31. EARLY AND INTERMEDIATE CHLOROPHYLL DIAGENESIS OF BLACK SEA SEDIMENTS: SITES 379, 380, AND 381

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INTRODUCTION

DSDP drilling activities in the Black Sea afforded an opportunity to continue the study of early chlorophyll diagenesis. Since the usual mass spectrometric analysis of thermally labile nonvolatile geochlorins was inadequate for our study, a new analytical mass spectrometric method based on a novel synthesis of a new class of compounds, the silylated hydroxyaluminum chlorins, was developed.

Twenty-five core samples, ranging from 0 to 1062 meters depth of burial (Pleistocene to Miocene) were analyzed. Shallow sediment samples contained chlorins with characteristics similar to those reported for the Pleistocene samples from Leg 15 Site 147 (Baker and Smith, 1973). Chlorins gave way to free-base porphyrins with increasing depth of burial, and small amounts of nickel porphyrins were found in deeper sediments.

The importance of depth of burial as a factor in maturation is re-emphasized by these data. All shallow samples (0-400 m) contain chlorins; however, intermediate diagenetic products (free-base porphyrins) occur in Site 380 samples at 484-1016 meters depth of burial. These deeper samples, containing the intermediate diagenetic products, can stratigraphically correlated with shallower samples of Site 381 where only chlorins are found.

Small amounts of nickel porphyrin were found in Pleistocene samples at and below 484 meters of burial. The distribution of these porphyrins with respect to other pigments present and the geologic age of the enclosing sediments suggest that they are more characteristic of the Pliocene and Miocene sediments than the overlying Pleistocene sediments. Because the distribution of these particular nickel porphyrins do not fit into the expected sequence typical of early and intermediate chlorophyll diagenesis, it is suspected that they migrated from older deeper sediments.

EXPERIMENTAL

All core samples were stored frozen until time of analysis; 9:1 mixtures of acetone:methanol were used for ball-mill extraction of pigments. Crude extracts of pigments were chromatographed over Sephadex LH-20 with THF. Further isolation and purification of chlorins and free-base porphyrins was made by HCl extraction after diazomethane derivitization. Nickel porphyrins were chromatographed over Grade III Alumina with cyclohexane: benzene (50:50). These methods, given sufficient amounts of pigment (0.5 μ g and greater), yielded samples of sufficient purity to permit mass spectrometric analysis.

Each step of the sample work-up was monitored by UV-visible spectrophotometry, using a Beckman ACTA CIII scanning spectrophotometer. Representative spectra are reported in Table 1.

A new technique for mass spectrometry of chlorins, silylation of hydroxyaluminum derivatives, was developed. In each case, the chlorin sample (9 to $37 \mu g$) was treated with an excess of LiAlH4 in anyhydrous THF (dried over LiAlH₄) under reflux for two hours (Baker and Billig, 1970). Conversion to the aluminum chelate was shown by the shift in the red band from that of the free-base (660-668 nm) to that of a typical metallochlorin with a red band at 635-640 nm. Sample work-up was completed by careful addition of redistilled water, producing the hydroxyaluminum chlorin. Chromatography over Alumina Grade III with THF as eluant was used to remove unreacted starting material and then 5% H₂O in THF to elute the chlorin derivative. The silvlation of the hydroxy group(s) was carried out by treatment with 0.1 ml BSA bis(trimethysilyl)-acetamide in 0.3 ml reaction vials at 80°C for 20-30 min. The solvent was evaporated under dry nitrogen and mass spectrometric analyses were made on a DuPont 491-BR mass spectrometer by the direct probe method. The temperature of the source was held at 260°C while the probe temperature was slowly raised from 180° to 260°C, the volatization range of the silvlated components. Multiple scans with increasing temperature were made to record peaks appearing at different temperatures.

The derivitization method provides a convenient, dependable way of obtaining mass spectra of chlorins since silylated hydroxyaluminum chlorins can be easily volatilized at temperatures in the range of 190°-230°C. This is in marked contrast with previous experience where underivitized chlorins yielded inconsistently to mass spectrometry and at times were destroyed on the probe.

Mass spectra of free-base and nickel porphyrins were also recorded using the solid probe. Probe temperatures ranged from 195° to 220°C for free-base porphyrins and 230° to 240°C for nickel porphyrins. Source temperatures were kept at 270° to 275°C while the

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probe temperature was slowly increased, expelling the more volatile nonporphyrin compounds, until the desired probe temperature was reached.

The data obtained from the mass spectrometric analyses of silylated hydroxyaluminum chlorins and the free-base and nickel porphyrins were given in Tables 2 and 3, respectively.

RESULTS

Three classes of tetrapyrrole pigments were found in the Black Sea: chlorins, free-base, and nickel porphyrins. The individual pigment yields and UVvisible spectrometric data are given in Table 1. The concentration (log scale) of each class is plotted versus depth of burial and strata from site to site in Figure 1. A brief summary of the results is now presented for each site.

Site 379

Six samples, ranging from 48 to 458 meters depth of burial, were examined for pigment content. Chlorins were abundant in the upper sections (Table 1, Figure 1), particularly in Section 379B-5-3. Chlorin concentration decreased with increasing depth and pigment was not detectable in Section 379A-50-4. A similar distribution pattern was observed for chlorins isolated from Site 147 (Leg 15) samples where a plot of log of pigment concentration versus depth was approximately linear (Baker and Smith, 1973); however, the range in depth of burial in that case was only 5 to 107 meters. The chlorin concentration decreases independent of percent organic carbon in both the Site 379 and Site 147 samples. Mass spectrometric analyses of chlorins obtained from this site are discussed together with those from Site 380. Data are given in Table 2.

No free-base or metalloporphyrins (or metallochlorins) were found in these samples, indicating that chlorophyll diagenesis had not progressed into the intermediate (free-base) stages.

Site 380

Fifteen Pleistocene, Pliocene, and Miocene samples, ranging from 0 to 1062 meters depth of burial, contained pigments ranging with depth from free-base

TABLE 1								
Sample and Pigment Data Obtained	From Black Sea Cores, Sites 379, 380, and 381							

Section	Geologic Age ^a	Lithologic Description	Depth of Burial ^a (m)	Organic Carbon ^a (% by wt)	Individual Yield ^b (ug/g)			UV-Vi	sible A (nand	bsorpti	on Spe	ctra			Pigment Type
379B-4-2	Pleistocene	Calc. dark gray	47.5-48.5	approx.	0.98		409			535		605		663	Chlorin
379B-5-3	Pleistocene	Calc, dark gray	77.5-78.5	0.51		(12	410	507		535		605		663	Chlorin
		mud		14144	30	10	412	505		537		607		666	Chlorin
						17	409	500		530		605		668	Chlorin
379B-9-3	Pleistocene	Calc, dark gray mud	153.5-1555	approx. 0.70	1.27		409			535		605		664	Chlorin
379A-25-6	Pleistocene	Calc. dark gray shale	233-234	0.66	0.14		406			532		600		660	Chlorin
379A-46-1	Pleistocene	Calc, med, gray shale	415.5-416.5	0.18	0.002									665	Chlorin
379A-50-4	Pleistocene	Calc. gray- green shale	458-459	0.28	none										
380-0-2	Pleistocene	Calc, gray mud	1.5-3		0.50		409	500		535		605		666	Chlorin
380-10-3	Pleistocene	Calc. brown gray mud	89-90		0.33		408	500		535		605		663	Chlorin
380-13-2	Pleistocene	Calc. dark gray mud	115.5-117		0.14		407	500		535		600		658	Chlorin
380-25-3	Pleistocene	Slightly calc. dark gray mud	231-232.5		trace									(660)	Chlorin
380-39-2	Pleistocene	Calc. dark gray mud	330-330.5		0.14		(407)					605		662	Chlorin
380A-3-3	Pleistocene	Calc. layers of light and med-	354.5-356		0.46	{0.21	400					595		661	Chlorin
	_	ium gray shale				0.25	394	495		530		590	645	666	
380A-8-0	Pleistocene	Cale. dark gray mud	399		0.005		(407)							668	Chlorin
380A-17-0	Pleistocene	Calc, gray mud	484.5		0.005		394		521		556				Nickel porphyrin
380A-21-3	Pleistocene	Calc. dark gray mud	525.5-527		0.008		395		521		554			1000000	Nickel porphyrin
380A-38-4	Pliocene	Dark gray mud	679-680.5		0.07						200	598		667	Chlorin
					0.07		400	498		528	564		618		Free-base porphyrin
2001 12 1	7041	ware and the second	044 6 046 F		0.02		394		521		220			110	Nickel porphyrin
360A-4/-4	rhocene	Caic. dark gray	/64.3-/63.5		0.07		400	100		610	864		619	003	Erea baca porphyrin
		mua			0.17		400	470	\$15	320	550		010		Nickel northvrin
3804-63-1	Miccene	Cale gray mud	012.013	1.90	0.12		374		515		220			668	Chlorin
50011051	Mocene	care. Bray mud	712-715	1.00	233		400	498		528	564		618	000	Free-base porphyrin
					0.05		396	170	518	020	554		010		Nickel porphyrin
380A-74-1	Miocene	Calc. dark gray	1016.5-1017.5		1.30		400	498	210	528	564		618		Free-base porphyrin
		shale			trace						555				Nickel porphyrin
380A-78-6	Miocene	Calc. gray shale	1062-1062.5	2.20	2.02 0.40		400 395	498	515	528	564 551		618		Free-base porphyrin Nickel porphyrin
381-2-3	Pleistocene	Slightly calc. black shale	12.5-13.5	1.07	1.89		409			534		605		665	Chlorin
381-9-0	Pleistocene	Calc. gray shale	76	0.42	0.006		407							659	Chlorin
381-23-6	Pleistocene/ Pliocene	Gray shale	207-208.5	0.95	0.05									663	Chlorin
381-37-3	Pliocene/ Miocene	Calc. gray shale	335-336.5	5.49	3.64		407	494				597		660	Chlorin
381-54-5	Miocene	Dark gray	500.5-502	1.72	0.04									644	Chlorin
		shale			0.10 0.03		400 395	498	518	528	564 552		618		Free-base porphyrin Nickel porphyrin

^aDates for much of the sedimentary section are still unresolved. Age determinations used here are from Jousé and Mukhina (this volume) and Ross (this volume).

^bPigment yield calculated by using the following molar extinction coefficients: pheophytin "a" = 63700 at 660 nm, free-base porphyrin = 6540 at 618 nm, and nickel porphyrin = 34820 at 550 nm.



Figure 1. Pigment concentration (log scale) vs. depth of burial, Sites 379, 380, and 381. Data for chlorins (\bullet), free = base porphyrins (\circ), nickel porphyrins (Δ) plotted here are given in Table 1. Stratigraphy was supplied by DSDP; only those horizons which can be traced from one site to another have been indicated (shown as A', A, B, C, D, and E).

Core Sample	Sephadex ^a Fraction	Approx. ^b HCl No. (%)		1	Mass Sp	ectru	n of Si	lyl Der	ivative			
379-5		32 19-32 19			722	714 714 712		694 694 692		664 664 664		
380-0	(1 - 3)	32			722	714				664		
380-10	(1 - 2)	19-32			720	712		692		664		
380-13	(1 - 2)	19-32			722	714				666		
	Compound ^C	Mol. Wt										
Pheophytin a Pyropheophorbide		870 534	(858)	796 796, 794	(770)	712	708	696 694	(682)	664 664		
Deoxomo Chlorin e	esopyropheoph 6	orbide 522 596	(860) 858		772, 770	712			684, 682		580	

TABLE 2 Mass Spectrometric Data of Silylated Hydroxyaluminum Derivatives of Black Sea Geochlorins and Selected Model Compounds

^a Sephadex LH-20 fraction numbers are given to indicate chromatographic behavior of geochlorins; note that only core 379-5 had a substantial amount of late-running chlorin fraction (5).

^b Approximate HCl numbers are the percent (by weight) of HCl used to extract the chlorin into the aqueous phase. An HCl Number of 32 is comparible with that of pheophytin *a*(HCl No. = 28-29) while 19 is comparible with pheophorbide (HCl No. = 15). H. Fischer and A. Stern, Die Chemie des Pyrrols, Band 11: Pyrrolfarbstoffe, Halfte 2, Akad. Verlag., Leiqzig, p. 55 and 59 (1940).

^cStructures for these model chlorin compounds are given in Figure 3.

chlorins to free-base and nickel porphyrins (Table 1, Figure 1). In contrast with Site 379, the chlorin concentration did not decrease monotonically with depth, but was greatest near the surface (380-0-2 and 380-10-3) and peaked again at 355 meters (380A-3-3).

Nickel porphyrins were found in Cores 380A-17 and 380A-21 (484 to 526 m) in which chlorins were absent. This finding seemed unusual because chlorins were abundant above and below these two samples; the nickel porphyrins are diagenetically out of place. Mass spectrometric analyses of nickel porphyrins from these cores showed that the molecular weight distributions were markedly different from those previously reported for marine sediments. Earlier, nickel DPEP and etio type porphyrins were reported as the only series (Baker et al., in press a, b). In contrast, these series were nearly absent in the Black Sea nickel porphyrins and a new series (455 + 14n) dominated the mass spectra. Molecular weight distributions of the nickel porphyrin fractions from two deeper samples (380A-38 and 380A-63) were similar to 380A-17 and 380A-21 (Table 3).

Whereas porphyrins of the etio series were present only at the level of detection in Samples 380A-17, 380A-21, 380A-38, and 380A-63, both nickel DPEP and etio type porphyrins became mass spectrometrically more observable in Core 380A-78.

In all samples, the molecular weights of the new and etio type nickel porphyrins were low, having 29 carbons or less. In previous Initial Reports (Baker et al., in press a, b) nickel porphyrins having 30 to 32 carbons predominated.

Sufficient pigment was available for demetallation of the Core 380A-78 nickel porphyrin fraction. A visible spectrum which could be duplicated by a mixture of rhodo porphyrin and etioporphyrin was obtained (Baker, 1966). Spectra of this nickel porphyrin fraction and its free base are shown in Figure 2.

Free-base chlorins and porphyrins, with the porphyrins predominating, were found in samples below 525 meters (380A-38 to 380A-63); below this depth all pigments increased with depth of burial. These relationships are depicted in Figure 1.

Mass spectrometric analyses of the free-base porphyrins are reported in Table 3. Five to six members of a DPEP homologous series, with m/e 476 and 462 being the major members, characterize every mass spectrum with the exception of the fraction isolated from Core 380A-47. In this case, the m/e values (530, 516, and 502) may indicate deoxophylloerythrin, a carboxylated porphyrin.

Site 381

Five samples, from 12 to 500 meters depth of burial, were extracted and their pigment content was compared with those of Sites 379 and 380. Most interesting was the finding that sediments representative of the same geologic age at Site 381 as at Site 380 contained different pigment assemblages (Figure 1). High concentrations of chlorins at 208 to 336 meters (Site 381) are perhaps correlatable with the high concentrations of free-base porphyrins in Site 380 cores at 680 and 765 meters. That sediments of the same age contain pigments of different stages of diagenesis indicates the importance of depth of burial as a maturation rate determining factor.

Free-base porphyrins, whose mass spectra were similar to those of Site 380 samples, were found in Core 381-54 of Miocene age. Nickel porphyrins also present

TABLE 3
Mass Spectrometric Data of Free-base and Nickel Porphyrins ^a From Sites 380 and 381
(peak intensities normalized to 100 for the most intense peak)

380A-17	Nickel porphy	rin									
	506	492	484	478	464		450	436			Etio series ^b
511	4	97	483		469	455		441			New series
37		33	87		81	100		442			455 + 14n
513	499		485	471		457	443				
5	5		12	11		15	10				457 + 14n
380A-21	Nickel porphy	rin									
	478	464		450	436		422				Etio series ^b
483	4	69	455		441	427		413			New series
41		61	77		100	92		79			455 + 14n
485	471		457	443		429	415				
7	8		13	14		15	12	-			457 + 14n
380A-38	Nickel porphy	rin				3					
	porpuj			478	464		450	436			Etio series ^b
511	4	197	483		469	455					New series
50		42	100		86	14					455 + 14n
612	400		405	471	1222	457					
15	499		485	4/1		457			5		
10				15		15					
380-4 / F	ree-base porph	iyrin	500								
100	510		502								
100	22		33								
380A-63	Nickel porphy	rin									h
532	518										DPEP series
			506	492		478	464		450	436	Etio series ^b
		511		497	483		469	455		441	New series
		30		44 '	82		86	100		52	455 + 14n
			499		487	471		457	443		
			3		11	7		20	6		457 + 14n
	Free-base por	nhvrin									
476	462	, in the second s	448	434		420					
47	100		34	40		19					
380A-74	Free-base port	hvrin									
476	462		448	434		420	406				
46	100		34	26		9	6	-			
3804-78	Nickel porphy	rin									
532	518		504	490							DPEP series
39	65		55	49	-						-2017028
	520	506		492	479		464	450			Etio series
	15	31		56	99	,	92	87	-		Dito Jelles
	1 (my child)			.e-#1	100		1000	400			N
			497		483	469	97	455			ASS + 14-
			28		93	100	0/				433 T 14h

380A-	78 Nickel porp	hyrin (Co	ont)									5
			499	485		471	457					
			9	13		16	12					457 + 14n
	Free-base p	orphyrin										
476	462		448	434		420						
94	100		63	37		22						
381-54	Nickel porph	yrin										
532	518		504									DPEP series
26	11		16									
		506		492	478		464	450		436	422	Etio series
		2	8	16	53		47	68		79	53	
		511	497		483	469		455	441		427	New series
		21	21		58	63		84	100		63	455 + 14n
	513		499	485		471	457		443	429		
	8		3	15		18	16		15	23		457 + 14n
	Free-base p	orphyrin										
476	462		448	434		420	406					
100	72		69	46		49	32					

TABLE 3 – Continued

^aThe peak heights for the Ni⁵⁸ 457 + 14n series has been adjusted for the Ni⁶⁰ isotope contribution from the corresponding Ni⁶⁰ 455 + 14n series, the corrected values were used to compute the normalized values in the table.

^bNickel porphyrins of the DPEP and etio types were just at the level of detection in all samples except for 380A-78 and 381-54; thus, only the presence of these series is noted and the peak intensities are not reported except for 380A-78 and 381-54. Correction for Ni⁶⁰ isotope contributions from the DPEP series were made.

in this core are similar to those found in Core 380A-78 (Table 3).

lost from pheophytin *a* during the derivatization. The major peaks are: m/e = 794(796), 694 and 664.

Mass Spectrometric Analyses of Silylated Hydroxyaluminum Derivatives of Geochlorins

Mass spectrometric data of silylated derivatives of Black Sea geochlorins and selected model compounds are given in Table 2. Four synthetic chlorins were selected for use as reference compounds and to serve as indicators of the following diagenetically related structural changes: (1) de-esterification (loss of phytol); (2) reduction of C-9 keto group, (3) decarbomethoxylation at C-10 position; and (4) isocyclic ring opening.

Only a partial structural interpretation of the mass spectra of the model compounds (Figure 3) has been made. However, observable differences between them can be pointed out. The m/e values of 858, 770(772), and 682(684) are indicative of chlorin e_6 , a chlorin in which the isocyclic ring is replaced by two carboxyl groups. Due to the basicity of the reaction mixture, rupturing of the isocyclic ring of pheophytin *a* occurred to some extent; the m/e values assigned to chlorin e_6 , therefore, appear along with values characteristic of pheophytin *a* (m/e = 796, 712, 708, 696, and 664).

The mass spectrum of the silylated derivative of pyropheophorbide, which lacks phytol and the C-10 carbomethoxyl group, cannot be clearly distinguished from that of pheophytin *a*. Apparently these groups are

However, when the reduction of the isocyclic ring is complete (loss of carbomethoxyl and keto groups) and the C-2 vinyl group is reduced to ethyl, as is the case in deoxomesopyropheophorbide, the mass spectrum is simplified and contains two major peaks (m/e = 712and 580).

Comparison with the mass spectra obtained for the model compounds permits the following statements concerning the structure of the geochlorins to be made: most of the geochlorins can be accounted for as a pheophytin a or pheophorbide type pigment since m/e values 712(714), 692(694), and 664(666) are present in the spectra of the unknowns. The significance of the m/e values of 720 and 722 is not presently known. That none of the geochlorins can be assigned the structure of deoxomesopyropheophorbide is evidenced by the lack of a major m/e peak at 580. This observation is reasonable because geochlorins having a structure similar to deoxomesopyropheophorbide would be expected at a much later stage of diagenesis than that of the samples studied. The degree of reduction of this particular model compound places it very close to the chlorin-porphyrin transition. If sufficient amounts of chlorin for derivatization had been present in samples of greater depth of burial, a deoxomesopyropheophorbide type pigment may have been found. (These deeper chlorins were found in association with free-base porphyrins.)



Figure 2 (a, b). UV-visible spectra of the nickel porphyrin fraction isolated from Core 381A-78, before (a) demetallation and after (b).

These data clearly indicate that chlorins with ruptured isocyclic rings, such as chlorin e_6 , are not present in the samples studied. Apparently, conditions during deposition and sediment compaction in the Black Sea were not those that permit isocyclic ring opening. Thus, the route by which chlorins such as chlorin e_6 are formed was not a major one, if operative at all.

Interpretation of mass spectra of silylated hydroxyaluminum geochlorins can be more complete after additional model chlorins are studied and structures correlated with fragmentation patterns. High resolution mass spectrometry is proposed in order to provide empirical formulas of significant mass spectral fragment ions. As this method is developed, more detailed structural information will become available. However, even at this stage, the method provides new insights into chlorin diagenesis.

Discussion

Based on the data obtained on 25 samples from the Black Sea, tetrapyrrole diagenesis has progressed from the early stages (pheophytin \rightarrow pheophorbide) to intermediate stages (chlorin-porphyrin transition). Freebase DPEP type porphyrins were abundant in deeper cores of Site 380, increasing with depth relative to the amount of chlorin present.

The UV-visible and mass spectrometric data of chlorins extracted from core samples of 0 to 200 meters depth of burial are indicative of pheophytin-like



Name	R ₁	R ₂	R ₃	R ₄
Pheophytin a	CH=CH2	0	COOCH3	CH ₂ CH=C-C ₁₆ H ₃₃
Pheophorbide a	CH=CH ₂	0	COOCH3	н
Pyropheophorbide a	CH=CH2	0	н	н
Deoxomesopyropheophorbide	сн ₂ сн ₃ or сн ₂ -сн ₃	н2	н	н
Chlorin e6	CH=CH ₂	а	а	н

 $^a{\rm The}$ isocyclic ring is broken and the substituent in the 6 position is COOH and CH_2 COOH in the γ position.

Figure 3. Structures of chlorin model compounds. Note a = the isocylic ring is broken and the substituent in the 6 position is COOH and CH₂COOH in the γ position.

chlorins. No trace of free-base or metalloporphyrin was found in these shallow sediments. Peake et al. (1974) reported that phyllo and etio type free-base porphyrins were mass spectrometrically observable in surface (0-68 cm) sediments of the Black Sea. However, these investigators did not report UV-visible spectra in support of these data. In contrast, in the study reported here, free-base porphyrins were found only in sediments at and below 500 meters depth of burial. These proved to be of the DPEP series; phyllo and etio series pigments were absent.

In addition, our chlorin mass spectrometric data (Table 2) do not support the speculation that homologous series, 14 mass units apart, exists in the chlorin fractions. A truncated series is initially observable only after diagenesis had progressed to the free-base porphyrin stage and then persists throughout the geoporphyrins, whether they are in the metallated or free-base form.

Site 380, drilled to a depth of 1073.5 meters, provided an opportunity to observe the transition of chlorins to free-base porphyrins. This transition is a dehydrogenation (aromatization of the 7, 8 bond, Figure 3) and is probably equivalent to the minimum diagenetic stage where hydrocarbons could be produced from their precursors. The initial appearance of free-base porphyrin was at 680 meters; as depth increased, the concentration of the porphyrin increased relative to the chlorin. At 912 meters, there was 20 times more free-base porphyrin than chlorin and chlorins were not observed below this depth.

The influence of depth of burial as a diagenetic factor was clearly demonstrated by the distribution of these products at Site 380. Stratigraphic horizons are traceable from site to site, as shown in Figure 1. Horizon D lies at 860 meters depth of burial at Site 380; at this depth, high concentrations of free-base porphyrins were found. In contrast, horizon D is shallower at Site 381 (350 m); only chlorins were found at this depth. In this case, free-base porphyrins appeared only in the Miocene core sample at 500 meters (381-54-5). The data presented here may indicate that depth of burial (and its corollary, temperature) is a more important factor in the maturation process of organic matter than geologic age.

Nickel porphyrins were present in the deeper Pleistocene and older sediments along with free-base porphyrin and/or chlorins. Exceptions to this generality are Cores 380A-17 and 380A-21 where the nickel porphyrin was the only observable pigment.

A minor portion of the nickel porphyrins, the DPEP series, had a molecular weight distribution similar to that of the free base (Table 3, Cores 380A-78 and 381-54). The major portion of the nickel porphyrins, though, is atypical and could not have arisen from simple insertion of nickel into the free-base porphyrin common to those strata. This conclusion is based on the previous finding of the similarities between the molecular weight distributions of nickel porphyrins and free-base porphyrins occurring together in the same sediment (Baker et al., in press a).

These are atypical nickel porphyrins as shown by the UV-visible spectrum, Figure 2. Both the spectra of the metallated and free-base porphyrins indicate a divergence from the DPEP and etio type of spectra observed in all earlier deep-sea studies. The mass spectra (Table 3) show that these are almost totally dealkylated nickel porphyrins with as few as four or five methylene groups attached to the porphyrin nucleus. Dealkylation has proceeded to a greater degree than previously noted in extracts from either deep-sea sediments or crude oil (Baker et al., 1967).

Because these nickel porphyrins are predominantly associated with the Pliocene and Miocene sediment samples and because of their lone occurrence in Cores 380A-17 and 380A-21, we suspect that their present distribution may be a result of upward diffusion from the older strata. This information together with the spectral data is offered as an explanation for the suggestion that these are not typical nickel geoporphyrins.

The Black Sea sediments have been described as being characteristically lacustrine with only a few marine phases present (Leg 42B summary). However, no distinctions can be made based on chlorophyll diagenetic products as to the source of the organic matter deposited in this basin. Marine sediments from Legs 40 and 41 contained products similar to those found in the Black Sea.

The data obtained from the hydroxyaluminum chlorins represents the most detailed analysis of these early products yet to be obtained. Application of this method to chlorins of marine origin may yet show differences in diagenetic products not discernible with less sophisticated methods used in the past. However, complete interpretation of early chlorophyll diagenetic products is presently lacking.

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