

J. Serb. Chem. Soc. 71 (7) 793–806 (2006)
JSCS – 3471

UDC 550.4"6153" "623":546.93'74"47
Original scientific paper

Geochemistry of the Cretaceous-Tertiary boundary (Fish Clay) at Stevns Klint (Denmark): Ir, Ni and Zn in kerogen

PAVLE I. PREMOVIĆ^{1,*}, MILENA M. KRSMANOVIĆ¹, BRATISLAV Ž. TODOROVIĆ²,
MIRJANA S. PAVLOVIĆ³, NIKOLA D. NIKOLIĆ¹ and DRAGAN M. DJORDJEVIĆ¹

¹Laboratory for Geochemistry, Cosmochemistry and Astrochemistry, University of Niš, P. O. Box 91, 18000 Niš, Serbia, ²Faculty of Technology, University of Niš, P. O. Box 79, 16000 Leskovac, Serbia and ³Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia
(e-mail: asteroid_2000@yahoo.com)

(Received 9 September 2005)

Abstract: Geochemical analyses of trace metals (Ir, Ni and Zn) in the kerogen of the black marl of the Cretaceous-Tertiary boundary succession (Fish Clay) at Stevns Klint (Højerup Church) were undertaken. The data for this kerogen were in accordance with a previous hypothesis¹ that this (insoluble) georganic polymer was derived from humic substances (mainly humic acids) of a nearshore soil. Substantial proportions of Ir, Ni and Zn within the kerogen structure were probably contained in these substances arriving at the sedimentary site. It is proposed that these humics were probably transported by acid surface waters (induced by the KT asteroid impact) into the shallow marine basin of Stevns Klint. It is also suggested that local leaching/weathering of the asteroidal impact fallout on the land near these waters played an important role in providing Ir, Ni and Zn for these substances. Apparently, Ir, Ni and Zn of the kerogen were created by the chondritic component of the impact ejecta fallout.

Keywords: geochemistry, Cretaceous-Tertiary boundary, iridium, nickel, zinc, kerogen, trace metals.

INTRODUCTION

The Fish Clay formation is a thin grey-to-black marl forming the KT boundary at Stevns Klint (eastern Denmark), Fig. 1. There it occurs in small marine basins between the Cretaceous white chalk and the overlying calcareous Tertiary formation. The lithology of Fish Clay near Højerup Church (hereafter Fish Clay) has been described by Christensen *et al.*² The authors differentiated four distinct layers within this boundary: a bottom layer II (Maastrichtian grey marl: 1–2 cm thick), middle layers III (black marl: *ca.* 2–5 cm thick) and IV grey to black marl: 3–5 cm thick) and a top layer V (light-grey marl: 5–7 cm thick). Layer II is underlain by

* Corresponding author.

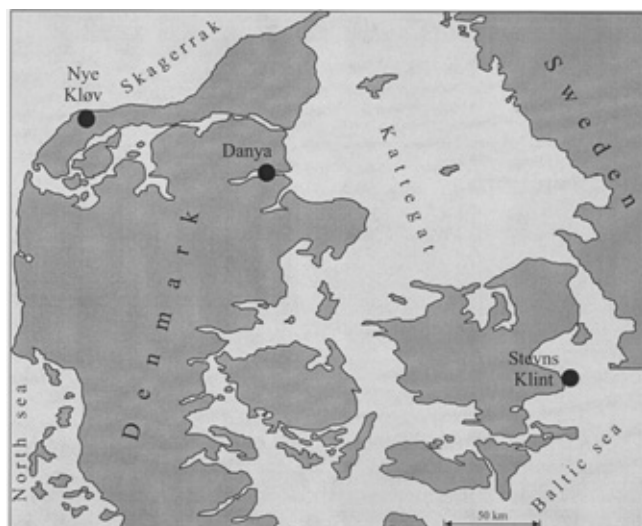


Fig. 1. Location of the samples of the Danish boundaries.

Maastrichtian chalk (I) and layer V is overlain by Danian cerithium limestone (VI). Elliot³ subdivided layer III into a red layer IIIA which is overlain by a black marl layer IIIB, Fig. 2. The layer IIIA is thin (0.3–0.5 cm) with a high content of microcrystalline pyritic spherules.⁴ The layer IIIB is black marl containing high amounts of Ir,^{5,6} kerogen enriched with Cu²⁺-porphyrins¹ and minute macroscopic pyrite (FeS₂), which are probably of postdiagenetic (secondary) origin.⁴

Palynological studies of Fish Clay by Hultbert^{7,8} indicate that layer II was deposited under normal marine conditions and that layer IIIB was deposited in a milieu strongly affected by a freshwater influx; whereas the top of layer IIIB, as well as layers IV and V were accumulated under a predominant marine influence. He suggested that local Maastrichtian freshwater agents (a river, streams, creeks), close to the shallow (*ca.* 100 m) marine basin at Stevns Klint, were the source for the detritus (including humics) of Fish Clay. According to this author, at some time during the deposition of Fish Clay, an abrupt increase of the outflow of terrestrial surface waters (mainly a river) at Stevns Klint occurred, resulting in the formation of the base part of the IIIB layer. A subsequent decrease in this outflow resulted in the formation of the top of IIIB (and afterward IV/V).

Alvarez *et al.*⁹ reported an anomalously high Ir concentration in IIIB. To explain this enhanced Ir concentration, the authors proposed a late Cretaceous asteroid impact on the Earth. Apart from Ir, IIIB is enriched in other metals: meteoritic Ni and non-meteoritic (terrestrial) metals, for example Cu*.^{1,11} Kyte *et al.*^{12,13} measured trace metals across Fish Clay on a very fine scale and proposed that only the IIIB/IV layers could be used to estimate the fallout (asteroidal matter + target rocks).

Geochemical analyses of the IIIB layer revealed that this rock contains up to *ca.* 3

* Note that Strong *et al.*¹⁰ also concluded that the Cu in the KT boundary succession at Flaxbourne River could only be derived from a terrestrial component within the impact fallout.

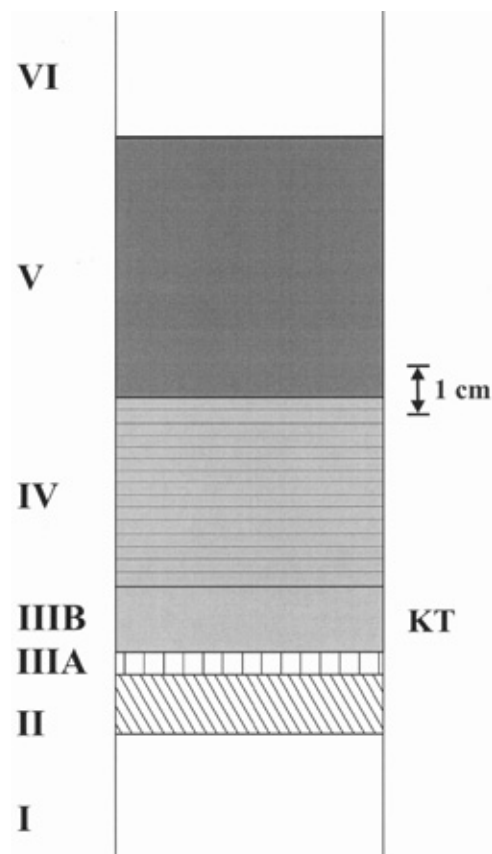


Fig. 2. Schematic illustration of the internal layering in a stratigraphic succession of Fish Clay.

% of kerogen.^{1,11,14} Geochemical extractions performed by Wolbach *et al.*¹⁵ indicated that the IIIB kerogen contains a predominance (> 90 %) of highly resistant terrestrial kerogen, a reactive marine kerogen and a minor fraction (< 1 %) of elemental carbon (soot/charcoal) particles. Premović *et al.*¹ suggested that IIIB kerogen represents a mixture of marine kerogen diluted with kerogen derived from soil humic substances of a nearby organic rich (oxic) soil at Stevns Klint (hereafter SK soil).

Trace metals have played an important role in determining the origin and nature of the KT successions and associated sediments worldwide. In many previous studies of Fish Clay, most attention was focused on trace metals present in the smectite. Much less regard has been paid to trace metals associated with IIIB kerogen. Schmitz *et al.*¹⁴ reported that kerogen separated from IIIB/IV kerogen concentrate exhibits enhanced concentrations of Ir, Ni and Cu. According to these authors, trace metal precipitation in Fish Clay was induced by various redox-controlled processes in connection with the decomposition of the abundant algal matter. Schmitz⁵ argued that the concentrated trace metals of IIIB/IV precipitated as sulfides from seawater; though the authors, also, pointed out that the ultimate ori-

gin of some of these metals (*e.g.*, Ir and Ni) may have been an Earth-impacting asteroid.

In this study, the metals Ir, Ni and Zn in IIIB kerogen were determined. They were chosen primarily because of their relatively simple chemistry in natural waters/sediments. In addition, two of the selected metals (Ni and Zn) show a similar geochemical behavior in natural (oxic/anoxic) waters. Special focus was given to Ir because this metal is probably the best tracer for the identification of the extraterrestrial matter in KT boundary successions. Essentially, this paper is complementary to our earlier studies^{1,11} and discusses broader aspects of the geochemistry of Ir, Ni and Zn in IIIB kerogen which may be important in understanding the geochemical/paleoecological events that occurred during the KT boundary.

EXPERIMENTAL

Dr. Helle Schummel collected bulk samples of IIIB from an outcrop 200 m south of Højerup Church. The rock sample was dried in an oven and carefully ground in an agate mortar. The fraction procedure was similar to that used by Premović *et al.*¹¹ and Saxby.¹⁶ The major steps in preparing the four fractions were:

1. Powdered rock (48 g) was treated (12 h) with acetate buffer: acetic acid (1 M)/sodium acetate (1 M) solution at pH 5.0¹⁷ to remove most of the carbonates. The soluble material constitutes the carbonate fraction.

2. The insoluble residue from (1) was demineralized further by repeated treatment with cold HCl (6 M, room temperature, 12 h). This acid solution removes the oxides/sulfides of Ir, Ni and Zn.

3. The insoluble residue from (2) was demineralized with boiling HCl (6 M, 80 °C, 12 h). This treatment removes most of soluble silicates. Silicate removal was checked by X-ray/FTIR analyses.

4. The insoluble part which remained after the previous treatment, was first demineralized (72 h) with a HF (22 M)–HCl (12 M) mixture at 80 °C and then with boiling HCl (12 M, 12 h). The remaining insoluble (mainly organic) portion was further extracted (Soxhlet, 72 h) for bitumen with a benzene: methanol (6:1, v/v) mixture. The final insoluble (1.8 % of the whole rock sample) represents IIIB kerogen.

The demineralized fractions were thoroughly rinsed with (twice redistilled and deionized) water, ensuring that these materials were sufficiently free from acid. Blank analyses involving solvents and reagents were also performed as control measures. Details on the procedure are given by Nikolić.¹⁸

X-Ray diffraction, Fourier transform infrared, electron spin resonance, scanning electron microscopy/microprobe analyses of the demineralized fractions of IIIB confirmed that dissolution was essentially complete and that a good selectivity was obtained at each stage of demineralization. However, the residual kerogen was not completely free of some fluorides, which precipitate from the HF/HCl solution of the aluminosilicate matrix.¹⁶

The whole rock sample and its demineralized fractions were analyzed for Ir, Ni and Zn by either Instrumental Neutron Activation Analysis (INAA) or Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). INAA Were carried out by Activation Laboratories Ltd., (Toronto, Canada). The reproducibility of the results from this analytical method was good. The analytical precision and accuracy were better than 30 % for Ir and 10 % for Ni and Zn.

A Spectroflame ICP-OES instrument was employed using Ar as the plasma gas. Energy dispersive spectrometry (EDS) was carried out with a Jeol JSM-35 electron microscope equipped with a Tracor TN-2000 energy dispersive X-ray spectrometer. The operating conditions for these analyses were: 25 keV accelerating voltage, 0.1 µA beam current, and a beam spot diameter of approximately 0.1 µm.

The above described demineralization was also performed of samples from other prominent KT successions (equivalent to Fish Clay), that is from the southernmost part of Stevns Klint close to

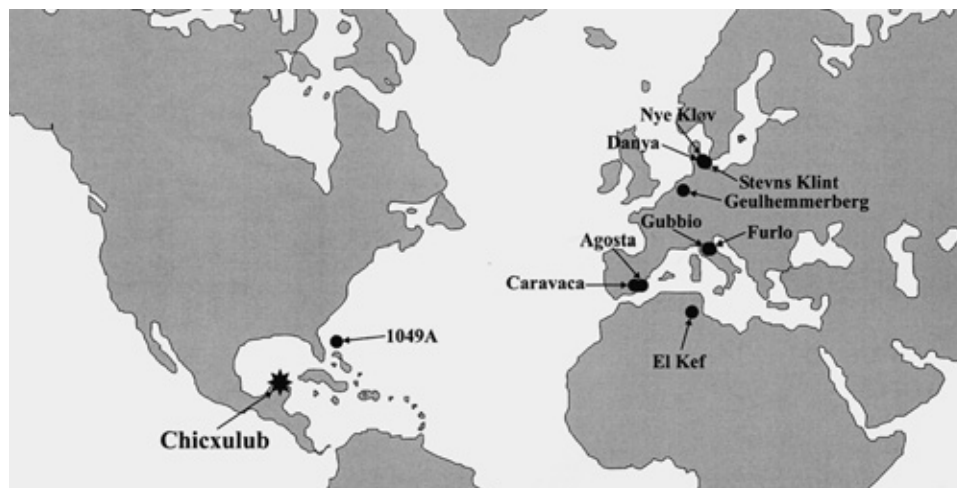


Fig. 3. Location map of the KT succession at Stevns Klint in relation to other KT boundary sections worldwide.

Rødvig (about 4 km from Højerup Church); Nye Kløv (*ca.* 320 km away from Stevns Klint) and Dania (*ca.* 220 km away from Stevns Klint) in western Denmark, Fig. 1; as well as Caravaca/Agosta (Spain), El Keef (Tunisia), Geulhemmerberg (Holland) and Furlo/Gubbio (Italy), Fig. 3.

RESULTS

Ir, Ni and Zn of IIIB kerogen. The contents of Ir, Ni and Zn in IIIB kerogen were determined and the analytical results are given in Table I. Blank levels were more than an order of magnitude lower than the given values. The determined concentrations of these trace metals are likely to represent the lower limits of their actual levels due to loss of a fraction of Ir, Ni and Zn (which are labile and loosely bound to IIIB kerogen) during the acid demineralization. The distribution pattern of Ir, Ni and Zn associated with IIIB kerogen is presented in Table I. It is noteworthy that the acid demineralization steps remove almost all the Ni and Zn.

TABLE I. INAA/ICP-OES Data for Ir, Ni and Zn in IIIB and IIIA kerogen (in ppm, otherwise indicated)

Metal	Whole-rock abundance	Kerogen abundance ^a	% ^b
Ir/ppb	40	500	25
Ni	330	737	3
Zn	340	25	< 0.5

^a The percentage of kerogen of the whole-rock sample was 1.8 %; ^b Amount of respective metal remaining in the IIIB kerogen

DISCUSSION

Cu²⁺-porphyrins, humic substances and the impact-induced acid surface waters. Geochemical analyses show that IIIB contains 1.8 % of kerogen, Table I. Premović *et al.*¹ reported that IIIA kerogen contains anomalously high level (up to

1000 ppm) of Cu and that this Cu is predominantly (> 90 %) in the Cu²⁺-porphyrin form. The kerogen content of Fish Clay increased abruptly with the accumulation of the basal part of IIIB and declined gradually towards the deposition of the top of IIIB and across IV.^{1,5} IV is also contains kerogen with Cu²⁺-porphyrins but this material is much less abundant than in IIIB. The underlying II/IIIA and overlying V layers contain no kerogen at all. Premović *et al.*¹ proposed that the upward decline of kerogen from its maximum in IIIB is simply a reflection of the decreasing proportion of terrigenous humic substances (HS) to the predominant authigenic/detrital inorganic materials (biogenic calcite/smectite). These authors also suggested that HS from a nearby (organic-rich) oxic soil at Stevns Klint were brought by acid (probably sulfate) surface waters (hereafter surface waters) induced by the Alvarez *et al.*⁹ impactor. These humics underwent later alteration by the low temperature diagenetic process to form IIIB/IV kerogen (enriched with Cu²⁺-porphyrins). The redox potential (*Eh*) fell during this process, creating strong anoxic conditions in IIIB (and in most of IV). The absence of kerogen in the II/IIIA/V layers suggests that their depositional environments were probably oxic, causing bioorganic matter (formed by photosynthetic planktonic microorganisms) to decompose completely after reaching the seafloor.

Premović *et al.*¹ concluded that Cu²⁺ chelation by humic free porphyrins must have occurred in the oxic solution of SK soil* under acidic (pH < 5) conditions prior to entering Fish Clay. Indeed, Cu²⁺ is available essentially only at pH < 5 and *Eh* > 0.1 V in H₂O – O₂ – CO₂ systems (*e.g.*, the solution of SK soil).^{20,21} According to several studies,^{22–24} Cu²⁺ chelation by porphyrins is exceedingly rapid (half-lives < 1 s⁻¹) and the rate of Cu²⁺ incorporation into porphyrins is nearly independent of the nature of the porphyrins themselves. Of course, the acid solution of SK soil, already enriched with Cu, would facilitate the formation of humic Cu²⁺-porphyrins.

Premović *et al.*¹ hypothesized that Cu²⁺-porphyrins in IIIB kerogen were formed by the rapid deposition of decaying green land flora, as a result of local (impact-induced) extinction events, including acid rainfalls/wildfires. In addition, the post-KT impact atmospheric photosynthesis was very likely interrupted for at least several months.⁹ For this reason, it is suggested that the probable source of free porphyrin structures within the humic skeleton was the chlorophylls of plant vestiges. Thus, it is reasonable to suggest that the IIIB layer, which is highly enriched with Ir,⁵ kerogen (enriched with Cu²⁺-porphyrins)¹ and impact-derived soot,¹⁵ may echo the first geochemical effects of the impact on the ecosystem of SK soil.

In contrast to Fish Clay, the nearby KT succession near Rødvig shows no presence of kerogen, indicating that this section was formed under oxic sedimentary conditions. The KT boundary successions at Nye Kløv/Dania contain a very low amount of kerogen (≤ 0.1 %) enriched with Cu²⁺-porphyrins.

* Note that moderately acidic soils have a pH 4.5–6.5.¹⁹

Trace metals and soil humic substances. The distinction between fulvic acids, humic acids and humin of soil is based on their aqueous solubility, which is mainly a consequence of their molecular weights. Fulvic acids are soluble at all pH values and have molecular weights near 1000. Humic acids are soluble below pH 2 and have molecular weights $> 10^4$; and humin (which is very dense) is insoluble at any pH. The HS of organic-rich soils, such as SK soil, show a strong cation exchange capacity, generally from 5–12 mmol g^{-1} , which is due the presence of functional groups such as carboxylic/phenolic acids. These groups are capable of forming coordination complexes (Stevenson²⁵ and references therein). The stability constants of these complexes are often in the range of 10^3 – 10^6 , hence the concentrations of trace metal ions in the soil solution at equilibrium are very small but the geochemical enrichment factors are large.

Under the acidic (pH < 5: see above) conditions of SK soil, fulvic acids would be soluble and they would chelate trace metals to form stable, but soluble complexes. Evidently, the surface waters would subsequently remove most of these complexes from the soil. Under the same conditions, humic acids are insoluble and their presence would result in the fixation of trace metals. Indeed, high levels of Cu/Cu²⁺-porphyrins are only found in the humic acids of a wide variety of organic-rich soils: recent soils (including peat-soils)^{26–28} and paleosols.²⁹

Considering that most of the IIIB kerogen is originally redeposited HS from SK soil,¹ it may be reasoned that much of its trace metals content is either detrital in the sense of having been brought into the marine basin at Stevns Klint already located in HS (*ex-situ* model) or authigenic in the sense of having been sorbed from the sedimentary seawater either by HS or by IIIB kerogen (*in-situ* model).

Ni and Zn: anoxic vs. oxic environment. Geochemical evidence indicates that IIIB (and most of IV) was deposited either under strong anoxic conditions or soon after deposition the conditions became strongly anoxic* ; under these conditions H₂S was present in the seawater overlying IIIB.¹¹ The question is whether the incorporation of Ni and Zn in the anoxic sedimentary environment of IIIB can account for their abundances in IIIB kerogen.

Under anoxic conditions, most of the Ni would be preferentially incorporated into FeS₂ and Zn would precipitate as insoluble solid ZnS.³⁰ In this way, an anoxic environment would act as a sink for these metals. In other words, the strong anoxic conditions of IIIB would be detrimental for the incorporation of the Ni and Zn in the seawater of IIIB into HS or IIIB kerogen.

The demineralizing steps remove most of the Fe (> 95 % of total Fe) in IIIB. The boiling-HCl step dissolves monosulfides [chalcopyrite (CuFeS₂), sphalerite (ZnS) and pyrrhotite (Fe_(1-x)S)], but not disulfides, such as FeS₂. Thus, it appears likely that a minor amount of FeS₂ is associated with IIIB kerogen. Since it is difficult to separate FeS₂ from the kerogen, this mineral may partially account for the proportions of some sulfide-related trace metal, such as Ir, Ni and Zn, of IIIB kerogen.

* Schmitz⁴ suggested that the abundant presence of the FeS₂ concretions enclosed within IIIB indicates that, 65 Ma after its formations, strong reducing conditions still prevail in IIIB.

The pyritization of trace metals was investigated in different anoxic marine sediments in the Gulf of Mexico by Huerta-Diaz and Morse.³¹ They reported that the general pattern for extent of pyritization shows that Ni \gg Zn. Accordingly, sedimentary FeS₂ is a moderately important sink for Ni and, generally, unimportant for Zn. Thus, Ni could partly reside within the FeS₂ associated with IIIB kerogen. As ZnS is completely soluble in cold HCl, it is very likely that this metal resides in IIIB kerogen.

The ICP-OES analysis indicated that IIIB kerogen contains on the average 2.7 % of Fe. Given that the EDS analysis of IIIB kerogen showed that approximately 10 % of its total Fe is in the form of FeS₂, it can be easily calculated that this material contains about 0.6 % FeS₂. Using this percentage value for FeS₂ and the average values for Ni (3100 ppm) and Zn (2300 ppm)* in FeS₂ microspherules of IIIB,⁴ it can be readily computed that a substantial proportion (> 95 %) of these metals are incorporated into IIIB kerogen. This crude estimation is consistent with the very low Ni content in FeS₂ grains reported by Graup *et al.*⁶ In addition, Balauz *et al.*³² reported that there is no relation between Ni and Zn and FeS₂ in IIIB. Furthermore, the abundance of Zn in IIIB kerogen is a strong indication of a high concentration of soluble Zn in the sedimentary environment. Rather high concentrations of this metal, however, are only present under well-oxidized conditions, whereas low abundances of soluble Zn are present under strong anoxic conditions.³³

Considering these facts, it must be concluded that the enriched association of Ni and Zn with IIIB kerogen does not reflect anoxic conditions but oxic conditions. As was the case with Cu,¹ Ni and Zn were probably incorporated into the HS of oxic SK soil. This conclusion is consistent with an early geochemical study which indicated a strong affinity of Ni and Zn for soil HS.³⁴

Erickson and Dickson³⁵ carried out mass balance calculations of trace metal influxes to surface seawater associated with the Alvarez *et al.*⁹ chondritic impactor. These calculations show that this water would be enriched by a factor of 660 (Ni) and 6800 (Zn). Assuming that 100 % of these metals were dissolved, their concentrations in the shallow (*ca.* 100 m) seawater at Stevns Klint would be about 78 ppb (Ni) and 2.2 ppb (Zn). Simple metal supply calculations suggest that this source would not be an adequate supply of Ni and Zn in IIIB kerogen. This supports our contention that Ni and Zn in IIIB kerogen are strictly detrital in character and originated from SK soil. The same conclusion was reached by Premović *et al.*¹¹ for Ni in IIIB smectite and by Premović *et al.*¹ for Cu in IIIB kerogen.** It is, however, unlikely that an ordinary soil would be adequate to explain the elevated values for Ni and Zn and a considerably abundant source is clearly needed to explain their enrichments.

* We consider that these values provide useful maximum values for Ni and Zn in the FeS₂ grains.

** Note that if the incorporation of Ni and Zn into HS occurred under acidic/oxidizing (pH \leq 6) conditions of SK soil then free N²⁺ and Zn²⁺ ions would be almost solely present in the soil solution.²¹

Recently, Frei and Frei³⁶ carried out a multi-isotopic/trace elements study of Fish Clay. According to these authors, the sudden changes in the Sr, Pb and Nd isotope compositions/ratios of this boundary indicate enhanced, acid-rain induced continental (local?) weathering. The same conclusion was obtained independently by Premović *et al.*¹ from their study of Cu/Cu²⁺-porphyrins within IIIB. Note that these researches also concluded that the source of the Cu of IIIB smectite/kerogen was probably the same.

Summarizing, the most plausible scenario is that HS (as the precursors of IIIB kerogen) already enriched with Ni and Zn were laterally transported from the top-soil at Stevens Klint onto the nearshore bed of Fish Clay. (This must also be true, to some extent, for IV kerogen). This resulted in the formation of IIIB kerogen enriched with Ni, Zn and Cu²⁺-porphyrins. This interpretation is in accordance with previous *ex-situ* scenario for IIIB kerogen (enriched with Cu and Cu²⁺-porphyrins) presented by Premović *et al.*¹

The impact fallout, HS and trace metals. Kyte *et al.*¹³ analyzed IIIA/IIIB for trace metals (in particular siderophiles) and suggested that only IIIA should be used to estimate primary ejecta fallout of the Alvarez *et al.*⁹ impact, as trace metals in higher layers arose mainly from secondary fallout material laterally transported from nearby localities on land. Kyte *et al.*¹³ suggested that only IIIA (usually referred to as the impact layer) is the sole representative of the original fallout in the sedimentary column of Fish Clay.

We reason that after immediate deposition of the primary airborne ejecta fallout into SK soil, secondary fallout from the surroundings was leached of its meteoritic/non-meteoritic trace metals by the surface waters. These metals were laterally transported by the same waters to SK soil where they were chelated by HS. Uptake of (chondritic/non-chondritic) trace metals by these humics probably occurred rapidly during early diagenesis. Perhaps regional/local conditions (*e.g.*, topography) were favorable for an efficient/concentrated accumulation of these metals in the solution of SK soil.

Ni and Zn in IIIB: chondritic vs. terrestrial origin. The simultaneous occurrence of Ir, kerogen enriched with Cu²⁺-porphyrins and the impact-derived soot are strong evidence that IIIB kerogen is closely coupled with the asteroidal impact. The concentrations of Ni and Zn within IIIB kerogen are 737 ppm and 25 ppm (Table I), respectively, which are much lower than the average Ni (11,000 ppm) and Zn (312 ppm) in C1 chondrite.³⁷ It is reasonable, therefore, to assume that most of the Ni and Zn within the IIIB kerogen ultimately came from a C1 chondritic component associated with the fallout covering the SK soil. Indeed, Davenport *et al.*^{38*} estimated that the top of the soil after the Alvarez *et al.*⁹ impact would be covered with fallout, having Ni one or two orders of magnitude greater than the contemporary average level of Ni (16 ppm) in soil.

* According to these authors, the impact infall would have Ni concentrations of between 133 – 1330 ppm, respectively.

The distribution patterns of Ni and Zn in most prominent marine KT successions are very similar of those of Fish Clay and these metals are well correlated with one another.³⁹ These authors suggested a chondritic origin of the anomalous Ni in these successions, including Fish Clay. High Zn in the successions of concern was, however, considered by Gilmour and Anders³⁹ to be of seawater origin. On the other hand, Strong *et al.*¹⁰ concluded that the Zn of the KT boundary section at the Flaxbourne River (N. Zealand), one of these KT boundary successions, could only be derived from a terrestrial component within the fallout.

Ir and IIIB kerogen. The Ir of IIIB most likely has the same meteoritic origin as it is found in enhanced levels at many KT successions worldwide. In general, Ir is associated with geoorganic matter in marine/continental sediments.⁴⁰ Schmitz *et al.*¹⁴ reported that about 50 % of the total Ir flux in Fish Clay is hosted by IIIB kerogen (1100–1500 ppm) and inferred that the HS in the SK soil probably played an important role in concentrating Ir in these geoorganics. Indeed, it appears that Ir has a high affinity for HS in natural waters. For example, Anbar *et al.*⁴¹ found that a large amount of these substances in rivers water enters the Baltic Sea, and about 75 % of riverine Ir accumulates in nearshore (brackish) waters similar to that of Stevns Klint.

The present analysis shows that IIIB kerogen contains as much as 500 ppb Ir (Table I) and that 22 % of this metal resides in this fraction. Schmitz⁴ reported that microspherules of FeS₂ in IIIB contain *ca.* 9 ppb of Ir. Using the above value of 0.6 % for FeS₂ in IIIB kerogen, a simple arithmetic reveals that an insignificant amount (0.02 %) of the total Ir in this kerogen is associated with this sulfidic mineral.

As Ni and Zn, the Ir would precipitate as highly insoluble IrS₂ and/or Ir₂S₃²¹ preferentially in the strong anoxic milieu of IIIB, although an anoxic environment may not be a major sink for Ir.⁴¹ Thus, Ir ions under these conditions would not be readily available for incorporation into the HS of the SK soil. It is more likely that this incorporation was an event which just preceded the accumulation of IIIB, *i.e.*, it occurred in the solution of the SK soil. It is, therefore, possible that a considerable part of the Ir inventory of IIIB kerogen resulted from the geochemical enrichment of the HS in the SK soil. If this is true then it infers that a large portion of the Ir anomaly of IIIB came through the geologically instantaneous influx of these substances (enriched also with Cu²⁺ porphyrins/soot) of the SK soil to the shallow seawater at Stevns Klint. This suggestion is in line with previous estimates of a fast deposition of IIIB.^{1,42}

IIIB is rich in calcareous dinoflagellates^{8,42} and the numbers of dyncocysts in Fish Clay increase *ca.* 10⁴ fold from II to IIIB, with no gradual decline before the Fish Clay.⁴³ Wendler and Willems⁴² reported that only a few specimens of calcareous dinoflagellates can be found above IIIB, *i.e.*, in IV/V. Thus, it can be qualitatively concluded that there is a good correlation between richness of dinoflagellate species, kerogen (enriched with Cu²⁺–porphyrins/soot) and Ir across the Fish Clay. Wendler and Willems⁴² suggested that the dinoflagellate analysis is compatible

with a sudden ecological change at Stevns Klint caused by the asteroidal impact at the KT boundary.

Redeposition of IIIB kerogen: sea level fall vs. impact. Fish Clay contains a very condensed/incomplete KT succession and belongs to the P0 foraminiferal zone of the earliest Danian.^{44,45} The biostratigraphic section at Stevns Klint indicates a sharp fall of the sea level at the KT boundary.⁴⁶ We may hypothesize that the redeposition of the HS (already enriched with Cu–porphyrins, soot, Ir, Ni and Zn) from the SK soil to the Fish Clay bed occurred during or shortly after the KT boundary, *i.e.* during a lowstand of the sea level at the KT boundary. An alternative hypothesis is that the impact at the KT boundary triggered some turbulence of the local terrestrial environment of Stevns Klint, instigating the transport of the HS of the SK soil to the site of Fish Clay.

In contrast to Fish Clay, Nye Kløv shows every indication of being temporarily a complete KT section characterized by a complete set of biostratigraphic zones.⁴⁴ This boundary is also marked by a few centimeters of thick marl enriched with cheto–smectite. Recently, Premović⁴⁷ showed that this (biostratigraphically true) KT boundary could have been formed by the coeval redeposition of smectite (enriched with Cu) and HS (enriched with Cu/Cu²⁺ porphyrins) from their original sites in the eastern part of the Danish Basin. Consequently, an erosion induced either by a sharp sea level fall or an impact-induced turbulence (*e.g.*, a river flooding) could readily translocate these materials even to the Nye Kløv site. In general, while sediments (*e.g.*, Fish Clay) are eroded in shallow areas during falls in the sea level, the eroded sedimentary material should collect in adjacent deeper parts of the basins (*e.g.*, Nye Kløv). If the second possibility is correct, then the impact which created the turbulence was either a relatively small impact which occurred in the relative vicinity of Stevns Klint or a distant but large impact. The fact that the KT boundary event is worldwide marked by Ir anomaly (and with other extraterrestrial signals) supports the large impact.

Keller *et al.*⁴⁸ presented evidence for multiple impacts during KT transition. The first impact (with no Ir anomaly) occurred at Chicxulub in the late Maastrichtian (*ca.* 65.3 Ma). This impact coincided with major Deccan volcanism. The second impact event (with Ir anomaly) occurred at the KT boundary (65 Ma) and the third one in the early Danian about 100 ky after the KT boundary. It is possible that Ir anomaly in IIIB kerogen represents the second (earliest) Danian impact event.⁴⁸ If it is assumed that the anomalous Ni and partly Zn in this kerogen also arose from the chondritic component of the fallout, then it is likely that their incorporation into the HS of the SK soil occurred at the KT boundary.

CONCLUSIONS

A previous geochemical study by Premović *et al.*¹ indicates that the HS in the SK soil can be regarded as the precursor of the IIIB kerogen. From the geochemis-

try of trace Ir, Ni and Zn associated with the IIIB kerogen, it may be deduced that most of these metals were originally bound with the HS in the acid (pH < 5) solution of the SK soil at Stevns Klint. Apparently, Ir, Ni and Zn of this material are derived from the chondritic component of the impact fallout. The HS of the SK soil probably had functional (carboxyl, porphyrin, *etc.*) groups which were able to chelate the trace metals of concern before they reached the sedimentary site of Fish Clay; this can account for their high contents in IIIB kerogen. The most plausible scenario is that the HS (already enriched with Ir, Ni, Zn and Cu²⁺-porphyrins/soot) were laterally transported by the (impact-induced) acid surface waters from the topsoil at Stevns Klint onto the nearshore site of Fish Clay. The lateral distribution of Cu²⁺-porphyrins implies that the KT boundary succession at Nye Kløv (north-western Denmark) were formed by erosion/emplacement of Fish Clay in eastern Denmark.

Acknowledgements: Dr. Helle Schummel (The Højerup sample) and Tove Damholt (the Rødvig sample), to whom our thanks go, collected the Fish Clay samples at Stevns Klint used in this work. We also thank the staff of Laboratoire de Mineralogie et Cristallographie de Paris (LMCP) and Instituto de Ciencias de la Tierra (ICT), without whose help, patience and understanding this paper would not have appeared. We are also indebted to LMCP/ICT for the use of their laboratory/instrumental facilities. Funding support from le Ministre Francais de l'Education National, de l'Enseignement Superieur et de la Recherche to P. I. P. for his stay at LMCP, Univeristé Pierre et Marie Curie (Paris), is gratefully acknowledged. P. I. P. also acknowledges the financial support, which was provided by the Programa Catedra y Consejo de Estudios de Postgrado for his pleasurable/fruitful stay at ICT (Universidad Central de Venezuela, Caracas). The Ministry of Science and Technology of Serbia (project 1235) financially supported in part this work.

ИЗВОД

ГЕОХЕМИЈА КРЕДА-ТЕРЦИЈАР ГРАНИЧНОГ СЛОЈА (FISH CLAY) ИЗ STEVNS KLINT-A (ДАНСКА): Ir, Ni И Zn У КЕРОГЕНУ

ПАВЛЕ И. ПРЕМОВИЋ¹, МИЛЕНА М. КРСМАНОВИЋ¹, БРАТИСЛАВ Ж. ТОДОРОВИЋ², МИРЈАНА С. ПАВЛОВИЋ³, НИКОЛА Д. НИКОЛИЋ¹ И ДРАГАН М. ЂОРЂЕВИЋ¹

¹Лабораторија за геохемију, космохемију и астирохемију, Природно-математички факултет, Универзитет у Нишу, б. бр. 91, 18000 Ниш, ²Технолошки факултет, Универзитет у Нишу, б. бр. 79, 16000 Лесковац и ³Институт за нуклеарне науке Винча, б. бр. 522, 11000 Београд

Извршена је геохемијска анализа трагова метала (Ir, Ni и Zn) у керогену црног лапорца креда-терцијар граничног слоја налазита (Fish Clay) у Stevns Klint-у (црква Нøјеруп). Подаци за овај кероген се слажу са претходним претпоставкама да је овај (нерастворни) геоорганички полимер настао од хумичних супстанци (углавном хумичних киселина) околног земљишта. Знатан део Ir, Ni и Zn у структури керогена је вероватно био садржан у тим супстанцама при њиховом преносу на место седиментације. Предпоставља се да су ови хумати вероватно транспортовани уз помоћ киселих површинских вода (узрокованих КТ астероидним ударом) у плитки морски басен Stevns Klint. Указано је такође да локално спирање овим водама астероидне падавине имало важну улогу у снабдевању Ir, Ni и Zn за хумичне супстанце. Вероватно да су Ir, Ni и Zn у керогену настали од хондритског дела астероидне падавине.

(Примљено 9. септембра 2005)

REFERENCES

1. P. I. Premović, N. D. Nikolić, I. R. Tonsa, M. S. Pavlović, M. P. Premović, D. T. Dulanović, *Earth Planet. Sci. Lett* **177** (2000) 105
2. L. Chistensen, S. Fregerslev, A. Simonsen, J. Thiede, *Bull. Geo. Soc. Denmark* **22** (1973) 193
3. W. C. Elliott, *Clays Clay Miner.* **41** (1993) 442
4. B. Schmitz, *Geochim. Cosmochim. Acta* **49** (1985) 2361
5. B. Schmitz, *Geology* **16** (1988) 1068
6. G. Graup, H. Palme, B. Spettle, *Lunar Planet. Sci.* **23** (1992) 445
7. S. U. Hulteber, *J. Micropalaeontol.* **5** (1986) 37
8. S. U. Hulteber, *J. Micropalaeontol.* **6** (1987) 35
9. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208** (1980) 1095
10. C. P. Strong, R. R. Brooks, S. M. Wilson, R. D. Reeves, C. J. Orth, X. Y. Mao, L. R. Quintana, E. Anders, *Geochim. Cosmochim. Acta* **51** (1987) 2769
11. P. I. Premović, N. Z. Pavlović, M. S. Pavlović, N. D. Nikolić, *Geochim. Cosmochim. Acta* **57** (1993) 1433
12. F. T. Kyte, Z. Zhou, J. T. Wasson, *Nature* **288** (1980) 651
13. F. T. Kyte, J. Sit, J. T. Wasson, *Earth Planet Sci. Lett.* **73** (1985) 183
14. B. Schmitz, P. Andersson, J. Dahl, *Geochim. Cosmochim. Acta* **52** (1988) 229
15. W. Wolbach, R. Lewis, E. Anders, *Science* **230** (1985) 167
16. J. D. Saxby, in *Oil Shale*, T. F. Yen, G. V. Chilingarian, Eds., Elsevier, Amsterdam, 1976, p. 103
17. M. Lyle, R. G. Heath, J. M. Robins, *Geochim. Cosmochim. Acta* **48** (1984) 1705
18. N. D. Nikolić, Vanadium and Physicochemical Conditions of Sedimentation, *Ph. D. Thesis*, University of Niš, Niš, 1999
19. G. J. Retallack, *Soils of the Past: an Introduction to Paleopedology*, Unwin Hyman, Boston, 1990, p. 519
20. R. M. Garrels, C. L. Christ, *Solutions, Minerals, and Equilibria*, Harper and Row, New York, 1965, p. 450
21. D. G. Brookins, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag, Berlin, 1988, p. 176
22. J. G. Erdman, J. W. Walter, W. E. Hanson, *Reprints Div. Pet. Chem. Am. Chem. Soc.* **2** (1957) 259
23. G. Cole, D. W. Doll, *J. Am. Chem. Soc.* **105** (1983) 4477
24. P. P. Zelmer, E. H. Mann, *Org. Geochem.* **5** (1983) 43
25. F. J. Stevenson, *Humus Chemistry: Genesis, Composition, Reactions*, Wiley, New York, 1994, p. 125
26. B. A. Goodman, M. V. Cheshire, *J. Soil Sci.* **27** (1976) 337
27. M. V. Cheshire, M. I. Berrow, B. A. Goodman, C. M. Mundie, *Geochim. Cosmochim. Acta* **41** (1977) 1131
28. A. L. Abdul-Halim, J. C. Evans, C. C. Rowlands, J. H. Thomas, *Geochim. Cosmochim. Acta* **45** (1981) 481
29. N. Senesi, G. Calderoni, *Org. Geochem.* **13** (1988) 1145
30. M. A. Huerta-Diaz, J. W. Morse, *Mar. Chem.* **29** (1990) 119
31. M. A. Huerta-Diaz, J. W. Morse, *Geochim. Cosmochim. Acta* **56** (1992) 2681
32. B. Bauluz, D. R. Peacor, W. C. Elliott, *Earth Planet. Sci. Lett.* **182** (2000) 127
33. R. P. Gambrell, J. B. Wiesepepe, W. H. Jr. Patrick, M. C. Duff, *Water Air Soil Poll.* **57-8** (1991) 359
34. B. Lakatos, J. Meisel, G. Mady, P. Vinkler, S. Sipos, *Proc. Inter. Peat Cong.*, Otaneimi, Finland 4, 1972, p. 341
35. D. E. Erikson, M. Dickson, *Geology* **15** (1987) 1014
36. R. Frei, K. M. Frei, *Earth Planet. Sc. Lett.* **203** (2002) 691
37. E. Anders, N. Grevesse, *Geochim. Cosmochim. Acta* **53** (1989) 197
38. S. A. Davenport, T. J. Wdowiak, D. D. Jones, P. Wdowiak, *Geol. Soc. Am. Spec. Pap.* **247** (1990) 71
39. I. Gilmour, E. Anders, *Geochim. Cosmochim. Acta* **53** (1989) 503
40. N. J. Evans, D. C. Gregoire, W. D. Goodfellow, B. I. McInnes, N. Miles, J. Veizer, *Geochim. Cosmochim. Acta* **57** (1993) 3149

41. A. D. Anbar, G. J. Wasserburg, D. A. Papanastassiou, P. S. Andersson, *Science* **273** (1996) 1524
42. J. Wendler, H. Willems, in: *Catastrophic Events and Mass Extinctions: Impact and Beyond*, C. Koeberl, K. G. Macleod, Eds., Geological Society of America Special Paper, 2002, p. 265
43. H. J. Hansen, R. Gwozdz, J. M. Hansen, R. G. Bromley, K. L. Rasmussen, *Earth Sci.* **8** (1986) 382
44. G. Keller, J. B. Lyons, N. MacLeod, C. B. Officer, *Geology* **21** (1993) 776
45. M. B. Hart, S. E. Fiest, G. D. Price, M. J. Leng, *J. Geol. Soc.* **161** (2004) 885
46. F. Surlyk, in: *Cool-Water Carbonates*. N. P. James, J. A. D. Clark, Eds., SEPM Special Publications, 1997, p. 293
47. P. I. Premović, *J. Serb. Chem. Soc.* **69** (2004) 555
48. G. Keller, W. Stinnesbeck, T. Adatte, D. Stüben, *Earth-Sci. Rev.* **62** (2003) 327.