

## 40. MINERALOGY AND GEOCHEMISTRY OF THE CRETACEOUS/TERTIARY BOUNDARY IN DEEP SEA DRILLING PROJECT HOLES 465 AND 465A<sup>1</sup>

Patrick Giblin,<sup>2</sup> Institut de Géologie, Université Louis Pasteur, 1, rue Blessig, F-67084 Strasbourg Cedex, France

### INTRODUCTION

The complete Paleocene section begins with the basal Tertiary *Globigerina eugubina* Zone. This zone occurs at 465A-3-3, 4 cm to 465A-3-3, 144 cm and belongs to Lithologic Unit I (Site 465 report, this volume), a homogeneous, white, moderately to highly disturbed nannofossil ooze.

Eleven samples spanning the Cretaceous/Tertiary boundary were analyzed by X-ray diffraction and spectrometry.

### METHODS

X-ray analyses of bulk samples were performed on a Phillips X-ray diffractometer under the following instrumental conditions: CuK $\alpha$  radiation, Ni filter, 38 Kv, 18 mA, 1°/min. Semi-quantitative estimation was made by comparison of (001) peaks of minerals on X-ray diffractograms. Samples for clay-fraction analyses were first treated with dilute hydrochloric acid (0.1N) to remove carbonates, according to the method described by Robert and Tessier (1974). Oriented clay aggregates are ethylene glycol and hydrazine treated and heated according to the methods of the Institut de Géologie, Strasbourg (Weber and Larque, 1978).

Semi-quantitative estimations of the amounts of clay minerals were made on the glycolated X-ray charts under the following conditions: CuK $\alpha$  radiation, Ni filter, 40 Kv, 20 mA, 2°/min.

Chemical analyses of major elements (%) and trace elements (ppm) on bulk samples were performed on an Arl-Sofica quantumeter, by arc spectrometry, according to the methods described by Ataman and Besnus (1965), Besnus and Lucas (1970), and Besnus and Rouault (1973). Concentrations of K and Na in solution were measured with the flame EEL 450 (Corning Medical) spectrophotometer. The relative precision is  $\pm 2\%$  for major elements and  $\pm 20\%$  for trace elements.

### MINERALOGY

#### Bulk Samples

Lithologic Unit I in Holes 465 and 465A is a homogeneous nannofossil and foraminifer-nannofossil ooze at the Cretaceous/Tertiary boundary. X-ray data (Table 1) show that the sediments contain mostly calcite and quartz. No opal-CT was found; quartz represents chert in Unit I. Goethite is associated with calcite.

#### Clay Minerals

Two samples (465-7,CC and 465A-3-6, 30–32 cm) with high carbonate contents provided no clays.

The prevalent clay minerals are smectites (Fig. 1), and their crystallinity differs in the two holes: in Hole

465, Core 10, smectite crystallinity is good; it is bad in the upper Maastrichtian sediments of Hole 465A.

Attapulgite occurs in all samples in small amounts. Sepiolite occurs only in a carbonate-rich sample (465-10-2, 70–72 cm), associated with clinoptilolite. This clinoptilolite was detected only on the  $< 2\text{-}\mu\text{m}$  X-ray diffractogram. Clinoptilolite is common in Cretaceous pelagic sediments (Stonecipher, 1976) and often associated with attapulgite and chert.

Some lath structures in the clay fraction have been observed (Plate 1). Micro-diffraction diagrams show that these are not palygorskite fibers, but are characteristic of clay monocrystals with the sheets orientated perpendicular to the electron beam. These clay minerals, according to X-ray diffraction, are smectite, but since we have no chemical analyses of the  $< 2\text{-}\mu\text{m}$  fraction, we are not able to specify which kind of smectite they are.

### GEOCHEMISTRY

In Unit I, carbonates are represented by coccoliths and foraminifers, and CaO contents are very high (42–55%), except in one sample (465A-4,CC) where goethite occurs and the Fe<sub>2</sub>O<sub>3</sub> content represents 40% of bulk material.

Many trace elements are lower than the detection limits, such as V, Co, Cr, Zn, and Ga (Table 2). The high contents of Sr and Ba are associated in part with the carbonates; the correlation coefficients between Ca and Sr ( $r = 0.60$ ) and Ca and Ba ( $r = 0.16$ ) are not significantly below their theoretical correlation coefficient ( $r = 0.68$ ). Some samples are enriched in SiO<sub>2</sub> (higher than three times Al<sub>2</sub>O<sub>3</sub>; Boström et al., 1972). These are explained by the occurrence of chert and by biogenic silica, as it has been observed in some samples in the clay fraction, from the dissolution of siliceous microfossils.

### DISCUSSION

Some problems occur in this study, in particular the method of formation of smectites, clinoptilolite, and attapulgite in a carbonate environment under reducing conditions. Clinoptilolite either must be authigenic (Stonecipher, 1976; Couture, 1977; McCoy and Zimmermann, 1977), or it must form from alteration of volcanic material (Bonatti, 1963; Hathaway and Sachs, 1965; Kastner, 1976; McCoy and Zimmermann, 1977); it has been observed replacing radiolarians (Berger and von Rad, 1972). In Holes 465 and 465A, clinoptilolite apparently is not associated with volcanic detritus, but with biosiliceous debris in a high-carbonate environment

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<sup>2</sup> Present address: Société Nationale Elf Aquitaine, Centre Micoulou, BP 65, 64000 Pau, France.

Table 1. X-ray mineralogy of the sedimentary deposits of the Cretaceous/Tertiary boundary, Holes 465 and 465A.

Sample (interval in cm)	Sample No.	Lithology	Age	Bulk-Sample Components (non-orientated powders)				<2- $\mu$ m-Fraction Components (orientated aggregates)					
				Calcite	Quartz	Goethite	Pyrite	Smectite	Illite	Attapulgite	Sepiolite	Clinoptilolite	
465-7,CC	—	Nannofossil-foraminifer	early Paleocene	100	—	—	—	—	—	(not enough clay)			
465A-3-1, 30-32	1			100	—	—	—	56	10	6	—	—	28
465A-3-6, 30-32	2	ooze with chert and pyrite		100	tr	—	—	—	—	(not enough clay)			
465A-3,CC	3			75	25	—	—	46	18	15	—	—	21
465A-4,CC	4			30	20	50	—	100	—	—	—	—	tr
465-10-1, 70-72	5	Nannofossil ooze	late Maastrichtian	100	—	—	—	51	13	20	—	—	14
465-10-2, 70-72	6	and foraminifer-nannofossil ooze		100	tr	—	—	49	18	7	9	—	15
465-10-3, 70-72	7			100	—	—	—	62	11	9	—	—	17
465-10-4, 70-72	8			100	—	—	—	65	10	9	—	—	15
465-10-5, 70-72	9			100	—	—	—	71	—	13	—	—	16
465-10,CC	10			94	6	—	—	57	17	—	—	—	26

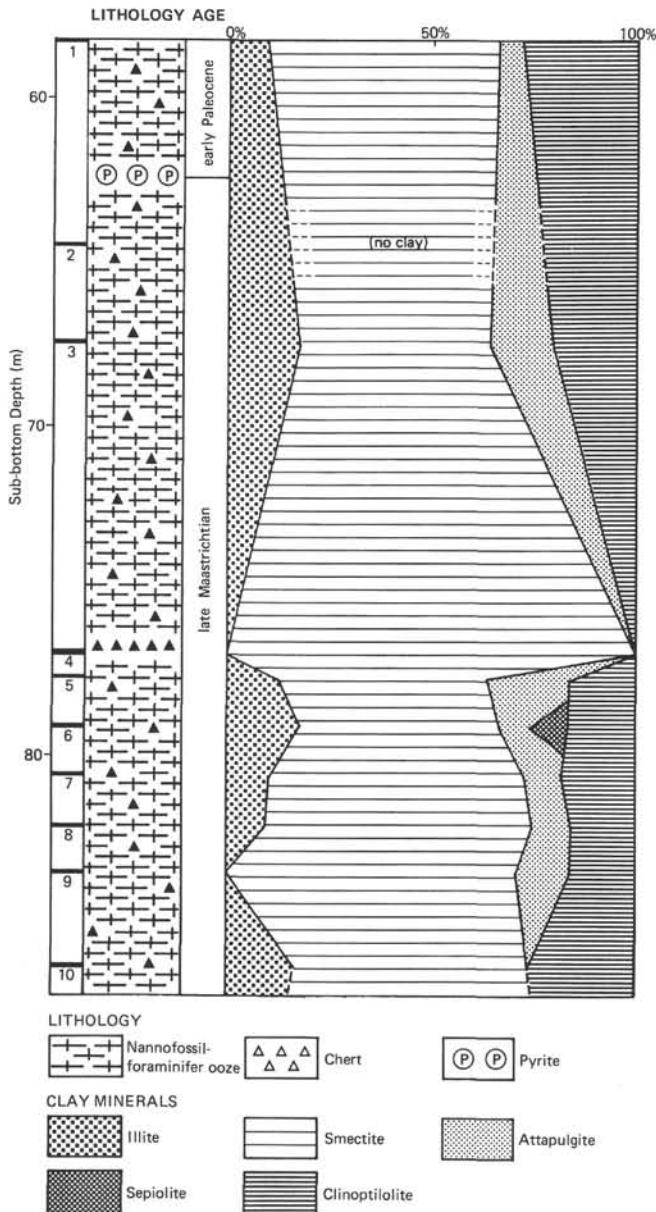


Figure 1. Abundance of clay minerals in Holes 465 and 465A.

which favors the formation of zeolite (McCoy and Zimmermann, 1977). The authigenic formation of such minerals by the transformation of cation-enriched opal at depth to opal-CT, and ultimately quartz, was suggested by Donnelly and Merrill (1977). Nathan and Flexer (1977) and Couture (1977) suggest that the presence of silica in active form (opal-CT) is a condition necessary for the formation of authigenic silicates by reaction with biogenic silica and interstitial water. Palygorskite (attapulgite-sepiolite) is widespread and abundant in Cretaceous clay and carbonate sediments of the Pacific (Couture, 1977). Several origins may be accepted: (1) directly precipitated from Mg-rich brines in an arid zone (Milot, 1964; Rateev et al., 1969); (2) diagenetic formation from montmorillonite (Hathaway and Sachs, 1965); (3) continental origin, suggested by Chamley and Milot (1975) and Froget and Chamley (1977); (4) neoformation in a hydrothermal environment (Hathaway and Sachs, 1965; Bonatti and Joensuu, 1968; Church and Velde, 1979); (5) authigenic formation from opal-CT (Donnelly and Merrill, 1977; Couture, 1977). Here it is not possible to fully resolve the problem of their method of formation. The present position in the Pacific of Holes 465 and 465A favors authigenic or diagenetic formation over detrital input.

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Table 2. Chemistry of samples of the Cretaceous/Tertiary boundary, Holes 465 and 465A.

Sample (interval in cm)	Sample No.	Major Elements (% oxides)										Trace Elements (ppm)										
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>4</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	L.O.I.	Sr	Ba	V	Ni	Co	Cr	B	Zn	Ga	Cu	Pb
465-7,CC	—	0.6	0.2H	0.23	54.4	0.1H	0.037	0.02H	0.14	0.05H	43.52	—	—	—	—	—	—	—	—	—	—	
465A-3-1, 30-32	1	0.8	0.3	0.45	54.8	0.1H	0.026	0.02	0.16	0.05H	43.68	1422	1345	5H	4	2H	5H	61	2H	2H	6	4
465A-3-6, 30-32	2	3.1	0.2H	0.26	52.9	0.7	0.035	0.02H	0.17	0.05H	42.67	810	952	5H	2H	2H	5H	7	2H	2H	4	2
465A-3,CC	3	22.5	0.2H	0.17	42.1	0.1H	0.028	0.02H	0.11	0.05H	33.91	774	898	5H	3	2H	5H	5H	2H	2H	3	2H
465A-4,CC	4	28.0	1.3	2.61	9.2	40.6	0.058	0.14	1.18	1.79	14.53	—	—	—	—	—	—	—	—	—	—	—
465-10-1, 70-72	5	0.8	0.2H	0.28	55.1	0.1H	0.017	0.02H	0.19	0.05H	43.69	1027	980	5H	2H	2H	5H	5H	2H	2H	2	2
465-10-2, 70-72	6	2.8	0.2H	0.25	54.1	0.1H	0.019	0.02H	0.19	0.05H	42.86	1363	702	5H	2H	2H	5H	51	2H	2H	2	2
465-10-3, 70-72	7	1.1	0.2H	0.28	55.0	0.1H	0.016	0.02H	0.17	0.05H	43.79	1442	768	5H	2H	2H	5H	54	2H	2H	2	2
465-10-4, 70-72	8	0.5	0.2H	0.28	54.8	0.1H	0.012	0.02H	0.18	0.05H	43.95	1246	741	5H	2H	2H	5H	12	2H	2H	5	2
465-10-5, 70-72	9	0.8	0.2H	0.28	54.9	0.1H	0.022	0.02	0.22	0.05H	43.84	1653	702	5H	850E	2H	61	71	2H	8	4	2
465-10,CC	10	4.6	0.2H	0.22	49.9	0.1H	0.020	0.02H	0.16	0.05H	41.70	770	530	5H	2H	2H	5H	5H	2H	2H	2H	2

Note: Major element oxides in percent of samples dried at 110°C; L.O.I. = loss on ignition at 1000°C. Trace element values in ppm of samples dried at 110°C; E = extrapolated value; — = no data; H = lower than the detection value.

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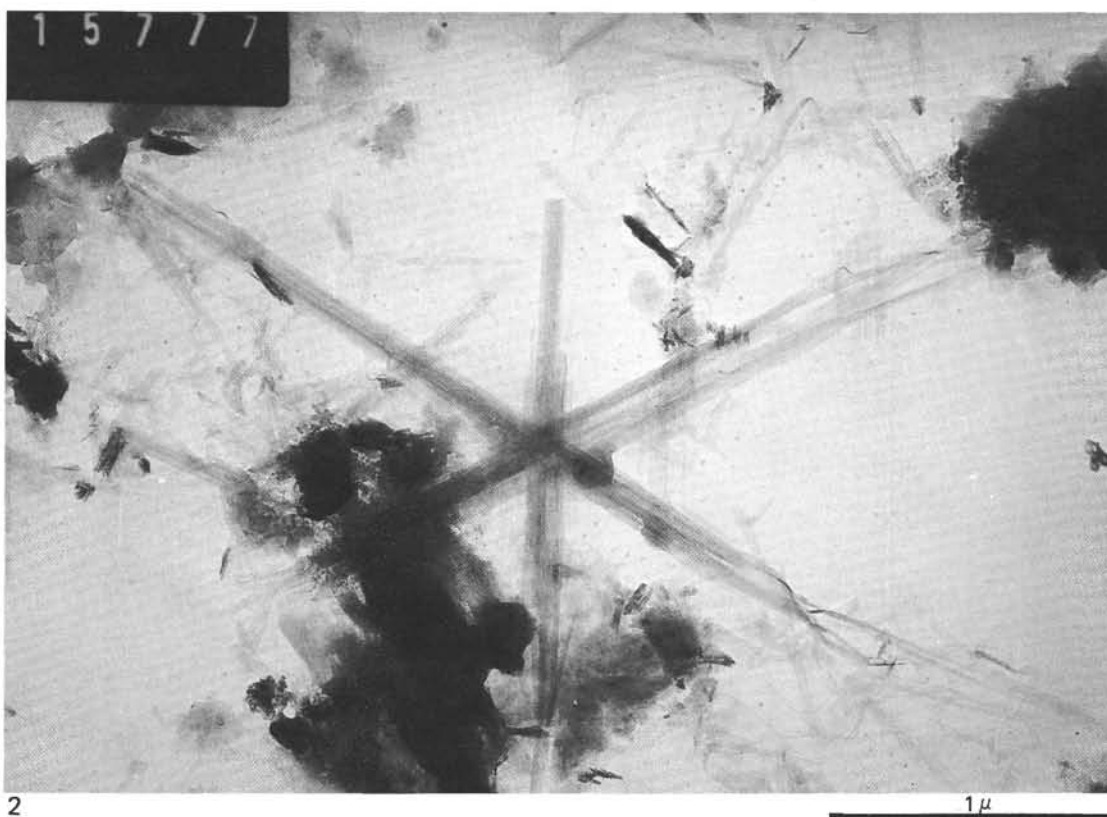
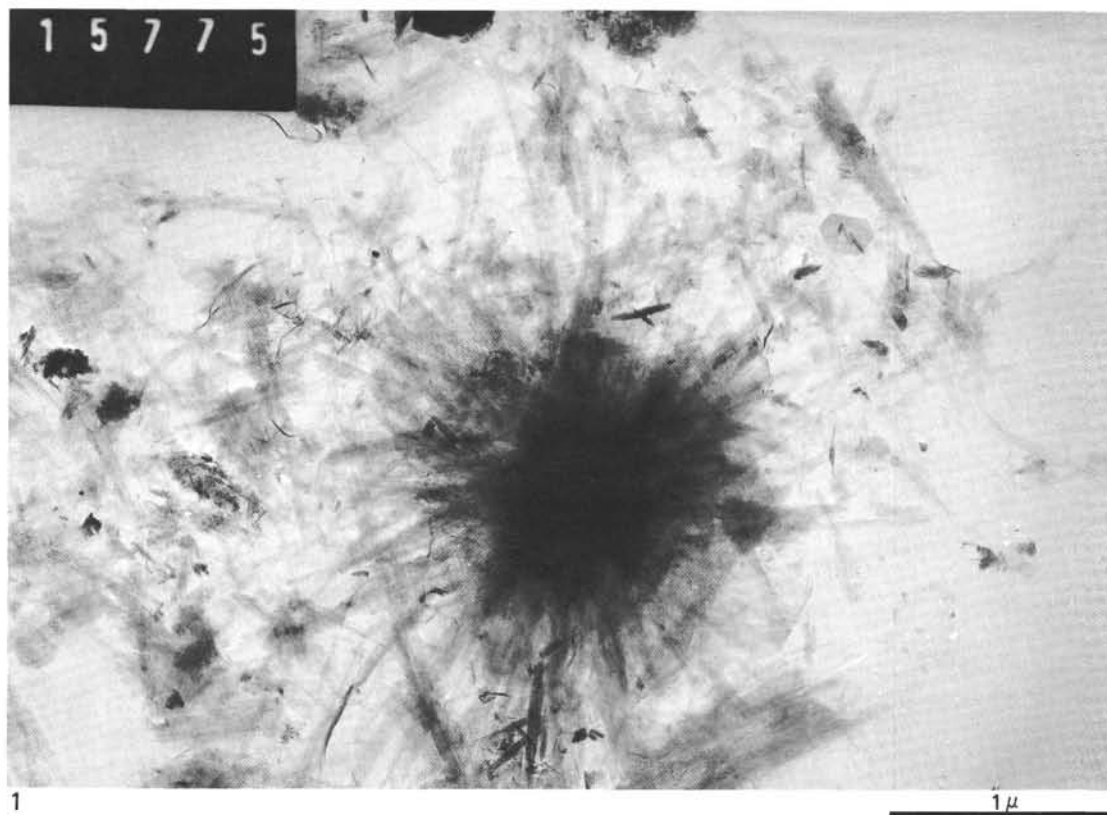


Plate 1. Transmission electron micrographs.

Figure 1. Transmission electron micrograph of the <math>< 2\text{-}\mu\text{m}</math> fraction of 465A-4,CC, showing a fibrous mineral.

Figure 2. Transmission electron micrograph of the <math>< 2\text{-}\mu\text{m}</math> fraction of 465A-4,CC, showing lath-shaped minerals. These minerals are described in the text as smectites. One can observed amorphous siliceous compounds associated with these lath-shaped minerals.