Reports

Copper Porphyrins in Deep-Sea Sediments: A Possible Indicator of Oxidized Terrestrial Organic Matter

Abstract. *Copper porphyrins have been isolated from deep-sea sediments collected during six legs of the Deep Sea Drilling Project–International Program of Ocean Drilling. These pigments are present in depositional areas receiving high inputs of terrestrially derived oxidized organic matter. Such areas include the Black Sea, the Bay of Biscay, the Blake-Bahama Basin, and slumped Miocene deposits off Cape Bojador on the west coast of Africa.*

We have identified copper porphyrins, previously unconfirmed in geological samples, in particular marine sediments; the evidence suggests that these porphyrins represent one branch of the chlorophyll degradation process. Biological copper porphyrins have been known for many years (*1*); however, the presence of native copper porphyrins in marine sediments has remained undocumented. We report their occurrence as components of some tetrapyrrole pigment mixtures isolated from marine sediments. These pigments occur in areas receiving large amounts of terrestrially derived organic matter which is either slowly accumulated, deposited from oxygenated bottom waters, or oxidized before deposition (*2, 3*). In contrast, copper porphyrins have been absent in basins that were anoxic at the time of deposition.

Copper porphyrins are typically found in association with nickel porphyrins, the most frequently encountered metalloporphyrins in deep-sea sediments. Copper and nickel porphyrins occur either alone or in combination with products of intermediate chlorophyll diagenesis such as free base deoxomesopyropheophorbide-like chlorins and free base deoxophylloerythroetioporphyrin (DPEP-type) porphyrins (*4*). Until now, nickel and vanadyl chelates (*5*) were thought to be the only late diagenetic products of chlorophyll (*6*).

Concentrations of total porphyrin pigments for organic-rich marine shales range from 120 μg per gram of wet sediment to a barely detectable value of 0.001 μg/g (*7*). More typically, concentrations of 1 to 10 μg/g are found. Copper porphyrins cochromatograph with nickel porphyrins and can constitute 10 to 80 percent of the mixture. We first noted their presence as a component of the metalloporphyrin mixture as a result of the abnormal position of the visible bands of the electronic spectrum. Both synthetic and naturally occurring nickel porphyrins have an α band at 550 to 552 nm and a β band at 512 to 514 nm, whereas in the copper porphyrins the comparable bands occur at 564 and 527 nm. Increasing proportions of copper porphyrin in a copper-nickel porphyrin mixture are revealed by a shift in the visible bands to between 557 and 560 nm and to between 518 and 522 nm, as illustrated by the spectrum of sample 47A-397-68-2 (Fig. 1A). Such spectral shifts have been duplicated in synthetic mixtures.

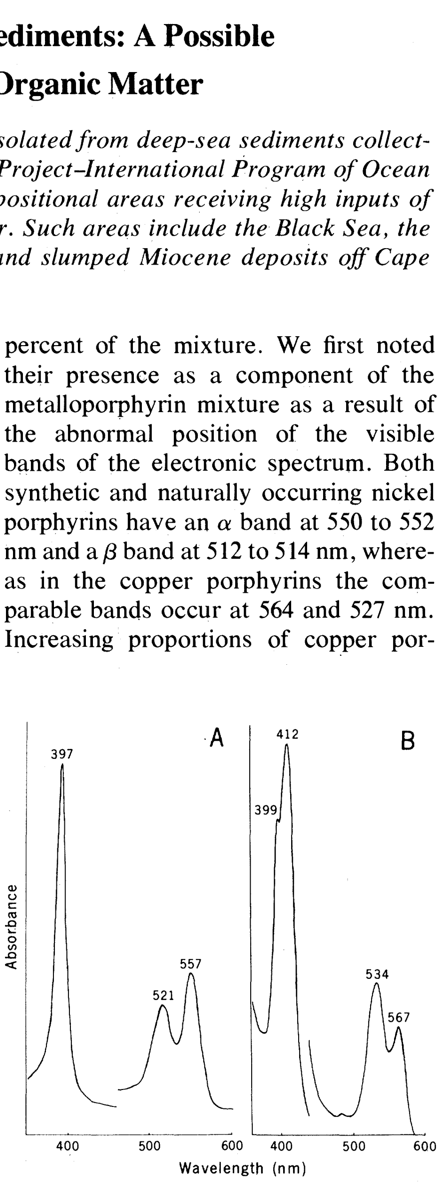

Fig. 1. Electronic spectrum of the nickel and copper porphyrin mixture from IPOD core sample 47A-397-68-2: (A) uncomplexed; (B) complexed with piperidine. The spectrum of a metalloporphyrin is typically composed of two bands in the visible region, which are labeled from right to left as bands α and β and a band usually 20 times as intense in the near ultraviolet, which is referred to as the Soret band. The α, β, and Soret bands for nickel etioporphyrin occur at the wavelengths 552, 514, and 395 nm. The band locations for copper etioporphyrin are 564, 527, and 399 nm. Approximately 80 percent of this sample was copper porphyrin; this estimate is based on the relative intensities of mass spectral peak intensities for the mass spectrum shown in Fig. 2.

The presence of copper porphyrins was further confirmed on the basis of diagnostic shifts in the Soret band resulting from complexation with piperidine (*8*). Synthetic copper etioporphyrin has a Soret band at 399 nm, whereas the piperidinate complex shows a branched Soret band with maximum absorbances at 399 and 410 nm. In contrast, nickel etioporphyrin has a Soret band at 395 nm and a branched Soret band for the piperidinate complex at 399 and 420 nm. The piperidinate complex for International Program of Ocean Drilling (IPOD) sample 47A-397-68-2 with the branched Soret band characteristic of copper porphyrins clearly evident is shown in Fig. 1B. In cases where copper porphyrins make up only a small fraction of the nickel and copper porphyrin mixture, only the branched Soret band characteristic of a nickel porphyrin is observed.

Mass spectrometric analyses of copper porphyrins isolated from deep-sea sediments show the presence of homologous series of etioporphyrins having as few as 23 (C_{23}) to as many as 32 (C_{32}) carbons. The centroid of the mass spectral envelope is usually at C_{25} to C_{28}. The mass spectrum of the porphyrin fraction from IPOD sample 47A-397-68-2 is shown in Fig. 2. In this sample the centroid of the spectral envelope is at a mass-to-charge ratio (*m/e*) of 455, corresponding to a C_{26} copper etioporphyrin having only five methylene groups attached to the tetrapyrrole ring with the envelope extending from C_{30} to C_{23}. This mass spectral envelope contrasts markedly with the envelopes of nickel and vanadyl porphyrins which typify late chlorophyll diagenesis in marine sediments that accumulated under anoxic conditions. In those cases, porphyrins of the DPEP series with carbon numbers of 32 to 30 predominate (*9*). In only five cases have copper porphyrins been found in either the DPEP series or with as many as 32 carbons (12 methylene groups).

A compilation of all occurrences of copper porphyrins in the Deep Sea Drilling Project–International Program of Ocean Drilling (DSDP/IPOD) core samples is given in Table 1. Included are samples ranging from Pleistocene to Cretaceous in age and collected at subsurface depths of burial of 255 to 1585 m. These data were used to evaluate two

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possible modes of origin of copper porphyrins in marine sediments. The possibility that these materials are artifacts of the separation scheme was considered and rejected for the following reasons. First, it is recognized that, even when special care is exercised, artifacts can result from chelation and breakdown of geochlorins during sample work-up. However, this source must be discounted because chlorins were not detected in every sample studied. In 7 of the 24 cases listed (Table 1), chlorins are totally absent. Furthermore, this mode of artifact formation could not account for the fact that copper porphyrins are observed as homologous series. A second possible route by which artifacts could be formed is chelation with inorganic copper during laboratory extraction of free base porphyrins. In this mode of formation, the molecular weight distributions of the laboratory artifacts would necessarily be identical to those of the free base DPEP-type porphyrins. However, this is clearly not the case since the copper porphyrins are generally greatly dealkylated (C_{25} to C_{28}) and typically of the etio series. The data thus indicate that copper porphyrins are native to these samples.

Mass spectrometric data show that copper is chelated with dealkylated etioporphyrins (C_{25} to C_{28}) in contrast with the DPEP-type porphyrins (c_{32} to C_{29}) characteristic of reducing marine environments. The fact that copper porphyrins are found to coexist with products of varying states of chlorophyll diagenesis formed under reducing conditions suggests that they are derived from a different source of organic material. We believe that their presence is indicative of terrestrially derived organic matter which has undergone oxidation before or during deposition. This suggestion is supported by the fact that copper porphyrins are absent from anoxic basins which receive terrestrial debris that has not been oxidized. An example is the absence of these pigments in lower Cretaceous samples from the Cape and Angola basins off the southwest coast of Africa and likewise in upper Cretaceous samples from the Cape Verde Rise and the Moroccan Basin (*10*). They were also absent in the lower Cretaceous black shales from the Bermuda Rise which were deposited under anoxic conditions; however, by the late Cretaceous, the bottom had become oxygenated and copper porphyrins were present in sediments of this age. Other localities where either deposition of terrestrially derived organic matter has occurred under oxygenated bottom conditions or during times of slow accumulation rates or where the land-derived material was oxidized prior to deposition include the Black Sea (*11*), the Cretaceous black shales of the Bay of Biscay and Blake-Bahama Basin, and the reworked Miocene sediments off Cape Bojador on the west coast of Africa.

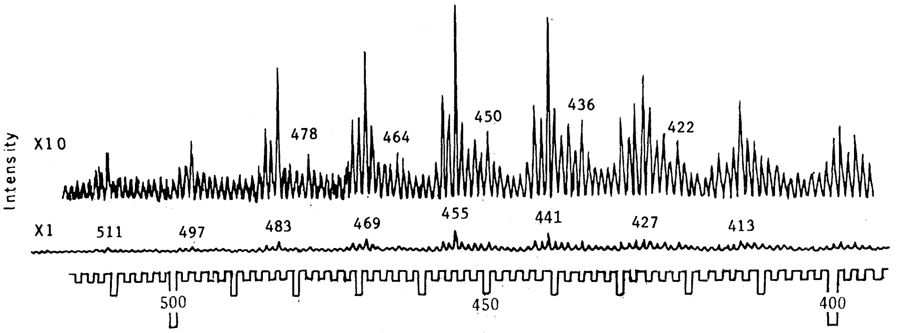

Fig. 2. Mass spectrum of the nickel and copper porphyrin mixture from IPOD core sample 47A-397-68-2. Molecular weights of the copper etioporphyrin homologous series are indicated on the ×1 scale; these values fall into the $^{63}Cu + (310 + 14n) - 2H^+$ series. Nickel porphyrins of the etio series, indicated on the ×10 scale, fall into the $^{58}Ni + (310 + 14n) - 2H^+$ homologous series. The mass spectrum is more complex because both metals have two major, naturally occurring isotopes (^{63}Cu = 69 percent, ^{65}Cu = 31 percent; ^{58}Ni = 67.8 percent, ^{60}Ni = 26.2 percent). Spectra of biisotopic metals, therefore, have a smaller peak corresponding to the higher-molecular-weight isotope of lesser abundance.

Table 1. Distribution of copper porphyrins and other pigments in deep-sea sediments containing substantial amounts of terrestrially derived organic matter. Thirty-six occurrences of copper porphyrins have been noted; however, only those for which both electronic and mass spectrometric data were available are given. Localities for the 24 samples listed by DSDP/IPOD leg number include the following: 38, Norwegian Sea; 42B, Black Sea; 43, Bermuda Rise; 44, Blake-Bahama Basin; 47A, off Cape Bojador, West Africa; 47B, south of Vigo Seamount; and 48, Bay of Biscay. The *Initial Reports of the Deep Sea Drilling Project* give the exact locations, geologic ages, and subbottom depths of burial of these samples.

Porphyrins						Free base chlorins	DSDP/IPOD sample designation
Copper etio	Copper DPEP	Nickel etio	Nickel DPEP	Vanadyl DPEP	Free base DPEP		
x		x					42B-380a-17-0, 42B-380a-21-3
x		x				x	43-387-35-3, 44-391c-9-3, 47A-397-68-2
x		x	x			x	43-387-16-2, 43-387-26-2, 44-391c-12-4
x	x	x	x			x	43-387-37-2, 43-387-49-4, 47B-398d-75-2, 47B-398d-122-5
x		x			x	x	38-341-(28-31), 42B-380a-38-4, 44-391a-20-2
x		x	x		x		42B-380a-78-6, 47A-397a-12-2, 47A-397a-16-4, 47A-397a-21-2, 47A-397a-23-4
x		x	x		x	x	42B-380a-63-1, 42B-381-54-5, 44-391c-10-3
x	x	x	x	x	x	x	43-386-43-3

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References and Notes

1. J. W. Buchler, in *Porphyrins and Metalloporphyrins*, K. M. Smith, Ed. (Elsevier, Amsterdam, 1975), p. 157.
2. Shipboard party, Leg 38, *Geotimes* **20** (No. 2), 24 (1975); shipboard party, Leg 43, *ibid.* **20** (No. 12), 18 (1975); shipboard party, Leg 44, *ibid.* **21** (No. 2), 23 (1976); shipboard party, Leg 47, *ibid.* **21** (No. 10), 21 (1976); shipboard party, Leg 48, *ibid.* **21** (No. 12), 19 (1976).
3. Shipboard party, Leg 42B, *ibid.* **20** (No. 10), 18 (1975).
4. For occurrences and structures of chlorophyll diagenetic products, see E. W. Baker, S. E. Palmer, K. L. Parrish, *Initial Rep. Deep Sea Drill. Proj.* **38**, 785 (1976); E. W. Baker, S. E. Palmer, W. Y. Huang, *ibid.* **42B**, in press; S. E. Palmer, W. Y. Huang, E. W. Baker, *ibid.* **43**, in press; E. W. Baker, S. E. Palmer, W. Y. Huang, *ibid.* **44**, in press; E. W. Baker and S. E. Palmer, *ibid.* **47A**, in press; S. E. Palmer and E. W. Baker, *ibid.* **47B**, in press; E. W. Baker and S. E. Palmer, *ibid.* **48**, in press.
5. The presence of vanadyl porphyrins in petroleum and bitumen was first reported in 1934 [A. Treibs, *Justus Liebigs Ann. Chem.* **510**, 42 (1934)]. Nickel porphyrins were identified 14 years later [E. A. Glebovskaia and M. V. Vol'kenshtein, *Zh. Obshch. Khim.* **18**, 1440 (1948)].
6. It is now possible to reconstruct the pathways by which nickel and vanadyl porphyrins arise in marine sediments. Chlorophyll a, the most common green pigment in plants, undergoes a series of diagenetic reactions including loss of magne-

sium, decarbomethoxylation, reduction, aromatization, decarboxylation, and devinylation to give rise to a group of free base porphyrins of the DPEP homologous series (308 + 14*m*, where *m* is 2 or greater). Porphyrins of the DPEP series retain the isocyclic ring characteristic of chlorophyll [E. W. Baker, in *Organic Geochemistry*, G. Eglinton and M. T. J. Murphy, Eds. (Springer Verlag, Berlin, 1969), p. 480]. The short series of DPEP-type free base porphyrins, usually consisting of C_{32} to C_{29}, then becomes chelated with either nickel or vanadyl, resulting in compounds stable in a field of increasing thermal stress. Subsequent reactions fall into the realm of early catagenesis. With increasing temperature (~50°C) the metalloporphyrins of the DPEP series are gradually converted to members of the etio series (310 + 14*n*, where *n* = 1 or greater) by rupture of the isocyclic ring followed by dealkylation (loss of methylene groups from the tetrapyrrole ring) and in special cases transalkylation. "Transalkylation" refers to the proposed free radical mechanism by which methylene units can be added (alkylation) or removed (dealkylation) from the tetrapyrrole ring. This process results in metalloporphyrins having homologous series in the range C_{39} to C_{27}. Since the reactions proceed with increasing temperature, chlorophyll diagenesis serves as a paleothermometer.

7. Core samples were stored frozen until the time of analysis; mixtures of acetone and methanol (9:1) were used for ball mill extraction of pigments. Metalloporphyrins were then isolated from the crude extractions by chromatography over neutral alumina (grade III). Nickel and copper porphyrins cochromatograph with a mixture of cyclohexane and benzene (1:1), whereas the more polar vanadyl porphyrins can be eluted with a mixture of benzene and tetrahydrofuran (1:1). Repeated chromatography of the porphyrins yields relatively pure fractions for electronic and solid probe mass spectrometry.
8. E. W. Baker, M. S. Brookhart, A. H. Corwin, *J. Am. Chem. Soc.* **86**, 4587 (1964); J. C. W. Chien, *ibid.* **100**, 1310 (1978).
9. E. W. Baker, S. E. Palmer, W. Y. Huang, *Initial Rep. Deep Sea Drill. Proj.* **40**, in press; *ibid.* **41**, 825 (1977); S. E. Palmer and E. W. Baker, *ibid.* **50**, in press.
10. Shipboard party, Leg 40, *Geotimes* **20** (No. 6), 22 (1975); shipboard party, Leg 41, *ibid.* **20** (No. 7), 18 (1975); shipboard party, Leg 50, *ibid.* **22** (No. 4), 24 (1977).
11. The Black Sea, presently an isolated inland sea with anoxic bottom waters, contains a complex sequence of Pleistocene sediments which reflect the climatic influence imposed by alternating glacial and interglacial stages. Anoxic conditions have existed in the Black Sea for approximately the last 7300 years. Before this, the basin underwent evaporitic, brackish water, and lacustrine phases [(*3*); D. A. Ross, in *The Geology of Continental Margins*, C. A. Burk and C. L. Drake, Eds. (Springer-Verlag, New York, 1974), p. 669].
12. This research was supported by the Oceanography Section of the National Science Foundation under grants OCE 74-12438 A02 and OCE 77-072773. We thank G. DeMott for laboratory assistance.

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Noble Gases in the Murchison Meteorite: Possible Relics of *s*-Process Nucleosynthesis

Abstract. *The Murchison carbonaceous chondrite contains a new type of xenon component, enriched by up to 50 percent in five of the nine stable xenon isotopes, mass numbers 128 to 132. This component, comprising 5 × 10^{-5} of the total xenon in the meteorite, is released at 1200° to 1600°C from a severely etched mineral fraction, and probably resides in some refractory mineral. Krypton shows a similar but smaller enrichment in the isotopes 80 and 82. Neon and helium released in the same interval also are quite anomalous, being highly enriched in the isotopes 22 and 3. These patterns are strongly suggestive of three nuclear processes believed to take place in red giants: the* s *process (neutron capture on a slow time scale), helium burning, and hydrogen shell burning. If this interpretation is correct, then primitive meteorites contain yet another kind of alien, presolar material: dust grains ejected from red giants.*

Noble gases in carbonaceous chondrites show complex isotopic patterns, dating back to the beginning of the solar system or even beyond. To resolve these patterns into their components, two techniques have proved especially useful: extraction of gases by stepwise heating, and mineral separation by chemical techniques. We have combined both in the present study.

One of the more enduring puzzles in this field is a xenon component enriched in both heavy and light isotopes (*1*–*4*), which has been attributed to fission of a superheavy element (*5*), or to nuclear processes in a supernova (*2, 3*). It is commonly designated by the acronym CCFXe (for carbonaceous chondrite fission xenon), although its fission origin has not yet been proved. This component resides mainly in chromite and amorphous carbon (*4, 6, 7*). These phases can be isolated by dissolving the bulk of the meteorite in HCl-HF, and etching the residue (0.5 to 2 percent) with oxidizing reagents to remove two other phases that contain large amounts of ordinary trapped (or "primordial") xenon: the organic polymer and "phase Q," a poorly characterized mineral that may be an Fe,Cr-sulfide (*5, 8*).

In our previous study of the Murchison C2 chondrite (*7*), we were only partly successful in removing trapped xenon, judging from the modest enrichment in the heavy xenon isotopes. The highest ^{136}Xe/^{132}Xe ratio was only 0.441, higher than the ratio in trapped Xe (0.310) but lower than the highest value found for the Allende meteorite [0.626 (*6*)]. We therefore devised a new procedure for removal of polymer and Q, involving alkaline oxidants such as $NaOH + H_2O_2$ or NaClO (*9*), in addition to the fuming nitric acid used previously. This procedure indeed dissolved ~ 90 percent rather than 55 percent of the residue, and left a sample (designated 1C10) that yielded a ^{136}Xe/^{132}Xe ratio as high as 0.53 on stepwise heating. But the fractions released at the highest temperatures showed some new and totally unexpected trends.

The large, 800°C xenon fraction (Table 1) seems to consist mainly of trapped xenon from the polymer, judging from the low release temperature and isotopic similarity to trapped meteoritic xenon (penultimate line in Table 1). The 1000° and 1100°C fractions show the usual traits of CCFXe: enrichments in the lightest three and heaviest two isotopes, and little change in the others, relative to ^{132}Xe. But starting with the 1200°C fraction, some new trends appear: isotopes 128 and 130 rise, whereas 129, 131, 134, and 136 fall, all to more extreme values than any observed in meteoritic or lunar samples in the 18 years since John Reynolds founded the field.

Although the two most anomalous fractions (1400° and 1600°C) are quite small, the anomaly is not an artifact of the blank correction. This correction is only 1 percent for the 1400°C fraction, and although it is larger (25 percent) for the 1600°C fraction, even the uncorrected ratios are quite anomalous (*10*).

It appears that a new kind of xenon component is present in the 1200° to 1600°C fractions. This can be verified by three-isotope plots, such as Fig. 1. On such a plot, mixtures of *n* components fall within an *n*-sided polygon of minimum area, whose vertices are the individual components. Xenon in carbonaceous chondrites normally behaves like a pseudobinary mixture, with all samples lying on a straight "mixing line" that joins trapped Xe (from Q and polymer) at the left and CCFXe (from chromite and carbon) off the scale to the right (*11, 12*). When air xenon is present, samples drift below the line, toward the atmospheric point.

All Murchison samples ever measured by us indeed lie on the mixing line, except for the 1100° to 1600°C fractions of Murchison 1C10. This deviation cannot be due to air xenon, because the points lie above rather than below the mixing line. Apparently these fractions contain a third xenon component, lying somewhere on the upper left in Fig. 1.

The isotopic pattern of this third component can be qualitatively inferred from the 1400° and 1600°C fractions (Table 1). Isotopes 128 and 130 are obviously enriched, and so is the normalizing isotope 132, judging from the parallel decrease of

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