ELSEVIER

Earth and Planetary Science Letters 177 (2000) 105–118

EPSL

www.elsevier.com/locate/epsl

Copper and copper(II) porphyrins of the Cretaceous–Tertiary boundary at Stevns Klint (Denmark)

Pavle I. Premović[a,*], Nikola D. Nikolić[a], Ivana R. Tonsa[a],
Mirjana S. Pavlović[b], Miroslav P. Premović[a], Dejan T. Dulanović[a]

[a] *Laboratory for Geochemisty and Cosmochemistry, Department of Chemistry, Faculty of Science, University of Niš, P.O. Box 91, 18000 Niš, Yugoslavia*
[b] *Institute of Nuclear Sciences Vinča, P.O. Box 522, 11001 Belgrade, Yugoslavia*

Received 10 February 1999; received in revised form 21 September 1999; accepted 28 January 2000

Abstract

High levels of copper(II) (Cu^{2+}) were found with the major part (> 90%) of the total Cu located in the smectite (Cu: 175 ppm) and kerogen (Cu: up to 1000 ppm) of the basal black marl of the Cretaceous–Tertiary (KT) boundary informal type sedimentary rock: the Fish Clay at Stevns Klint, Denmark. Anomalous abundance (4000 ppm) of the kerogen Cu^{2+}-porphyrins in this marl was detected by electron spin resonance. A model is proposed in which the enormous acid rains (caused by the KT asteroid impact) washed out the humics (already enriched with Cu^{2+}/Cu^{2+}-porphyrins) of the top horizon of the nearby oxic soil into the Fish Clay Basin during the KT event.

Keywords: copper; porphyrins; K–T boundary; electron paramagnetic resonance; smectite; kerogen; acid rain

---

1. Introduction

During the debate about the Stevns Klint Cretaceous–Tertiary (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. [1] attributed the metal enrichment in the Fish Clay at Stevns Klint (hereinafter referred to as the Fish Clay) to an accumulation of mainly terrigenous material with minor amounts of clay minerals of diagenetic origin. These authors subdivided this boundary rock into four beds from the bottom bed II (Maastrichtian grey marl) to the top bed V (Danian Cerithium limestone) with the basal (Maastrichtian) bryozoan chalk as the bed I.

In a benchmark paper, Alvarez et al. [2] attributed the anomalous concentrations of Ir (and other so-called meteoritic/partly meteoritic metals) in the Fish Clay to global fall-out of extraterrestrial materials. According to these authors, this sedimentary accumulation was produced by the impact event and reflects an intimate mixture of the meteoritic and impact ejecta. In the following 10 years, such Ir anomalies have been detected almost all over the world, in both hemispheres

---

* Corresponding author. Fax: +381-18-46-460; E-mail: pprem@gea.ciens.ucv.ve

PII: S0012-821X(00)00030-3

and in marine and continental sections [3]. Kyte et al. [4] suggested that only beds III and IV (hereinafter referred as III and IV) of the Fish Clay can be used to estimate the primary asteroidal fallout. As an alternative to the extraterrestrial hypothesis, a volcanic model was proposed for the Ir abundance in the Fish Clay beds [5]. None of the above theories, however, explain all of the observed features of the Danish KT boundary rocks.

Geochemical analyses of the Fish Clay beds revealed that not only Ir (and other meteoritic/partly meteoritic metals), but also non-meteoritic (terrestrial) trace metals (such as Cu and V) are also present in these materials [1,4,6]. Whilst considerable attention has been paid to meteoritic metals present in the Fish Clay, less regard has been given to terrestrial metals (e.g. Cu).

The Cu concentration in the Earth's crust ranges from 24 to 55 ppm, in soils from 20 to 30 ppm and in carbonaceous sedimentary rocks from 20 to 200 ppm. In the Fish Clay, the Cu content ranges from 50 to 80 ppm [1,4,7] and, thus, is of the same order of magnitude as in other carbonaceous sedimentary rocks [8,9]. Sedimentary Cu is usually associated with organic matter, Fe/Mn oxides, clays and other minerals [8]. The distribution and chemical nature of Cu in III were thus studied with the object of gaining some further insight into the geochemistry of Cu during the III forming process. Interest was particularly centered on terrestrial sources of Cu.

The foundation of modern organic geochemistry is associated with Treibs' suggestion that sedimentary extractable (alkyl) metalloporphyrins are principally the diagenetic end products of chlorophylls and bacterio-chlorophylls [10]. Nickel(II) (Ni^{2+}) and vanadyl (VO^{2+}) alkyl porphyrins are the two principal types of metalloporphyrins found in carbonaceous sedimentary rocks. Recent electron spin resonance (ESR) work in our laboratory has shown that kerogens isolated from ancient carbonaceous sedimentary rocks of marine origin also contain significant amounts of VO^{2+} porphyrins (VO^{2+}-P) incorporated into the kerogen structure. 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 [11].

Although the widespread occurrence of VO^{2+}-P and Ni^{2+}-P in ancient sedimentary rocks from different depositional environments has been reported, there are few reports of porphyrins complexed to Cu^{2+}. The occurrence of extractable Cu^{2+}-P is perhaps best authenticated by Palmer and Baker [12] and Baker and Louda [13,14] who isolated such species in very low concentrations (< 1 ppm of the total organic C) from a number of immature sedimentary rocks, giving evidence based on accurate mass spectrometric measurements. Palmer and Baker [12] and Baker and Louda [13,14] proposed that these Cu^{2+}-P may derive from, and be markers for, oxidized terrestrial organic matter redeposited in a marine environment.

Previous geochemical studies of humic substances (i.e. humic and fulvic acids) of soils (including peat soils) have shown large differences between humic fractions; though these substances cannot be regarded as distinctly different, but merely as part of a continuum of compounds varying in both polarity and molecular weight [15]. On the other hand, despite the fact that the fulvic acids of soils contained a significant percentage of the total Cu, an extremely weak ESR signal ascribed to Cu^{2+} was observed. This signal was attributed to Cu^{2+}-non-porphyrin complexes in which Cu^{2+} is coordinated with the oxygen atoms of the fulvic carboxylic groups. Cu^{2+}-P are found in (insoluble-acid hydrolyzed) humic acid fractions in a wide variety of organic-rich soils: recent soils (including peat soils) [16–18] and paleosols [19]. It has been suggested that these humic Cu^{2+}-P are largely derived from the plant chlorophylls of soil under oxidizing conditions.

We also report here an anomalous high concentration of Cu^{2+}-P (4000 ppm: determined by ESR) incorporated into the kerogen structure of III. The Nye Kløv and Dania boundaries in the Jylland sequences near Stevns Klint were, also, investigated by ESR spectroscopy for the presence of Cu^{2+}-P in kerogen. These boundary layers are mineralogically identical to that at Stevns Klint [20].

2. Experimental

The experimental techniques/methods have already been described earlier [6]. ESR experiments (at room temperature) were performed using Varian X-band [6] and Q-band [21] spectrometers.

Hyperfine splitting constants and *g*-values for all X- and Q-band spectra were measured from line positions and corrected for second-order effects. Refinements of these values were accomplished by computer simulation of the spectra using a program for spin quantum number $s = 1/2$ systems.

3. Geochemical association of Cu

To obtain an indication about the chemical nature of the Cu present in III, this boundary material was analyzed for Cu by both atomic absorption spectrometry (AAS) and emission spectrometry at various stages of demineralization. The results are given in Table 1. It is obvious that Cu occurs in various forms, including adsorbed on the smectite ($>60\%$ of the total Cu) and organically bound within the kerogen (ca. 30% of the total Cu). Finally, the ascorbic acid+H_2O_2 test [22] indicates that a very low concentration (10 ppm) of Cu is resident in the sulfide fraction of III. For comparison, we list in Table 2 the Cu contents of smectite of other four beds of the Fish Clay and of the KT boundary rocks from other than the Stevns Klint locality: for the Nye Kløv/Dania sites. The Cu contents of the Nye Kløv/Dania kerogens could not be estimated, however, due to the small size of the kerogen samples. The Cu contents of the III/IV kerogens were also determined by instrumental neutron activation analysis (INAA) and the results are summarized in Table 3. Although the INAA data of Cu seem to be systematically lower than the AAS data [23] both values overlap considering the analytical uncertainties. Schmitz et al. [24] also analyzed the Fish Clay beds for Cu and their Cu values are consistent with our values. Besides the Fish Clay the other two most Ir-rich marine KT boundaries are found at Caravaca (Spain) and at Woodside Creek (New Zealand). It is of interest that the clay/organic fractions of the beds of these two boundaries contain enhanced concentrations of Cu (up to 310 ppm) [7].

The X-band (Fig. 1a) and Q-band (Fig. 1c) ESR spectra of the III kerogen are typical of Cu^{2+}-P. The X-band spectrum resembles that of the Cu^{2+}-P associated with the above mentioned organic-rich recent soils [16–18] and paleosols [19]. The ESR spectrum of 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 linewidths 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

Table 1
Geochemical data for the Danish KT boundaries: III

Fraction	Sediment (±5 wt%)	Cu[a] (±25 ppm)	Total Cu (±5 wt%)
Carbonate	< 50	30	< 20
Sulfide	5	10	< 1
Smectite	30	175	> 60
Kerogen*	3	800	30
Sediment	100	90[b] 80[c]	100

*Elemental analysis (%): C: 63.0, H: 5.1, N: 1.4, S: 1.6 and O: ca. 29 (by difference); H/C: 1.0, O/C: >0.3 and N/C: 0.2.

[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.

Table 2
Geochemical data for the Danish KT boundaries: kerogen and smectite of the KT boundary layers

The Fish Clay beds	Geochronology	Lithology	Thickness (cm)	Kerogen (wt%)	Cu* (ppm)	V*[a] (ppm)	Cr*[a] (ppm)	Ir*[b] (ppb)
V	Danian	chalk	–	n.a.	55	–	145	n.a.
IV	Danian	marl	6.0	0.5**	75	170	280	54
III	Danian	marl	3.0	3.0**	175	195	380	77
II	Danian	marl	1.0	<0.2	35	80	280	10
I	Maastrichtian	bryozoan chalk	–	n.a.	35	–	135	–
Nye Kløv*	Danian	marl	–	<0.1**	<50	180	470	–
Dania	Danian	marl	–	<0.1	<50	200	190	–

*In the smectite fraction.
**Kerogen enriched with Cu^{2+}-P.
n.a., not analyzed.
There is a systematic uncertainty of 10–20% for each metal.
[a] Premović et al. [6].
[b] Elliot [50].

anisotropic nuclear hyperfine interactions to the linewidth [25]. Small-scale ESR experiments on the IV/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 ESR spectra of the Cu^{2+}-P (Fig. 1b,d) were computed 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 anisotropic hyperfine parameters (which were adjusted to give the best fit of the experimental spectra, Fig. 1a,c) are shown in Fig. 1. We were unable to find evidence for the departure from axial symmetry in either the experimental or simulated spectra.

4. Boundary seawater and Cu^{2+}

Of importance is that the syngenetic carbonate fraction of III contains a very low concentration (<30 ppm) of Cu (Table 1). Microscopic inspection of a thin section of III indicates that it contains predominantly calcite ($CaCO_3$) derived exclusively from calcerous algal plates (coccoliths $>95\%$). The Cu^{2+} ion is characterized by an ionic radius of 1.00 Å [26]. Thus, Cu^{2+} may substitute for the Ca^{2+} ion in the calcite matrix since both have the same charge [27,28]. This would involve the direct incorporation of Cu^{2+} from the Danish KT seawater into the III calcite or metabolic uptake by the coccolith organisms. The low Cu concentration of III (<30 ppm) in the biogenic calcite phase, which is comparable with those in the beds II/V [22], indicates that Cu^{2+} was not present in enhanced concentration in the KT seawater of the Fish Clay Basin. On the other hand, the con-

Table 3
Geochemical data for the Danish KT boundaries: III/IV

	Sediment (± 0.5 wt%)	Cu (± 50 ppm)[a]	Cu^{2+}-P (± 100 ppm)[b]	Cu (± 50 ppm) as Cu^{2+}-P	Fraction (wt%) as Cu^{2+}-P
Kerogen III	3.0	600	4000	550	>90
Kerogen IV	<0.5	200	>1000	–	–

[a] The Cu content determined by INAA.
[b] The Cu^{2+}-P content determined by ESR [23]: the Cu^{2+}-P content calculated from the Cu^{2+} concentration using 440 as the average porphyrin molecular weight [14].

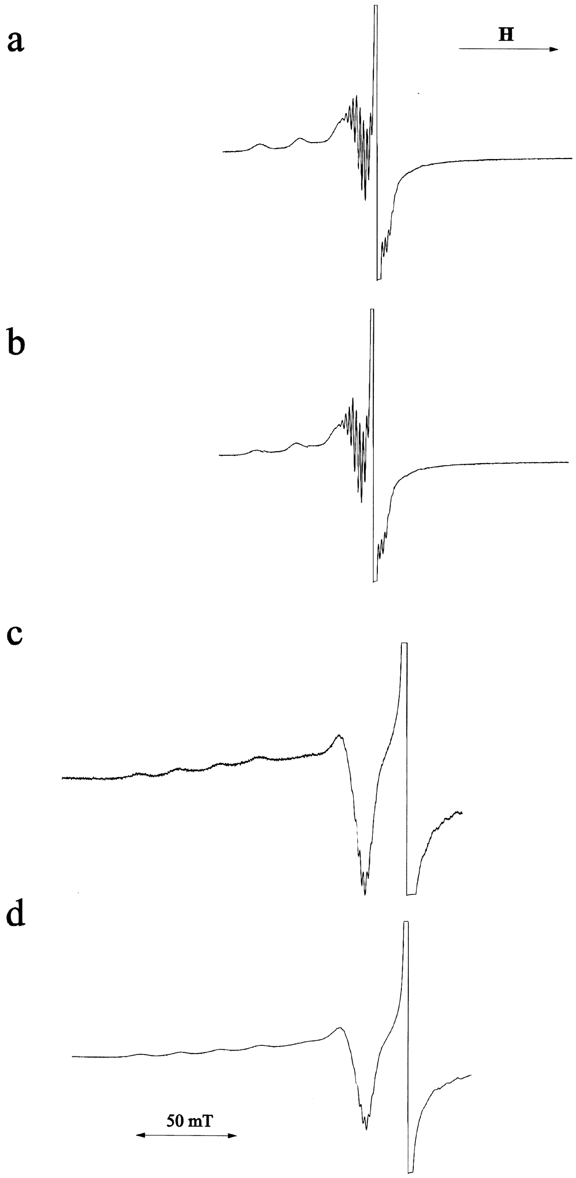

Fig. 1. First-derivative room-temperature anisotropic ESR spectra of Cu^{2+}-P in the III kerogen: (a) experimental X-band; (b) simulated X-band; (c) experimental Q-band and, (d) simulated Q-band [21] spectra. Anisotropic hyperfine Cu^{2+}-P parameters are: $A_{\parallel} = 19.9 \pm 0.1$ mT; $A_{\perp} < 1.0$ mT; $g_{\parallel} = 2.189 \pm 0.002$; $g_{\perp} = 2.039 \pm 0.001$ and $a^{N} = 1.45 \pm 0.10$ mT.

centration of Cu is ca. 3×10^6 times (in the III kerogen) and 6×10^5 times (in the III smectite) its concentration (0.3 ppb: mainly as Cu^{2+}) in average seawater [29].

5. Boundary kerogen

According to Hansen et al. [30] and Schimtz et al. [24] the III kerogen mainly represents the remains of freshwater algae (*Botryococcus*), brackish dynocysts and marine green algal group of prasinophytes. The dominant phase of the III kerogen concentrate is organic matter: of the 3% III (Tables 1–3), which survived laboratory demineralization procedure, about 97% consists of organic matter. Elemental analysis (Table 1) shows that the III kerogen has a low atomic H/C ratio (1.0) and a high O/C ratio (>0.3) and these values are characteristic of a transitional type II–III kerogen. A well-preserved marine kerogen typically has a relatively high atomic H/C ratio (≥ 1.2) and a low atomic O/C ratio (<0.1) [31]. The low H/C and high O/C values obtained for the III kerogen infer dilution of the marine kerogen (derived from water-column photosynthate) by terrestrial kerogen (derived from terrigenous humics with low H/C). As a rule, the terrigenous component of the transitional type of kerogen is derived essentially from terrestrial humic substances of organic-rich soils [31]. There are, however, alternative origins of this type of kerogen: it may be either reworked/oxidized kerogen from older marine sedimentary rocks or kerogenous material which was exposed to subaerial weathering (including forest fire/biological oxidations). According to Wolbach et al. [32] the III kerogen concentrate contains: a predominantly ($>90\%$) highly resistant kerogen of terrestrial origin and a reactive kerogen of ma-

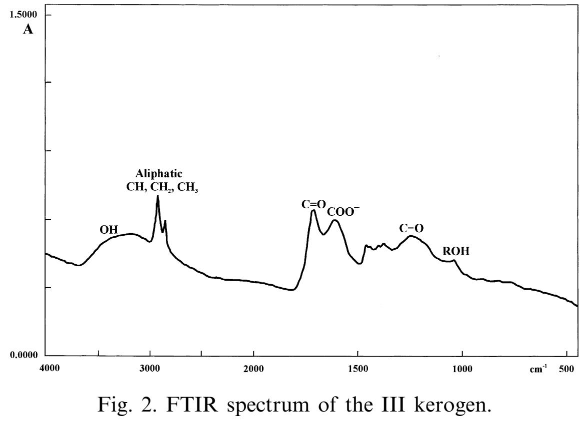

Fig. 2. FTIR spectrum of the III kerogen.

rine origin and a minor amount ($<1\%$) of elemental carbon particles which resemble soot/charcoal from forest fires or marine sedimentary rocks. In other words, the kerogen components within III have more than one origin, i.e. the III kerogen is therefore a hybrid or polygenetic material.

The FTIR spectrum of a representative sample of the III kerogen is presented in Fig. 2. The assignment of the most characteristic bands in this spectrum is based on the FTIR spectra of coals and kerogens [33]:

1. The broad band centered around 3400 cm^{-1} is due to OH groups.
2. The peaks around 2920 and 2850 cm^{-1} are due to aliphatic, CH, CH_2 and CH_3, groups.
3. The band around 1700 cm^{-1} is due to $C=O$ of carbonyl and carboxyl groups.
4. The band at 1550–1600 cm^{-1} is characteristic for ionized carboxyl groups (COO^-).
5. The band around 1250 cm^{-1} is characteristic for C–O of phenolic groups.
6. The band around 1050 cm^{-1} is presumably due to alcohol groups (ROH).

In conclusion, it may be stated that the FTIR spectrum of the III kerogen is similar to the spectra of terrestrial immature kerogens (including lignites and subbituminous coals) and reworked/oxidized kerogens [33].

6. Cu^{2+}/Cu^{2+}-P within the boundary kerogen

Electron microprobe spectra of the III kerogen 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 this kerogen showed S (up to 3%) and Cu (up to 1000 ppm). The association of Cu with kerogen in different sedimentary rock types is not a rare phenomenon and is discussed in a number of articles. For instance, Patterson et al. [22] showed that a portion of the Cu in the Julia Creek bituminous shale (Cretaceous, Australia) is closely associated with the 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 most important result of the laboratory leaching experiment is that Cu/ Cu^{2+}-P show a strong association with the III kerogen. The percentage of the total Cu found in the kerogen concentrates is greater in the kerogen-rich samples (e.g. the III kerogen versus IV kerogen, Table 3). Geochemical analysis also indicates that the III kerogen which contains a significant amount of Cu also contains a significant amount of Cu^{2+}-P, Table 3. These observations infer that the origin of the kerogen Cu/Cu^{2+}-P is related to the origin of the III kerogen, i.e. its humic precursors.

The data in Table 3 indicate that Cu in the III kerogen (600 ppm, determined by INAA) is predominantly in the Cu^{2+}-P form (550 ppm, determined by ESR): it constitutes $>90\%$ of the total Cu. Apparently, the rest of Cu is, at least, 'invisible' for ESR at room temperature. The most plausible explanation is that the 'invisible' Cu is in a diamagnetic state, either as Cu^{2+} in the cluster structures which involves strong Cu–Cu magnetic interactions, or, less probable, as Cu^{1+} which has no unpaired electron. Indeed, the redox diagram for Cu [34] indicates that, regardless of physicochemical conditions (i.e. oxic versus anoxic milieu) in natural waters, Cu^{2+} is the only Cu ion available for incorporation into the humic structures and the smectite skeleton.

7. Detrital nature of the kerogen Cu^{2+}-P

Geochemical data provide strong evidence that III 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 [6]. In most cases, the kerogen of this rock type is thought to be derived from humic substances with suitable functional (including porphyrin) groups which may form coordination complexes with Cu^{2+} [35]. However, under strong anoxic sedimentary conditions (such as those of the Julia Creek black shale) most of Cu^{2+} is precipitated as sulfides; Cu^{2+}-P is exceedingly labile under these conditions [36], but they preserve porphyrins [37]. The general absence of Cu^{2+}-P in sedimentary rocks from shallow marine depositional paleoenvironments (e.g. the Julia Creek carbonaceous rock) is consistent with such a rationalization. In other words, the anoxic sedimentation conditions of III were rather unfavorable for the formation of the kerogen Cu^{2+}-P. The evidence which supports the idea that the kerogen Cu^{2+}-P were not formed in situ (i.e. within III) is: (a) an exceptionally high concentration (4000 ppm, Table 3) of the kerogen Cu^{2+}-P within III and (b) the low concentration (10 ppm, Table 1) of Cu associated with the sulfide phase of III. These results suggest that the kerogen Cu^{2+}-P are strictly detrital in character, i.e. were transported to the Fish Clay site.

8. Organic oxic soil

In an oxic sedimentary environment Cu^{2+} is readily chelated to humic substances (and is adsorbed on the clay surface), which leads to the enrichment of this ion in the sedimentary rocks (such as III); thus, in this type of environment, Cu^{2+} is capable of metallating humics [35] and their free porphyrins [16,38,39]. If the above reasoning is correct, we can only surmise that Cu^{2+} chelation by the free porphyrins within humic substances had to occur in an aerated aqueous environment (e.g. an organic-rich oxic soil) prior to entering the Fish Clay Basin. As Cu^{2+} precipitates as hydrous oxides under mild acid conditions ($pH \geq 5.1$) [26] this indicates that the soil milieu in which humic Cu^{2+}-P were formed must have been acidic ($pH \leq 5$). According to Palmer and Baker [12] Cu^{2+}-P in marine sedimentary rocks represent a redeposited form of eroded/oxidized pigments originally present in terrestrial organic accumulations (e.g. peats) and were suggested as biomarkers for terrestrial influx. In essence, porphyrins in terrestrial sedimentary rocks are commonly complexed with Cu^{2+} [14]. It is noteworthy that our ESR measurements indicate that the concentration of Cu^{2+}-P in the III kerogen is in the range of 4000 ppm (Table 3), which is, at least, > 4000 times higher than its concentration in organic matter of immature marine rocks studied by Baker et al. [12–14]. On the other hand, the amount of Cu^{2+}-P in the III kerogen is comparable with the Cu^{2+}-P contents of humic insoluble-acid hydrolyzed fractions of recent soils [16–18] and paleosols [19]. Obviously, Cu^{2+}/Cu^{2+}-P in the III kerogen are not homogeneously distributed but are associated with a specific part of this material which originated from its terrestrial humic precursors. Hence, we propose that terrestrial humic substances played an important role in the Cu^{2+}/Cu^{2+}-P transport and fixation through the III column. Indeed, the soil humics show a far greater affinity for Cu^{2+} than marine humic matter [26]. In addition, Goodman and Cheshire [16,38] have shown that the soil humic substances have a relatively great capacity for the uptake of Cu^{2+} as Cu^{2+}-P when they are treated with aqueous solutions containing Cu^{2+} ions.

Controls on accumulation of humic matter in sediments and sedimentary rocks are imperfectly understood and have been a subject of debate for many years [15]. Modern studies of sedimentary tetrapyroles indicate that the free porphyrin content of sedimentary humics is very sensitive to the duration of exposure of these materials to air O_2 [14]. For this reason, long residence time in a partially watered milieu of organic-rich oxic soils may result in relatively low ratios of free porphyrins to total organic matter. In fact, preferential degradation of chlorophylls in oxic soils begins during senescence or shortly after the death of plants [14]. Therefore, a high concentration of Cu^{2+}-P within the III kerogen structure is not expected. However, geochemical studies of metalloporphyrins indicate that metal ions (such as Cu^{2+}) contribute essentially to the chemical stability of the porphyrins in sedimentary environments through geologic time [14]. In consequence, the incorporation of Cu^{2+} into the porphyrin nuclei gives these pigments enough extra-stability to permit their survival even under unfavorable aerobic conditions of oxic soils.

Notable is the absence of V in the III kerogen, a point overlooked in the paper by Premović et al. [6]. Under typical aerobic conditions, the most stable forms of V in aqueous solution are generally vanadate ions $H_nVO_4^{n-3}$ [6]. As a consequence, the V species involved in adsorption processes appear to be anionic, resulting in a relatively low affinity for both sedimentary humic substances [40] and clay minerals [41]. Indeed, laboratory experiments by Shiller and Boyle [40] have shown that complexation by humic materials is not a major factor in determining the aquatic behavior of the $H_nVO_4^{n-3}$ ions. On the other hand, in anoxic/acid media, humic substances may reduce vanadate ions to VO^{2+} accompanied by chelation [6]. Consequently, in an anoxic sedimentary environment, V is almost solely present as VO^{2+} and is available for complexation with both humic substances [42] and clays [43]. Thus, the absence of V in the III kerogen is consistent with the formation of its humic precursors (hereinafter referred as the III humics) in an oxic soil.

9. Redeposition of terrestrial humics

The kerogen concentrate of the Nye Kløv boundary rock also contains 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 [11]. This indicates that the humics (as the progenitors of the III/Nye Kløv kerogens) came from a common source at a considerable distance and were ponded in marine Danish KT Basin. This conclusion is in accordance with terrestrial/detrital hypothesis for these organic materials.

In the light of the above, we suggest that the redeposition of humic substances of a freely drained (oxic) soil, near the Fish Clay Basin, served as the ultimate source of the III kerogen. Supporting this view is the observation that the acid-insoluble mineral fraction of III contains more than 20% of the sand and silt particles (including well-rounded quartz and feldspar grains) of local terrestrial origin ([1,24,44], this work). Indeed, modern studies of sedimentary rocks show that silt in marine sedimentary rocks is mainly of terrestrial origin and most of it is produced during soil formation [26]. Evidently, Cu^{2+} of the III humics must have had its source rock on land from the surrounding area. An exceptionally high concentration of Cu (600 ppm, Table 3) in the III kerogen implies that Cu in the source rock was greater than normal. The leached Cu (as Cu^{2+}) of this rock reached the organic-rich oxic soil near the Fish Clay Basin either through solution, or in-transit adsorption by terrigenous humic material that was carried into the soil by streams draining the source rock area.

Hansen et al. [30] estimated an average sedimentation rate for the bed I (grey chalk) of ca. 7×10^{-3} cm yr^{-1}. If the Fish Clay represents a sudden influx of fine terrigenous material into the basin, then this marl may be considered to represent a more rapid accumulation then a normal deposition of chalk. So, we can probably safely multiply by 10 the sedimentation rate of bed I in order to arrive at an approximate rate of accumulation of III: i.e. 7×10^{-2} cm yr^{-1}. If we conservatively assume that this rate prevailed at the Stevns Klint locality, we calculate that the (maximum thickness) 3 cm of III represents ca. 30 years of sedimentation. In our opinion, even this figure is a considerable overestimate of the actual time for accumulation of III within the Fish Clay deposit.

10. Impact of acid rains

Schmitz [7] suggested that the Danish boundary rocks were probably deposited as a result of a basin wide regression. A strong case for the relation between the oceanic regressive event and the presence of Cu^{2+}-P in marine sedimentary rocks has been previously presented by Baker and Louda [14]. However, the formation of III containing initially humic substances from a soil is difficult to attribute to the regression at the end of the Cretaceous, as it was relatively instantaneous (≤ 30 years) when compared to the lengthy time of the sea withdrawal. Another possibility could be that the KT impact event caused large, rapid (but unpredictable) fluctuations of sea-level depending on the nature of the impact (land, ocean, etc.). For instance, an oceanic impact could produce waves with the initial amplitude of several kilometers [45]. Alternatively, massive draining of a preexisting soil by acid rains caused by either the asteroid impact or volcanic escalations could, also, produce a high influx of humic materials into the Fish Clay Basin during or immediately after the KT event [46]. Prinn and Fegley [46] have, however, argued that the chemical (weathering/leaching) effects of such volcanism would be much less severe than those of the impact produced nitrogen(II) oxide (NO), largely because of the slow rate of volcanic addition.

It is also noteworthy here that the presence of kerogen (enriched with Cu^{2+}/ Cu^{2+}-P) in the Fish Clay commences abruptly with III (Table 2). This is consistent with the abrupt input of terrestrial humic materials into the Fish Clay Basin during the KT event suggested by Premović et al. [6]. These authors also proposed 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 the kerogen content (Table 2), the kerogen Cu^{2+} content (Table 2) and the Cu^{2+}-P content (Table 3) from III to IV is in line with such a claim. These observations are very compatible with the sudden effects of a large meteoritic KT impact. Indeed, all experimental studies have shown that the rate of metal (e.g. Ir) enrichment of the Fish Clay was the greatest in early stages of the rock accumulation (i.e. during the KT event) and declined almost exponentially with time after the event.

Experimental studies and observations on modern soils suggest that there is a steady decrease in humic content with the depth through the soil profile. Accordingly, the top (eluvial) horizon usually contains the most of humic materials within a particular soil. Lower horizons are made mainly from mineral matter and contain minor amount of humics [26]. Tentatively, we suggest that the sudden and sharp increase of the kerogen content in the basal black marl (i.e. III) could be explained by abrupt removal of humics of the top horizon which was first washed out from the source soil by the KT acid rains. During the later stages of development the soil detritus from the lower horizons swept in the Fish Clay Basin. This ultimately led to the sharp drop in the kerogen content (i.e. its humic precursors) from III to IV. The inorganic geochemical data on the Fish Clay can thus be reasonably well explained under the hypothesis that this boundary partly represents redeposited materials (by the impact acid rains) of the top horizon of a near-by organic-rich oxic soil.

Simple calculation based on the Cu^{2+}-P content of the III kerogen (Table 3) indicates that about 3% of the total N (1.4%) in this material occurs as Cu^{2+}-P. The large excess of total elemental N over that accounted for the Cu^{2+}-P content of the III kerogen suggests that other metalloporphyrins (e.g. Ni^{2+}-P, Ga^{3+}-P, Mn^{3+}-P or Fe^{3+}-P) or even free porphyrins might be also present within the III kerogen structure; Ga^{3+}-P, Mn^{3+}-P and Fe^{3+}-P were identified in humic coals [14]. This, however, is only a postulate and is supported by circumstantial evidence though relatively high concentrations of Ni and Fe have been detected in the III kerogen concentrate [7]. Wolbach et al. [47] pointed out that in III N is 20-fold enriched over the values of underlying Cretaceous (I/II) or overlying Tertiary (IV/V) beds: the N/C ratio is 0.20 (similar to our value of 0.2, Table 1), compared with 0.03–0.05 in most of the Fish Clay beds. These researchers attributed such an enhanced abundance of N to an enhanced preservation of nitrogen compounds augmented by nitrosylation by HNO_2 from acid rains caused by the asteroid impact.

11. Boundary smectite and Cu

The origin of the III smectite (mainly Mg-smectite) has been variously attributed to the alteration of impact glass [48], to detritus swept in during the sea-level regression [7] or to alteration of volcanic ash [49]. According to Schmitz [7] the abundant presence of the microfossils of dinoflagelletes in III [23] infers a near shore origin of the III smectite as these microplants are brackish- or fresh-water species [7]. Premović et al. [6] suggested that the Danish KT boundary clay represents weathered clay (along with some asteroid/local materials) that was transported to the Danish boundary sites during or immediately after the KT event. These authors claimed that most of terrestrial metals (e.g. V) associated with the

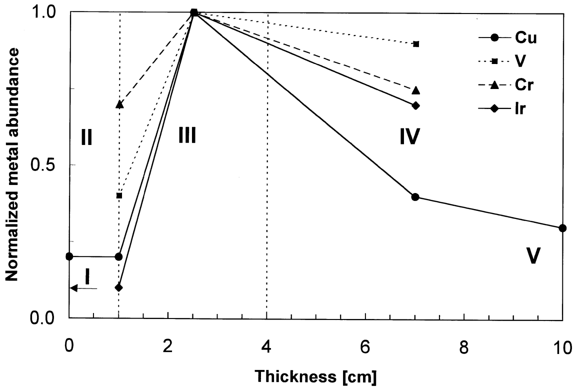

Fig. 3. Distribution of Cu, V, Cr and Ir within the smectite (II, III, IV and V) normalized to the metal content of the III smectite.

smectite fraction are strictly detrital in character, i.e. were transported to the Danish boundary sites already contained in clay.

Table 2 shows the Cu contents within the smectite fractions of the beds I–V of the Fish Clay because the smectite appears to be the major carrier of Cu (Table 1). The difference in the abundance of Cu in the clay fractions of the Fish Clay layers have been noted before by Schmitz et al. [24]. Fig. 3 shows the distribution of the normalized values of the average Cu contents of the smectite within the beds I–V. For comparison, Table 2 lists, also, the contents of: V, Cr (as a typical partly meteoritic metal) and Ir (as a typical meteoritic metal). The normalized average abundances of these three metals are also presented in Fig. 3. Five generalizations can be drawn from the data presented in Table 2 and Fig. 3: (1) the modest Cu enrichment of the Fish Clay smectite begins with the reduced black marl III, but not with the lower (underlying) layers I/II; (2) the III smectite is only 2.5 times higher in Cu than the average sedimentary clay (50–70 ppm [8,9]); (3) the III smectite is enriched in Cu by 5 times in comparison with smectite in the beds I/II below III; (4) the smectite within the beds IV/V above III always contains more Cu than its counterpart in the layers I/II below III; and (5) analytical data for V and Cr [6] and Ir [50] show that the III smectite is enriched 2.5 times (V), >2 times (Cr) and >7 times (Ir) in comparison with smectite of the underlying bed II. In short, these results indicate that Cu, V, Cr and Ir show similar and moderately pronounced abundance peak in the smectite fraction of III.

Despite the fact that the III smectite contains more than half of the total Cu no ESR signal characteristic for Cu^{2+} within the III smectite skeleton is observed. The most likely reason is that almost all of Cu is in a diamagnetic state, as Cu^{2+} in the cluster structures which involves strong Cu^{2+}-Cu^{2+} magnetic interactions.

12. Separate formation of humics and smectite

The absence of V in the III kerogen and the abundant presence of both V (195 ppm) and VO^{2+} (215 ppm) in the III smectite [6,23] imply that the III humics and the III smectite had different sites of formation. Sedimentary clays originated in oxic soils rarely exist in pure form; they usually have a high content of hydrous oxide precipitates of Fe, Al and Mn linked to them. They occur in the clay-size (<2 μm) fraction and are usually mixed with clays. However, in the more rigorous weathering environment (e.g. in a tropical climate of the Fish Clay Basin during the late Cretaceous) these oxides may often be even more abundant than clay minerals in a sedimentary rock [26]. On the contrary, our mineralogical analysis indicates that the III smectite is extremely pure containing only trace amounts of illite and non-phyllosilicate minerals strongly arguing for the separate sites of formation of the III humics and the III smectite. Another piece of evidence for the separate formation sites of these two sedimentary components of the Fish Clay is the low chemical stability of Cu^{2+}-P in contact with the smectite due to a facile demetallation of Cu^{2+}-P in the presence of clays [51].

13. Separate origins of Cu^{2+} and VO^{2+}: primary/secondary nature

Modern studies of the behavior of trace metals in various environments indicate that V shows a high mobility in either neutral or alkaline milieu (as $H_nVO_4^{n-3}$) and a medium mobility in reducing media (as VO^{2+}) [6]. It should be noted that the smectites are largely derived from volcanic materials (including glass) and their formation from parent volcanoclastic materials frequently takes place in an alkaline environment [52]. This might especially be true for the Fish Clay which contains pyroclastic labradorite and Mg-smectite thought to have been produced by basaltic volcanism [6]. Our recent ESR analysis indicated that 85% of the total V (195 ppm) in the III smectite occurs as VO^{2+} (215 ppm) [23]. According to Premović et al. [6] the V abundance in III may be related largely to terrestrial source(s) which are crustal and mantle (volcanism, hydrothermalism). These authors concluded that VO^{2+} within the III smectite is of the primary origin, i.e. it was incorporated into the clay skeleton during the smectite genesis. Also significant is that the Cu^{2+} and VO^{2+} incorporation into the smectite structure generally seems to be mutually exclusive: the incorporation of Cu^{2+} into the smectite skeleton requires an oxic milieu and VO^{2+} a more reducing environment. Thus, the results reported herein imply separate origins for Cu^{2+} and VO^{2+} within the III smectite. The fact that no joint occurrence of Cu^{2+} and VO^{2+} in the clays or the clay fractions of sedimentary rocks has been ever reported strongly supports such a contention.

Unlike VO^{2+}, Cu^{2+} shows a medium degree of mobility only in an oxidizing/acid environment (e.g. acid rains). Considering that the Cu^{2+} and VO^{2+} probably had separate origins and that VO^{2+} is likely to be the primary ionic constituent of the III smectite, it is almost certain that Cu^{2+} is of the secondary nature, i.e. it was introduced into the III smectite (formed elsewhere) rather than a syngenetic ionic entity. This incorporation probably took place during the clay emplacement (from its original site to the Danish KT boundaries). Relatively high concentrations of Cu of the smectite and the kerogen within III imply that the source of Cu of this smectite and the III humics was probably the same. It is, also, possible to speculate that a transmetallation reaction between Cu^{2+}-P of redeposited humic substances and the clay was responsible for the Cu enrichment of the III smectite. However, the fact that the kerogen content of III is ca. 10 times lower than the smectite content excludes such a possibility.

Going on the assumption that the III kerogen is derived through the redeposition of humic materials of an oxygenated soil into the Fish Clay Basin (as we suggested above), we offer the following model (illustrated in Fig. 4) as a first approximation to the processes involved.

During or immediately after the KT impact event acid rains weathered out the smectite from its original site (which was probably located near the Fish Clay Basin) on elevated land and ponded

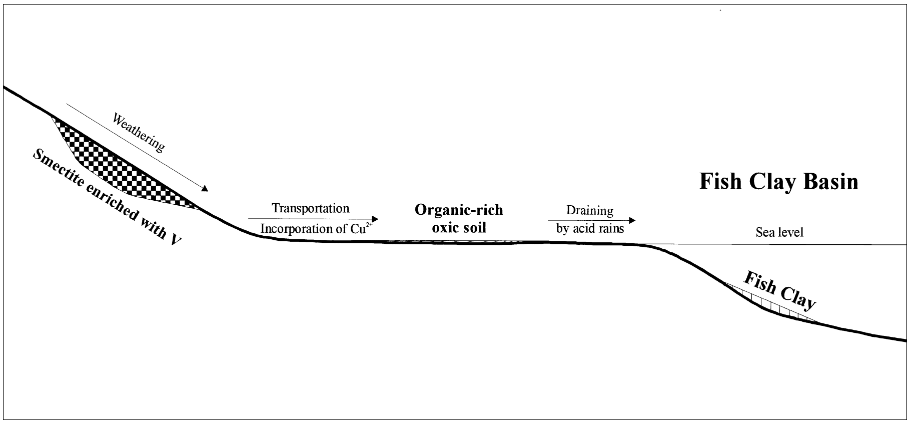

Fig. 4. Proposed model for geochemical relations between the smectite (enriched with V), the organic-rich oxic soil and the Fish Clay Basin.

it into the basin. Simultaneously the near-by oxic soils abundant in humics (likely in the form of collodial materials) enriched with Cu^{2+}-P then were washed away by these rains to its present day sedimentary locations (such as Stevns Klint/Nye Kløv).

14. Conclusions

From the above we can draw the following conclusions:

1. High concentrations of Cu were found in the kerogen (Cu: up to 1000 ppm) and the smectite (Cu: 175 ppm) of the basal black marl (i.e. III) of the Fish Clay at Stevns Klint, Denmark.
2. Anomalous high content (4000 ppm) of Cu^{2+}-P was detected in the III kerogen by electron spin resonance.
3. It is suggested that the III kerogen derived from the humics (already enriched with Cu^{2+}/Cu^{2+}-P) of an oxic soil near the Fish Clay Basin. The analysis of Cu^{2+}-P within the III kerogen was a critical result prompting this conclusion.
4. A model is proposed in which enormous acid rains (caused by the KT asteroid impact) redeposited the humics of the top horizon of the near-by oxic soil into the Fish Clay Basin.
5. Geochemistry of V and VO^{2+} within the III smectite and mineralogical data of this clay imply that the III humics and the III smectite had different sites of formation.

Acknowledgements

This work is dedicated to the memory of Professor Slobodan Ristić who passed away during 1993 and will be missed by all, especially those of us who were his students. We are thankful to both the IPG Institution (France) and Ministry of Science and Technology (Serbia) for the support of this work. Funding support from le Ministère français de l'Education National, de l'Enseignement Superieur et de la Recherche to P.I.P. for his stay at Université Pierre et Marie Curie (Paris) is gratefully acknowledged. We are also indebted to the donor of the KT samples Dr. H.J. Hansen. The paper was reviewed by two anonymous journal referees whose detailed comments are acknowledged with thanks.*[A.C.]*

References

[1] L. Christensen, S. Fregerslev, A. Simonsen, J. Thiede, Sedimentology and depositional environment of Lower Danian Fish Clay from Stevns Klint, Denmark, Bull. Geol. Soc. Denmark 22 (1973) 193–212.

[2] L.W. Alvarez, W. Alvarez, F. Asaro, H.V. Michel, Extraterrestrial cause for the Cretaceous–Tertiary extinction, Science 208 (1980) 1095–1108.

[3] R.R. Brooks, Analytical chemists and dinosaurs, Can. J. Chem. 65 (1987) 1033–1041.

[4] F.T. Kyte, Z. Zhou, J.T. Wasson, Siderophile-enriched sediments from the Cretaceous–Tertiary boundary, Nature 288 (1980) 651–656.

[5] F.L. Sutherland, Volcanism around K/T boundary time: its role in an impact scenario for the K/T extinction events, Earth Planet. Sci. Rev. 36 (1994) 1–26.

[6] P.I. Premović, N.Z. Pavlović, M.S. Pavlović, N.D. Nikolić, Physicochemical conditions of sedimentation of the Fish Clay from Stevns Klint, Denmark, and its detrital nature: vanadium and other supportive evidence, Geochim. Cosmochim. Acta 57 (1993) 1433–1446.

[7] B. Schmitz, Origin of microlayering in worldwide distributed Ir-rich marine Cretaceous/Tertiary boundary clays, Geology 16 (1988) 1068–1072.

[8] D.E. Baker, J.P. Senft, Copper, in: B.J. Alloway (Ed.), Heavy Metals in Soils, Blackie Academic and Professional, London, 1995, pp. 179–205.

[9] R.R. Brooks, R.D. Reeves, X.H. Yang, D.E. Ryan, J. Holzbecher, J.D. Collen, V.E. Neall, J. Lee, Elemental anomalies at the Cretaceous–Tertiary boundary, Woodside Creek, New Zeland, Science 226 (1984) 539–542.

[10] A. Treibs, Chlorophyll- und Häminderivate in organischen Mineralstoffen, Angew. Chem. 49 (1936) 682–686.

[11] P.I. Premović, M.S. Pavlović, N.Z. Pavlović, Vanadium in ancient sedimentary rocks of marine origin, Geochim. Cosmochim. Acta 50 (1986) 1923–1956.

[12] S.E. Palmer, E.W. Baker, Copper porphyrins in deep-sea sediments: A possible indicator of oxidized terrestrial organic matter, Science 201 (1978) 49–51.

[13] E.W. Baker, J.W. Louda, Highly dealkylated copper and nickel etioporphyrins in marine sediments, in: P.A. Schenck, J.W. de Leeuw and G.W.M. Lijmbach (Eds.), Advances in Organic Geochemistry 1983, Pergamon Press, Oxford, 1984, Org. Geochem. 6, 183–192.

[14] E.W. Baker, J.W. Louda, Porphyrin in the geological record, in: R.B. Johns (Ed.), Biological Markers in the

Sedimentary Record, Elsevier, Amsterdam, 1986, pp. 125–225.

[15] F.J. Stevenson, Humus Chemistry: Genesis, Composition, Reactions, John Wiley and Sons, New York, 1982.

[16] B.A. Goodman, M.V. Cheshire, The occurrence of copper–porphyrin complexes in soil humic acids, J. Soil Sci. 27 (1976) 337–347.

[17] M.V. Cheshire, M.I. Berrow, B.A. Goodman, C.M. Mundie, Metal distribution and nature of some Cu, Mn and V complexes in humic acid: An electron paramagnetic resonance study, Geochim. Cosmochim. Acta 41 (1977) 1131–1138.

[18] A.L. Abdul-Halim, J.C. Evans, C.C. Rowlands, J.H. Thomas, An EPR spectroscopic examination of heavy metals in humic and fulvic acid soil fractions, Geochim. Cosmochim. Acta 45 (1981) 481–487.

[19] N. Senesi, G. Calderoni, Structural and chemical characterization of copper, iron and manganese complexes formed by paleosol humic acids, Org. Geochem. 13 (1988) 1145–1152.

[20] M.R. Rampino, R.C. Reynolds, Clay mineralogy of the Cretaceous–Tertiary boundary clay, Science 219 (1983) 495–498.

[21] B. Clozel, Les défauts paramagnétiques induits par irradiation dans les kaolinites, Approche experimentale et implications geochimiques, Ph.D. Dissertation, Paris 7 Université, 1991.

[22] J.H. Patterson, A.R. Ramsden, L.S. Dale, J.J. Fardy, Geochemistry and mineralogical residences of trace elements in soil shales from Julia Creek Queensland, Australia, Chem. Geol. 55 (1986) 1–16.

[23] N.D. Nikolić, Vanadium and Physicochemical Conditions of Sedimentation, Ph.D. Dissertation, University of Niš, 1999.

[24] B. Schmitz, P. Andersson, J. Dahl, Iridium, sulfur isotopes and rare earth elements in the Cretaceous–Tertiary boundary clay at Stevns Klint, Denmark, Geochim. Cosmochim. Acta 52 (1988) 229–236.

[25] B.A. Goodman, J.B. Raynor, Electron spin resonance of transition metal complexes, Adv. Inorg. Chem. Radiochem. 13 (1970) 135–362.

[26] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, CRC Press, Boca Raton, FL, 1984.

[27] A. Heydemann, Adsorption aus sehr verdünnten Kupferlösungen an reinen Tonmineralen, Geochim. Cosmochim. Acta 15 (1959) 305–329.

[28] M.L. Franklin, J.W. Morse, The interaction of manganese(II) with the surface of calcite in dilute solutions and seawater, Mar. Chem. 12 (1982) 241–254.

[29] D.M. Hirst, Geochemistry of sediments from eleven Black Sea cores, in: E.T. Degens, D.A. Ross (Eds.), The Black Sea Geology, Chemistry and Biology, Memoir 20, Am. Assoc. Petr. Geol., Tulsa, OK, 1974, pp. 430–435.

[30] H.J. Hansen, R. Gwozdz, K.L. Rasmussen, High-resolution trace element chemistry across the Cretaceous–Tertiary boundary in Denmark, Rev. Esp. Paleont. 1987, 21–29.

[31] B.P. Tissot, D.H. Welte, Petroleum Formation and Occurrence, Springer Verlag, Berlin, 1984.

[32] W. Wolbach, R. Lewis, E. Anders, Cretaceous extinctions; evidence for wildfires and search for meteoritic materials, Science 230 (1985) 167–170.

[33] P.G. Rouxet, P.L. Robin, G. Nicaise, Characterization of kerogens and their evolution by infrared spectroscopy, in: B. Durand (Ed.), Kerogen-Insoluble Organic Matter from Sedimentary Rocks, Editions Technip, Paris, 1980, pp. 163–190.

[34] D.G. Brookins, Eh–pH Diagrams for Geochemistry, Springer-Verlag, Berlin, 1988.

[35] D.M. McKnight, G.L. Feder, E.M. Thurman, R.L. Wershaw, J.C. Westall, Complexation of copper by aquatic humic substances from different environments, Sci. Total Environ. 28 (1983) 65–76.

[36] J.W. Buchler, Static coordination chemistry of metalloporphyrins, in: K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, pp. 157–231.

[37] M. Brongersma-Sanders, On conditions favoring the preservation of chlorophyll in marine sediments, in: Proc. 3rd World Petrol. Congr., The Hague, Sect. I, 1951, pp. 401–411.

[38] B.A. Goodman, M.V. Cheshire, Electron paramagnetic resonance evidence that copper is complexed in humic acid by the nitrogen of porphyrin groups, Nature New Biol. 244 (1973) 158–159.

[39] P. Hambright, Dynamic coordination chemistry of metalloporphyrins, in: K.S. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, pp. 233–278.

[40] A.M. Shiller, E.A. Boyle, Dissolved vanadium in rivers and estuaries, Earth Planet. Sci. Lett. 86 (1987) 214–224.

[41] B. Wehrli, Vanadium in der Hydrosphäre; Oberflächenkomplexe und Oxidationskinetik, Ph.D. Dissertation, ETH Zürich, 1987.

[42] M.D. Lewan, Geochemistry of Vanadium and Nickel in Organic Matter of Sedimentary Rocks, Ph.D. Dissertation, University of Cincinnati, Cincinnati, OH, 1980.

[43] B. Wehrli, W. Stumm, Vanadyl in natural waters: adsorption and hydrolysis promote oxygenation, Geochim. Cosmochim. Acta 53 (1989) 69–77.

[44] N.J. Evans, D.C. Gregoire, W.D. Goodfellow, N. Miles, J. Veizer, The Cretaceous–Tertiary fireball layer, ejecta layer and coal seam: Platinium-group element content and mineralogy of size fractions, Meteoritics 29 (1994) 223–235.

[45] R.H. Dott, Episodic sedimentation: how normal is average? How rare is rare? Does it matter?, J. Sediment. Petrol. 53 (1983) 5–23.

[46] R.G. Prinn, B. Fegley, Bolide impacts, acid rain, and biospheric traumas at the Cretaceous–Tertiary boundary, Earth Planet. Sci. Lett. 83 (1987) 1–15.

[47] W. Wolbach, I. Gilmour, E. Anders, C. Orth, R. Brooks, Global fire at the Cretaceous–Tertiary boundary, Nature 334 (1988) 665–669.

[48] M. Kastner, F. Asaro, H.V. Michel, W. Alvarez, L.W. Alvarez, The precursor of the Cretaceous–Tertiary bound-

ary clays at Stevns Klint, Denmark, and DSDP hole 465a, Science 226 (1984) 137–143.

[49] W.C. Elliott, J.L. Aronson Jr., H.T. Millard, E. Gierlowski-Kordesch, The origin of the clay minerals at the Cretaceous/Tertiary boundary in Denmark, Geol. Soc. Am. Bull. 101 (1989) 702–710.

[50] W.C. Elliot, Origin of the Mg-smectite at the Cretaceous/Tertiary (K/T) boundary at Stevns Klint, Denmark, Clays Clay Miner. 41 (1993) 442–452.

[51] F. Bergaya, H. VanDamme, Stability of mettaloporphyrins adsorbed on clays. A comparative study, Geochim. Cosmochim. Acta 46 (1982) 349–360.

[52] C.E. Weaver, L.D. Pollard, The Chemistry of Clay Minerals, Elsevier, London, 1973.