Cretaceous-Tertiary boundary layer at Stevns Klint (Denmark): copper and copper(II) porphyrins

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High concentrations (up to 4000 ppm) of copper(II) porphyrins have been detected in the kerogen of the Cretaceous/Tertiary (KT) boundary informal type sediment, the Fish Clay, at Stevns Klint, Denmark. These pigments have also been found in the Danish KT sediment at Nye Kløv, which is about 300 km away from Stevns Klint. However, copper(II) porphyrins cannot be detected in the Danich boundary rock of the Dania site, which is separated from Stevns Klint by about 200 km. It is proposed that the kerogen copper(II) porphyrins are derived from humic materials of terrestrial (peat/soil) sources already enriched with these compounds, which were redeposited in the Danish KT boundary Basin. In addition, our results show that the kerogen copper(II) porphyrins are present, for comparison, in the Permian Kupferschiefer shale from Poland. The amounts are comparable to those in the Fish Clay kerogen. To our opinion, the same processes responsible for the kerogen copper(II) porphyrin enrichment have occurred in the Stevns Klint KT boundary sediment and in the Kupferschiefer.

Key words: copper, porphyrins, kerogen, electron spin resonance.

The foundation of modern organic geochemistry is associated with Treibs' suggestion that sedimentary extractable (alkyl) metalloporphyrins are principally diagenetic end products of chlorophylls and bacterio-chlorophylls.[1] Nickel (Ni) and vanadyl (VO^{2+}) alkyl porphyrins are the two principal types of metalloporphyrins found in petroleums and carbonaceous sedimentary rocks, however, recent electron spin resonance (ESR) work in our laboratory have shown that the kerogens isolated from ancient carbonaceous sedimentary rocks of marine origin also contain significant amounts of VO^{2+} porphyrins incorporated into the kerogen structure.[2] It is generally agreed that the incorporation of the porphyrin nuclei into the kerogen matrix is essentially due to abiotic, diagenetic reactions and modifications of initial humic substances and associated chlorophylls.

We report here the wide occurrence of high concentrations of copper(II) porphyrins (named Cu^{2+}-P) (up to 4000 ppm) incorporated into the kerogen struc-

tures of the Cretaceous-Tertiary (KT) boundary layers from the Stevns Klint locality (Denmark). In addition, the Nye Kløv and Dania boundaries in the Jylland sequences near Stevns Klint were similarly investigated by ESR spectroscopy for the presence of Cu^{2+}-P in kerogen. These boundary layers are mineralogically identical to that at Stevns Klint.[3] For comparison, a study was conducted on Cu^{2+}-P of the kerogen of metalloferrous Permian Kupferschiefer (Poland) of comparable origin and geologic/geochemical history.

Cu^{2+}-P are found in acid-insoluble (humic acid) fractions in a wide variety of soil environments: recent soils[4-6] and paleosols.[7] These humic Cu^{2+}-P are largely derived from land plant chlorophylls under oxidizing conditions of the peat/soil formation. Although the widespread occurrence of VO^{2+}-P and nickel porphyrins in ancient sediments from different depositional environments has been reported, they are few reports of porphyrins complexed to Cu^{2+}. The occurrence of extractable Cu^{2+}-P is perhaps best authenticated by Palmer and Baker[8] and Baker and Louda[9,10] who isolated such species in very low concentrations (<1 ppm TOC) from a number of immature sedimentary rocks, giving evidence based on accurate mass measurement.[8] Baker and Louda[9,10] proposed that these Cu^{2+}-P may derive from, and be markers for, oxidized terrestrial organic matter redeposited in a marine environment.

During the debate about Stevns Klint KT boundary deposition, several genetic models were discussed in order to explain the source and enrichment processes for the base metals present in the boundary layer. Christensen *et al.*[11] attributed the metal enrichment in the Stevns Klint KT boundary layer (that is the Fish Clay) to an accumulation of mainly terrigenous materials with minor amounts of clay minerals of diagenetic origin. These authors subdivided the Fish Clay into four layers from the bottom bed II to the top bed V. In a benchmark paper, Alvarez *et al.*[12] explained the anomalous iridium (Ir) concentrations in the KT boundary layer at Stevns Klint, to global fall-out of extraterrestrial materials. According to these authors, the Stevns Klint boundary was produced by the impact event and consists of a mixture of terrestrial ejecta and meteoric material. Kyte *et al.*[13] suggested that only beds III and IV of the Fish Clay (hereinafter referred to as III and IV) can be used to estimate the primary asteroidal fallout. However, geochemical analyses of the KT layers revealed that not only Ir (and other meteoric/partly meteoric metals), but also non-meteoric terrestrial trace metals, such as Cu and V, are substantially enriched in these materials.

Most authors have concluded that metals of terrestrial origin in the Fish Clay were derived from natural aqueous solutions, enriched with these elements, in contact with unconsolidated sediment. Premović *et al.*[14] suggested that the Danish KT boundaries represent weathered clay (mainly smectite) (along with some asteroid/local materials) that was redeposited at the Danish boundary sites after the KT event. These authors claimed that most of terrestrial metals associated with the smectite fraction are strictly detrial in character, *i.e.,* were transported to the Danish boundary sites already contained in clay. Elliot *et al.*[15] argued that the anomalous

metal enrichments of the Fish Clay are comparable with those of the Kupferschiefer shale. These authors suggested that metals in the Fish Clay are derived from the same kind of "non-impact" sources that contributed to the high metal contents in the Kupferschiefer rock. They postulated that the same processes were responsible for the metal enrichment in the Fish Clay as in the Kupferschiefer rock.

The average Cu concentration in the Earth's crust ranges from 24–55 ppm and in soils from 20–30 ppm. Cu is usually associated in sediments with organic matter, the Fe/Mn oxides, sedimentary clays and other minerals.[16] In the Fish Clay, the Cu content ranges from 50 – 80 ppm[11,13] and is thus, of the same order of magnitude as in other ancient shaly type sedimentary rocks of marine origin.[17]

EXPERIMENTAL

Emission spectrometry

A PGS-2 plane grating spectrograph (Carl Zeiss, Jena) was used with an attachment for photoelectric detection, an arc plasma excitation source, and a Bausch and Lomb diffraction grating as the monochromator.[18]

Atomic absorption spectrometry (AAS)

A Perkin-Elmer model 4000 atomic absorption spectrometer was used with a Perkin-Elmer platinum hollow-cathode lamp and a nitrous oxide/acetylene burner head.[14]

Instrumental neutron activaiton analysis (INAA)

The kerogen samples and corresponding standards of $(NH_4)_3VO_4$ were irradiated simultaneously in the TRIGA MK II reactor at a neutron flux of 4×10^{12} n cm^{-2} s^{-1}. The γ-induced activity of Cu isotopes was measured on a germanium Ge(Li) detector connected to a 4000 channel analyser (Canberra).[19] The kerogen Cu contents were also determined by inductively coupled plasma-atomic emission spectroscopy (ICP-EAS).[20]

Electron microprobe

All analyses were obtained with a Jeol JSM-35 electron microscope equipped with a Tracor TN-2000 energy dispersive X-ray (EDX) spectrometer. Operating conditions for EDX analyses were at 25 keV accelerating voltage, 0.1 μA beam current, and a beam spot diameter of approximately 3 μm.[14]

Electron spin resonance (ESR)

ESR measurements were performed on the finely-ground powders of the samples which were trnsferred to an ESR quartz tube (4 mm o.d., 3 mm i.d.). Spectra were recorded on a Bruker ER-200 series ESR spectrometer with either a Bruker ER-044 X-band bridge or a Bruker ER-053 Q-band bridge, using standard 100 kHz field modulation. X-band measurements were made at 9.3 GHz utilizing a rectangular TE cavity, and those at 35 GHz Q-band using a cylindrical TE cavity. Further details of the ESR measurements are given in Ref. 21.

The *g*-values and hyperfine coupling constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for which $g = 2.0055 \pm 0.0001$ and the nitrogen hyperfine splitting, $a_N = 1.309 \pm 0.001$ mT.[22] A quartz sample tube was used for Fremy's solution (*ca.* 10^{-3} M) that was taped on the exterior of the sample tube.

RESULTS

To obtain an indication about the chemical nature of the Cu present in III, this boundary material was analysed by both AAS and emission spectrography for Cu determination at various stages of demineralization. The results are given in Table

Ia. It is obvious that the Cu occurs in various forms, including adsorbed on smectite (50%) and organically bound within the kerogen (30%). Schmitz *et al.*[23] presented data on the Stevns Klint boundary samples, in which the Cu content was as high as in our case. According to these authors, 30% of total Cu is associated with the III kerogen. The kerogen Cu contents were determined by both INAA and ICP-AES and the results are summarized in Table Ib. Finally, the ascorbic acid + H_2O_2 test[24] indicates that a very low concentration (<10 ppm) of Cu is resident in the sulfide fraction of III.
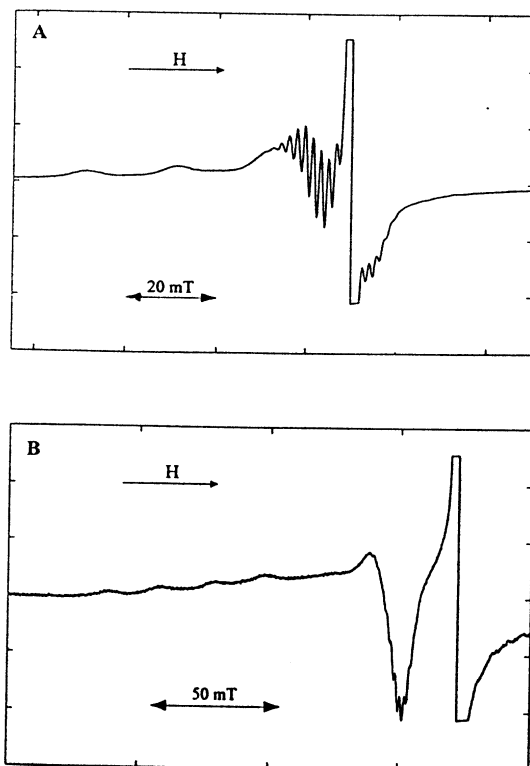

Fig. 1. First-derivative room-temperature anisotropic ESR spectra of Cu^{2+}-P in the III kerogen: a) X-band; b) Q-band[20] spectra. Anisotropic hyperfine Cu^{2+}-P parameters are: $A_{||}$ = 19.9 ± 0.1 mT; $A_\perp$ = <*1.0 mT*; $g_{||}$ = 2.189 ± 0.002; $g_\perp$ = *2.039* ± 0.001; a^N = 1.45 ± 0.10 mT.

The III kerogen occurs typically as organic laminae when viewed perpendicular to the bedding. EDX spectra of areas which are substantially free of Si, Al, Ca and Fe always show S as the major component and sometimes with Cu as a minor component. Electron microprobe analyses of the III kerogen showed S (up to 3%) and Cu (up to 1000 ppm). These results are consistent with the previously known organic associations of Cu.[16] The association of Cu with kerogen in different sediment types is not a rare phenomenon and is discussed in a number of articles. For instance, Patterson *et al.*[25] showed that Cu in the Julia Creek bituminous shale (Australia) is closely associated with kerogen. According to these authors, the Cu

is associated mainly with sulfides (75% of the total Cu) and to a lesser extent with kerogen (12%) and clay (10%).

The X-band (Fig. 1a) and Q-band (Fig. 1b) ESR spectra of the III kerogen are typical of Cu^{2+}-P. The X-band spectrum resembles that Cu^{2+}-P associated with recent soils[4-6] and paleosols.[7] The Cu^{2+}-P in the III kerogen (Fig. 1a) consists of four lines which are almost equally spaced, but not of equal width. These lines are attributed to the Cu nucleus, which has a nuclear spin of 3/2. Superimposed on each Cu hyperfine absorption are nine absorptions due to the four N nuclei, each of spin 1 on the narrowest Cu hyperfine line. The spacing of the N hyperfine structure is 1.45 mT. The line widths of the Cu hyperfine lines increase with magnetic field from 8 mT (for the nuclear quantum number $m_I = -3/2$) up to 13 mT (for $m_I = 1/2$). The asymmetry of the Cu hyperfine structure is, partly, attributed to the contribution of the anisotropic nuclear hyperfine interactions to the linewidth.[26] Small-scale ESR experiments on the IV and Nye Kløv kerogens gave similar but not identical results. However, ESR analysis of the Dania kerogen shows no evidence for Cu^{2+}-P above the limit of detection of 20 ppm.

Simulated powder spectra were computed using a Fortran program for $s = 1/2$ systems, modified to include two different hyperfine interactions. The first- and second-order perturbation theories were used for the metal (Cu) and ligand (N) nuclear hyperfine interactions, respectively. The simulated spectra were compared with the experimental ones in order to estimate the anisotropic hyperfine parameters. The best fitted anisotropic hyperfine paramteres (which were adjusted to give best fit of the experimental spectrum) are shown in Fig. 1. We were unable to find evidence for the departure from axial symmetry in either the experimental or simulated spectra.

DISCUSSION

No analysis of the nature of the kerogen in the Fish Clay has been made so far, but it is likely that the kerogen mainly represents the remains of terrestrial (fresh water) algae (*botryococcus*) and to a lesser extent bacteria.[27] The observation that the Cu observed in III occurs in the inorganic fraction and is predominantly associated with the kerogen component of the rock suggests that the origin of the Cu is related to the origin of the III kerogen and its humic precursor(s). According to Premović *et al.*[14] terrestrial humic substances played an important role in terrestrial metal transport and fixation through the III boundary column. These authors also suggested that during the deposition of IV the input of terrestrial humic substances was considerably reduced or ceased to exist at all. The sudden and sharp drop in both the Cu and Cu^{2+}-P contents from III to IV (Table Ib) is in line with such a claim.

Geochemical data and observations provide strong evidence that the III layer was deposited either under anoxic conditions or soon after deposition the conditions became anoxic and H_2S was present in both the layer and the overlying seawater.[14]

In general, the kerogen of this rock type is thought to be derived from lipid-enriched humic substances.[28] One of the most important characteristics of these substances is their high sequestering ability for Cu^{2+}. Humic substances with suitable functional (including porphyrin) groups form coordination complexes with Cu^{2+}. However, under strong anoxic sedimentary conditions (such as those of the Julia Creek black shale) most of the Cu^{2+} is precipitated as sulfides and free Cu^{2+}-P is exceedingly labile;[29] though such conditions preserve porphyrins. On the other hand, in oxic sedimentary environments, Cu^{2+} is the predominant Cu species in aqueous solution which is capable of metallating humic porphyrin sites. If this is correct, we can only surmise that Cu^{2+} chelation by humic porphyrin sites must occur in oxygenated freshwaters prior to entering the III marine KT deposition milieu. The fact that $< 2\%$ of total Cu in the III layer is present as sulfides support such a contention and indicates that Cu^{2+} incorporation into porphyrin site(s) of terrestrial humic materials just preceded the redeposion of these substances into the marine Stevns Klint KT Basin.

TABLE I. Geochemical data for the III and IV boundary layers

(a) The III layer

Fraction	Sediment [±5%]	Cu^a [± 10 ppm]	Total Cu [%]
Carbonate	40	10	5
Sulfide	<2	<10	<1
Smectite	30	150	50
Silicate	25	50	15
Kerogen	3	800	30
Sediment	100	86^b 100^c	100

[a]The Cu content determined by AAS; [b]The Cu content obtained by summation of the fraction Cu concentrations, determined by AAS; [c]The Cu content determined by emission spectrography[14]

(b) The III/IV layers

Total sediment [± 0.5%]		Cu[± 50 ppm]	Cu^{2+}-P[±100ppm]^a
Kerogen III	3.0	700^b 750^c	4000
Kerogen IV	0.3	400^b 450^c	2000

[a]The Cu^{2+}-P content determined by ESR.[14] The Cu^{2+}-P content calculated from the Cu^{2+} concentration using 440 as the average porphyrin molecular weight;[8] [b]The Cu content determined by ICP-AES; [c]The Cu content determined by INAA

Relative abundance of VO^{2+} and the absence of kerogen VO^{2+}-P in the III layer,[14] as well as the high concentration of the III kerogen Cu^{2+}-P are indications that the kerogen Cu^{2+}-P within the III layer is strictly detrital in character, *i.e.*, was transported to the III deposition site already contained in humic materials (as the III kerogen precursor(s)). The general absence of Cu^{2+}-P in sediments from shallow marine depositioinal paleoenvironments with abundant VO^{2+}-P (*e.g.*, sedimentary

millieu of the Julia Creek rock) is consistent with such rationalization. The III kerogen has a surprisingly low atomic H/C ratio (0.9) and a high O/C ratio (>0.3), which indicate intensive (surface) oxidation. Kerogen typically has a relatively high H/C atomic ratio and a low O/C atomic ratio. The concentration of oxygen-containing molecules and the possible contribution of oxygen from surface oxidation and degradation could readily produce H/C < 1 and O/C > 0.3 in the III kerogen before its rapid burial in the Stevns Klint Basin during the KT event.

The kerogen concentrate of the Nye Kløv boundary sediment contains also a relatively high Cu^{2+}-P (< 1000 ppm). This rock was deposited in the same marine basin, although separated by about 300 km from the Stevns Klint location. This fact indicates that the redeposition of the kerogen Cu^{2+}-P came from a common source(s) at a considerable distance. However, in contrast to the III layer the Nye Kløv analogue was redeposited in aerated (oxic) seawater.[14] These facts are in accordance with the detrial hypothesis for the kerogen Cu^{2+}-P which was displaced from its original deposition site and ponded in the Danish KT Basin.

The Kupferschiefer shale is thought to have accumulated in anoxic bottom waters of a shallow, stratified epicontinental sea, the Zechstein Sea (Germany/Poland).[30] The high content of amorphous (laminated) organic matter is derived mainly from algae/cyanobacteria, and to lesser amount from green sulphur bacteria (*Chlorobiceae*).[31] The X-band/Q-band ESR spectra of the kerogen Cu^{2+}-P from the Kupferschiefer rock samples are similar to those of the Fish Clay samples, although the kerogen Cu^{2+}-P contents were lesser (< 2000 ppm). However, in contrast to the Fish Clay, the Kupferschiefer rock contains high concentrations of both VO^{2+}-P and Ni^{2+}-porphyrins (> 3000 ppm).

Organic/inorganic geochemical studies by Püttmann *et al.*[32,33] indicate that the Kupferschiefer Basin acted as a geochemical trap. Accordingly, Cu^{2+} was accumulated in the Kupferschiefer location from ascending oxidizing solutions (brines) which transported high amounts of the metal ion from L. Permian red beds into the Kupferschiefer Basin. Nevertheless, given the high concentrations of VO^{2+}-/Ni^{2+}-porphyrins, it seems more likely that the kerogen Cu^{2+}-P are detrital. In other words, we suggest that the kerogen Cu^{2+}-P in the Kupferschiefer originated, also, from an external humic source(s) that contributed to the high content of these species.

One of the biggest problems of the Danish KT boundary layers has been the many speculations on and search for the (ultimate) source rocks of terrestrial metals (such as red beds or metal-bearing volcanics) which are missing in the Danish KT Basin.[14] From available geochemical data, it appears that the Fish Clay and the Kupferschiefer shale exibit a striking resemblance in geochemical fine details. For instance, in both rocks the bulk of Ir (and other platinum metals) is associated with the kerogen fraction: a value of 600 ppm is reported by Kucha[34] in the Kupferschiefer kerogen and 590 ppm in the III kerogen.[23] Considering that the Fish Clay and Kupferschiefer rocks belong to the same Zechstein Basin and they are separated

from each other by only 400 km[34] then these geochemical similarities (including the ubiquitous presence of the kerogen Cu^{2+}-P) might not be after all a mere coincidence. In our opinion, the striking similarities between the Fish Clay and the Kupferschiefer shale show that these two rocks are somehow generically related.

Results, to date, lead us to propose that the enhanced erosion of near-by terrestrial Kupferschiefer accumulations during or immediately after extraterrestrial-caused KT event is the prime force in translocating terrestrial metals to marine KT boundary sediments of the Danish Basin. At the moment this suggestion remains an open question and we have to wait until more geochemical data on both the Danish KT boundary sedimentary rocks and the Kupferschiefer rock are available for a more substantiated interpretation.

CONCLUSIONS

(1) High concentrations of both Cu (up to 1000 ppm) and Cu^{2+}-P (up to 4000 ppm) have been found in the kerogen structures of the Danish KT boundary layers (the Fish Clay) at Stevns Klint and Nye Kløv.

(2) It is suggested that the kerogen Cu^{2+}-P are derived from the enhanced erosion of terrestrial humic accumulations (*e.g.,* peats/soils) during or after the extraterrestrial caused KT event.

(3) Similar the kerogen Cu^{2+}-P have been detected in near-by L. Permian Kupferschiefer shale from Poland.

(4) The striking similarities (in some fine geochemical details) between the Danish KT boundary rocks and the Kupferschiefer rock imply that these rocks are generically related.

И З В О Д

КРЕДА-ТЕРЦИЈАР ГРАНИЧНИ СЛОЈ НА ЛОКАЛИТЕТУ STEVNS KLINT (ДАНСКА):
БАКАР И БАКАР(II) ПОРФИРИНИ

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Детектоване су високе концентрације бакар(II) порфирина (до 4000 ppm) у керогенима креда/терцијар (КТ) граничног типа седимента, Рибља глина на локацији Stevns Klint, Данска. Ови пигменти су такође нађени у данском КТ седименту на локацији Nye

Kløv која је удаљена око 300 km од Stevns Klint-a. Међутим, нисмо успели да детектујемо бакар(II) порфирине у данској граничној стени из Dania предела који је удаљен око 200 km од Stevns Klint-a. Предложено је да керогенски бакар(II) порфирини потичу од хумичних материјала из копнених извора (тресет/земљиште), већ обогаћених овим једињењима, депонованих у данском KT басену. Наши резултати показују да су керогенски бакар(II) порфирини присутни у пермским Kupferschiefer шкриљцима из Пољске у количинама које се могу упоредити са онима из керогена Рибље глине. По нашем мишљењу, процеси који су контролисали обогаћење керогенским бакар(II) порфиринима Stevns Klint граничног седимента су одговорни и за висок садржај ових пигмената у Kupferschiefer-y.

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