27. TETRAPYRROLE PIGMENTS FROM IPOD LEG 47B, HOLE 398D

Susan E. Palmer, Department of Geology, and Earl W. Baker, Department of Chemistry, Florida Atlantic University, Boca Raton, Florida

INTRODUCTION

We analyzed the tetrapyrrole content of 13 samples from Site 398 that range in age from Miocene to Early Cretaceous and at a sub-bottom depth from 400 to 1660 meters. Site 398 is located 90 km off the coast of northern Portugal, south of the Vigo Seamount.

Most surprising was the presence of chlorins in both the shallow (400 m) and deeper (1070-1660 m) samples; the presence of chlorins is usually indicative of thermally immature sediments. Previously, chlorins were not found below 1000 meters, but more typically gave way to free-base and metalloporphyrins at that and greater depths (Baker et al., 1978a, c). An anomalously low temperature gradient of $1°C/100$ m reported by the Leg 47B shipboard party could explain the presence of these diagenetically immature pigments below 1000 meters. The depositional environment and nature of the organic matter deposited, however, may also play a significant role in the observed diagenetic products.

A second surprising feature of these cores is the absence of free-base porphyrins. Free-base porphyrins indicate an intermediate stage of chlorophyll diagenesis (referred to as the chlorin-porphyrin transition). Perhaps the free-base porphyrins were formed and later erased from the record; thus, chlorins and nickel porphyrins occur together.

Total pigment content ranged from 1.0 μg/g to a nondetectable amount (the average value for the 13 samples studied was 0.11 μg/g); however, only two samples (from Cores 75 and 122) contained more than 0.1 μg/g. For comparison, average pigment concentrations for samples from off the west coast of Africa ranged from 0.06 μg/g (Leg 47A) to 5.5 μg/g (Leg 41) and 8.0 μg/g (Leg 40).

EXPERIMENTAL

Samples collected for organic geochemical studies were stored at 2 to 4°C for 3 weeks while in transit from *Glomar Challenger* to the DSDP depository at Scripps Institution of Oceanography. The cores were stored frozen thereafter until time of analysis. One hundred grams (wet weight) of sediment were extracted with acetone:methanol (9:1) in a ball mill until the extract was devoid of pigment. Type and quantity of pigment was determined by spectrophotometry using a Perkin-Elmer 575 scanning spectrophotometer. Crude extracts from samples taken from Cores 75 and 122 were chromatographed over Sephadex LH-20 with THF (20 × 2.5 cm bed dimensions). Separations of chlorins from nickel porphyrins were made by partition between HCl and ethyl ether. Nickel porphyrins were then chromatographed over Alumina Grade III with cyclohexane:benzene (1:1). Ratios of the α (552 nm) to β (516 nm) visible wavelength band intensities were computed for each nickel porphyrin fraction.

Solid probe mass spectrometric analyses were made on the nickel porphyrin fractions from Cores 75 and 122 using a Dupont 491-BR mass spectrometer. Source and probe temperatures were 280° to 320°C. Although analyses were attempted on porphyrin isolates from Cores 81, 84, 97, and 118, interpretable spectra were not obtained, probably because of insufficient sample material.

RESULTS AND DISCUSSION

Individual pigment yields, organic carbon content, and geologic age for Hole 398D samples are given in Table 1. Cenozoic samples (Cores 5 and 37) are primarily carbonate and contain only trace amounts of chlorin. This trend was noted in earlier studies (Baker et al., 1978a, b; Baker and Palmer, this volume, Part 1, Leg 47A Report). In contrast, nickel porphyrins are present in the Lower Cretaceous samples. These are usually at higher concentrations than the chlorins, which are present in only 55 per cent of these samples.

Only two of the samples (from Cores 75 and 122) shown in Table 1 contain 0.1 μg/g or more pigment. For this reason, electronic spectra of chlorins were obtained for only these samples. The organic extract of the Core 75 sample was separated by Sephadex LH-20 chromatography into two chlorin fractions: an early-running fraction containing about 20 per cent of the total chlorins and a later-running fraction which contained the bulk of the chlorins. The electronic spectral data for these two fractions are slightly different. The early-running fraction has a red band at 660 nm, while the red band for the late-running fraction is at 658 nm. Further purification of the chlorin fractions through partition between HCl and ethyl either required 10 to 30 per cent HCl (by wt.) to extract the early-running fraction from the ether layer. However, most of the pigment in the later-running fraction was extractable with only 10 to 20 per cent HCl. In contrast, isolation of the geochlorins from the Core 122 sample resulted in only one column fraction which was readily extracted from ether with 10 to 20 per cent HCl. In this case, the red band was at 647 nm. Geochlorins with absorbances in this region are reported for Cretaceous samples from Leg 43 and often occur with free-base porphyrins (Palmer et al., 1979).

TABLE 1
Tetrapyrrole Pigment Data From Leg 47B, Site 398

Section No.	Geologic Age[a]	Lithologic Description	Sub-bottom Depth (m)[a]	Organic Carbon (% by wt.)	Pigment Concentration[b] (μg/g)	Electronic Spectrum (nm)							Pigment Type
398D-5-3	Middle Miocene	Gray chalk	395-404	0.2	0.001							660	Chlorin
398D-37-3	Late Paleocene	Light br. chalk	756-765	0.1	no pigment								
398D-69-2	Early Cretaceous (Albian)	Calc. dark gray shale	1069-1079	0.6	0.001							660	Chlorin
					0.004		397		520	559			Nickel porphyrin[c]
398D-75-2	Albian	Sl. calc. black shale	1136-1145	0.3	0.75	0.16	400	(500)		560	590	660	Chlorin
						0.59	401	(506)	534	556	590	658	Chlorin
					0.3		399		520	555			Nickel porphyrin
398D-81-2	Albian	Sl. calc. black shale	1202-1212	0.6	0.02		397		518	552			Nickel porphyrin
398D-84-4	Albian	Sl. calc. black shale	1231-1240	0.5	0.007							660	Chlorin
					0.02		397		520	554			Nickel porphyrin
398D-90-5	Albian	Black shale	1288-1297	0.9	0.006		397		518	553			Nickel porphyrin
398D-97-3	Albian	Sl. calc. black shale	1345-1354	2.0	0.005							660	Chlorin
					0.03		395		516	552			Nickel porphyrin
398D-101-3	Albian	Black shale	1383-1392	0.7	0.003		395		516	552			Nickel porphyrin
398D-106-5	Aptian	Calc. dark green shale	1430-1440	0.5	0.003		398		522	560			Nickel porphyrin[c]
398D-118-5	Aptian	Dark green and calc. black shale	1544-1554	0.5	0.02		396		517	553			Nickel porphyrin
398D-122-5	Aptian	Calc. gray shale	1582-1592	0.6	0.1		402				593	647	Chlorin
					0.18		397		519	554			Nickel porphyrin
398D-130-5	Barremian	Calc. gray shale	1658-1668	0.5	0.02							661	Chlorin
					0.005		395		516	552			Nickel porphyrin

[a] Data obtained from Leg 47B Hole Summary.
[b] Individual pigment yields calculated by using the following molar extinction coefficients: pheophytin "a" = 63,700 at 660 nm, nickel porphyrin = 34,820 at 550 nm.
[c] The electronic spectra are similar to copper porphyrin.

Earlier studies containing more comprehensive observation of the changes in the geochlorin fraction with depth (Baker et al., 1978c, d) indicated that chlorins extracted from the more deeply buried cores have lower HCl numbers (i.e., 10) and form the late-running fraction on Sephadex columns. In addition, the UV-visible red bands shifted noticeably with increasing geologic age and depth of burial, from 663 to 660 to 658 nm and even as low as 640 nm. Metallochlorins have red bands at 640 nm, however, the pigments discussed here are extractable into HCl, a characteristic of free-base chlorins and porphyrins. The data given here for samples from Cores 75 and 122, coupled with earlier data, suggest that de-esterification and reduction of the geochlorin molecule increases with sub-bottom depth.

It is remarkable, however, that these compounds at these depths have not undergone aromatization resulting in conversion to the free-base porphyrin. Free-base porphyrins are the expected intermediate diagenetic products and have been observed in sediment samples from the Black Sea (DSDP Leg 42B) as well as in Cenozoic and Cretaceous samples from the Atlantic (Legs 38 through 44) where they occur either alone or with chlorins and/or nickel porphyrins. In contrast, free-base porphyrins are absent from these mixtures, which suggest a conversion to dihydroxyporphyrins whose electronic spectra would not be unlike those of chlorins derived more directly from chlorophyll (Baker and Smith, 1975). Whether dihydroyporphyrins occur in sediments or are artifacts formed by sample handling (for example, in this case by unfrozen storage, see experimental section) is not known. It has been long established that chelation with nickel or vanadyl has a stabilizing effect on the porphyrin nucleus. Porphyrins chelated with nickel are more likely to survive than those remaining in the free-base state. If the Cretaceous sediments in Hole 398D were deposited under oxidizing conditions, either explanation (i.e., conversion to dihydroxyporphyrins, or selective preservation of metal chelates) could explain the observations.

The ratio of the visible light absorbance bands, α (552 nm) and β (518 nm), of the nickel porphyrins are reported in Table 2. A gradual shift in the α/β ratio occurs with increasing depth; porphyrins from shallower samples have ratios of 1.8 to 2.0 while deeper samples have ratios of 2.2 to 2.5. A similar trend is found in nickel porphyrin isolated from Miocene core samples of Leg 47A at approximately the same depths of burial. However, the change for the Leg 47A samples is faster and the trend more noticeable. Samples from Cores 75 through 97 are Albian in age and (with the exception of the Core 90 sample) have similar lithologies and nickel porphyrin α/β ratios of 1.8 to 2.0. It is the deeper samples, Cores 101 through 130, that display a

TABLE 2
α/β Ratios of Nickel Porphyrins From Leg 47B Core Samples

Section No.	α/β
398D-75-2	2.0
398D-81-2	1.8
398D-84-4	1.8
398D-90-5	2.0
398D-97-3	1.8
398D-101-3	2.1
398D-118-5	2.2
398D-122-5	2.2
398D-130-5	2.5

TABLE 3
Mass Spectrometric Data for Metalloporphyrin Fractions Isolated From Leg 47B, Site 398 Cores[a]

	Carbon Number									
	32	31	30	29	28	27	26	25		
398D-75 nickel porphyrins	532	518	504	490	476	462	448	434	m/e	DPEP series
	16	*23*	*37*	*35*	*34*	*49*	*35*	*30*	I	
	534	520	506	492	478	464	450	436		etio series
	5	*6*	*25*	*37*	*98*	*74*	*100*	*58*		
Odd molecular weight porphyrins[b]	537	523								455 + 14n
	14	*14*								
			511	497	483	469	455	441		457 + 14n
			24	*28*	*52*	*52*	*56*	*45*		

$$\frac{\Sigma \text{I DPEP}}{\Sigma \text{I etio}} = 0.6$$

% 455 + 457 series = 28%

	32	31	30	29	28	27	26	25		
398-122 nickel porphyrins	532	518	504	490	476					DPEP series
	75	*76*	*100*	*93*	*60*					
	534	520	506	492	478					etio series
	27	*26*	*40*	*46*	*70*					
Odd molecular weight porphyrins	537	523								455 + 14n
	75	*46*								
				497						457 + 14n
				55						

$$\frac{\Sigma \text{I DPEP}}{\Sigma \text{I etio}} = 2.0$$

% 455 + 457 series = 22%

[a] Peak intensities (I) have been normalized to 100 for the most intense peak and peak heights for nickel porphyrins of the etio series have been corrected for the Ni^{60} contribution from the corresponding DPEP series.

[b] These metalloporphyrins have molecular weights coincident with copper DPEP and etioporphyrins.

are present in each series with only one peak, typically a C-32 to C-30 porphyrin, being the most intense. Lower molecular weight members (C-29 to C-25) of nickel porphyrins of the DPEP and etio series occur with the odd molecular weight series in samples from the Black Sea and in other Cretaceous samples from the Atlantic, the most demonstrative example being from Section 47A-397-68-2 (Baker and Palmer, this volume, Part 1). The 28 per cent contribution of the odd molecular weight series plus accompanying nickel etioporphyrins lowers the DPEP/etio ratio to less than 1:1 in the Core 75 sample, where a 3:1 or 2:1 ratio is expected for samples of the same age and depth (roughly 1100 m).

In contrast, the Core 122 sample contained a nickel porphyrin fraction which has only five members of both series and a smaller component of the odd molecular weight series. This is reflected in both the visible and mass spectrometric determinations of relative amounts of nickel DPEP and etio porphyrins (Tables 2 and 3). The relative amounts of the two nickel porphyrin series (DPEP/etio = 2.0) support the idea that these sediments have not undergone substantial thermal treatment as suggested above by the abundance of chlorins at this depth.

The relatively low pigment yields, in comparison with the results obtained in the previous studies of Lower Cretaceous samples where the organic carbon content was roughly 0.5 to 2 per cent, are also noteworthy. Only the two samples discussed above (from Cores 75 and 122) contained more than 0.1 µg/g of pigment. The organic carbon values were not high in either case (0.3 and 0.6%). Perhaps the discrepancy between the amount of organic carbon and the concentrations of extractable pigments is related to inhomogenity of the sediments and also to the presence of detrital oxidized terrestrial organic material. This may account for the samples having approximately 1 to 2 per cent organic carbon that contained only small amounts of extractable pigments. In turn, short-term high input of organic matter, perhaps even in the form of turbidity flows as indicated for the Barremian-lower Aptian strata (Leg 47 Shipboard Party, 1976), could account for the irregular trends in pigment concentrations observed. The presence of oxidized terrestial material may be coincident with the occurrence of odd molecular weight metalloporphyrins.

In contrast with the more detrital nature and oxidizing environment suggested for the Lower Cretaceous sediments from Hole 398D at over 1000 meters depth

of burial, the Cretaceous sediments of the Cape and Angola basins (Leg 40) in the South Atlantic, also clastic in nature and now buried at 1000 to 1100 meters, were deposited in euxinic stagnant basins. This difference in depositional environments is seen to influence the resulting diagenetic products of chlorophyll that either are carried into the environment or formed *in situ*.

ACKNOWLEDGMENTS

REFERENCES

Baker, E. W. and Smith, G. D., 1975. Chlorophyll derivatives in DSDP Leg 14, 20, 26, 27 and 29 sediments. *In* Ingle, J. C., Karig, D. E., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 31: Washington (U.S. Government Printing Office), p. 905–909.

Baker, E. W., Palmer, S., and Huang, W. Y., 1978a. Chlorin and porphyrin geochemistry of DSDP Leg 40 Sediments. *In* Bolli, H. M., Ryan, W. B. F., et al., *Initial Reports of the Deep Sea Drilling Project,* Supplement to Volumes 38, 39, 40 and 41: Washington (U.S. Government Printing Office), p. 639-648.

————, 1978b. Intermediate and late diagenetic tetrapyrrole pigments, Leg 41: Cape Verde Rise and Basin. *In* Lancelot, Y., Seibold, E., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 41: Washington (U.S. Government Printing Office), p. 825-838.

————, 1978c. Early and intermediate chlorophyll diagenesis of Black Sea sediments: Sites 379, 380 and 381. *In* Ross, D., Neprochnov, Y., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 42, Part 2: Washington (U.S. Government Printing Office), p. 707-716.

————, 1978d. Miocene and Cretaceous tetrapyrrole pigments from Leg 44, Site 391. *In* Benson, W. E., Sheridan, R. E., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 44: Washington (U.S. Government Printing Office), p. 639-644.

Palmer, S. E., Huang, W. Y., and Baker, E. W., 1979. Tetrapyrrole pigments from Bermuda Rise: DSDP Leg 43. *In* Tucholke, B., Vogt, P., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 43: Washington (U.S. Government Printing Office), p. 657-662.

Shipboard Party — Leg 47, 1976. Passive continental margin, *Geotimes,* v. 21, p. 21-14.