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Cretaceous – Paleogene boundary Fish Clay at Højerup (Stevns Klint, Denmark): Zn, Pb and REE in kerogen

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Abstract: Geochemical analyses of Zn, Pb and rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in the kerogen of the black marl at the Cretaceous – – Paleogene boundary Fish Clay at Højerup were performed. Substantial proportions of the Zn, Pb and rare earths were probably contained in terrestrial humic substances (the kerogen precursor) arriving at the marine sedimentary site. This is in accord with a previous hypothesis that kerogen is mainly derived from humic acids of an oxic soil in of the adjacent coastal areas of eastern Denmark. It is also suggested that humics enriched in Zn, Pb and rare earth elements were transported mainly through fluvial transport into the deposition site of the Fish Clay. Local weathering/leaching of the impact–eject fallout on the land surface and local terrestrial rocks by impact-induced? acid surface waters perhaps played an important role in providing Zn, Pb and rare earths to these humic substances. Apparently, chondritic and non-chondritic Zn originated from the impact fallout; Pb and rare earth elements were most likely sourced by exposed rocks in the coastal areas of eastern Denmark.

Keywords: geochemistry; Cretaceous – Paleogene boundary; zink; lead; rare earth elements; kerogen.

INTRODUCTION

Fish Clay is a thin grey-to-black marl marking the Cretaceous – Paleogene boundary (KPB) at Stevns Klint in eastern Denmark, Fig. 1A. A detailed lithology of the Fish Clay at Højerup was described by Premović *et al.*[1] The authors differentiated three distinct layers across the boundary section: the bottom layer III (black marl), the middle layer IV (grey to black marl) and the top layer V (light-grey marl). Layer III is underlain by late Maastrichtian chalk. Layer V is

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overlain by Danian Cerithium Limestone (VI). Elliott [2] subdivided layer III into a red layer IIIA (0.2–0.5 cm) overlain by a black marl layer IIIB (2–5 cm), Fig. 1B. Layer IIIB shows high contents of Ir[3,4] and the kerogen is enriched in Cu^{2+}-porphyrins.[5] Layer IIIB also contains minute macroscopic pyrite (FeS_2), probably of postdiagenetic origin.[6] Layers IIIB/IV are considered here to constitute the main part of the KPB section.

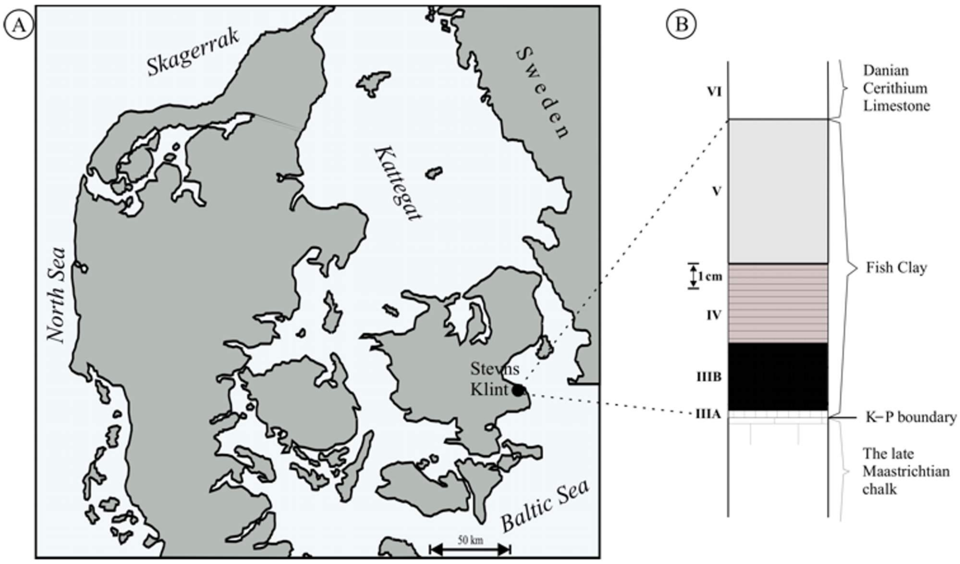

Fig. 1. A) Geographic location map of the sample from the Danish K–P boundary section. B) Lithological profile of the internal layering of the Fish Clay.

Alvarez *et al.*[7] reported an anomalously high Ir concentration in layer IIIB. To explain this enhanced Ir concentration, they proposed a late Cretaceous asteroid impact on the Earth.[8] In addition to Ir, layer IIIB is also enriched in other trace metals, such as: meteoritic or partly meteoritic Ni, Co, Au and some non-meteoritic terrestrial metals.[9]

The late Cretaceous impact is thought by most researchers to have occurred at the Chicxulub location (Yucatan Peninsula, Mexico). Shukolyukov and Lugmair[10] analyzed Cr in layers IIIA and IIIB employing high precision mass spectrometry and found that their Cr isotopic compositions strongly suggest that the impactor comprised C1 carbonaceous chondrite-type material. Very recently, Trinquier *et al.*[11] showed that the Cr isotopic signature of layer IIIB exhibits an isotopic ratio which would represent a mixture of a carbonaceous chondrite of CM2 type with terrestrial material in the ratio 3.8–6.8 % and that a single impactor may account for this signature.

Geochemical analyses of layer IIIB revealed that it contains up to *ca*. 3 % kerogen.[5,12,13] The kerogen content of the Fish Clay increased abruptly with an accumulation of the basal part of layer IIIB and declined gradually towards the top of layer IIIB and across IV.[3] Layer IV also contains kerogen but much less abundant than in layer IIIB. The underlying late Maastrichtian chalk and layer IIIA, and the overlying layer V contain no kerogen. Layer IIIB and, probably, layer IV were deposited under continuous anoxic bottom-water conditions[5,13] which prevailed 65 Ma after its formation.[6]

In many previous studies of Fish Clay, most attention was focused on the trace metals present in smectite, but much less attention was paid to trace metals associated with the IIIB kerogen. Very recently, Premović *et al.*[14] reported a geochemical study of Ni in the kerogen of layer IIIB. In the present study, Zn and Pb in the IIIB kerogen were determined. These elements were chosen primarily because of their relatively simple chemistry in natural waters and sediments. Zn and Pb show a similar geochemical behavior in natural oxic or anoxic waters. La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, which belong to the rare earth elements (REE), were also analyzed. REE comprise a highly coherent geochemical group and are characterized by a large and unique similarity in their geochemical properties. The present study is complementary to earlier studies[1,5,13] and may be important for the understanding of the geochemical and paleoecological events that occurred during the deposition of the KPB section.

EXPERIMENTAL

The experimental techniques and methods were described in a previous paper.[14]

RESULTS

Zn, Pb and REE of the IIIB kerogen

Geochemical analysis showed that layer IIIB contains 1.8 % of kerogen, made up mainly (> 95 %) of organic matter, Table I. The IIIB kerogen contains high organic S (*ca.* 1.6 %) and low S (< 0.2 %), ascribed to finely disseminated FeS_2 embedded into the kerogen skeleton; this material contains no or very little non-pyritic sulfate S.[14] The contents of Zn, Pb and REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in the IIIB kerogen were determined and the analytical results are given in Table I. The blank levels were more than an order of magnitude lower than the given numbers. The concentrations of Zn, Pb and REE are likely to represent the lower limits of their actual levels due to loss of a fraction of these elements which are labile and loosely bound to the IIIB kerogen during the acid demineralization. The distribution pattern of Zn, Pb and REE associated with the IIIB kerogen is also presented in Table I. Of note, the acid demineralization steps remove almost completely Zn.

DISCUSSION AND INTERPRETATION

Zn and Pb: Anoxic vs. *oxic environment*

As sedimentary FeS_2 is generally an unimportant sink for Zn and Pb and because ZnS and PbS are completely soluble in cold HCl, it is very likely that these two metals are bound to the IIIB kerogen. Humics (mainly humic acids) in coastal soil can be regarded as the progenitor of the IIIB kerogen.[1,5,14] It is possible that incorporation of Zn and Pb into the humics occurred under the anoxic sedimentary environment of layer IIIB (*in-situ* model). However, under these conditions, most of the Zn and Pb would precipitate as insoluble solid sulfides.[15] In this way, an anoxic environment would act as a sink for these metals. Strong anoxic conditions of layer IIIB would be adverse for the incorporation of Zn and Pb into the humics. It can thus be concluded that the enriched association of Zn and Pb in the IIIB kerogen does not reflect anoxic but oxic conditions. Indeed, the excess of these two metals in the IIIB kerogen is a strong indication of their rather high concentrations as free ions and/or soluble complexes. Indeed, high soluble Zn is only present under well-oxygenated conditions of sedimentation.[16] Consequently, the Zn and Pb of the IIIB kerogen were probably incorporated into humic structures during the early diagenesis of the humics in the oxic milieu of coastal soil. The fact that the humics were enriched in Zn implies that the solution of the coastal soil was of relatively low pH because this metal is not very soluble at pH > 5.[17] Moreover, if the incorporation of Zn and Pb into the humics occurred under acidic and oxidizing conditions of coastal soil then predominantly free Zn^{2+} and Pb^{2+} ions would be almost solely present in the soil solution.[18]

TABLE I. INAA/ICP-OES Data for the abundances of Zn, Pb and REE in the IIIB kerogen and in C1 chondrite

Metal		Whole-rock	Kerogen[a]	Content, %[b]	C1 Chondrite
Zn	ppm	340	25.0	< 0.5	312
Pb	ppm	na[c]	12.5	–	2.47
La	ppb	na	34.8	–	234.7
Ce	ppb	na	61.0	–	603.2
Nd	ppb	na	< 5.0	–	452.4
Sm	ppb	na	4.5	–	147.1
Eu	ppb	na	1.6	–	56.0
Tb	ppb	na	1.0	–	36.3
Yb	ppb	na	8.6	–	162.5
Lu	ppb	na	1.3	–	24.3

[a]Percentage of kerogen of the whole-rock sample is 1.8 %. the IIIB kerogen is composed of > 95 % organic matter with *ca.* 4.7 % of S (determined by INAA); [b]percentage of total metal remaining in the IIIB kerogen; [c]not analyzed

Zn and Pb in the IIIB kerogen: chondritic vs. *terrestrial origin*

An enigmatic finding in the IIIB kerogen is a marked Zn enrichment (340 ppm), which is comparable with the average Zn (312 ppm) in C1 chondrites. This suggests that the Zn in the IIIB kerogen could be augmented by chondritic volatiles of the impactor. Strong *et al.*[19] suggested that the Zn in the KPB deposit at the Flaxbourne River was derived from crustal rocks. Here, it is suggested that the high Zn in the IIIB kerogen was probably primarily sourced by chondritic and non-chondritic materials of the impact fallout.

The concentration of Pb in the IIIB kerogen is almost 6 times higher than its mean abundance in C1 chondrites, Table I. If the Pb originated from the chondritic component of the impact fallout, it would necessitate rather drastic concentrations of the metal during the weathering/leaching of the impact fallout and it seems likely that the Pb arose from a terrestrial source. Indeed, geochemical studies of this metal in layer IIIB strongly indicate that it is probably of terrestrial origin.[20,21] Here, it is suggested that the Pb originated from the rock(s) exposed in the coastal areas; its predominant species in coastal soil could, therefore, be complexes of Pb^{2+} ions with humics.

REE of the IIIB kerogen

REE have been used as proxy indicators for reconstructing the Eh and pH conditions of ancient sedimentary environments.[22] Except for Ce, REE in natural waters commonly occur in the 3+ oxidation state and exhibit very similar geochemical properties.[18] Layers IIIB and IV contain relatively high concentrations of REE and the bulk (> 90 %) of the total rare earths resides in the apatite phase.[12] These authors concluded that most of these elements precipitated from seawater at Stevns Klint.

The REE of the IIIB kerogen are largely incorporated into its structure because they do not form sulfides. The REE signature of the IIIB kerogen is approximately comparable to the REE signature of North American Shale Composite (NASC[23]) but highly enriched in REE relative to C1 chondrites, (Table I; Fig. 2). It seems improbable, therefore, that a C1 chondritic source could have made an important contribution to the REE in the IIIB kerogen.

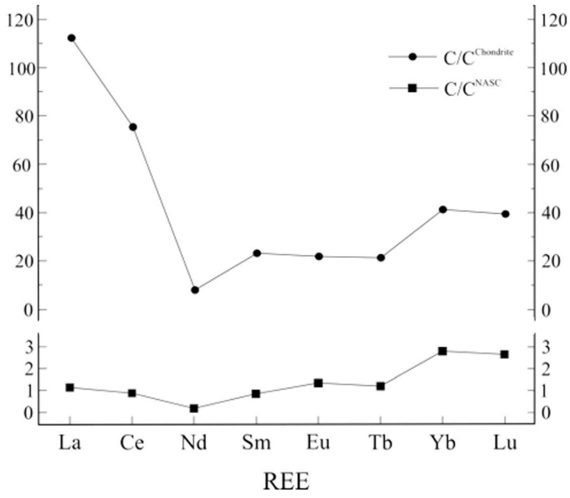

Fig. 2. Distribution of REE in IIIB kerogen normalized relative to REE in the NASC (■)[23] and chondrite (●).[36]

A prominent feature of various ancient and modern marine sedimentary environments and the associated waters is the strongly negative Ce and Eu anomalies and, less commonly, zero and positive anomalies.[24–29] In addition, the REE pattern of the authigenic component of marine sediment is, in general, the mirror image of the most common non-flat pattern for seawater. In contrast, marine waters show both a flat shale type pattern[27] and an absence of a Ce anomaly.[30]

The IIIB kerogen displays a flat pattern with no Ce and Eu anomalies (Table I; Fig. 2), indicating that its REE, probably, did not originate from seawater. It is rather likely, therefore, that this kerogen (*i.e.*, humics in the coastal soil) must have inherited the rare earths from the surface waters. The REE patterns of the surface waters with the exception of the negative Ce anomaly usually reflect the REE compositions of the lithologies along their flow paths.[31] Thus, it is suggested that ultimately the REE of the IIIB kerogen were perhaps sourced by rocks exposed on the adjacent land.

The mobility of REE in natural (oxic and anoxic) waters is mainly controlled by their ability to form complexes with organic and inorganic ligands. Several studies have indicated extensive association of REE with terrigenous humics[32–35] and that these types of complexes dominate in acid surface waters enriched in humics.[29] It is, thus, rather likely that the REE were initially complexed with humics in the coastal soil.

We offer a model as a first approximation to the geochemical processes involved, Fig. 3. It is thus suggested that chondritic and non-chondritic Zn was leached from impact-ejecta fallout on land probably by impact-induced? acid surface waters. Pb and REE were most likely removed by the same waters from the rocks in the coastal areas of eastern Denmark. Zn, Pb and REE were then chelated by the humics of coastal soil and this uptake occurred rapidly during early diagenesis. Local conditions, such as topography (*e.g.* highlands *vs.* lowlands) were perhaps favorable for an efficient and concentrated accumulation of these metals and REE in the humics-rich coastal soil. These humics were then fluvially transferred to the sea and further to the area where the Fish Clay was deposited, Fig. 3.

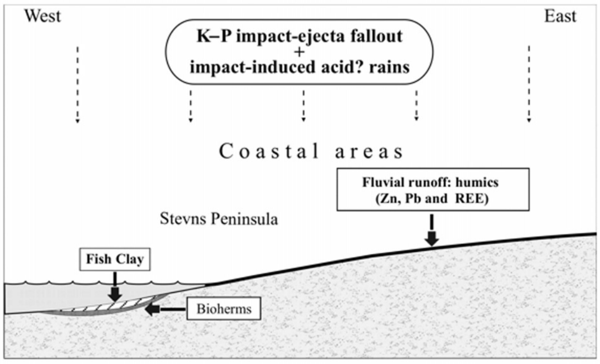

Fig. 3. Proposed model for the geochemical relations between the impact-ejecta fallout, humics in the coastal soil and Fish Clay at Stevns Klint.

CONCLUSIONS

In summary, the IIIB kerogen enriched in Zn and Pb were probably derived from the humics (mostly humic acids) enriched in these metals. These humics in the coastal soil were fluvially transported to the site of deposition of the Fish Clay, Fig. 3. This must also be true for the IV kerogen. This interpretation is in accordance with a previous *ex-situ* scenario for the IIIB kerogen enriched in Cu and Cu^{2+}-porphyrins.[5]

From the geochemistry of Zn, Pb and REE associated with the IIIB kerogen, it may be deduced that most of these metals and REE were originally bound with these humics in an acidic ($pH < 5$) and oxic soil of the adjacent coastal areas in eastern Denmark. Apparently, chondritic and non-chondritic Zn was most likely augmented by the impact-ejecta fallout through the leaching by the impact-induced? acid surface waters. Pb and REE were also leached by the same waters from the rocks on the adjacent land. Humics having functional carboxyl and phenolic groups were able to chelate Zn, Pb and REE before they were deposited in the Fish Clay; this chelation can account for their high content in the IIIB kerogen. The most plausible scenario is that humics and associated Zn, Pb and REE were fluvially transferred onto the Fish Clay site at the KPB.

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ИЗВОД

КРЕДА – ПАЛЕОГЕН ГРАНИЧНИ СЛОЈ FISH CLAY СА HØJERUP-А (STEVNS KLINT, ДАНСКА): Zn, Pb И REE У КЕРОГЕНУ

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Урађене су геохемијске анализе Zn, Pb и елемената ретких земаља (La, Ce, Nd, Sm, Eu, Tb, Yb и Lu) у керогену црног лапорца из креда – палеоген граничног слоја Fish Clay са Højerup локације. Знатан део Zn, Pb и елемената ретких земаља, вероватно, је био садржан у копненим хумичним супстанцама (претечи керогена) при дотоку на место морске седиментације. Ово је у складу са претходним претпоставкама да кероген, углавном, потиче од хумичних киселина из земљишта околне приобалне области источне Данске. Такође, претпоставља се да су хумичне супстанце обогаћене Zn, Pb и елементима ретких земаља пренете површинским водама, углавном, до места седиментације Fish Clay-а. Спирање киселим површинским водама астероидне падавине на околном земљишту и стенама, вероватно, је играло значајну улогу у обогаћивању наведених хумичних супстанца цинком, оловом и елементима

ретких земаља. Изгледа да хондритски и не-хондритски Zn потиче од астероидне падавине; Pb и ретке земље, највероватније, потичу од околних стена у приобалној области источне Данске.

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