

20. MINERALOGY AND ORIGIN OF CLAY MINERALS, SILICA AND AUTHIGENIC SILICATES IN LEG 14 SEDIMENTS

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ABSTRACT

Preliminary X-ray, SEM, TEM, and optical mineralogical results are reported to discuss the paragenesis, age distribution, and origin of clay minerals, silica modifications and authigenic silicates found in nine drilling sites of Leg 14 of the Deep Sea Drilling Project, located off northwestern Africa and northeastern South America.

Most noncarbonate minerals are diagenetic alteration products of volcanic ashes. Continent-derived clay minerals, such as mica-illite, kaolinite, and chlorite (rare), are frequent only in terrigenous sediments, especially off the Amazon River and off Cape Blanc. Smectites, mainly normal montmorillonite (+greenish nontronite, and hectorite-saponite), are the dominant clay minerals in sediments of all ages and sites. Montmorillonite, ultimately derived from the decomposition of volcanic glass, is especially abundant in volcanogenic clays and ashes, nannofossil marl-oozes, hemipelagic siliceous oozes, and brown pelagic clays. A mixed-layer mineral, consisting of regularly interstratified chlorite and trioctahedral montmorillonite, occurs mainly in pelagic clays.

Four types of amorphous or microcrystalline silica were observed in siliceous oozes and silicified mudstones and bedded cherts: (a) unaltered, amorphous opal (in siliceous organisms); (b) unidimensionally disordered low-cristobalite (-tridymite), either cryptocrystalline ("opal-cristobalite") or as fibrous "lussatite" needles, slowly crystallizing from closely-packed silica gel spheres (in cherts of intermediate maturity); (c) macrocrystalline fibrous chalcedony; and (d) cryptocrystalline quartz, commonly filling recrystallized radiolarian tests and forming the matrix of homogenized, mature, quartz-rich cherts.

Palygorskite, commonly associated with small amounts of sepiolite, is an abundant constituent of volcanogenic white (and brown) clays, carbonaceous clays, some siliceous muds, "white" lussatite cherts, and pelagic clays, all of Latest Cretaceous to Paleogene age. A diagenetic origin from degraded bentonitic clays by precipitation from magnesium-rich solutions with excess silica, derived from the devitrification of silicic ash and/or the dissolution of opaline organisms is suggested. The maximum occurrence of sepiolite is farther from shore than that of palygorskite.

Authigenic clinoptilolite, the only zeolite identified in all sites, has a similar age range (minimum age: Middle Miocene; minimum depth of burial: 120 meters) and paragenesis as palygorskite. It has also been formed diagenetically from the devitrification of volcanic glass and palagonite, especially in pelagic and volcanogenic brown clays and black carbonaceous shales, and at least 20 million years after their deposition.

High-temperature sanidine, possibly also of authigenic origin by hydrothermal solutions, was found in Late Cretaceous pyroclastic clays and altered vitreous ashes, associated with volcanic glass, palagonite, and montmorillonite.

INTRODUCTION AND ACKNOWLEDGMENTS

This paper intends to present our preliminary results of a reconnaissance mineralogical study of all representative sediment types encountered during Leg 14 of the Deep Sea Drilling Project (see also chapter by Berger and von Rad, this volume). A more detailed report on the petrography and diagenesis of the cherts and authigenic sediments is being prepared by the authors in cooperation with O. W. Flörke.

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PROCEDURE

Small sediment samples (a few cm³) were collected on board the *Glomar Challenger* by U. von Rad immediately after the cores were split. These samples were kept under refrigeration in small sealed PVC vials. Layers of special interest sampled at small intervals for this study included graded and homogeneous sand, silt, and ash layers, vari-colored volcanogenic and pelagic clays and marl oozes, black shale-dolomite silt cycles, as well as indurated and semi-consolidated shales, cherts and limestones.

From about 100 carefully selected samples, X-ray diffraction analyses were made by H. H. Rosch in the X-ray laboratory of the Bundesanstalt für Bodenforschung (see Tables 1 and 2). A Phillips Norelco Diffractometer was used with the following instrumental settings: Cu K α radiation, (mostly) LiF monochromator, 0.5° per minute scanning speed. The types of samples used were: a) untreated dry powder specimens, b) glycerine or ethylene-glycol saturated, oriented specimens, and c) random-orientation specimens ("texturarm"). Bulk samples were usually X-rayed; but, in a few cases, selected grain-size fractions (<32 μ , <63 μ , 32-63 μ , etc., see Tables 1 and 2) also were analyzed. Of about 20 carbonate-rich samples, both total and formic-acid-dissolved, carbonate-free samples were studied. The relative abundances of the different mineral phases were roughly estimated and grouped into four categories: main constituent (approximately >40%), abundant (about 20-50%), common (about 10-20%), and traces (about 3-10%). X-ray-amorphous constituents (for example volcanic glass, opaline organisms, and carbonaceous matter) and components in amounts too small to be detected by X-ray diffraction analysis were added in Tables 1 and 2 after optical determination in smear slides, thin-sections and coarse fractions. Comparison of smear-slide with X-ray semiquantitative estimates show poor correlation for quartz and feldspar (higher by X-ray) and pyrite, iron-oxides, zeolites (lower X-ray). The remaining constituents, especially the estimates of carbonate, and total clay percentages show fair correlation.

Smear slides, thin sections of consolidated and artificially impregnated sediments, and coarse fractions (different sieve-size intervals) were photographed with a "ZEISS-Photomikroskop II" and studied with a binocular microscope by U. von Rad at Hannover (see also Berger and von Rad, this volume).

Transmission and scanning electron microscope analyses helped in the identification of silica minerals, palygorskite, sepiolite, and clay minerals.

CLAY MINERALS

Mica-Illite

Mineralogy

In this preliminary study, mainly based on X-ray diffraction analyses, the different 10 Å mica minerals, such as clay-sized illite (hydromuscovite), and coarser-grained muscovite, biotite, and sericite were not differentiated. Smear slide and thin-section studies (see Berger and von Rad, this volume), however, show that brown and green biotite are more frequent than light-colored mica (muscovite) in the silt and sand fractions of nearly all samples.

The degree of crystallinity of the 10 Å mica phases ranges from nearly amorphous (Figure 1e, Figure 3) to well-ordered "illite" (Figure 1b) and well-ordered mica (Figure 1a, probably biotite). Transitional stages can be observed (Figure 1c and 1d).

The structural state of the main constituents of each sample (for example, mica, palygorskite) is expressed by the "disordering degree" in the next to last column of Tables 1 and 2. In this column "no signature" means "well-ordered," and "disordering common" means "nearly X-ray amorphous."

Occurrence

The mica minerals, together with kaolinite, are most abundant in terrigenous sand layers (135-7, 141-6, 142-2 to 6, for example). They are common constituents of cherts (135-8), of volcanogenic sediments (136-3-8), of pelagic sediments (associated with montmorillonite) and of zeolite-rich muds and carbonaceous shales (for example, in 144A-5). Traces of mica were found in most marl oozes and clays. Compared with the abundance of mica in recent sediments, reported by Griffin *et al.* (1968) for the equatorial Atlantic between northwestern Africa and the Amazon River (30-60 per cent), the comparatively small amount in the mainly montmorillonitic Cretaceous and Tertiary sediments of that region is surprising. Mica appears to be more frequent in Neogene than in Paleogene and Cretaceous sediments.

Origin

The mica minerals are most likely terrigenous components transported by high-altitude winds, by river discharge and currents from the adjacent continents. The high amount of tropospheric dust transported by high-altitude (13 to 15 kilometers) and high-velocity (100 to 140 km/h) westerly jet streams, blowing during the summer months from northwestern Africa (10-30° N latitude) is well known (Arrhenius, 1959; Folger, 1970). Trade wind transport from the arid regions of North Africa into the equatorial Atlantic

has been observed over a distance of 2000 kilometers to the Caribbean Islands, with a maximum between the Canary and Cape Verde Islands (our Sites 139-141). On the other hand, riverborne terrigenous material is transported in large amounts into the western equatorial Atlantic by the Amazon and Orinoco Rivers.

Chlorite

Chlorite is a rather rare clay mineral at all Leg 14 sites. It is frequently associated with mica and kaolinite in terrigenous, graywacke-type sand layers, especially at Sites 135 (Core 7) and 142 (Cores 1-6, see Figure 1a). It occurs also in Cretaceous sediments, for example in carbonate-cemented tuffs (136-5c), and in pelagic, partly zeolitic clays (137-7 and 8, 141-9, 144-6). For these sediments, the possibility of a secondary origin—as an alteration product of other clay minerals—cannot be excluded, but authigenesis in the marine environment is not as likely to occur.

Chlorite is the typical "high-latitude clay mineral" of the world ocean (Griffin *et al.*, 1968, p. 434); it is derived from the continental erosion of metamorphic and sedimentary rocks in the polar and subpolar regions. It is not surprising therefore, that chlorite is either absent or of minor importance in the equatorial sediments of Leg 14.

Kaolinite

Next to montmorillonite, kaolinite is the second most important clay mineral in most samples, especially at the drilling sites adjacent to the African and South American continents, where it occurs in terrigenous sediment layers.

The different degree of crystallinity is expressed by the character of the 7.2 Å kaolinite-chlorite peak (Figure 1a-d). On electron microscope micrographs (Plate 1, Figure 5), one can recognize the tabular crystals with pseudo-hexagonal outlines.

Abundant kaolinite—together with mica and chlorite—occurs in the Pliocene-Pleistocene feldspar-rich graywackes of Site 142 off the Amazon River. In the surface sediments off northeastern South America, between 20 and 30 per cent kaolinite was reported by Biscayne (1965), Griffin *et al.* (1968) and Rateev *et al.* (1966). Kaolinite, a typical low-latitude mineral, is usually formed in tropical regions undergoing intense lateritic weathering of feldspars. It is then transported as suspended matter by the Orinoco, Amazon, and especially the São Francisco River (northeastern South America) into the Atlantic. The Congo and Niger Rivers also carry kaolinite-rich (10 to 30 per cent) sediments from Africa into the equatorial Atlantic (Griffin *et al.* 1968).

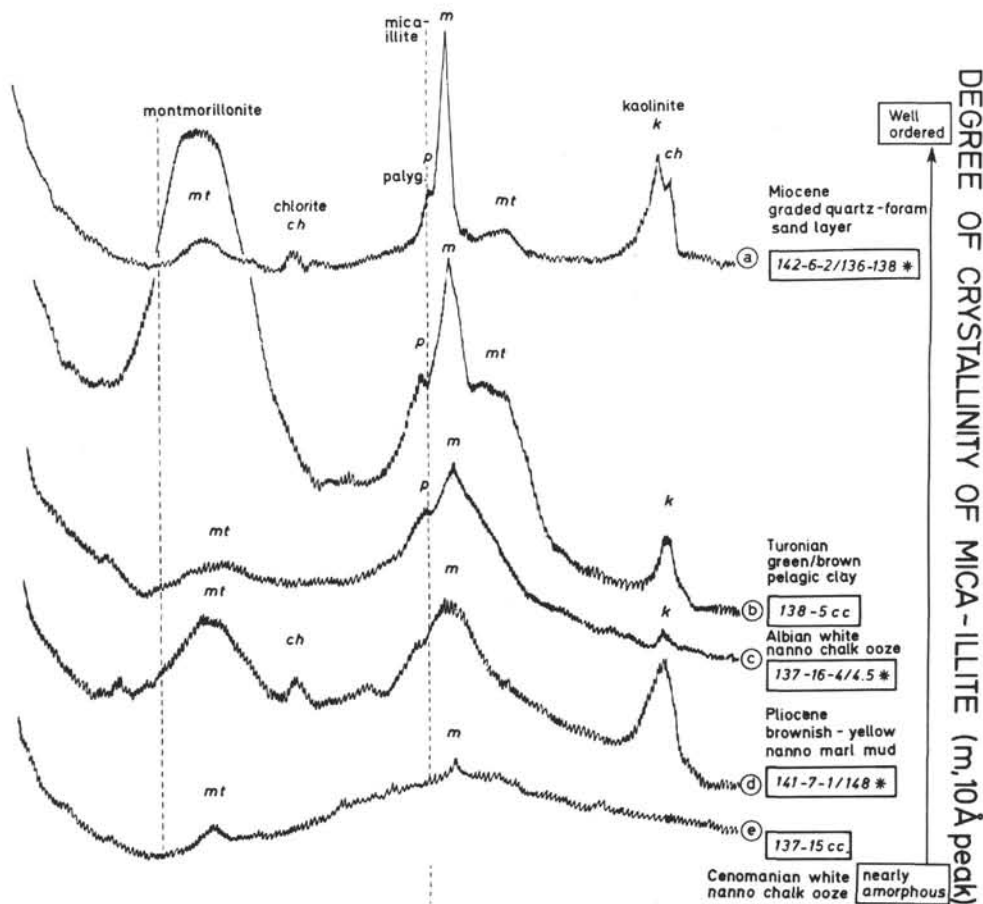


Figure 1. Degree of crystallinity of mica-illite (10 Å peak). Note transitional series from nearly amorphous (base) to well ordered mica-illite (Sample 142-6-2, 136-138 cm, top). X-ray diffraction traces, instrumental settings see text.

In general, kaolinite content appears to increase toward the continents: Sites 135, 139, 142 and 144—with high kaolinite proportions in terrigenous sediment are all located on or near the continental rise and less than 600 kilometers offshore.

At most sites, there is a tendency for kaolinite to occur only in sediments younger than latest Cretaceous/Paleogene (Sites 135, 136, 138, 140, 141). Only at Sites 137 and 144 was kaolinite found in sediments of Middle Cretaceous age.

Smectites

Minerals of the smectite or montmorillonite group (Correns, 1950; Brown, 1961) are the most important clay minerals in almost all samples from the different environments encountered in the deep-sea sediments of Leg 14. Most of the montmorillonite was probably formed *in situ* by halmyrolysis from devitrified magnesium-rich volcanic glass and palagonite (Peterson and Griffin, 1964; Nayudu, 1964; Griffin *et al.*, p. 440).

Minerals such as montmorillonite, zeolites, and pyroxenes, derived from volcanic sources, play an important role, because of the small amount of terrigenous clay minerals (illite, kaolinite, etc.) reaching the Equatorial Atlantic and because of the relatively low rate of deposition. On the other hand, there is a direct input of montmorillonite minerals from the continents, either by rivers draining degraded volcanic formations and arid desert soils, such as the Amazon River with 30 per cent montmorillonite (Gibbs, 1965) and the Nile River (Rateev and Emel, Yanov, 1966), or by suspended transport from volcanic islands, such as Madeira and the Cape Verde Islands (Correns, 1937, p. 284). Montmorillonite can also be derived from degraded illite (loss of K⁺). The surface sediments (Holocene-Pleistocene) of the Equatorial Atlantic between northwestern Africa and the Amazon River contain only 20 to 30 per cent montmorillonite in the total clay mineral fraction (Rateev *et al.*, 1966; Griffin *et al.*, 1968). In all Late Cretaceous and Tertiary sediments of Leg 14, the montmorillonite percentages are probably much higher than in the surface sediments, which are highly influenced by Quaternary terrigenous supply.

Montmorillonite

“Normal” montmorillonite with the basal reflex expanded to 17 Å in ethylene-glycolated, oriented specimens, is the main smectite mineral. It is the predominant constituent (>40 per cent) of (a) brown and pink volcanogenic clays (for example, 136-5-1, 136-8-2), (b) brown and greenish-gray zeolite-rich pelagic clays (for example, 137-5cc, 137-6-1), often associated with palygorskite, (c) hemipelagic siliceous silty clays (for example, 140-3-2, 74-78 cm), and (d) nannofossil marl oozes (for example, 137-8-1, 28-29 cm). It is also abundant (20 to 50 per cent) in altered ash layers (for example, 138-6-2, 144 cm), carbonaceous cherts (for example, 135-8-1), in the clay matrix of terrigenous silts and sands (for example, 141-SW 1; 140-8-3, 3 cm), and in dolomitic silty clays (for example, 138-6-2, 46-67 cm). Montmorillonite occurs, however, in considerable amounts (up to 20 per cent) in most other sediment types of all sites, irrespective of their age. The only exception is Site 142, off the Amazon River, where

mica-illite, kaolinite, and chlorite are more abundant than montmorillonite (see Tables 1 and 2).

One can easily understand the high proportion of montmorillonite in the Middle to Late Cretaceous altered vitreous ash layers (see Plate 1, Figures 3, 5) and brown volcanogenic clays. It is associated there with appreciable amounts of brown sideromelane (partly palagonitized), white pumice spherules, high-temperature sanidine, pyroxene and (sometimes) palygorskite-sepiolite. Most of the original sideromelane glass in the pyroclastic sediments was probably penecontemporaneously devitrified into palagonite and transformed into a bentonitic (montmorillonite-rich) clay during early diagenesis. The excess SiO₂, Al₂O₃, CaO, Na₂O and K₂O (which were formed during the halmyrolytic devitrification process) account for the formation of authigenic minerals, such as clinoptilolite, palygorskite, opal-cristobalite, and (?) authigenic K-feldspar (see Nayudu, 1962; Bonatti, 1965, 1967; Hay and Ijima, 1968; Füchtbauer and Müller, 1970, pp. 169, 569).

In addition, montmorillonite is also the main clay mineral in purely pelagic sediments—for example, at Site 140, where volcanogenic constituents (volcanic glass, pumice, K-feldspar; altered ashes) are absent or very rare. It is possible that this montmorillonite was originally formed in a different environment (for example, near submarine volcanic centers or volcanic islands) and was then transported in suspension together with terrigenous debris (quartz, mica-illite, kaolinite) to its site of deposition.

Nontronite (?)

Although not confirmed by X-ray diffraction analysis, the clay mineral nontronite, an iron-rich smectite, was tentatively identified in several smear slides of green volcanogenic sands and silts (see Plate 1, Figure 1 and 2). These layers (such as, 136-8-2, 10-11 cm) contain large amounts (>50 per cent) of greenish to straw-yellow phyllosilicate minerals of intermediate birefringence and positive relief. They occur as concretions in silt- and sand-sized spherules with furrows and contraction cracks, ellipsoids and tubules—which are probably derived from altered pumice—and as irregular aggregates. According to Arrenhius (1963), Bonatti (1965, 1967) and Nayudu (1962), nontronite originates from the slow diagenetic decomposition of basaltic glass, or from the quick hydrothermal reaction of hot lava at its contact with sea water.

Hectorite-Saponite

The main constituent of two brown clay samples is a mineral of the saponite-hectorite series (trioctahedral Al-Mg montmorillonite). This mineral is characterized by a (001) basal reflex, displaced to 19.5 Å in oriented, ethylene-glycol saturated specimens, by (060) interference peaks at 1.530 Å, and by the absence of 2.60-Å and <2.50-Å peaks. According to Kerr (1937) and Nagelschmidt (1938) these characteristics agree with the indices of the hectorite-saponite series (see also Brown, 1961 and Grim, 1968). Both samples are pelagic, brown silty clays of Late Cretaceous age (136-5-1, 120-124 cm; 137-4-2, 130 cm), in which hectorite-saponite is associated with palygorskite, sepiolite and clinoptilolite (Plate 1, Figure 6). The mineral is possibly a diagenetic alteration product of a bentonitic clay.

Mixed-layer Chlorite-Montmorillonite

Because of the small percentage of interstratified clay minerals it is difficult to make more than a tentative interpretation of their crystallographic structure. The combined observations of several X-rayed samples have shown this mineral to be a regular (1:1) interstratification of chlorite and trioctahedral montmorillonite (Earley *et al.*, 1956) (if optimally preserved) with the following experimental data:

Untreated Material		Glycolated Sample		Heated to 500°C		(hkl)
I	d(Å)	I	d(Å)	I	d(Å)	
5	30.1	8	32.4	10	22.2	(001)
10	14.9	10	16.0	10	11.8	(002)
3	7.4	4	8.0 ₅	5	5.9 ₂	(004)
—	—	—	—	—	—	(001)

The mixed-layer mineral occurs in Late Cretaceous to Paleogene, green, phyllosilicate sands (136-8-2, 10 cm; 141-9-1, 63 cm), in pelagic brown clays (141-8-2, 36-48 cm), in a nannofossil-marl mud, underlying a multicolored mineralized zone (136-8-2, 27-30 cm), and, as traces, in cherts (140-7-CC). It is always associated with montmorillonite, and in some cases also with palygorskite, kaolinite and chlorite.

SILICA PHASES AND AUTHIGENIC SILICATES**Silica Phases (Modifications) in Cherts**

By comparing the texture and structure of silicified sediments, the mineralogy of the matrix, and the nature, preservation and filling of siliceous organisms, the cherts of Leg 14 were classified into four descriptive and possibly also genetic groups. Heterogeneous and generally "young" cherts, rich in well-preserved opaline skeletons, "opaline" matrix and disordered low-cristobalite (lussatite) are of early diagenetic origin. Two transitional types exist between this "immature" chert and the "mature" late-diagenetic end product of this succession, a homogenized, quartz-rich chert of Late Cretaceous age with all opaline skeletons converted to quartz (see Berger and von Rad, Chapter 26, this volume).

The silica of these cherts originated in most cases from the partial or complete dissolution of opaline skeletons of diatoms, silicoflagellates, radiolarians, and sponge spicules during diagenesis at high pH-conditions; in a few cases the devitrification of volcanic glass or the degradation of smectites might have contributed some silica (SiO₂). The silica was redeposited by colloidal precipitation as "opal-cristobalite" (low-cristobalite and "lussatite") under low pH-conditions (Mizutami, 1966; Ernst and Clavert, 1969). This happened often in the presence of organic material within the pore space of bedded carbonaceous shales, terrigenous silts, and nannofossil marl muds. The silicified layers normally occur as distinct beds within black, carbonaceous, often zeolite-, palygorskite-, and dolomite-rich shales, zeolitic marls and hemipelagic, quartzose, diatom muds and silts. Nodular cherts associated with carbonate oozes, as described by Beall and Fischer (1969, Leg 1), Pimm *et al.* (1970, Leg 6), and Heath and Moberly

(1971, Leg 7) appear to be absent. The diagenetic processes leading from the original opaline skeletons in siliceous oozes through the intermediate phases of low-cristobalite to chalcedonic and microcrystalline quartz are mainly dependent on time, temperature, and the pH and fluid pressure of the pore solutions (Mizutami, 1966; Ernst and Clavert, 1969).

The youngest chert (earliest Miocene) was found at the lowest depth (660 meters, Site 139-7) and belongs to the immature opaline type. Most cherts, however, are of Late Cretaceous to Paleogene (Eocene) age. The minimum depth of burial is 150 meters (Late Cretaceous, Site 144-3).

Four silica varieties ("phases") were distinguished in the silicified mudstones and cherts of Leg 14 by optical microscopy, X-ray diffraction, scanning and transmission electron microscope analysis: (a) amorphous opal, (b) disordered low cristobalite-tridymite and "lussatite", (c) chalcedonic and (d) cryptocrystalline quartz.

Amorphous Opal

Genuine, unaltered opal (that is, nearly X-ray amorphous, hydrous silica) is rare. The X-ray pattern of skeletal opal in siliceous clays shows a broad diffuse hump centered at about 4.1 Å (Figure 3: Sample 139-7). Figure 3 reveals also other diffuse bands between 11 and 7.5 Å in silica-rich sediments, representing amorphous scattering. The degree and type of *amorphous scattering* (given also in Tables 1 and 2) depends on the proportion and kind of X-ray amorphous or cryptocrystalline material, mainly opal, or in other cases also volcanic glass and organic matter. Significant indications of "peaks" near 10.5 Å suggest amorphous palygorskite (?), "peaks" at 10 Å illite (?), and "peaks" near 9.5 Å clinoptilolite as nearly X-ray amorphous admixtures in these sediments (see Figure 3).

Nearly X-ray amorphous opal is preserved as opaline tests of siliceous organisms in post-early Eocene, hemipelagic sediments, deposited at high rates of sedimentation. Some "immature" cherts ("porcelanites") contain also opaline (?) fossil tests. In most cherts the matrix consists of dehydrated and aged opal, diagenetically transformed into low-temperature cristobalite (lussatite), and finally into chalcedonic and microcrystalline quartz.

Disordered Cristobalite-tridymite ("Lussatite")

"Lussatite" is an irregular structural interstratification of cristobalite-layers (cubic densest packing) with tridymite layers (hexagonal densest packing); that is, a unidimensionally highly disordered fibrous low-temperature cristobalite. The cryptocrystalline-spherulitic variety can be called "opal-cristobalite" or simply "low-cristobalite". The X-ray diffraction pattern shows broadened, but well-defined bands and missing peaks at low d-values (Flörke 1955, 1967, personal communication 1971; Tröger, 1967, p. 95, Jones and Segnit, 1971; Mizutami, 1966). Apparently the cristobalite is of low-temperature (<80°C) diagenetic origin, originating from dissolved skeletal opal or devitrified volcanic glass, and re-precipitated in the pore space of pelagic clays, marls and terrigenous silts (cf. Flörke, 1955; Ernst and Clavert, 1969; Hathaway *et al.*, 1970; Heath and Moberly, 1971). The high degree of unidimensional stacking disorder is caused by a very low temperature origin and the lack of foreign ions favoring further nucleation (Flörke, 1955).

The X-ray diffraction pattern (see Figures 2b, 3, 5b) combines the main broad $d(111)$ -cristobalite peak between 21.7 and $21.9^\circ 2\theta$ with a number of other cristobalite peaks and peaks typical for low-temperature tridymite (for example, at 20.6° , 23.3° and $36^\circ 2\theta$).

Scanning electron micrographs (Plate 2, Figure 1) show that the silica forms closely-packed, globular bodies (spherulites) of uniform size and with a diameter ranging from 3 to 8 (maximum 20) microns. The interior of each silica spherule consists of a network of minute irregularly-oriented lussatite (s.s.) fibers and needles (Plate 2, Figure 2), probably slowly crystallized from the amorphous silica gel (O. W. Flörke, personal communication, 1972). Similar silica gel spherules, but of much smaller size (0.15 to 0.35 microns), have been described from precious opal, where they are formed by chemical exsolution within the vitreous state and grown by deposition of silica onto a precipitated nucleus. In precious opal these globular pseudocrystals are stacked in hexagonal densest-sphere packing and cemented by silica (Sanders, 1964; Jones *et al.*, 1964; Nissen and Wessicken 1970, 1971). The silica spherules in the cherts of Leg 14 are less uniform in size and apparently distributed at random in the matrix or concentrated in the tests of partly dissolved siliceous organisms. Minute spherules and polygonal grains (0.2 to 1 micron in diameter), aligned in a "cobblestone-pattern" were observed on transmission electron micrographs of freshly broken chert surfaces and tentatively identified as low-cristobalite ("opal-cristobalite").

Macrocrystalline Chalcedony

Macrocrystalline chalcedonic quartz is the typical secondary silica cement forming the casts of partly recrystallized radiolarian tests and sponge spicules in cherts of intermediate maturity (cf. Berger and von Rad, Chapter 26, this volume). It is usually present as sheave-like bundles of radiating length-fast fibers filling the lumina of siliceous organisms. The growth starts from one or a few centers of crystallization, mostly at the outer rim toward the open space in the center of the fossil test. Both microcrystalline ($<1\mu$), length-fast chalcedony and fibrous (length-slow) microcrystalline quartz ("quarzin") are disordered quartz ($\pm H_2O$) and practically indistinguishable in thin-sections.

Microcrystalline Quartz

Micro- or cryptocrystalline quartz ($<1\mu$), including microcrystalline chalcedony and "quarzin", is the main constituent of most cherts, especially of the more "mature", quartz-rich types. The extremely fine-grained, interlocking quartz grains in random orientation and with "pin-point birefringence" (Folk and Weaver, 1952) are part of the chert matrix, or they fill the lumina of radiolarians.

Palygorskite-Sepiolite

Both palygorskite (=attapulgit) and sepiolite are hydrated high-Magnesium chain silicates. Because of their similar facies association and paragenesis, both minerals are treated together here.

Palygorskite

Mineralogy

The well-crystallized varieties (such as, 138-3-1, 122-123 cm; 140-6-2, 95-98 cm; see Figure 2 and Figures 4c and 4f)

show good agreement with the X-ray diffraction data for palygorskite given by Bradley (1940), De Lapparent (1938) and by Caillere and Henin (1961). The characteristic 10.5 \AA reflex of palygorskite is not influenced by polar organic molecules (glycolation) and does not change its position after heating the sample to 300°C . Therefore the mineral can not be confused with expandable (for example, mixed-layer) clay minerals.

Less well-crystallized varieties of palygorskite with different degrees of crystallinity are shown in Figure 4. The six X-ray traces demonstrate a continuous series ranging from excellently crystallized palygorskite with a high and pronounced 10.5 \AA peak (Figure 4f) to a very poorly crystallized sample (Figure 4a) with large X-ray-amorphous proportions (see also Figure 3). Apparently the mineral can exist in a transitional between amorphous and crystalline stage.

Clusters and aggregates of elongated needles and fibers, typical for both palygorskite and sepiolite, can be observed in transmission electron micrographs of ash fragments and pelagic clays (Plate 1, Figures 4-6).

Paragenesis and Age

Palygorskite is the dominant or second-most abundant constituent in several samples from Leg 14, most of them of pre-Miocene age. It usually occurs in: a) brown, yellow, and especially, white volcanogenic clays in Cores 5-8 of Site 136 (Late Cretaceous-Paleogene), always associated with traces of sepiolite; b) carbonaceous clays (135-8); c) light-greenish-gray to "white" dolomitic siliceous muds and palygorskite-lussatite cherts of Mid-Eocene age and older (Site 140, Cores 3, 5, 6); d) pelagic clays of several sites (135-7, 137-2, 138-3, 141-6, 144-3).

In most cases, the sediments containing palygorskite (and sepiolite) are of latest Cretaceous to Paleogene age deposited at low sedimentation rates. The youngest palygorskite is of Maestrichtian (Site 135, 144) or of Eocene-Oligocene age (137, 138). Core 141-6 is the only exception with relatively young (? Miocene) palygorskite.

Sepiolite

Mineralogy

In none of the analyzed samples, is sepiolite an abundant or main constituent. Its presence, however, can be recognized by the significant (110)-reflex at 12.1 \AA which can not be confused with that of any other clay mineral. The position of this peak does not change after glycolisation; also, it is not influenced by cations heating up to more than 250°C (Figure 2a).

The d-spacings and reflex intensities of the sepiolites found in Leg 14 sediments correspond well with those reported by Caillere and Henin (1961) from different localities. Judging from the degree of crystallinity (see Figures 4a-4d, and 4f), most of the analyzed sepiolites appear to correspond with the sepiolite described by Brindley (1959) from the type locality of Eski Chehir (Turkey).

Paragenesis

In all studied samples sepiolite is a subordinate admixture of palygorskite-rich clays. It is especially

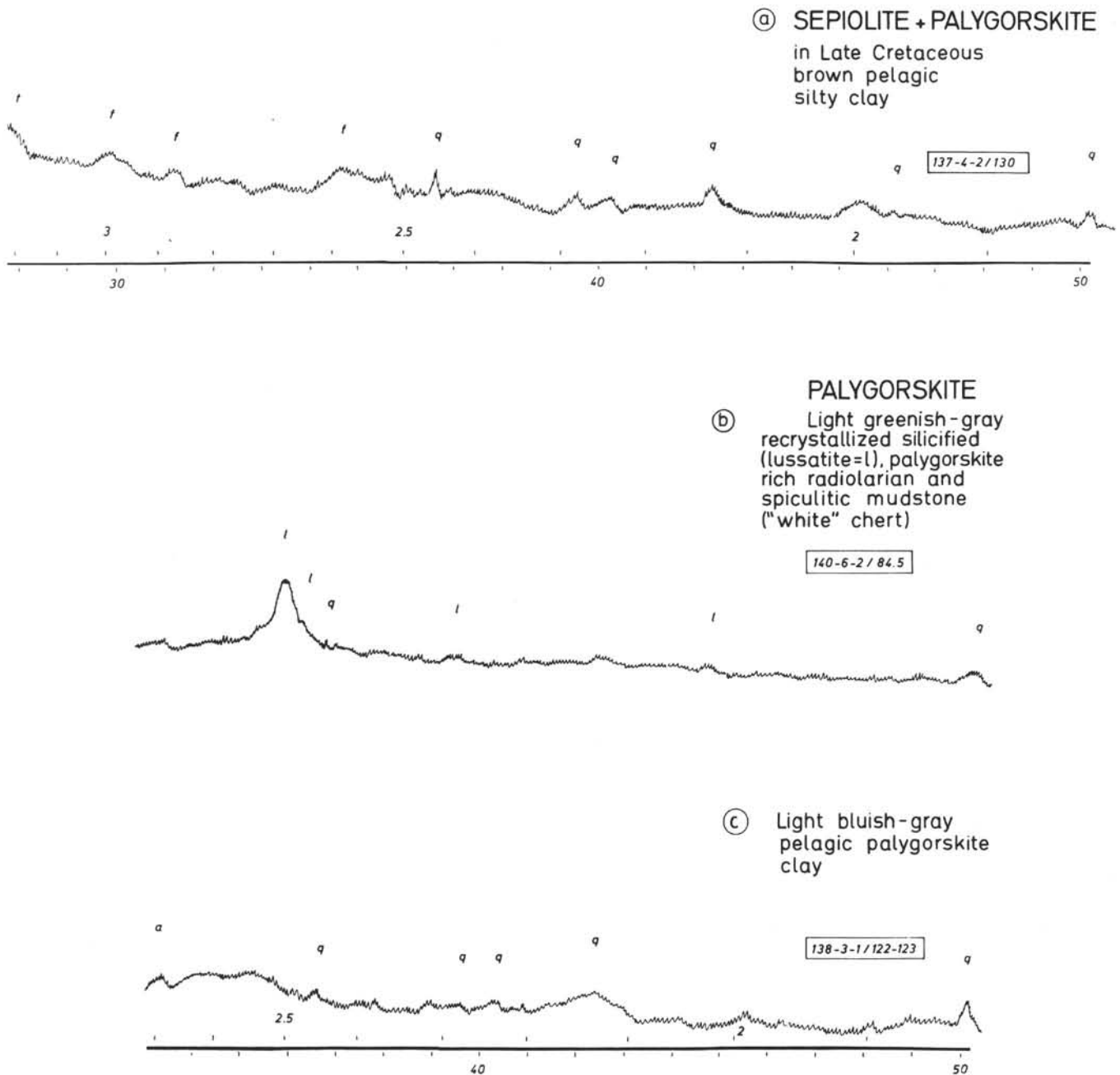


Figure 2. a) Sepiolite and palygorskite in brown clay (137-4-2, 130 cm). b) Palygorskite and "lussatite" (disordered cristobalite-tridymite) in white chert (140-6-2, 84.5 cm). c) Palygorskite-rich pelagic clay (138-3-1, 122-123 cm).

abundant in a sample of a Cenomanian yellow volcanogenic clay within the multicolored mineralized zone of Core 136-8-2, and in a Maestrichtian pelagic brown clay (137-4-2, 130 cm). In that sample sepiolite is associated with hectorite-saponite, palygorskite, and authigenic clinoptilolite and rhodocrosite (see Table 2).

Genesis of Palygorskite and Sepiolite

Both palygorskite and sepiolite are hydrated magnesium-rich silicates formed under unusual conditions (excess

magnesium and silica content), mostly in the marine environment, but also in fresh water lakes. Wollast *et al.* (1968) were able to produce, experimentally, a hydrated Mg-silicate similar to sepiolite by direct precipitation from sea water, rich in hydrous silica, under earth-surface conditions (25°C, 1 atmosphere). The presence of sepiolite and palygorskite in Cretaceous to Recent deep-sea sediments has proved that these minerals are also stable (or at least metastable) at much higher pressures (>700 bars) and lower temperatures (1 to 2°C at the sea floor). The direct

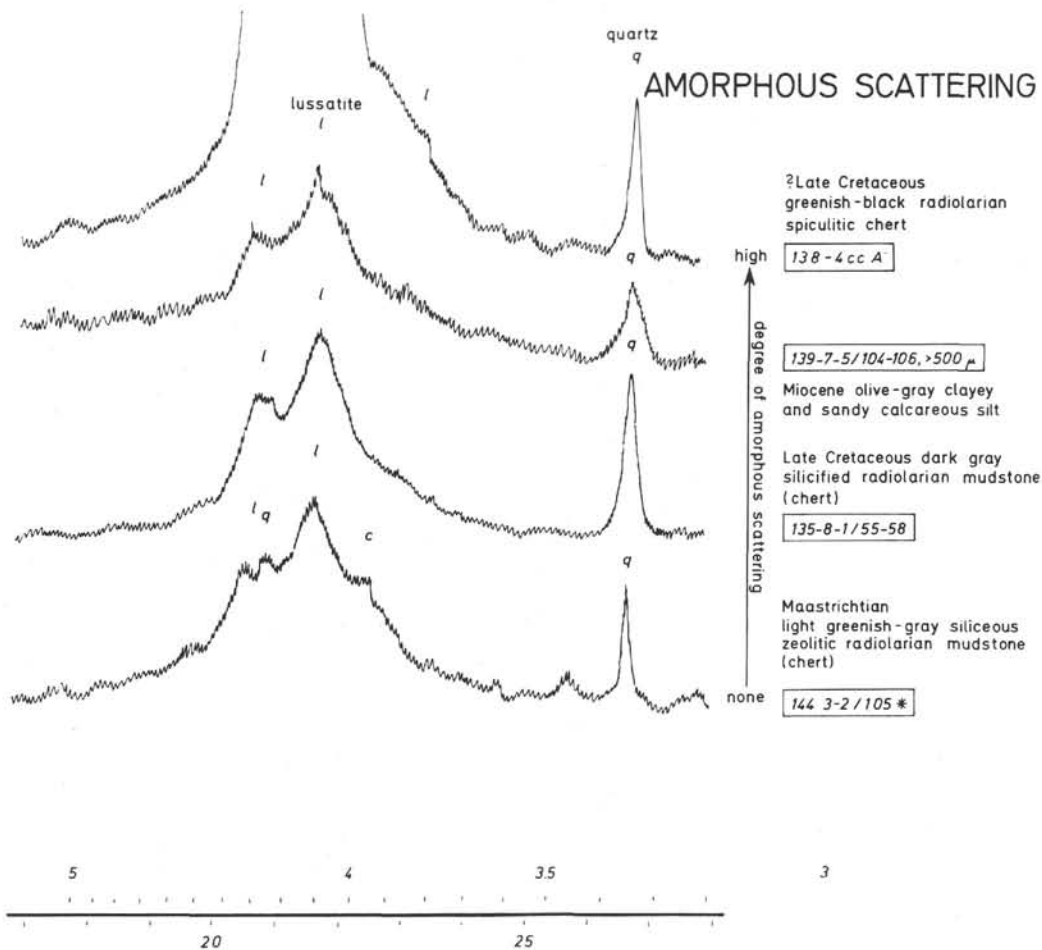


Figure 3. Degree of amorphous scattering in opaline sediments and cherts. Note increase of degree of amorphous scattering from Sample 144-3-2, 105 cm (base) to 138-4-CC (top).

precipitation from sea water appears to be the exceptional case under extreme (for example, lagoonal) conditions. Diagenetically, these Mg-silicates can be formed in the pore spaces of montmorillonitic clays by the interaction with magnesium-rich pore solutions, especially in sediments of Miocene and older age (Füchtbauer and Müller, 1970, p. 193; Hathaway *et al.* 1970).

The deposits of palygorskite and sepiolite which are documented in the literature may be assigned to four major genetic types of facies associations (see also Hathaway and Sachs, 1965):

1) Evaporitic sequences in highly saline or alkaline fresh-water environments (desiccating lakes) and in highly saline lagoons, where sepiolite and palygorskite are directly precipitated from magnesium-rich brines in arid zones (Millot, 1960, 1964; Rateev *et al.*, 1963). A similar origin was suggested also for their formation in restricted ocean basins, such as the Red Sea and a restricted Mesozoic Proto-Atlantic Ocean (Heezen *et al.*, 1965; Peterson *et al.*, 1969).

2) Diagenetic formation of palygorskite and sepiolite from degraded montmorillonitic clays by magnesium-rich solutions. The magnesium-ions may be either stripped from sea water, or derived from hydrothermal solutions, for example by the serpentinization of feric minerals (Bonatti and Joensuu, 1968). In the marine environment saturation

for the magnesium-rich sepiolite and the magnesium- and aluminum-rich palygorskite can only be reached if enough silica hydrogel is present in the pore spaces (Hathaway and Sachs, 1965). This excess silica may be derived from one or several of three sources:

a) the devitrification of volcanic glass and palagonite in silicic ashes to montmorillonitic clays where SiO₂ is liberated at high pH conditions. (In clinoptilolite-bearing ashes and tuffs the pH may go up to 10); the association of montmorillonite, clinoptilolite, and residual volcanic glass is typical for this origin (Hathaway and Sachs, 1965);

b) the dissolution of opaline tests of siliceous organisms (association with contemporaneous radiolarian and spiculitic cherts and calcareous oozes);

c) the introduction of SiO₂ by rivers draining regions of lateritic weathering;

3) Hydrothermal alteration of serpentine, where magnesium and silica ions are liberated.

4) Detrital origin: eolian and/or suspension transport from a continental source, for example from arid regions in Africa (Senegal), where palygorskite was reported by Wirth (1968).

A continental source was also suggested for the palygorskite found in the Red Sea (Muller, 1961) and in the Persian Gulf, where a terrestrial supply of reworked older

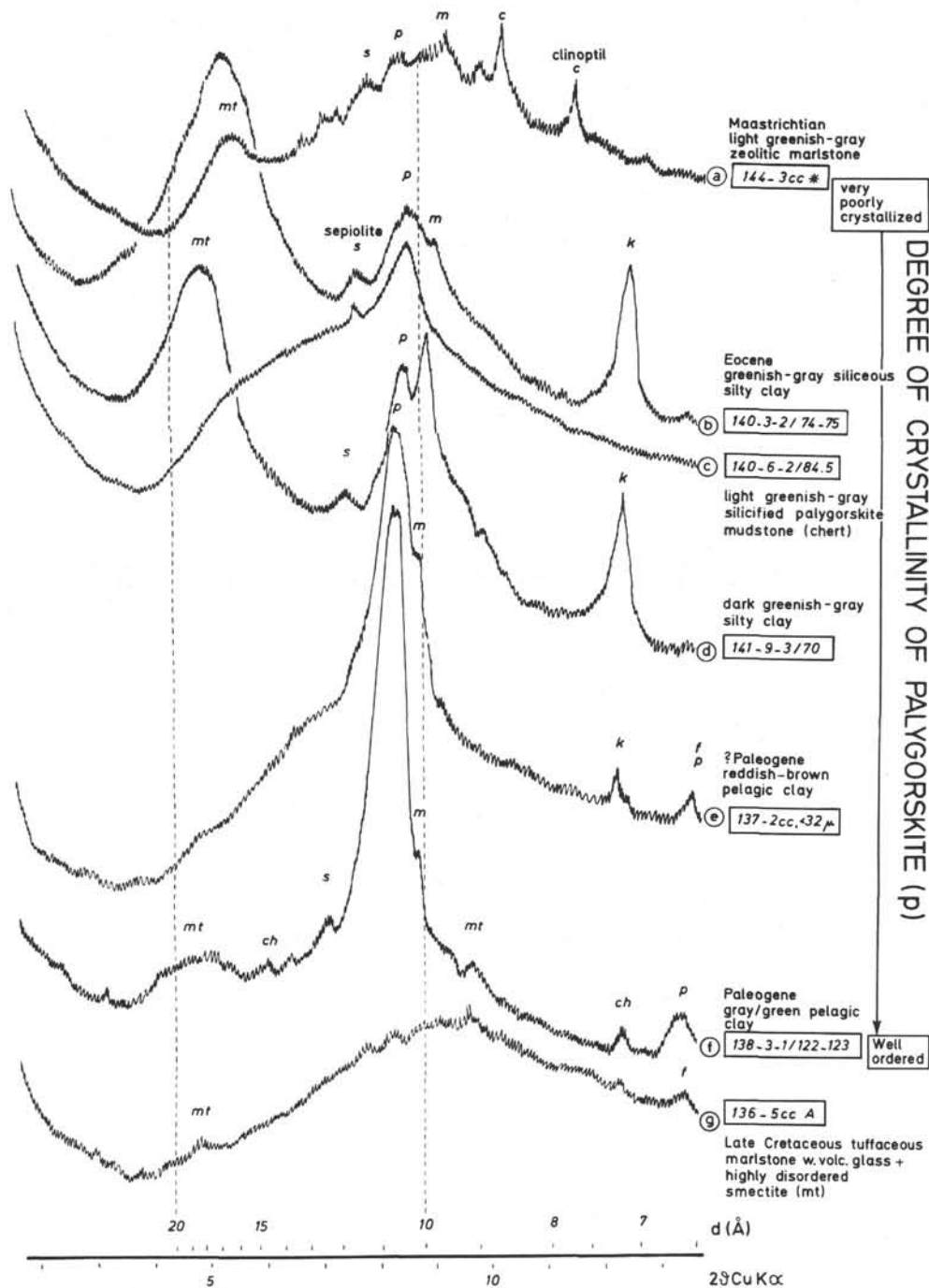


Figure 4. Degree of crystallinity of palygorskite (see text).

palygorskite from certain Persian rivers was proven by Hartmann *et al.* (1971, p. 48).

The genesis of palygorskite and sepiolite in deep-sea sediments is still somewhat enigmatic. The occurrence of these minerals, reported by Bonatti and Joensuu (1968) from the Western North Atlantic and by Hathaway and Sachs (1965) from the Equatorial Atlantic near the mid-Atlantic Ridge is connected with clinoptilolite-rich montmorillonitic clays. Peterson *et al.* (1970, p. 417) and Rex (in Peterson *et al.* 1970) described a thick Paleogene (?) section of palygorskite-sepiolite clays associated with dolomitic cristobalite-sepiolite cherts and varicolored volcanic tuffs from Site 12 in the Cape Verde Basin. All of

these examples probably belong to the diagenetic type (2a). The same origin (silica from the devitrification of altered ashes) can be assigned to the white and brown palygorskite-rich volcanogenic clays of Leg 14 (Site 136). The white layer in Core 135-8-1 (146 centimeters) is probably an altered ash. The magnesium-content of the palygorskite and sepiolite found in the orange and yellow clays of the multicolored mineralized zone in Core 136-8-2, might indeed have been derived from hydrothermal solutions.

As the distance from the African continent increases between Sites 139-140-138-137, kaolinite appears to give way to montmorillonite which in turn gives way to palygorskite (see also Hathaway and Sachs 1965, p. 863).

The highest sepiolite content occurs in Site 137, farthest from shore.

In many samples of pelagic and hemipelagic clays (for example, 137; 140-3,6; 141-6,7) palygorskite is associated with montmorillonite, kaolinite and quartz. It is possible that much of the palygorskite (aqueous magnesium-silicate) originated from the slow diagenetic degradation of montmorillonite (aqueous magnesium-alumosilicate), with kaolinite (aqueous pure alumosilicate) and silica as by-products (Schreyer, 1970, and personal communication, 1972).

The palygorskite of the pelagic brown clays, siliceous muds, and of the "white" palygorskite-lussatite cherts (for example, 140-3, 140-6-2, see Table 2) might have a different origin. In the case of these sediments, it is easier to derive the excess silica from the partial dissolution of opaline fossil tests. A detrital origin for the palygorskite is unlikely, since its proportion does not increase toward the continents. The restriction of palygorskite and sepiolite to Late Cretaceous and Paleogene sediments, and its common paragenesis with slowly-deposited montmorillonitic clays and authigenic clinoptilolite, clearly suggests a diagenetic origin. The minerals are apparently not forming today. A minimum age of about 20 to 25 million years, slow rates of deposition, montmorillonitic clay as a parent material, and the presence of excess silica from different sources appear

to be prerequisites for the formation of palygorskite and sepiolite.

Zeolites (Clinoptilolite)

Mineralogy

Although zeolitic clays are relatively frequent in the sediments of Leg 14, it is surprising that only the mineral clinoptilolite, a silica-rich variety of the zeolite heulandite, was found. None of the remaining zeolites could be identified, not even the mineral phillipsite which was reported to be the dominant zeolite of the post-Miocene sediments of Leg 2 (Peterson *et al.*, 1969; see also Pimm *et al.* 1970).

Two varieties of clinoptilolite can be distinguished on the X-ray diffraction patterns (see Figure 5):

a) a "normal" clinoptilolite, similar to the type clinoptilolite from Hector, California (Mumpton, 1960), typical for all sites off northwestern Africa (135-141), and,

b) an "untypical" clinoptilolite (c' in Figure 5A) which has 9.8 and 11.2° (2θ) peaks that have characteristic intensities, reproducibly different from normal clinoptilolite. The differences in peak intensities might be due to isomorphous substitution (J.C. Hathaway, written communication, June 1971). This variety of clinoptilolite was found only in sediments from Site 144 (Demerera Rise).

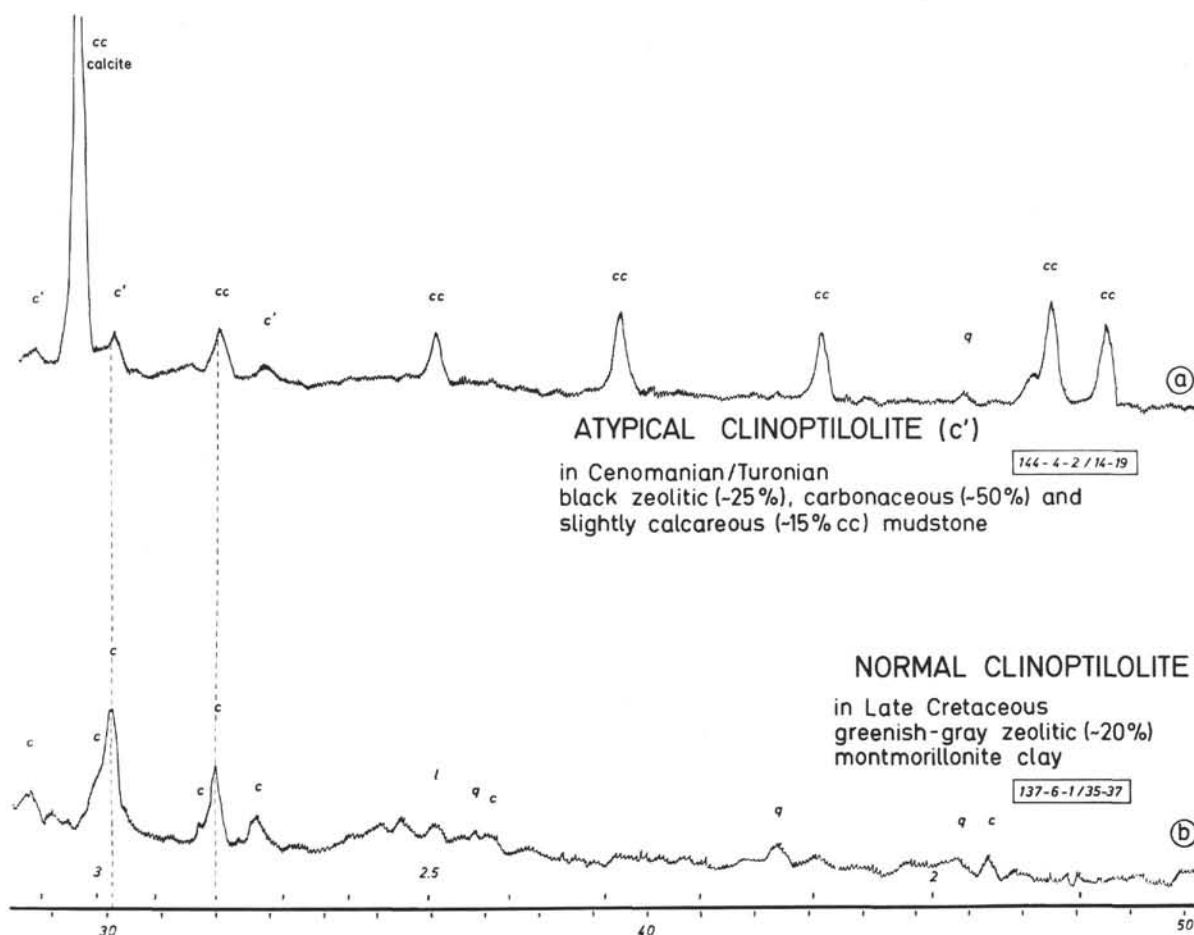


Figure 5. X-ray diffraction traces of clinoptilolite-rich pelagic sediments. a) A typical clinoptilolite (relative heights of the 9.8 and 11.2° 2θ peaks are reproducibly different from the normal clinoptilolite below). b) Normal clinoptilolite in sample 137-6-1, 35-37 cm.

Because of their resistance to thermal attack after heat treatment at 800°C, both varieties were positively identified as clinoptilolite and safely distinguished from heulandite which has similar X-ray diffraction peaks but becomes amorphous after heat treatment beyond 350 to 500°C (Mumpton, 1960; Mason and Sand, 1960; Shepard, 1961; Hathaway and Sachs, 1965).

Paragenesis

Clinoptilolite is common in similar sediments and lithofacies as the minerals palygorskite and sepiolite, namely,

a) In brown and greenish-gray pelagic smectite clays, for example 137-4, 5 and 6 (see Plate 2, Figure 3 and 4), where more or less euhedral clinoptilolite crystals and laths (partly as radiolarian casts) make up to more than 30 percent of the silt (and sand) fraction;

b) in black carbonaceous shales, for example in 135-8, 137-7, 138-6, 144A-5 and 6 (see Table 1);

c) as traces (only optically determined) in volcanogenic clays and ashes in Site 136.

Genesis and Age Range

Clinoptilolite is an authigenic mineral forming diagenetically from the devitrification of volcanic glass in an alkaline environment at very low temperatures (Deffeyes, 1959; Mason and Sand, 1960; Füchtbauer and Müller 1970; Tröger 1967, p. 782). Thus, it is commonly associated with volcanic ashes rich in volcanic glass, montmorillonite and silica (for example, opal). According to Ijima and Utada (1971) the minimum temperature of its formation is between 41 and 49°C at burial depths beyond 800 to 1900 meters (on land). Approximate pressures between 0.5 and 0.7 kb (corresponding to a water depth of 5000 meters plus 300 meters of sediment) can be inferred. But age appears to be more important than depth of burial. The youngest clinoptilolite is Middle Miocene, but most zeolitic samples range from Latest Cretaceous to Paleogene in age.

Youngest Clinoptilolite in Leg 14 Sediments

Site	Core	Age	Approximate Depth Below Sea Floor
135	7	Maestrichtian	430 m
137	3	Paleogene/Latest Cretaceous	150 m
138	5	Campanian	330 m
140	3	Middle Eocene	320 m
141	8	? Oligocene- Miocene	120 m
142	8	Middle Miocene	530 m
144	3	Maestrichtian	165 m

In the continental margin sediments off Florida clinoptilolite is mostly of Oligocene age and older; no post-Miocene zeolites have been discovered (Hathaway *et al.*, 1970). It is therefore likely that clinoptilolite is diagenetically precipitated within the pore spaces of bentonitic clays. At Site 137, it also commonly fills radiolarian tests (see Berger and von Rad, this volume). These sediments were deposited at low rates at least 20 million years ago, and buried by at least 100 meters of

sediment. The abundance of clinoptilolite in the brown and greenish-gray smectite clays of Paleogene age at Site 137 points toward an ultimately volcanic origin (alteration of current-transported reworked silicic ash?) for these sediments.

In a silicified radiolarian mudstone (144-3-2), small clinoptilolite laths have grown into the interior of open fossil pores. In this case, no ash layer nor any volcanogenic sediments were found in the stratigraphic column. It is possible that clinoptilolite was precipitated directly from Ca-alkali- and silica-rich pore solutions during the early diagenetic silicification of the mudstone.

Furthermore, clinoptilolite is common in black carbonaceous shales and marls. This association can be explained by the decrease of solubility of silica in the presence of decaying organic matter. Carbonates are dissolved at those low-pH conditions and silica is precipitated from migrating pore solutions producing carbonaceous cherts (for example 135-8-1) and, if less silica is available, clinoptilolite or palygorskite (see also Hathaway *et al.*, 1970).

High-temperature K-feldspar (sanidine)

Some samples from reddish-brown, partly laminated pyroclastic clays and red, altered, vitreous ash layers of late Cretaceous age in Site 136 Cores 5 (5) and 6(1-2) contain a few percentage of a euhedral monoclinic (sometimes pseudorhomboidal) low-relief mineral (Plate 2, Figures 5 and 6) that was first thought to be some unknown zeolite. The mineral could, however, be identified from its X-ray pattern (Figure 6) and photomicrographs (see Plate 2, Figures 5 and 6) as a high-temperature K-feldspar (J.C. Hathaway and F.J. Eckhardt, personal communication). The two values of (060) plot at the high-sanidine end of the high sanidine-high albite series in a study by T. L. Wright (1968, Figures 2 and 3). The same high sanidine was found in pyroclastic clays of Oxfordian age near the basement-basalt contact at Site 105 of Leg 11 in the Northwest Atlantic Basin (Hathaway, personal communication; Lancelot *et al.*, in press). At Site 105, the high sanidine also occurs in a brightly laminated zone together with volcanic glass, palagonite, and montmorillonite, as at Site 136 (see Table 2). It is likely that the high sanidine has the same volcanic origin in both associations. The sanidine could have been formed either by hydrothermal solutions or from altered glass during diagenesis (authigenesis), or it could have been directly crystallized during a submarine volcanic eruption and later incorporated into the ash layers and volcanogenic clays.

Authigenic K-feldspar is apparently also abundant in some of the Pacific cores of Leg 6 (R. L. Hay, personal communication, May 1971).

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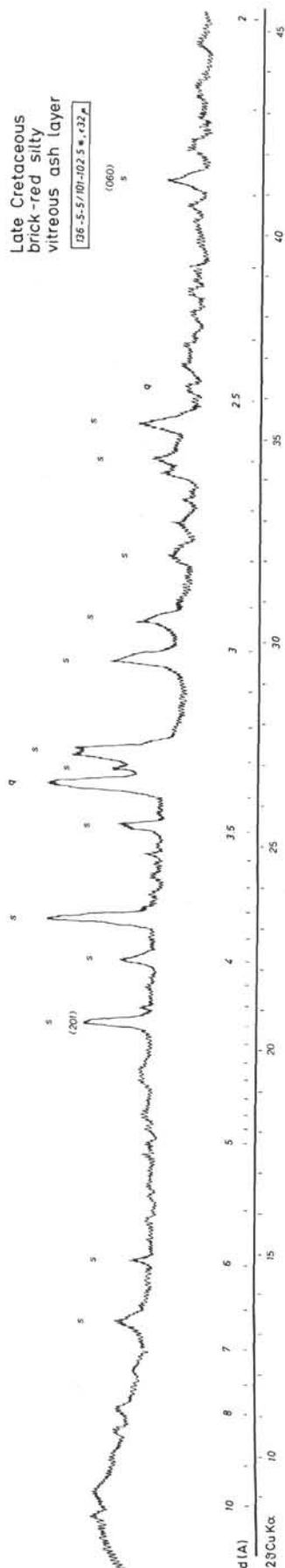


Figure 6. X-ray diffraction diagram of high-temperature sanidine (see text, determination courtesy of Dr. J. C. Hathaway).

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TABLE 1
X-ray Mineralogy of Characteristic Sediment Types (in stratigraphic order). X-ray amorphous constituent are added after optical determinations

Sample Designation	Sample Interval (cm)	Size Fraction Analysis Sed total sample unless indicated otherwise	X = carbonate dissolved (decarbon)	Sediment Description	Terrigenous Minerals							Mostly secondary or authigenic minerals						Zeolites	Biogenous & Secondary Carbonates				Optical Determination only	Interpretation of X-ray trace						
					Quartz	Feldspar (or plagioclase)	K' feldspar	Mica-illite	Kaolinite	Chlorite	Hematite (or Fe oxide, in general)	Goethite	FeS ₂	?	Phosphate	Sulfates	Montmorillonite group		Mg-Silica-ag.	Sec. SiO ₂	Calcite	Dolomite			Siderite (FeCO ₃)	Ankerite	Rhodochrosite (MnCO ₃)			
I. Biogenous																														
1) Calcareous marl chalk oozes (muds)																														
Plio.-Pleist.	141-6-4	92	X	Brown nannofossil chalk/marl ooze 73% CaCO ₃	●	●		•	•	+	+					●						■							•	
	141-6-4	92			●	●		•	•	+	+																			•
	141-7-1	148-150	X	Brownish yellow nannofossil marl mud 20.2% CaCO ₃	▲	●		●	●	+						•							■						•	
	141-7-1	148-150			▲	•		▲	●	+							○	•											•	
Miocene	136-4-1	55		Brown quartzose nannofossil-bearing mud	▲	•		●	●						•	●							○						○	
	141-7-2	99 (SiO) <20μ			●			•	●															●						
Turon.-Maestr.	137-7-1	85-86	X	Olive-gray nannofossil marl	●						●					•	●					■						•	○	
	137-7-1	85-86			▲			•										○											•	
	144-3	CC	X	Light green-gray zeolitic marlstone	●	•		•								•	•					■						•	•	
	144-3	CC			●			•										•	•										•	
"Middle" Cretaceous (?Apian-Cenoman.)	136-8-2	27-30	X	Gray nannofossil marl mud	●	•		●				●	●		○	•						■						•	●	
	136-8-2	33.5		Light gray nannofossil marl ooze	•	•		•															■							
	137-8-1	18-20		Greenish-gray nannofossil marl ooze	▲			•									•	○					■						•	
	137-8-1	18-20			▲													•	○					■					•	
	137-8-1	28-29		Very dark gray nannofossil marl mud	▲			●				+						●						○				●	●	

PLATE 1

Transmission Electron Micrographs and Smear Slide
Photomicrographs of Smectites, and Palygorskite-
Sepiolite Needles

- Figures 1, 2 Sample 136-8-2, 10 cm (smear slide, X63). Yellowish-green sandy clay, rich in quartz, mica-illite, greenish phyllosilicate mineral (? nontronite), and mixed-layer mineral (X-ray analysis). 2: Same, crossed-nicols.
- Figure 3 Sample 136-6-2, 94 cm (TEM of clay suspension, X30,000). Montmorillonite-rich light-colored ash fragment. Note thin, irregular montmorillonite flakes of different sizes with folded and curled edges. All TEM and SEM photos were made by Miss L. SCHEUERMANN (Bundesanstalt f. Bodenforschung).
- Figure 4 Same sample as in Figure 3 (TEM, X30,000). Dark ash fragment (rich in montmorillonite, long palygorskite fibers and (?)glass shards.
- Figure 5 Sample 141-8-2, 36-48 cm (TEM, X30,000). Reddish-yellow silty palygorskite clay, rich in quartz, mica-illite, chlorite, kaolinite, montmorillonite, and mixed-layer mineral (X-ray analysis). Note kaolinite with pseudohexagonal outlines parallel (001), smectite (thin, irregular flakes), and clusters of palygorskite.
- Figure 6 Sample 137-4-2, 130 cm (TEM, X30,000). Brown silty clay (Late Cretaceous) with common quartz, mica-illite, abundant hectorite-saponite (light-gray flakes?), and common palygorskite and sepiolite fibers and needles (according to X-ray analysis). Palygorskite and sepiolite can be distinguished only by X-ray diffraction.

PLATE 1

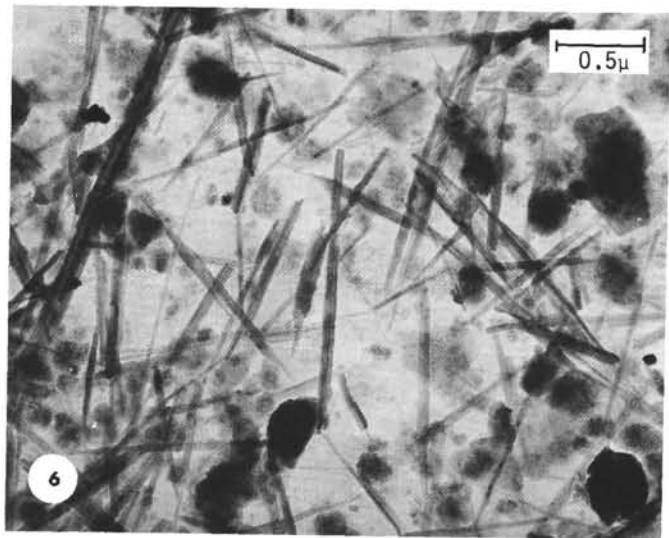
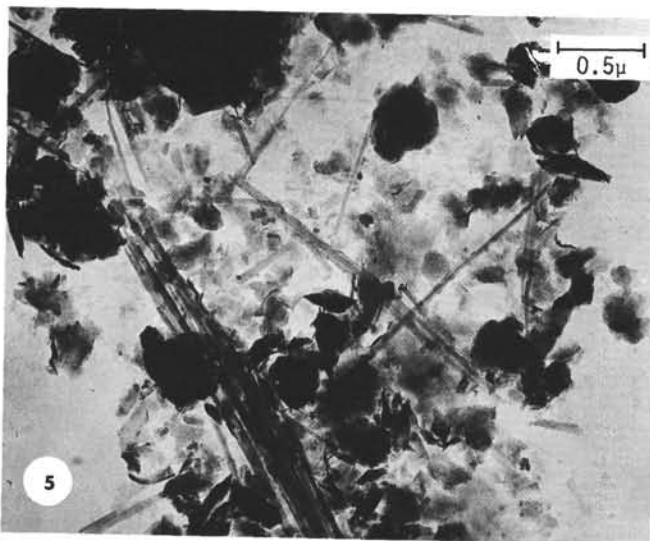
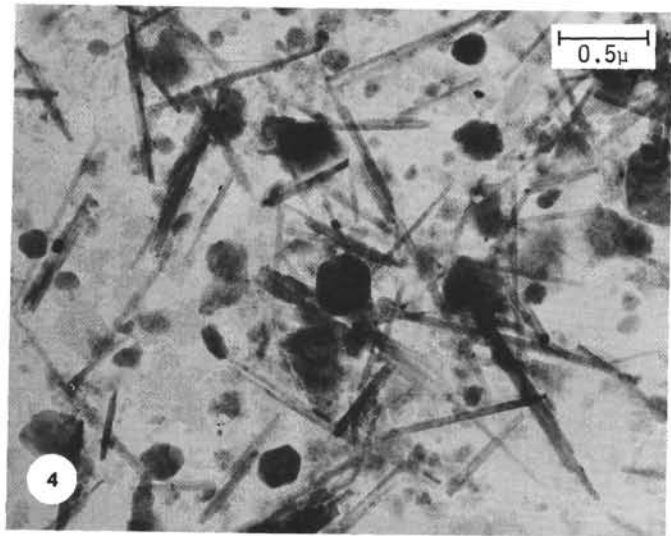
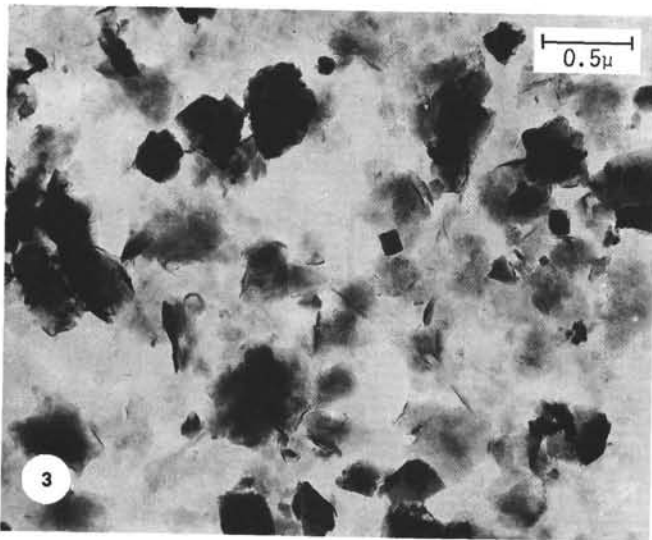
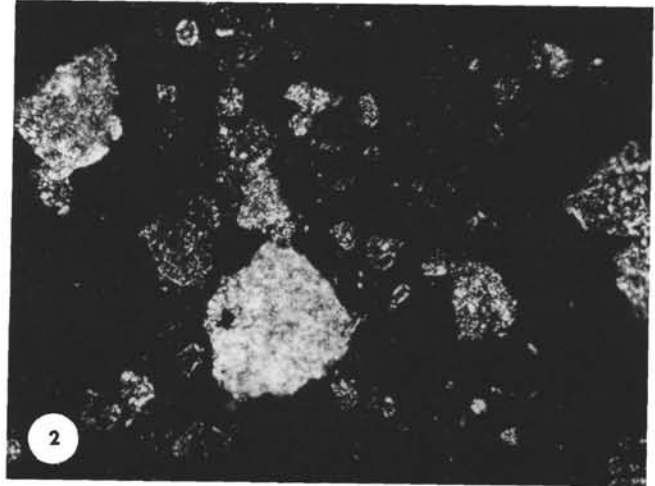
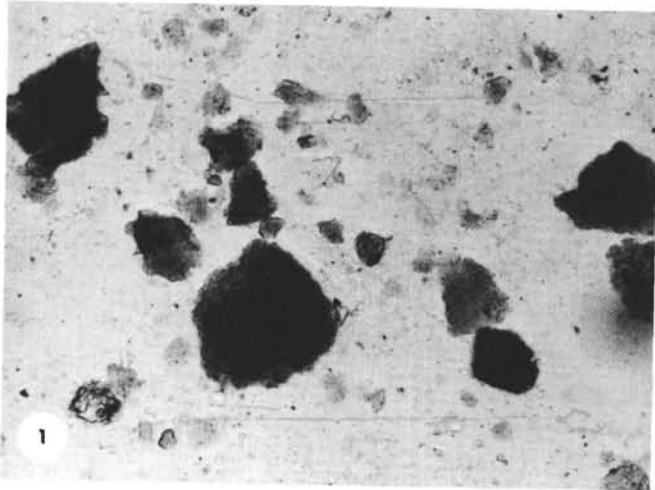


PLATE 2

Scanning Electron Micrographs of Opal-Lussatite and
Smear Slide Photomicrographs of Clinoptilolite and
High-Temperature Sanidine

- Figure 1 Sample 140-5-cc (SEM, $\times 1000$). SiO_2 spherules and globular bodies (? opal-lussatite) in Late Cretaceous palygorskite-rich opal-lussatite chert.
- Figure 2 Sample 135-8-1, 55-58 cm (SEM, $\times 5000$). Silica in Late Cretaceous carbonaceous chert (radiolarian mudstone): ?opal, partly recrystallized to "lussatite" laths and platelets(?).
- Figure 3 Sample 137-6-1, 30 cm (smear slide, $\times 160$). Late Cretaceous brown zeolitic clay with about 20 per cent stubby clinoptilolite laths (strong negative relief).
- Figure 4 Sample 137-5-cc, 32-63 μ (smear slide, $\times 160$). Paleogene brown zeolitic clay with long (60 μ), ?twinned clinoptilolite crystal (monoclinic outline).
- Figure 5 Sample 136-6-2, 94-95 cm (smear slide, $\times 200$). High-temperature sanidine (X-ray determination by Dr. J. C. Hathaway), ?twinned, in brown altered vitreous ash layer (see text).
- Figure 6 Sample 136-6-2, 94-95 cm (smear slide of sieve fraction 32-63 μ , plain light, $\times 125$). High-temperature sanidine (as in Figure 5). Note pseudorhomboidal outline and cleavage of monoclinic sanidine.

PLATE 2

