's diagram (1984), these glasses have an andesitic to dacitic composition.

Clay Mineralogy

The clay mineral assemblage contains illite (30%-45%), kaolinite + chlorite (15%-25%), and smectite (20%-30%) (Figs. 1 and 3). Generally chlorite is more abundant than kaolinite, but the amount of kaolinite increases with the silt content. The two minerals are represented in roughly equal amounts in Samples 650A-15X-1, 13-14 cm, and 650A-15X-1, 65-96 cm. The clay fraction of firm muds is composed of the same species as in soft muds, but the relative proportions are slightly different. In particular, the percentage of smectites is about 5%-10% higher (Figs. 1 and 3).

The v/p Biscaye's Index (1965) is low or negative, indicating "badly crystallized" smectites (Thorez, 1976), with disorders in the stacking of the layers. The diffraction bands between 14 Å and 17-18 Å after glycolation and between 10 Å and 14 Å after heating at 490°C (Fig. 2) mark the occurrence of interstratified structures of (14_c-14_{sm}) type. In addition, after glycolation, a little shoulder on the peak at 10 Å on the side toward lower 2θ values suggests the presence of $(10-14_{sm})$ type mixed-layers. The content of these interstratified structures is about 10%-15% of the clay mineral assemblage.

For the firm muds, the $d(060)$ at about 1.50 Å indicates the occurrence of dioctahedral smectites (Brown, 1963; Desprairies, 1983). After Li saturation and heating at 250°C, the shift of the (001) reflection to 18 Å confirms that beidellite is the main com-

Table 1. Chemical composition of bulk samples; oxides (wt%), C, and N (wt%).

	Sample (interval in cm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	TOTAL	C	N	C N
Hole 650A	18X-01, 6-7	55.0	18.0	6.2	0.05	3.2	1.0	1.2	3.1	0.8	88.55	3.0	0.5	6
	18X-01, 9-10	50.0	19.0	6.9	0.06	3.7	1.7	1.9	5.2	0.95	89.41	2.8	0.5	5.6
	18X-01, 13-14	57.0	16.8	5.7	0.05	3.0	0.95	1.8	4.0	0.75	90.05	2.1	<0.4	-
	18X-01, 95-96											0.8	<0.4	-
	18X-01, 96-97					-	not analyzed	-				3.4	0.5	6.8
	18X-01, 99-100											3.0	0.5	6
	18X-02, 147-148	56.0	16.2	5.0	0.04	2.7	0.7	1.5	3.4	0.8	86.34	3.5	0.5	7
	18X-02, 149-150	52.0	18.0	6.3	0.03	3.1	1.0	1.8	3.6	0.7	86.53	3.6	<0.4	-
	18X-CC, 3-4	55.0	15.6	4.9	0.04	2.6	0.8	1.2	3.1	0.9	83.14	3.5	<0.4	8.7
	43X-01, 3-5	49.0	20.0	5.3	0.07	3.0	2.1	0.9	4.9	0.7	85.97	3.5	<0.4	-
Hole 651A	11R-03, 132-135 M	45.0	14.1	10.0	0.08	7.3	1.8	1.8	2.1	0.7	82.88	8.3	<0.4	-
	12R-01, 16-19	41.0	12.9	7.3	0.05	6.9	2.3	0.8	2.9	0.6	75.35	2.2	<0.4	-

Table 2. Selective extraction analyses. Data (wt%) related to the carbonate-free sediment. A = cold HCl reagent (pH 3); B = citrate, bicarbonate, dithionate reagent (pH 7); C = acid ammonium oxalate reagent (pH 3).

	Sample (interval in cm)	Si			Al			Fe			K	
		A	B	C	A	B	C	A	B	C	A	C
Hole 650A	18X-01, 6-7	1.3	3.4	0.5	0.8	0.9	1.2	0.8	6.9	2.0	2.0	1.9
	18X-01, 9-10	0.9	3.8	0.4	0.9	1.5	2.7	0.5	9.2	2.8	2.2	4.1
	18X-01, 13-14	1.3	2.5	0.5	1.6	1.3	2.0	0.6	6.8	1.5	2.4	1.7
	18X-01, 95-96	2.1	5.8	0.2	2.6	3.8	4.7	0.9	5.2	1.3	0.5	3.2
	18X-01, 96-97	1.3	1.8	0.9	1.1	1.3	2.5	0.6	5.9	2.6	2.5	5.6
	18X-01, 99-100	1.2	3.0	0.6	1.1	1.0	1.5	0.9	9.1	3.1	2.2	2.1
	18X-02, 147-148	1.6	3.3	0.4	2.8	1.8	3.0	0.6	6.4	2.6	3.8	7.3
	18X-02, 149-150	1.1	3.1	0.8	4.5	1.2	3.6	1.1	5.6	1.8	5.1	8.8
	18X-CC, 3-4	1.2	4.2	0.5	2.0	1.6	2.5	0.8	8.0	3.7	3.3	4.6
	43X-01, 3-5	1.3	3.7	1.2	1.3	1.2	2.8	1.3	8.0	3.4	2.4	6.9
Hole 651A	11R-03, 132-135 M	1.9	5.2	1.3	4.3	2.9	9.0	1.6	6.8	5.8	5.6	18.4
	12R-01, 16-19	2.3	6.0	2.9	1.9	3.9	9.3	1.9	12.0	10.2	3.0	16.1

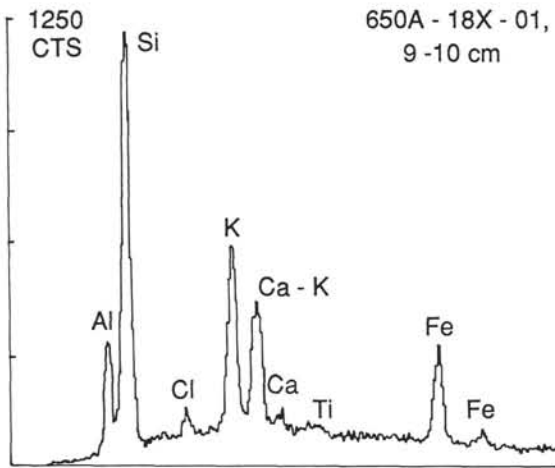


Figure 2. EDS analysis of secondary growth on a clay particle. Firm mud.

Table 3. Chemical composition (%) of volcanic glasses (Sample 650A-18X-1, 95-96 cm).

Run	19	20	21	22	23
SiO ₂	56.05	62.37	63.14	63.94	61.23
Al ₂ O ₃	14.57	15.83	17.34	15.33	18.48
Fe ₂ O ₃	9.93	6.38	4.55	6.67	5.43
MnO	.25	.17	.06	.13	.13
MgO	8.53	1.18	.99	1.64	1.05
CaO	7.41	4.77	5.51	4.69	6.45
Na ₂ O	2.01	2.98	3.88	2.51	3.43
K ₂ O	.99	2.76	2.28	2.85	1.93
TiO ₂	.67	.83	.55	.72	.58
Total	100.41	97.27	98.30	98.48	98.71

ponent of the "swelling complex" (Fig. 4). According to chemical analyses of the fraction below 0.5 μm and data obtained by W.D.S. microprobe analyses on dispersed particles (Table 4), it is a potassic ferriferous beidellite, with some Mg in the octahedral position.

The high proportion of exchangeable interlayer potassium in smectites of the firm muds is substantiated by the quantities of this element extracted by the acid ammonium oxalate reagent (Table 2). Beidellites of this type have been described by Desprairies (1981) and Parra et al. (1985).

Montmorillonite must constitute only a small percentage of the smectite because it was not possible to detect a significant shift to 10 Å of the (001) reflection after the Greene-Kelly's test (Fig. 4).

Transmission electron microscope investigations on the firm muds clay fraction show the presence of some "opaque smectites" or "folded smectites" almost identical to those recognized by Hoffert (1980) and Chamley et al. (1985) (Fig. 6, Plate 1). According to these authors it is indicative of the alteration of volcanogenic material, particularly basalts (Hoffert, 1980). The "folded smectites" are less abundant in the soft mud where smectites essentially correspond to the "fleecy smectites" morphological type of Chamley et al. (1985) (Fig. 5, Plate 1).

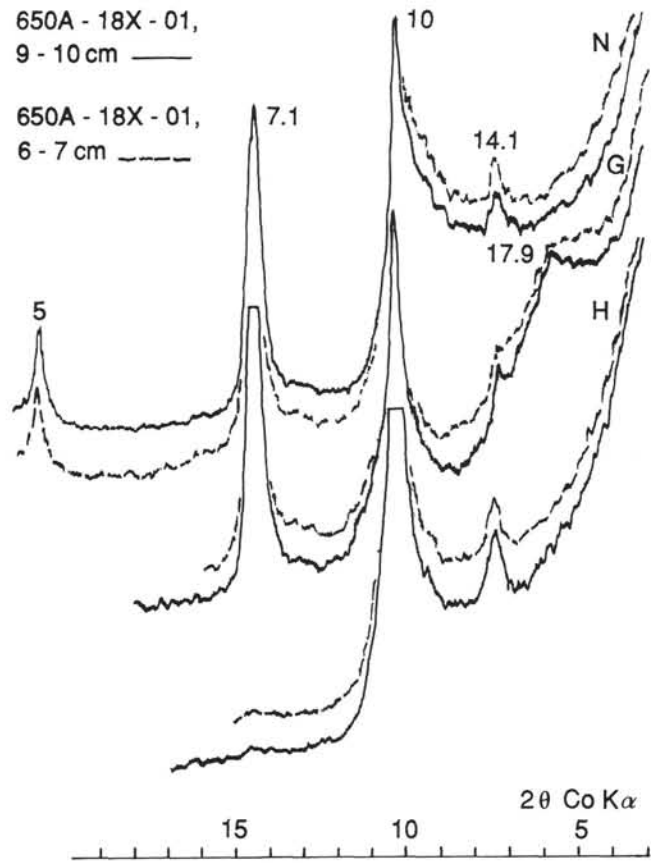


Figure 3. XR-diagrams. Soft mud (broken line) and firm mud (solid line). < 2-μm fraction.

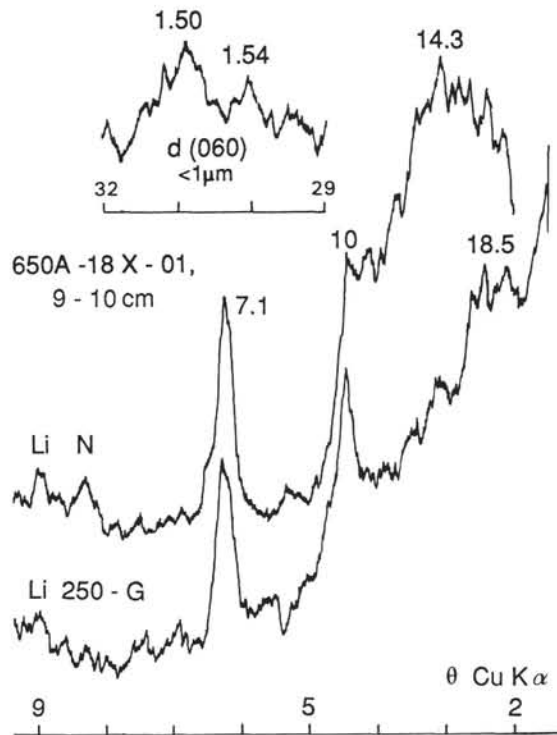


Figure 4. XR-diagrams. Clay fraction of a firm mud. Greene-Kelly's test and d(060) lattice dimension.

Table 4. Chemical composition (%) of smectites at Hole 650A. Comparison with K-Fe beidellites of the northeast Atlantic. (Calculated data for anhydrous composition, 10%-15% H₂O.)

	Chemical analyses fraction < 0.5 μm		Microprobe analyses ----- average values		K, Fe beidellites of the NE Atlantic (*)
	a	b	a	b	
	SiO ₂	57.11	55.99	59.07	55.36
Al ₂ O ₃	22.56	22.56	19.68	22.85	20.40
Fe ₂ O ₃	7.81	9.91	9.03	10.10	12.99
MnO	.05	.06	.07	.36	-
MgO	3.85	4.08	3.58	3.29	3.36
CaO	.58	.53	1.06	.86	.70
Na ₂ O	.58	.35	.77	1.04	-
K ₂ O	3.61	4.20	4.04	3.83	3.13
TiO ₂	.93	.82	.68	.46	1.16
Total	97.08	98.50	97.98	98.15	97.10

a = Sample 650A-18X-01, 9-10 cm b = Sample 650A-43X-01, 3-5 cm

(*) Average of the 4 analyses given by Parra, et al., 1985.

Recalculated values for anhydrous composition.

To summarize, most smectites are potassic feriferous beidellite, morphological types of which essentially correspond to "fleecy smectites" but firm muds also show "folded smectites" and "opaque smectites." The exact composition of secondary growths could not be determined, but they certainly also correspond to a beidellite mineral type.

Site 651A

Bulk Composition and S.E.M. Observations

Mudstones

The bulk mineralogy of samples is given in Figure 1. The mudstones 651A-11R-3, 132-135 cm, and 651A-12R-1, 16-19 cm, contain about 60%-70% clay minerals, 10%-15% feldspars (mainly plagioclase), 5%-7% calcite, and a few percent quartz and zeolite. Observation of thin sections shows that zeolite crystals are mainly localized inside intra-element spaces such as chambers of foraminifera (Fig. 9, Plate 2). They also may occur as a rim surrounding detrital grains but never build a network of crystals throughout the mudrock. Despite the fact that detrital grains are microscopically difficult to recognize, because of their very fine grain size, these mudstones also contain some fragments of basaltic lavas and grains of yellowish glass (probably palagonite). These particles were better observed in the silty sandstone facies (Sample 651A-11R-3, 132-135 cm, Fig. 8, Plate 2).

The selective extraction by the acid ammonium oxalate reagent points to the very low content of amorphous aluminosilicate compounds and the free iron extracted by the citrate-bicarbonate-dithionite reagent is, at best, around 1% (Table 2). The organic matter is lower than 1% (Table 1).

The scanning electron microscope observations of these samples show two microfacies. Sample 651A-11R-3, 132-135 cm, appears to be mainly made up of joined folded sheets with very numerous secondary growths similar to those described for the firm muds from Hole 650A (fine bulges, "papilla," or "bacteria"-like particles) (Figs. 11, 12, Plate 2). As these samples do not contain amorphous material, these silico-aluminous secondary growths (Fig. 5) also correspond to a clay mineral. They can grow on any substrate, in particular on detrital grains (Fig. 12, Plate 2), or coccoliths (Fig. 13, Plate 3). In this way, clay miner-

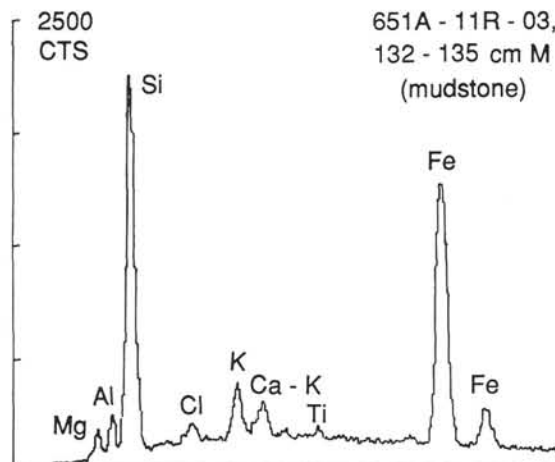


Figure 5. EDS analysis of authigenic clay particle. Mudstone.

als build a frame of diagenetic bridges. In Sample 651A-12R-1, 16–19 cm, clays make a densely packed mass that almost completely conceals detrital or biogenic components (Fig. 14, Plate 3). This mass is organized in aggregated clusters of coalescent particles from 0.3 to 0.8 μm in length (Fig. 15, Plate 3). Each particle resembles those of secondary growths seen in indurated sediments of Hole 650A and identical shapes are visible in places (Fig. 16, Plate 3).

Silty Sandstone

In the silty sandstone (Sample 651A-11R-3, 132–135 cm) which overlays the mudstone (Sample 651A-11R-3, 132–135 cm), clays do not represent more than 35% of the bulk sediment. The detrital grains, several millimeters in length, consist mainly of numerous fresh potassic feldspars together with rather fresh plagioclases (with a composition of andesine to labradorite) and fragments of basic lavas in variable states of alteration. Analyses of feldspathic microlites on the less altered basaltic clasts indicate a labradorite composition (Table 5). Additionally, scattered in the rock, there are altered yellowish to brownish glass fragments, vesicular in places (Fig. 8, Plate 2) resembling palagonitized clasts (cf. Bernoulli et al., 1978); some mafic minerals (particularly pyroxenes) are also visible.

In addition, this sample contains numerous crystals of philipsite in rosettes or bundles which form a rim around volcanogenic grains (Figs. 9 and 10, Plate 2). Clay minerals show the same morphological characteristics as those of the underlying mudstone (joined and folded particles with secondary growths).

Clay Mineralogy of Mudstones

The clay fraction of the two mudstones 651A-11R-3, 132–135 cm, and 651A-12R-1, 16–19 cm, have approximately the same composition; it consists of about 5%–10% chlorite + kaolinite, about 10% illite and about 70%–80% smectites (Figs. 1 and 6). The “swelling complex” proportion is therefore much larger than in firm muds from Hole 650A. The v/p Biscaye's index close to 0.3 marks a rather poorly crystallized structure.

All the layers expand to 17–18 Å (Fig. 7). Thus, according to the Greene-Kelly's test, there is no montmorillonite. The XR diagrams show two more or less weakly defined $d(060)$ peaks at about 1.505 Å and 1.52–1.525 Å. The peak near 1.52 Å may in-

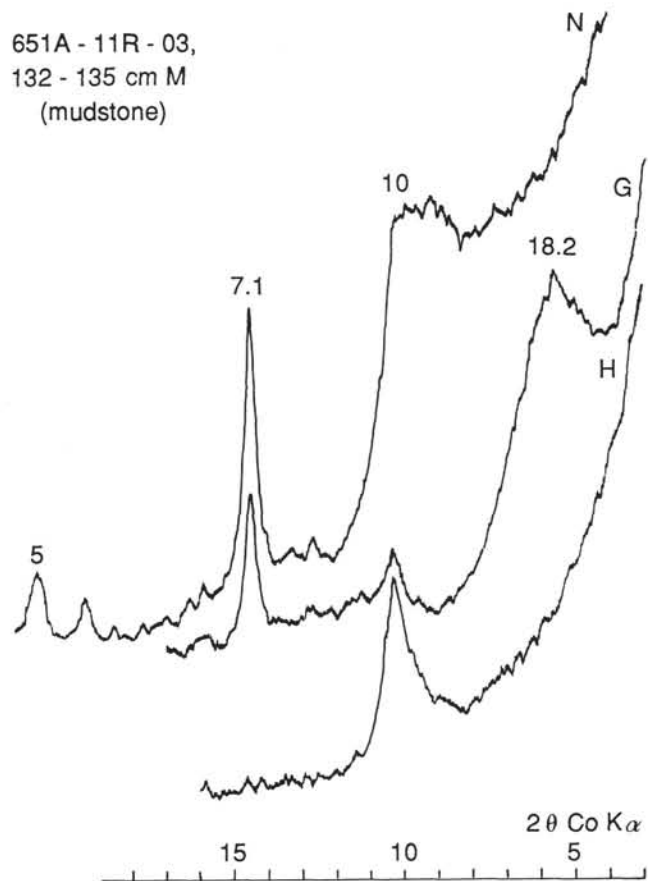


Figure 6. XR-diagrams. Mudstone. < 2- μm fraction.

Table 5. Microanalyses of plagioclases (Sample 651A-11R-3, 132–135 cm, sandstone part).

Run	32	33	34	22
SiO ₂	48.00	49.52	48.05	50.00
Al ₂ O ₃	31.85	31.07	32.17	30.90
Fe ₂ O ₃	.60	.47	.52	.87
MnO	.01	.08	.05	.04
MgO	.03	.01	.01	.12
CaO	15.29	14.62	15.32	14.17
Na ₂ O	2.54	2.84	2.36	2.75
K ₂ O	.83	.31	.40	.55
TiO ₂	.01	.01	.01	.03
Total	99.16	98.93	98.89	99.43

dicate the existence of saponite-type layers in addition to ferriferous dioctahedral structures (Brown, 1963; Desprairies, 1983) despite the MgO content which is only about 10% (Table 6).

The infrared investigations give some detail to this mineralogical problem (Fig. 8). Both samples give the same spectra. In the high frequencies field one observes only an absorption band at 3620–3625 cm^{-1} besides the strong adsorption band near 3420 cm^{-1} (interlayer H₂O vibration). The characteristic bands of saponite or Fe saponite layers at 3550 and 3678 cm^{-1} (Farmer, 1974; Van der Marel and Beutelspacher, 1976; Parra et al., 1985) are not present. This fact and the absence, in the low frequencies field, of absorption bands at 685 cm^{-1} and toward 650 cm^{-1} shows that the smectites, for the most part or in totality, correspond to a beidellite-type mineral (Parra et al., 1985).

Thus, from the presence of two (060) reflections at 1.50–1.505 Å and 1.52–1.525 Å, and the absence of saponite, it follows that a very large proportion or the whole of the “swelling complex” consists of Fe-Mg beidellites identical to those described by Chamley et al. (1985) (they were named Mg beidellites by these authors). This conclusion is corroborated by chemical analyses of the bulk purified clay fraction (< 1 μm) and by microchemical W.D.S. analyses of dispersed clays, seeing that measured values are close to data given by Chamley et al. (1985) (Table 6).

As stated above, it is not possible in these mudstones from Hole 651A to recognize precisely authigenic phases from detrital ones because of the abundance of secondary growths. But, in view of the very large amount of Fe-Mg beidellite, it is very likely that a part of this “swelling complex” is detrital.

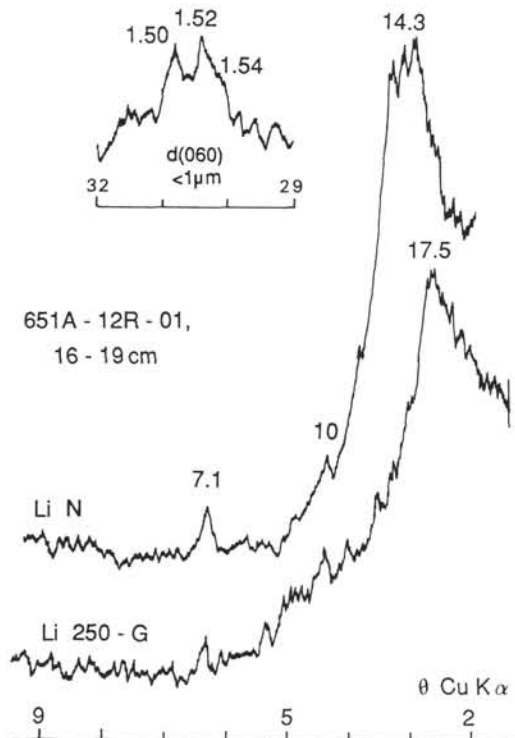


Figure 7. XR-diagrams. Clay fraction of a mudstone. Greene-Kelly's test and d(060) lattice dimension.

Transmission electron microscope investigations show two main morphological types of smectites:

1. The first consists of small sheets of smectites more or less transparent to the electron beam (Fig. 17, Plate 3), that resemble the "transparent smectites" of Chamley et al. (1985).
2. The second shows large opaque layers of "folded smectites" (Chamley et al., 1985) often outlined by a felting of thin elongated, curved or folded particles (Figs. 17 and 18, Plate 3). These smectites closely resemble those identified in the vicinity of the East Pacific Ridge basalts by Hoffert (1980).

These two morphological types are about equally represented. According to the microanalyses coupled with the T.E.M. observations (analyzed surface is about 0.04 μm²) the composition of "transparent smectites" and "folded smectites" are not very different from each other (Table 7).

To summarize, mudstones from Hole 651A show a large development of authigenic clays, the composition of which is close to that of the primary (sedimented) smectites and would correspond to ferriferrous magnesian beidellites. The morphological types of sedimented and authigenic smectites correspond to the "transparent smectites" and to the "folded smectites" of Chamley et al. (1985).

DISCUSSION

Cohesion and induration of studied samples do not result from carbonate diagenesis. Soft muds are as rich or richer in carbonate than firm muds and mudstones (Fig. 1) and S.E.M. observations do not show any pore-bridging by carbonates. Elements are not linked either by siliceous or silico-aluminous components (no visible lepispheres, very weak amounts of amorphous Si and Al extracted by selective reagents).

Table 6. Chemical composition (%) of smectites at Hole 651A—comparison with Fe-Mg beidellites of the East Mariana Basin. (Calculated data for anhydrous composition, 10%–15% H₂O.)

	Chemical analyses fraction < 1.0 μm		Microprobe analyses ----- average values		Fe-Mg beidellites of the East Mariana Basin (*)
	a	b	a	b	
SiO ₂	56.16	56.01	54.76	52.96	53.24
Al ₂ O ₃	14.61	16.94	14.06	15.58	17.89
Fe ₂ O ₃	11.91	12.21	12.85	13.49	11.80
MnO	.08	.07	.15	.13	.10
MgO	11.18	8.46	12.00	10.50	9.19
CaO	.18	.12	.54	.38	1.09
Na ₂ O	.36	.12	.39	.32	1.09
K ₂ O	1.82	2.43	1.87	2.39	2.85
TiO ₂	.10	.12	.33	.43	1.28
Total	96.40	96.48	96.95	96.18	98.53

a = Sample 651A-11R-03, 132-135 cm M (mudstone part)

b = Sample 651A-12R-01, 16-19 cm

(*) = Data according to Chamley, et al., 1985.

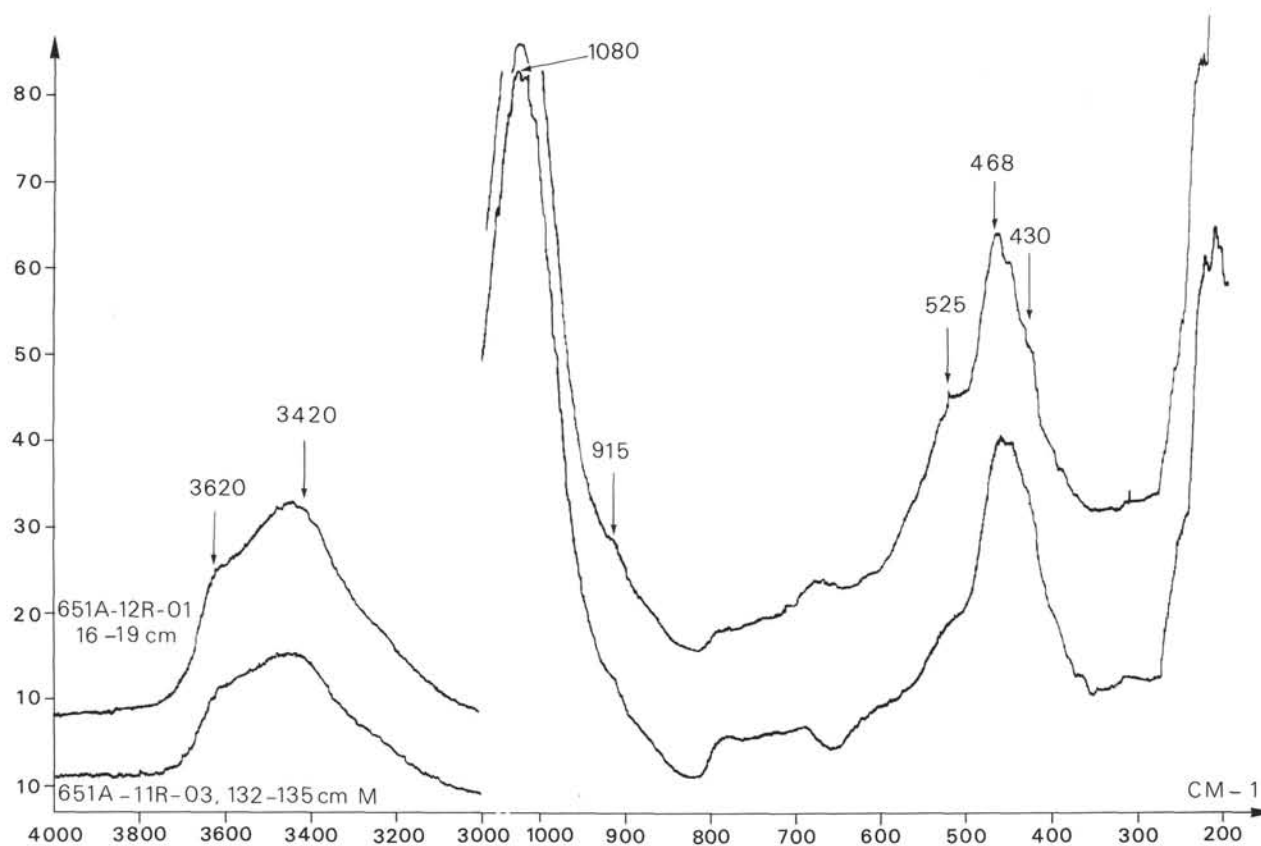


Figure 8. IR spectra of the clay fraction. Mudstones.

The cohesion of firm muds of Hole 650A and the induration of mudstones of Hole 651A appear essentially as a consequence of *in situ* silicate and, in particular, clay authigenesis. This diagenetic process creates secondary growths on previously sedimented particles that, finally, are linked by diagenetic bridges. It is a well known phenomenon and numerous examples of pore-bridging by smectites (and other clay minerals) have been shown by Welton (1984). Figures 1-3, Plate 1, and Figures 11-15, Plates 2 and 3, give evidence of a gradual increase in the proportion of secondary authigenic clays, resulting in a gradual loss of porosity and leading to changes from soft muds to firm muds and finally to mudstones.

Zeolites appear to contribute to the induration phenomenon only in the Samples 651A-11R-3, 132-135 cm (mudstone and sandstone), and 651A-12R-1, 16-19 cm. But, even in these samples, phillipsite crystals seem to play a moderate role as a cement, because of their very preferential localization in intra-element pores and as a rim around interspersed clastic particles.

Smectites may directly precipitate from hydrothermal fluids (cf. synthesis in Cole and Shaw, 1983). But, in the case of the studied samples, this hypothesis must be ruled out. The two Sites 650A and 651A are not in a marginal position within the Marsili and Vavilov basins and the occurrence of an intrusive body in the Pleistocene sediment column has not been signaled

Table 7. Semiquantitative E.D.S. microanalyses of "transparent smectites" and "folded smectites" (Sample 651A-11R-3, 132-135 cm, mudstone part).

"Transparent smectites" count up : 538 sec.			"Folded smectites" count up : 470 sec.		
Si	267825 shots	Si/Al = 3.61	Si	351734 shots	SI/Al = 4.31
Al	74152	Si/Fe = 4.28	Al	81433	Si/Fe = 3.86
Fe	62529	Si/Mg = 5.35	Fe	91030	Si/Mg = 5.79
Mg	50014	Si/K = 10.16	Mg	60691	Si/K = 10.55
Ca	12086	Al/Mg = 1.48	Ca	15432	Al/Mg = 1.34
K	26351		K	28019	
Ti	7033		Ti	8079	

in the vicinity of Sites 650 and 651 (Kastens, Mascle, et al., 1987, 1988). Silicate diagenesis could otherwise hardly result from convective flow of heated marine connate fluids, because studied samples are localized at about 290 m (Hole 651) and 200 or 470 m (Hole 650) above the volcanic basement, and no fault serving as a fluid pathway has been signaled in this area (Kastens, Mascle, et al., 1987, 1988).

Neither is a low temperature combination of Fe-oxyhydroxides and biogenic silica as discussed by Chamley and Millot (1972); Dymond and Eklund (1978); Hoffert (1980) and others (cf. synthesis in Cole and Shaw, 1983) very plausible. Despite the detailed techniques used, we did not find significant siliceous biogenic debris. High productivity of siliceous microorganisms, such as would serve as a source for the large amount of Si necessary for 2/1 clay genesis, does not appear commonly in the Mediterranean Sea. Such blooms as for instance in the Santorin Caldera (Chamley and Millot, 1972) or in a small basin located on the eastern slope of the Tyrrhenian Sea, in the most internal, presently submerged, portion of southern Apennines (Castellari and Sartori, 1978), seem to be local. Moreover, the smectites crystallizing from alteration of biogenic silica would correspond to iron-rich beidellites (nontronite) or Fe-montmorillonites (Dymond and Eklund, 1978; Hein et al., 1979; Cole and Shaw, 1983), clay mineral forms different from those recognized in the samples studied.

From the previous lines of evidence and from the large amount of volcanogenic material in the cores of Holes 650A and 651A (Shipboard Scientific Party in Kastens, Mascle, et al., 1987) it is possible to infer that authigenesis of clays have resulted mainly from *in situ* low temperature alteration of volcanoclastic particles. According to downhole temperature measurements or geothermal gradients (Shipboard Scientific Party in Kastens, Mascle, et al., 1987), temperature is currently about 25°–30°C at the depths of sampling for both Holes 650A and 651A. So, it may be assumed that ambient temperature of these sediments deposited at about 200 m, 300 m, or 470 m above the volcanic basement was also below 50°C during their diagenesis. Chamley and Giroud d'Argoud (1978), however, studied Leg 42A samples and concluded that the transformation of volcanogenic material to clay minerals is not common in volcanoclastic sediments of the Mediterranean Sea. Actually, andesitic and dacitic volcanic glasses of Sample 650A-18X-1, 95–96 cm, for instance, do not contain evidence of alteration, and increase of volcanogenic material corresponds to a significant reduction in the proportion of clays (Fig. 1). But, considering the composition and the size of parental volcanogenic elements as discussed below, there may exist no contradiction between the proposed hypothesis and these previous observations on the sediments of the Mediterranean Sea.

Samples of Hole 651A show that the sediments of indurated sections were enriched with small particles of basaltic composition (microlitic lavas and palagonitized glass), the susceptibility to alteration of which results from their composition and small size. Thus, it is understandable that these sediments show authigenic mineralogical growths, whereas layers containing more siliceous ashes or glasses, like those interbedded in common deep-sea sediments of the Mediterranean Sea, and similar to the ones considered by Chamley and Giroud d'Argoud (1978) "rarely show any characteristic authigenic clay mineral growth" (Chamley and Giroud d'Argoud, 1978).

For samples of Hole 650A, it is not possible to assert definitely that the formation of authigenic clay minerals results mainly from alteration of grains of basaltic composition because the latter remain markedly subordinate with respect to more siliceous volcanoclastic and siliciclastic grains. Although volcanogenic grains and plagioclase appear essentially fresh, it is theoretically possible, considering their high percentage of

sediments, that they could provide ions necessary for clay authigenesis. However, the latter hypothesis does not fit in well with the localization of firm muds in particular intervals, since volcanoclastics are abundant throughout Core 18X for instance. Here also, the same process as in Hole 651A appears the most plausible hypothesis since it is supported by indirect evidences as indicated below.

An *in situ* low temperature alteration of basaltic particles as the main source of clay authigenesis is substantiated by several arguments both for samples from Hole 650A and for samples from Hole 651A:

1. At Holes 650A and 651A, layers of indurated sediments are generally well correlated with peaks of Ca/Mg ratio of the interstitial water. Mg is depleted whereas Ca is enriched (Kastens, Mascle, et al., 1987, p. 317). This type of geochemical modification, frequently observed in DSDP Sites, has been attributed to low temperature diagenesis by many authors (Desprairies, 1981, and references therein). In mudstones rich in basic volcanic material studied by Desprairies (Leg 60, Mariana Trough and Trench), the Ca/Mg gradient expresses the low temperature alteration of volcanic material and authigenesis of Mg-enriched smectites.

2. Mudstones from Holes 651A and firm muds from Hole 650A contain morphological types of smectites that denote volcanic influences (Hoffert, 1980; Chamley et al., 1985).

3. Ferriferous and magnesian beidellites, like those in Hole 651A, have been commonly noted in sedimentary environments located in the vicinity of submarine basaltic outcrops which supply erosion or alteration materials (Hoffert, 1980; Desprairies, 1981; Chamley et al., 1985). The magnesian smectites (saponite) are commonly the result of submarine alteration of basaltic lavas (Kurnosov, 1982). Thus, ferriferous and magnesian beidellites may be the result or re-equilibration of magnesian smectites in a marine environment, with loss of Mg and gain of Fe and K (Hoffert, 1980). But they may also correspond to a transition towards a chloritic structure (Chamley et al., 1985). Concerning the potassic-ferriferous beidellites from Hole 650A, a part of them might have resulted from re-equilibration, on the seafloor, of detrital smectites derived from the continent but, a large proportion of this mineral most likely represents the end-member equilibrium phase of a submarine transformation of the Fe, Mg smectites (Parra et al., 1985). The affinity for K of the dioctahedral smectites with replacement in the tetrahedral layer explains their enrichment with regards to this element (Rico-Gamboa, 1984).

At Hole 651A, the proportion of land-derived terrigenous material is low. Very likely, sediments, in particular fragments of basaltic rocks, originated mainly from the slopes of the Vavilov seamount located about 20 km south of Hole 651A. The Vavilov seamount corresponds to an imposing volcanic complex consisting of a series of thick basaltic pillow lava flows and, according to the petrographic study of some samples, glassy altered cortex and vitreous to hyalocrystalline zones surrounding fresh-looking vesicular basalt were found (Robin et al., 1987). Also reported was a breccia composed of basaltic clasts (Robin et al., 1987). Basalts of this volcano, the upper part of which is late Pleistocene, fall into the mildly alkaline series (Robin et al., 1987).

At Hole 650A, the geographic origin of basic volcanogenic material is more difficult to determine. The distance between the Vavilov volcano and Hole 650A (about 120 km) could explain the more aluminous and potassic composition of beidellite and the larger proportion of terrigenous material. The Marsili volcano is closer to Hole 650A (about 35 km to the east); it comprises tholeiitic basalts (Kastens et al., 1986) overlaid with

alkaline basalts (Selli et al., 1977; Colantoni et al., 1981) and is therefore also another probable source.

Whatever the precise geographic origin of the parental material, it originated from basaltic seamounts of the Tyrrhenian Sea. Clay or clay and zeolite authigenesis, with subsequent induration, appear as an indirect consequence of inputs of this material in sediments.

Considering geochemical requirements, authigenic mineralogical growths are certainly favored by isolation of deposits with respect to seawater. Authigenic ferrous and magnesian smectites indicate that interstitial waters are enriched in these elements. The neoformation of 2/1 clays with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio close to 4, requires sufficiently rich Si solutions. It is known also that phillipsite can crystallize in solutions with a seawater composition (Glaccum and Boström, 1976; Stonecipher, 1976); but the occurrence of this mineral in some indurated levels may also reflect a decrease of the Na/K ratio of interstitial solution with respect to seawater (Bernoulli et al., 1978 and references therein). The amounts of K required for authigenesis of phillipsite were probably delivered *in situ* by altered basic volcanogenic fragments enriched in this element (Hart, 1970; Melson and Thompson, 1973; Seyfried and Bischoff, 1979; Staudigel and Hart, 1983). In the same manner, the induration of Eocene volcano-sedimentary deposits from the South Pacific was explained by their isolation from seawater (Hoffert et al., 1978; Hoffert, 1980).

CONCLUSION

At Holes 650A and 651A, Pleistocene sediments consisting of turbiditic inputs rich in variable volcanoclastics interbedded with hemipelagic deposits contain some indurated layers. They are firm muds (Hole 650A) and mudstones (Hole 651A) located about 200 m and 470 m or 290 m, respectively, above the volcanic basement. The cohesion is mainly due to authigenic smectites forming secondary growths and diagenetic bridges between grains. Phillipsite contributes to cementation only in mudstones of Hole 651A but, even in these samples, it plays only a subordinate role in the induration phenomenon. The authigenic smectites are ferrous and magnesian beidellites in the mudstones from Hole 651A and potassic ferrous beidellites in the firm muds from Hole 650A. They have approximately the same composition as the sedimented smectites.

In samples of Hole 651A, authigenesis of clays appears to have resulted from low temperature *in situ* alteration of fine basaltic material (lavas detritus and palagonitized glass) concentrated in the upper part of graded turbidite layers. These volcanoclastics have been generated by the Vavilov Seamount made up of basalts with tholeiitic affinity. In samples of Hole 650A, although less evident, the source of clay authigenesis may be also basaltic clasts originated either from the Vavilov or from the Marsili seamounts made up of tholeiitic to alkaline basalts.

The induration phenomenon appears as an indirect consequence of an increase in the contribution of intrabasinal material to volcanoclastic sedimentation in the area of Sites 650 and 651.

Also probably promoting authigenic mineralogical growths, was a relative isolation from the seawater chemical environment.

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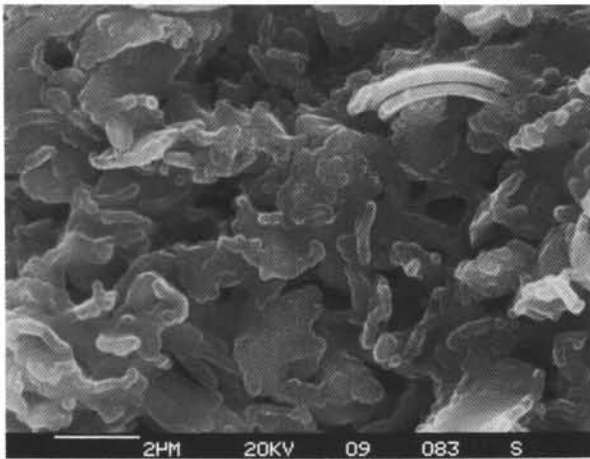
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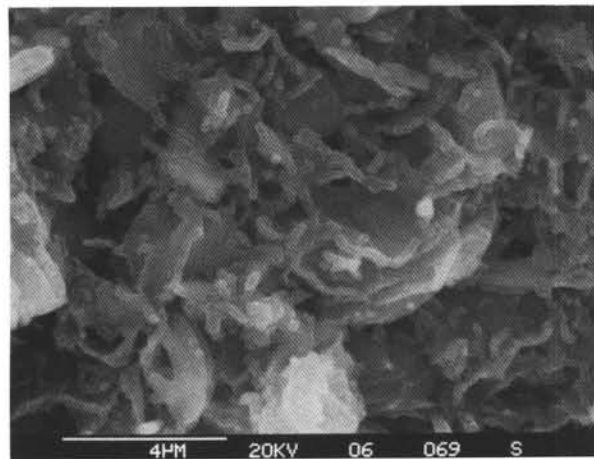
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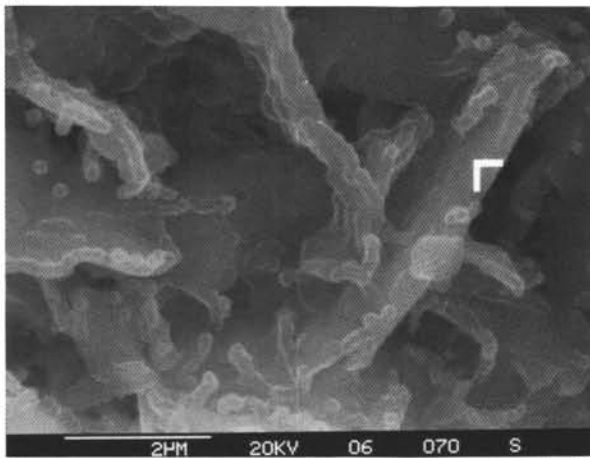
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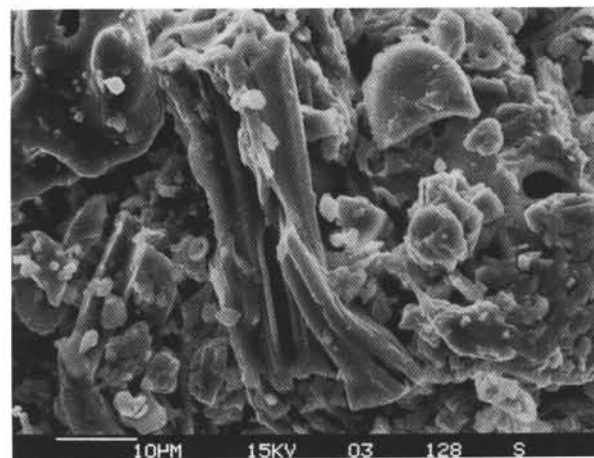
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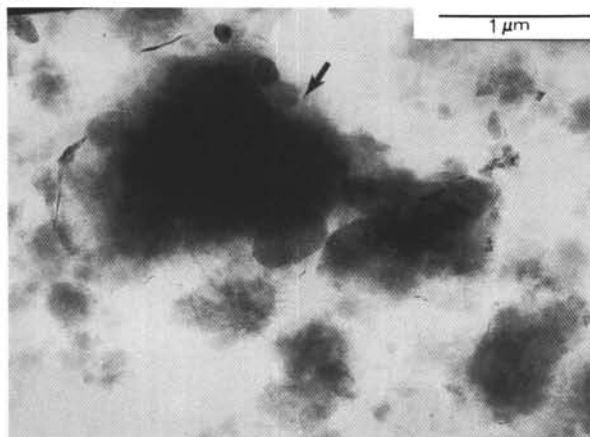
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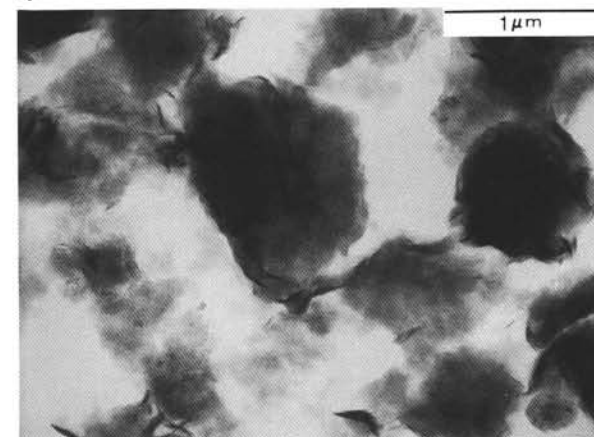
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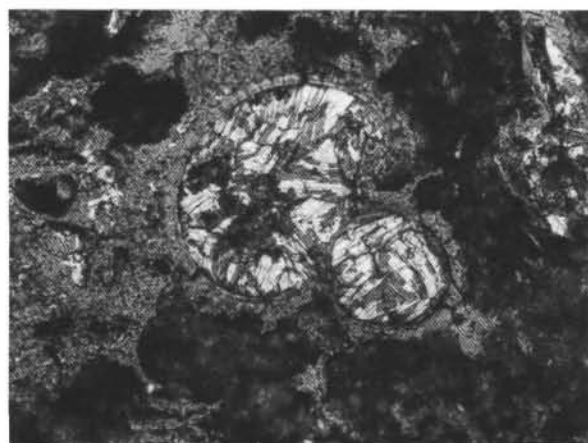


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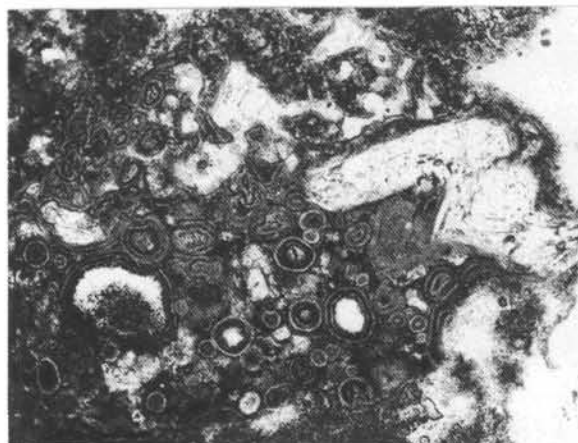
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Plate 1. 1. Sample 650A-18X-2, 149-150 cm. Microstructure of a poorly indurated sediment. 2. Sample 650A-18X-1, 9-10 cm. Microstructure of a firm mud. Note the occurrence of numerous gently folded clay sheets in which the terrigenous and biogenic particles are embedded. 3. Same sample, detail. Clay sheets show numerous tiny secondary growths both on their (001) faces and their edges. 4. Sample 650A-18X-1, 95-96 cm. Volcanic glass fragments with gas tubes. The majority of these volcanogenic grains have an andesitic composition, some have approximately a dacitic composition. Note the fresh appearance of the clean elongated glassy particle in the center of the photograph. 5. Sample 650A-18X-2, 149-150 cm. TEM. "Fleece smectites" (arrow) almost similar to the morphological type described by Chamley et al. (1985). < 1- μ m fraction. 6. Sample 650A-18X-1, 9-10 cm. Assemblage with several "folded smectites" (Chamley et al., 1985). < 0.5- μ m fraction.



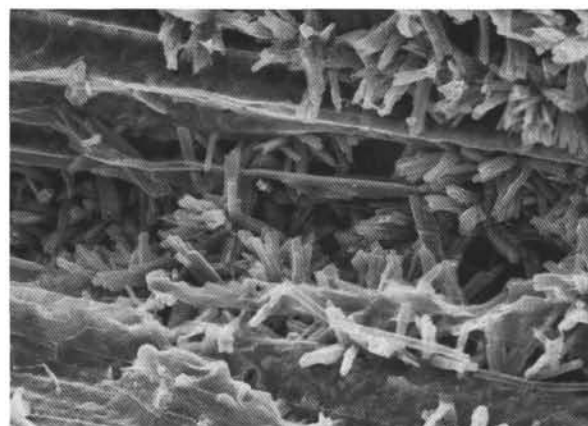
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50 μm



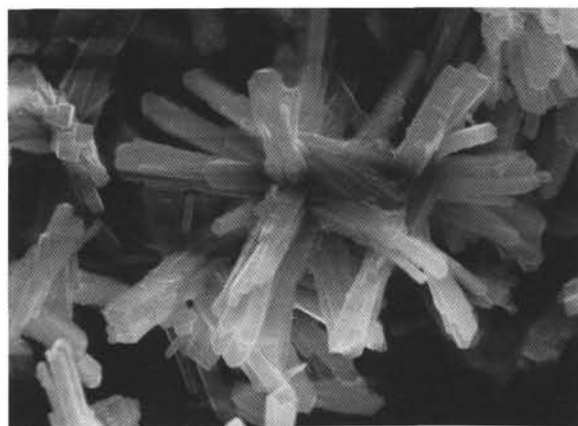
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100 μm



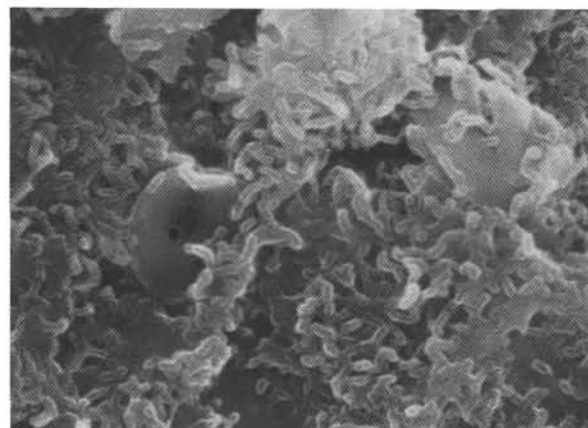
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10 μm



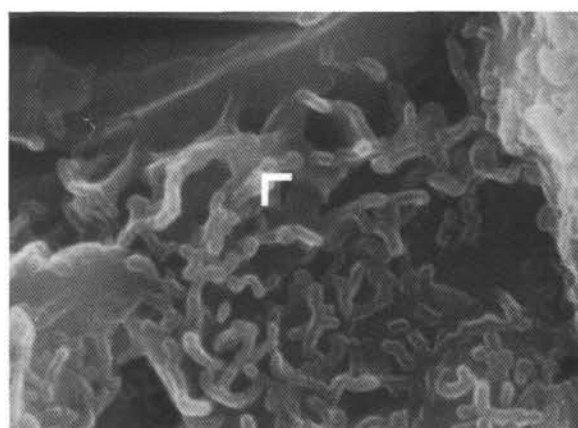
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10 μm



11

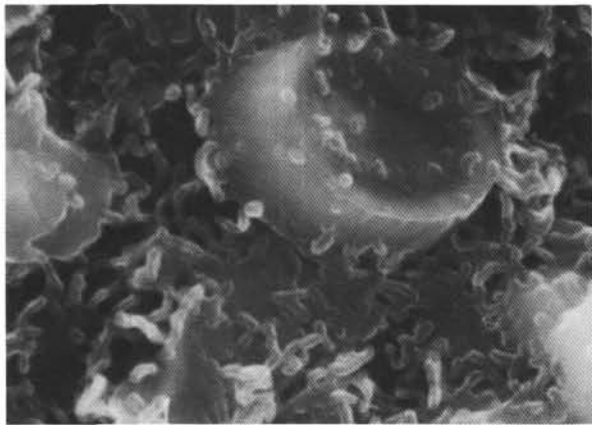
2 μm



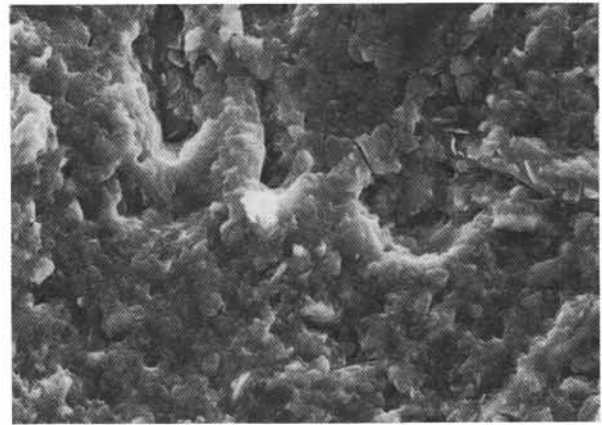
12

1 μm

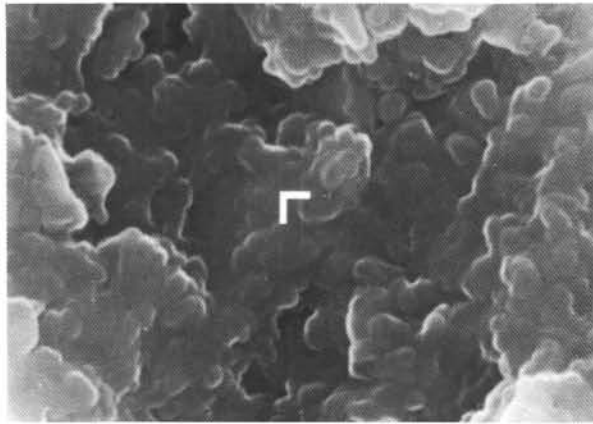
Plate 2. 7. Sample 651A-12R-1, 16–19 cm. Zeolite crystals (phillipsite) in a foraminiferal chamber. 8. Sample 651A-11R-3, 132–135 cm, sandstone part. Altered basaltic glass fragment with a vesicular structure. 9. Same sample. Authigenic pore-lining phillipsite crystals developed on a volcanic particle. 10. Detail of 9. Rosette of phillipsite crystals. 11. Sample 651A-11R-3, 16–19 cm, mudstone part. Aspect of the clay material mainly composed of gently folded sheets. 12. Detail of 11. Clay minerals appear linked to each other and form diagenetic bridges plainly visible on the side of the detrital fragment.



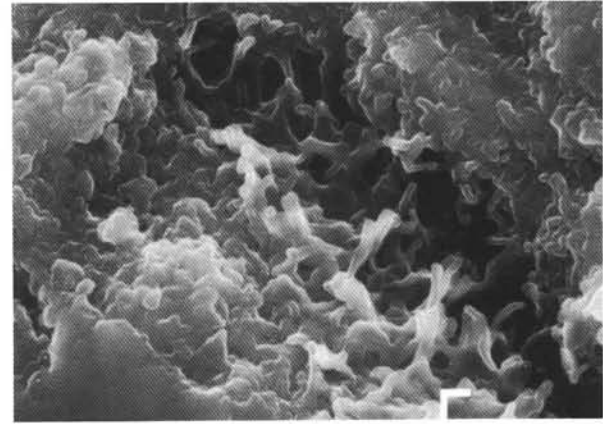
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2 μm 

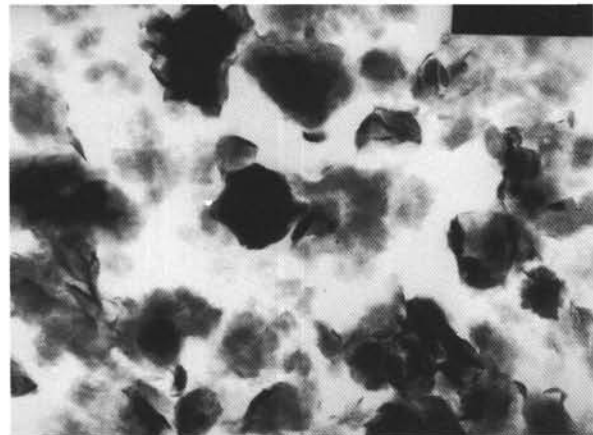
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10 μm 

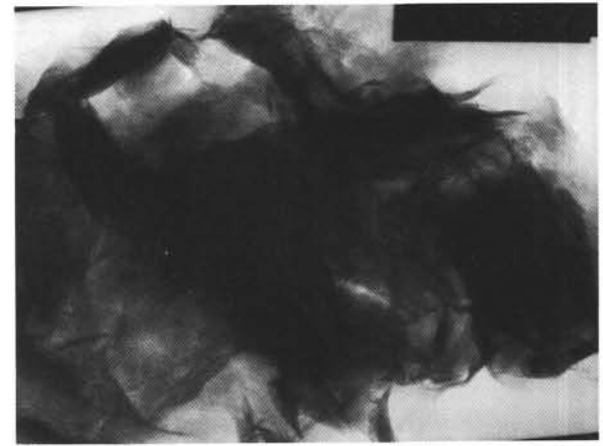
15

1 μm 

16

2 μm 

17

1 μm 

18

0.5 μm

Plate 3. 13. Sample 651A-11R-3, 132-135 cm, mudstone part. Growth of clays on a carbonated biogenic particle (probably a coccolith). 14. Sample 651A-12R-1, 16-19 cm. Homogeneous and more or less massive aspect of the microstructure. 15. Detail of 14. 16. Same sample. Transition to a morphological clay type similar to that of Sample 651A-11R-3, 132-135 cm, mudstone part. 17. Same sample. TEM. Clay assemblage is essentially made up of opaque "folded smectites" with some "transparent smectites." 18. Same sample. TEM. Detail of "folded smectites" constituting an aggregate.