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Cretaceous – Paleogene boundary Fish Clay at Højerup (Stevns Klint, Denmark): trace metals in kerogen

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Key words. – Geochemistry, Cretaceous–Paleogene boundary, Trace metals, Rare earth elements, Kerogen

Abstract. – Geochemical analyses of trace metals (Ir, Ni, Co, Cr, Zn, Au and Pb) and rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in kerogen of the black marl at the Cretaceous–Paleogene boundary Fish Clay at Højerup have been undertaken. Substantial proportions of the trace metals 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 were transported mainly through fluvial transport into the site of the deposition of the Fish Clay. The local weathering/leaching of the impact-ejecta fallout on the land surface or local terrestrial rocks by impact-induced? acid surface waters perhaps played an important role in providing trace metals and rare earths for these humic substances. Apparently, chondritic Ir, Au, Ni, Co, Cr and chondritic and non-chondritic Zn originated from the impact fallout; Pb and rare earth elements were most likely sourced by the rocks exposed in the coastal areas of eastern Denmark.

Argile Crétacé–Paléogène de frontière Fish Clay à Højerup (Stevns Klint, Danemark) : oligo-métaux dans le kérogène

Mots clés. – Géochimie, frontière Crétacé–Paléogène, Fish Clay, Oligo-métaux, Eléments de terre rare, Kérogène

Résumé. – La composition en éléments-traces métalliques (Ir, Ni, Co, Cr, Zn, Au et Pb) et en terres rares des kérogènes extraits des marnes sombres de la formation Fish Clay (Crétacé-Paléocène) à Højerup a été déterminée. Une part importante de ce stock d'éléments provient probablement des substances humiques terrestres à l'origine des kérogènes, déposées en milieu marin. Ces résultats confirment l'hypothèse que ces kérogènes proviennent d'acides humiques issus des sols oxydants des domaines côtiers du Danemark oriental. Nous proposons que les substances humiques aient été transportées par les fleuves jusqu'au milieu de dépôt de la formation Fish Clay. Il est possible que les substances humiques aient été enrichies en éléments traces et en terres rares par le lessivage des particules remobilisées par un impact météoritique ou par l'altération des roches par des pluies acidifiées par un tel impact. Ainsi, les éléments Ir, Au, Ni, Co, Cr pourraient être d'origine chondritique, le Zn pourrait avoir une double origine (chondritique et non-chondritique) ; le Pb et les terres rares auraient été enrichis à partir des roches des zones côtières.

INTRODUCTION

The Fish Clay appears to be a very condensed and incomplete Cretaceous–Paleogene (K–P) succession probably corresponding to planktonic foraminifer Zone P0 of the earliest Danian [Keller *et al.*, 1993; Hart *et al.,* 2004; Rasmussen *et al.,* 2005]. The Fish Clay is a thin grey-to-black marl marking the K–P boundary at Stevns Klint in eastern Denmark (fig. 1A). The lithology of the Fish Clay at Højerup was described by Christensen *et al.* [1973]. The authors differentiated four distinct layers across the boundary section: the bottom layer II (thin grey marl), the middle layer III (black marl), IV (grey to black marl) and the top layer V (light-grey marl). However, very recent lithostratigraphic study indicates that transitional layer II should not be included in the Fish Clay member since it forms the very top of the latest Maastrichtian bryozoan chalk I [Surlyk *et al.,* 2006]. Layer V is overlain by the Danian Cerithium Limestone (VI). The Cerithium Limestone and the Fish Clay form infillings of small basins of the latest Maastrichtian bryozoan bioherms [Surlyk, 1997; Surlyk and Håkansson, 1999; Hart *et al.,* 2004]. Elliott [1993] subdivided layer III into a red layer IIIA (0.2-0.5 cm) overlain by the black marl layer IIIB (2-5 cm) (fig. 1B). Layer IIIB shows high contents in Ir [Schmitz, 1988; Graup *et al.*, 1992] and kerogen is enriched in Cu^{2+}-porphyrins [Premović *et al.,* 2000]. Layer IIIB also contains minute macroscopic pyrite (FeS_2) which is probably of postdiagenetic origin [Schmitz, 1985]. Layer IIIB is here considered to constitute the main part of the K–P boundary section. There is, however, no sharp boundary between layers IIIB and IV and it makes it difficult to distinguish the top of layer IIIB and the base of layer IV. Deposition of the Maastrichtian chalk occurred in a rather shallow epicontinental sea, but within the euphotic zone, in about

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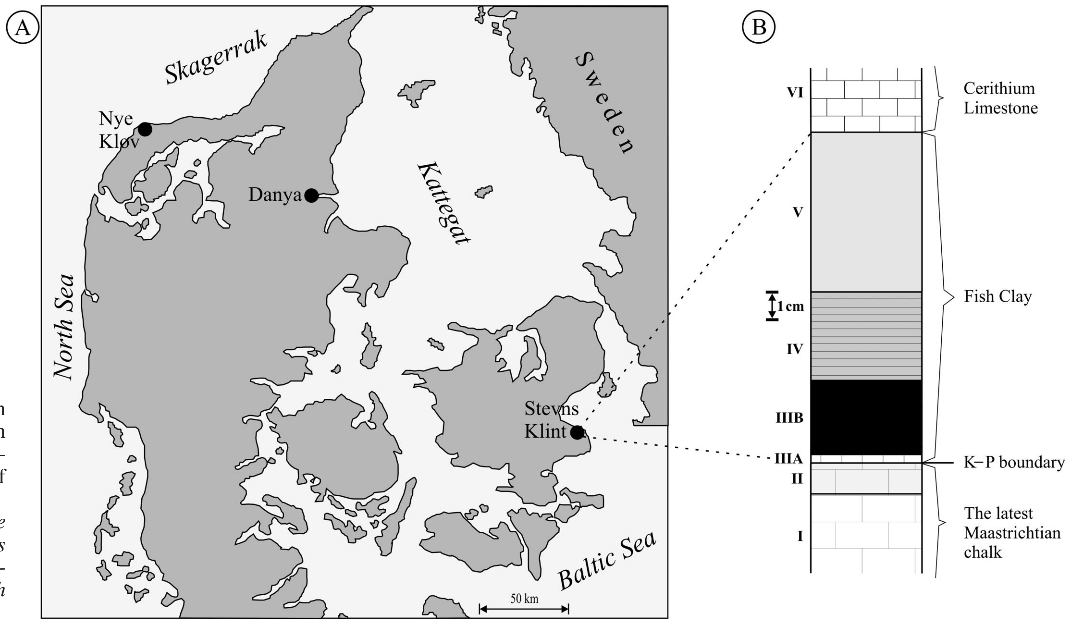

FIG. 1. – A) Geographic location map of the samples from Danish K–P boundary section. B) Lithological profile of the internal layering of the *Fish Clay.*
FIG. 1. – A) *Carte géographique de localisation des échantillons prélevés à la limite K-P au Danemark.* B) *Profil lithologique de la succession Fish Clay.*

150 m [Bromley, 1979]. The Fish Clay succession probably represents a much shallower depositional environment than this chalk.

Alvarez *et al.* [1980] 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. Apart from Ir, layer IIIB is enriched in other trace metals such as: meteoritic or partly meteoritic Ni, Co, Au and non-meteoritic terrestrial metals, for example Cu [Christensen *et al.*, 1973; Premović *et al.*, 2000]. Kyte *et al.* [1980, 1985] measured trace metal concentrations across the Fish Clay on a very fine scale and proposed that only layer IIIA could be used to estimate the amount of fallout (asteroidal matter + target rocks).

The late Cretaceous impact is thought by most workers to have occurred at the Chicxulub location Yucatan Peninsula, Mexico (fig. 2). Shukolyukov and Lugmair [1998] analyzed Cr in layers IIIA and IIIB employing a 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.* [2006] have shown that Cr isotopic signature of the Fish Clay exhibit an isotopic ratio which would represent a mixing of a carbonaceous chondrite of CM2 type with terrestrial material in a 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 [Schmitz *et al.*, 1988; Premović *et al.*, 1993, 2000]. Geochemical extractions performed by Wolbach *et al.* [1985] indicate that the IIIB kerogen contains a predominant (> 90%) highly resistant humic kerogen, a reactive marine kerogen, and a minor fraction (< 1%) of elemental carbon particles (soot). Wolbach *et al.* [1985] suggested that a significant quantity of the soot in layer IIIB could be concentrated from surface waters of the coastal areas.

Premović *et al.* [2000] suggested that the IIIB kerogen represents a mixture of marine kerogen diluted by (humic) kerogen derived from humics of an organic-rich oxic soil of the adjoining coastal areas in the eastern Denmark (hereafter coastal soil). The kerogen content of the Fish Clay increased abruptly with accumulation of the basal part of layer IIIB and declined gradually towards the deposition of the top of layer IIIB and across IV [Schmitz, 1988; Premović *et al.*, 2000]. Layer IV also contains kerogen but much less abundant than in layer IIIB. The underlying layers IIIA and II, and the overlying layer V do not contain any kerogen. Premović *et al.* [2000] proposed that the upward decrease in kerogen from its maximum in layer IIIB is simply a reflection of the decreasing proportion of humics to the predominant inorganic materials, mainly biogenic calcite and smectite.

The presence of kerogen and macroscopic FeS_2, the fine lamination and the lack of bioturbation throughout layer IIIB indicate that this layer was deposited under continuously anoxic bottom-water conditions [Premović *et al.*, 1993, 2000]. The same is probably true for most of layer IV. In addition, Schmitz [1985] suggested that the abundant occurrence of FeS_2 concretions in layer IIIB indicates that 65 Ma after its formation strongly reducing conditions still prevail in this layer. In stark contrast to layer IIIB, the absence of kerogen and FeS_2 in layers IIIA and V suggest that their depositional environments were probably oxic.

Trace metals have played an important role in determining the nature of the K–P boundary strata worldwide. In many previous studies of the Fish Clay, most attention has been focused on trace metals present in smectite. Much less attention has been paid to trace metals associated with the IIIB kerogen. Schmitz *et al.* [1988] reported that the kerogen separated from layers IIIB and IV exhibits enhanced concentrations of Ir, Au, Ni, Cr and Cu; in the present study Ir, Au, Ni, Co, Zn, Cr and Pb in the IIIB kerogen were determined. These elements were chosen primarily because of their relatively simple chemistry in natural waters and sediments. Some of these metals (Ni, Co, Zn and Pb) show a similar geochemical behaviour in natural oxic or anoxic waters. Special focus has been on Ir, Au, Cr, Ni and Co because these metals are probably the best tracers for

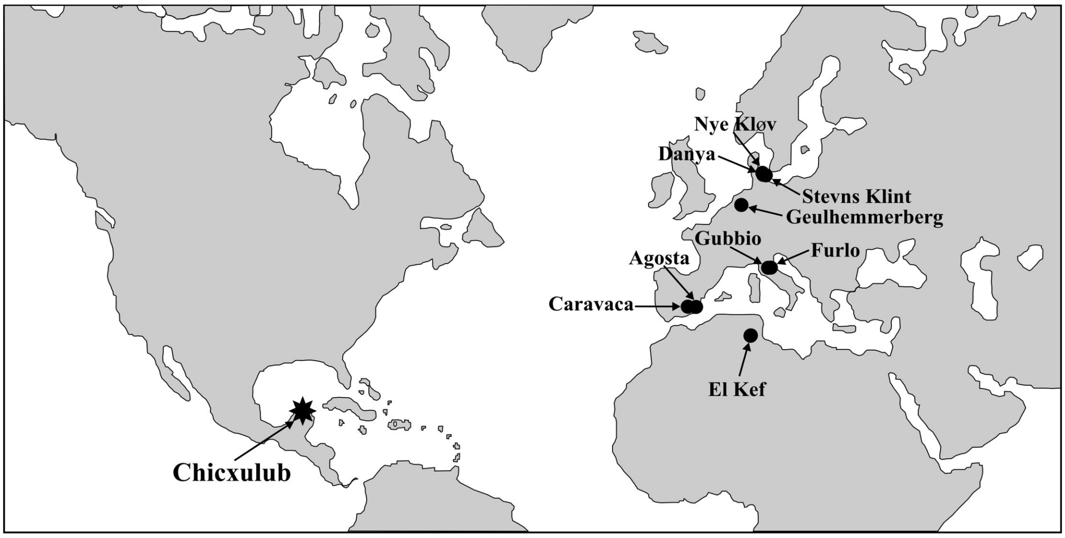

FIG. 2. – Geographic location map of the K-P succession at Stevns Klint in relation to other K–P boundary sections worldwide.
FIG. 2. – *Carte géographique de localisation de la succession K-P à Stevns Klint par rapport aux autres successions K-P dans le monde.*

identification of the extraterrestrial matter in K–P boundary strata in contrast to Zn and Pb which are typical terrestrial metals. We also analyzed La, Ce, Nd, Sm, Eu, Tb, Yb and Lu which belong to the rare earth elements (REE). REE comprise a highly coherent geochemical group and are characterized by a great and unique similarity in geochemical properties. The present study is complementary to our earlier studies [Premović *et al.*, 1993, 2000] and discusses broader the aspects of the geochemistry of trace metals and REE in the IIIB kerogen, which may be important for the understanding of the geochemical and palaeoecological events that occurred during deposition of the K–P boundary strata.

METHODS

A bulk sample of layer IIIB was collected by Dr. Helle Schummel 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 fractionation procedure is similar to that used by Saxby [1976] and Premović *et al.* [1993]. The major steps in preparing the four fractions are:

1– powdered rock (48 g) was treated (12 hrs) with acetate buffer: acetic acid (1 M)/sodium acetate (1 M) solution at pH 5.0 [Lyle *et al.*, 1984] 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 hrs). This acid solution removes the oxides and sulfides of Ir, Au, Fe, Ni, Co, Zn, Cr and Pb;

3– the insoluble residue from (2) was demineralized with boiling HCl (6 M, 80°C, 12 hrs). This treatment removes most of the soluble silicates;

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 hrs). The remaining insoluble mainly organic portion was further extracted (Soxlet, 72 hrs) for bitumen with benzene: methanol (6: 1, v/v) mixture. The final insoluble residue (1.8% of the whole rock sample) represents the IIIB kerogen.

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 [1999].

The X-ray diffraction, Fourier transform infrared and scanning electron microscopy and microprobe analyses on the demineralized fractions of layer IIIB confirm that dissolution was essentially complete and that a good selectivity was obtained at each stage of demineralization. However, residual kerogen was not completely free of some fluorides which precipitate from the HF/HCl solution of the aluminosilicate matrix [Saxby, 1976].

The whole rock sample and its demineralized fractions were analysed for trace metals and REE (except Pb) by Instrumental Neutron Activation Analysis (INAA). INAA was carried out by Activation Laboratories Ltd. (Toronto, Canada). The reproducibility of the results from this analytical method is good. Analytical precision and accuracy were better than 30% for Ir and Au, and 10-20% for the remaining trace metals.

Minor Fe and trace Pb in the IIIB kerogen were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas. Total uncertainty (including accuracy error) of the analysis for Pb is about 10%.

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. Operating conditions for these analyses were at 25 keV accelerating voltage, 0.1 μA beam current, and a beam spot diameter of approximately 0.1 μm. The Fe content of the IIIB kerogen was obtained by averaging 50 EDS analyses performed on a pressed pellet of the kerogen.

We also performed the above demineralization of the samples from the prominent K–P boundary section (equivalent to Fish Clay) at the southernmost part of Stevns Klint close to Rødvig (about 4 km south of Højerup), Nye Kløv (ca. 320 km northwest of Stevns Klint), Dania (ca. 220 km away northwest of Stevns Klint) (fig. 1A) in western Denmark, and Caravaca and Agosta (Spain), El Kef (Tunisia), Geulhemmerberg (Holland) and Furlo and Gubbio (Italy) (fig. 2).

RESULTS

Trace metals, REE, and minor Fe of the IIIB kerogen

Geochemical analysis shows that layer IIIB contains 1.8% of kerogen made up mainly (> 95%) of organic matter (table I). The contents of trace metals (Ir, Ni, Co, Cr, Zn, Au and Pb), REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) and minor Fe in the IIIB kerogen were determined and the analytical results are given in table I. Blank levels are more than an order of magnitude lower than given numbers. The concentrations of trace metals and REE are likely to represent lower limits of their actual levels due to loss of a fraction of these metals which are labile and loosely bound to the IIIB kerogen during the acid demineralization. The distribution pattern of trace metals and REE associated with the IIIB kerogen is also presented in table I. Note that the acid demineralization steps remove almost completely Ni, Co and Zn.

The ICP-OES analysis indicates that the IIIB kerogen contains on the average 2.7% of Fe. Given that the EDS analysis shows that approximately 10% of the total Fe is in the form of FeS_2, it can be calculated that this material contains about 0.6% FeS_2. The demineralizing steps remove most of the Fe (> 95% of total Fe) in layer IIIB, dissolving mainly Fe oxides and monosulfides [chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and pyrrhotite ($Fe_{(1-x)}S$)], but not disulfides such as FeS_2. Since it is difficult to separate FeS_2 from the IIIB kerogen it is likely that a minor amount of this iron mineral is associated with it. Thus, FeS_2 may partially account for the proportions of some sulfide-related trace metals.

The pyritization of trace metals was investigated in different anoxic marine sediments in the Gulf of Mexico by Huerta-Diaz and Morse [1992]. They reported that the general pattern for the degree of pyritization for Fe and trace metals shows that Fe > Co > Ni > Zn > Cr = Pb. Accordingly, sedimentary FeS_2 is a moderately important sink for Ni and Co, and generally unimportant for Zn, Cr and Pb. Thus, Ni and Co could partly reside within FeS_2 of layer IIIB because Co^{2+} and Ni^{2+} substitute isomorphously for Fe^{2+} in the FeS_2 lattice, due to similar ionic radii. Because ZnS and PbS are completely soluble in cold HCl it is very likely that these two metals are bound to the IIIB kerogen. This must also be true for Cr which also shows a rather low affinity for incorporation into FeS_2 and does not form sulfides [Brookins, 1988].

Elemental and EDS analyses indicate that 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. Given that the IIIB kerogen contains 4.7% S as measured by INAA (table I), it can easily be calculated that this material contains no or very little non-pyritic, sulfate S.

In contrast to the Fish Clay at Højerup, we did not detect kerogen neither in the Fish Clay at Rødvig nor in the marine boundary clays at Caravaca and Agosta, El Kef, Geulhemmerberg and Furlo and Gubbio; the Danish boundary clays at Nye Kløv/Dania have very low kerogen contents (≤ 0.1%) enriched in Cu^{2+}-porphyrins.

DISCUSSION AND INTERPRETATION

Cu^{2+}-porphyrins, humic substances and the impact-induced acid surface waters

Premović *et al.* [2000] suggested that humics were brought to the Fish Clay site by fluvial-influenced acid (probably sulfate) surface waters induced by the Alvarez *et al.* [1980] impactor (fig. 3). Indeed, the many studies of the K–P events indicate that the Alvarez *et al.* [1980] impactor could generate acid rain(s) at the K–P boundary. The opponents of the Alvarez *et al.* [1980] impactor usually suggest that gigantic volcanic eruptions (e.g. Deccan Traps in India) could produce similar acid rainfall(s). Vast amounts of mainly SO_2, generated by this impact, would be globally dispersed and would quickly be converted into H_2SO_4 aerosols that would act as nucleation sites for acid rain. Recently, Frei and Frei [2002] carried out multi-isotopic and trace elements studies of the Fish Clay and found that the sudden

TABLE I. – INAA/ICP-OES data for the abundances of trace metals, REE and minor Fe in the IIIB kerogen, and in C1 chondrite.

TABL. I. – *Résultats INAA/ICP-OES pour les métaux en trace, les éléments de terre rare et le fer dans le kérogène IIIB et la chondrite C1.*

Metal		Whole-rock	Kerogen[a]	[%][b]	C1 chondrite
Ni	ppm	330	737	3	11000
Co	ppm	50	41	2	502
Zn	ppm	340	25	0.5	312
Cr	ppm	150	158	4	2660
Pb	ppm	na[c]	12.5	-	2.47
Ir	ppb	40	500	25	481
Au	ppb	25	475	40	140
Fe	%	1.3	2.7	< 4	19.04
La	ppb	na	34.8	–	234.7
Ce	ppb	na	61	–	603.2
Nd	ppb	na	< 5	–	452.4
Sm	ppb	na	4.5	–	147.1
Eu	ppb	na	1.6	–	56.0
Tb	ppb	na	1	–	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] na: not analyzed.

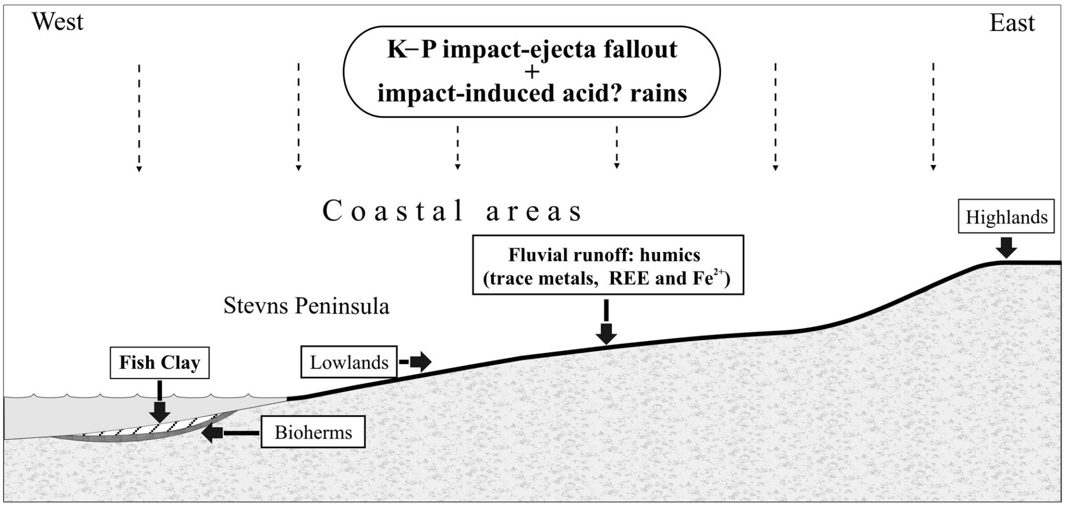

FIG. 3. – Proposed model for geochemical relations between the impact-ejecta fallout, humics in the coastal soil and Fish Clay at Stevns Klint.
FIG. 3. – *Modèle des relations géochimiques entre les retombées d'impact, les substances humiques dans le sol côtier et la succession Fish Clay à Stevns Klint.*

changes in Sr, Pb and Nd isotope compositions and ratios indicate enhanced, acid-rain induced local continental weathering.

Premović *et al.* [2000] reported that the IIIB kerogen contains anomalously high levels (up to 1000 ppm) of Cu and that this Cu is predominantly (> 90%) in the Cu^{2+}-porphyrin form. They concluded that Cu^{2+} chelation by humic-free porphyrins must occur in the humics-rich oxic coastal soil under acidic conditions prior to entering the Fish Clay. Indeed, Cu^{2+} is available essentially only at $pH < 5$ and Eh (redox potential) > 0.1 V in $H_2O – O_2 – CO_2$ systems [Garrels and Christ, 1965; Brookins, 1988]. Nevertheless, soil solutions even at pH 5 may contain Cu^{2+} because of the formation of complexes between this ion and humic substances. Moderately acidic soils have a pH of 4.5-6.5 [Retallack, 1990].

Cu^{2+} chelation by porphyrins is exceedingly fast (half-lives $< 1\ s^{-1}$) and the rate of the Cu^{2+} incorporation into porphyrins is nearly independent of the nature of the porphyrins themselves [Erdman *et al.*, 1957; Cole and Doll, 1983; Zelmer and Mann, 1983]. The acid solution of coastal soil, already enriched in Cu, would facilitate the formation of the humic Cu^{2+}-porphyrins.

The results of many geochemical studies have shown that organic matter derived from marine (sapropelic) sources (primarily dead phytoplankton) in anoxic sediments such as layer IIIB is considered to be more easily bio-degraded than organic matter derived from terrestrial (humic) sources (mainly land plants). This is because the latter contains higher concentrations of biologically resistant macromolecular (refractory) compounds. Thus, the predominant presence of resistant humic kerogen in layer IIIB may reflect substantial bio-degradation of organic matter derived from dead phytoplanktons [predominantly dinoflagellates: Hansen *et al.*, 1986; Wendler and Willems, 2002]. In oxic layers IIIA and V humic and marine organic matter were probably completely bio-decomposed before and/or after reaching the seafloor.

Refractory bioorganic matter in anoxic layer IIIB has subsequent to deposition undergone alteration by a low temperature early diagenetic process of remineralization (or oxidation) to form humics (enriched in Cu^{2+}-porphyrins). Under anoxic conditions of this layer the remineralization was probably mediated by bacteria. These humics were further transformed into kerogen (enriched also in Cu^{2+}-porphyrins) during the late diagenesis. The abundant presence of kerogen enriched in Cu^{2+}-porphyrins in the Fish Clay is unique among the K–P boundary strata worldwide and perhaps reflects very specific geochemical circumstances. The simultaneous occurrence of most likely cosmogenic Ir, impact-derived soot and kerogen enriched in Cu^{2+}-porphyrins are strong evidence that this kerogen is closely coupled with an asteroid impact. Premović *et al.* [2000] hypothesized that Cu^{2+}-porphyrins in the IIIB kerogen was formed from the humics derived from decaying green land flora, as a result of local impact-induced extinction events including acid rainfall and wildfire. In addition, the post-K–P impact atmospheric photosynthesis was very likely interrupted for at least several months [Alvarez *et al.*, 1980]. We suggest therefore that a probable source for the free porphyrin structures within the humic skeleton was chlorophylls of green plant vestiges on land (litter). It is reasonable then to suggest that the IIIB kerogen enriched in the impact-derived soot/Cu^{2+}-porphyrins, may echo the first environmental stresses of the end-Cretaceous impact event on the ecosystem of Denmark or even of Europe.

Trace metals and soil humic substances

Aquatic humic substances are the largest fraction of dissolved organic matter in natural waters [Thurman, 1985]. These substances are ubiquitous in geochemical processes including trace metal complexation and transport. However, humics are composed of a complexed mixture of organic compounds with varying chemical and structural characteristics and trace metal functional groups. The distinction between fulvic acids, humic acids and humin of soil is based on their aqueous solubility, which is primarily a consequence of their molecular weights. Humic and fulvic acids make up about 80% of dissolved organic matter in natural waters [Thurman, 1985]. Fulvic acids are soluble at any pH and have molecular weights near 1000. Humic acids are soluble below pH 2 and have molecular weights > 10^4, and humin which is very heavy is insoluble at any pH. Humics of organic-rich soils, such as coastal soil, show a strong cation exchange capacity, generally from 5-12 mmol g^{-1}, which is due to the presence of functional groups such as carboxylic and phenolic acids. These groups are capable of forming coordination complexes [Stevenson, 1994, and references therein]. Stability constants of these complexes are often in the range of 10^3-10^6, so that concentrations of trace metal ions in soil solution at equilibrium are very small and geochemical enrichment factors are large.

Under the acidic (pH < 6) conditions of coastal soil, fulvic acids would be soluble and they would chelate trace metals to form stable, but soluble complexes. Evidently the fluvial-influenced surface waters would remove most of these complexes from this soil afterwards. Under the same conditions, humic acids are insoluble and their presence would result in fixation of trace metals. Indeed, high levels of Cu and Cu^{2+}-porphyrins are only found in humic acids of a wide variety of organic-rich soils such as: recent soils, including peat-soils [Goodman and Cheshire, 1976; Cheshire *et al.*, 1977; Abdul-Halim *et al.*, 1981] and paleosols [Senesi and Calderoni, 1988].

Fe, Ni, Co and Zn: anoxic vs. oxic environment

An important mechanism of the bacterial degradation of bio-organic matter below the seawater-anoxic sediment interface is usually bacterially mediated reduction. The by-products of such biogeochemical process are mainly HS^- and H_2S that in turn may generate the formation of FeS_2 if detrital Fe^{2+} is present [Coleman and Raiswell, 1995, and references therein] and trace metal sulfides such as ZnS within the sedimentary rocks. In general, the quantity of Fe^{2+} ions brought into marine sedimentary basins depends on the dispersal of clays transported *via* fluvial runoff to the marine environment. Also, pH could determine the form of Fe available (Fe^{2+} *vs.* Fe^{3+}). Therefore, we accept the conservative view that virtually all pyritic and organic S in the IIIB kerogen is generated during early diagenesis in a strongly anoxic sedimentation milieu, rich in H_2S.

As pointed out before, most of the IIIB kerogen is originally redeposited humic substances, so we may reason that much of its trace metals is either detrital in the sense of having been brought to the site of the Fish Clay already located in humics (*ex-situ* model) or authigenic in the sense of having been sorbed from the seawater by humics (*in-situ* model). It is possible that incorporation of Ni, Co and Zn in the humics occurred under the anoxic sedimentary environment of layer IIIB (*in-situ* model). However, under these conditions most of Ni and Co would be incorporated into FeS_2 or precipitate as insoluble solid sulfides and Zn would precipitate as insoluble solid ZnS [Huerta-Diaz and Morse, 1990]. In this way the anoxic environment would act as a sink for these metals. Strong anoxic conditions of layer IIIB would be adverse for the incorporation of Ni, Co and Zn of the seawater into humics. We can thus conclude that the enriched association of Ni, Co and Zn in the IIIB kerogen does not reflect anoxic but oxic conditions. Indeed, the excess of Zn in the IIIB kerogen is a strong indication of a rather high concentration of soluble metal. On the other hand, high soluble Zn is only present under well-oxygenated conditions of sedimentation [Gambrell *et al.*, 1991]. Like Cu [Premović *et al.*, 2000], Ni, Co and Zn of the IIIB kerogen were probably incorporated into humic structures during the early diagenesis of humics (*ex-situ* model) in the oxic milieu of coastal soil. This conclusion is compatible with a geochemical study of Ni and Co in modern soils which indicates a strong affinity of these two metals for soil humics [Lakatos *et al.*, 1972]. The fact that humics were enriched in Ni, Co and Zn implies that the solution of coastal soil was relatively low in pH because these metals are not very soluble at pH > 5 [Swaine, 1980]. Moreover, if the incorporation of Ni, Co and Zn into humics occurred under acidic and oxidizing conditions of coastal soil then predominant free Ni^{2+}, Co^{2+} and Zn^{2+} ions would be almost solely present in this solution [Brookins, 1988]. The content of Fe incorporated into the IIIB kerogen is as high as 2.7%, implying that coastal soil also received a high input of detrital Fe. Thus, this soil may have differed in composition from an ordinary oxic soil, possibly, because of its excess of trace Ni, Co, Zn and minor Fe. Note that Fe is very insoluble under oxidizing conditions above pH 4 and precipitates as various oxides [Kraemer, 2004].

In summary, the IIIB kerogen was probably derived from humics (largely humic acids) enriched in Ni, Co, Zn. These humics in 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 of Premović *et al.* [2000].

The impact fallout, humics and trace metals

Chondritic and non-chondritic trace metals in the marine K–P strata sourced by the impact fallout can be divided into primary and secondary. The primary trace metals would represent the part associated with the impact-ejecta airfall which settled directly onto the seafloor. The secondary trace metals arose from weathering/leaching of the impact fallout settled on land which afterwards was transferred to marine sedimentary sites by rivers. Kyte *et al.* [1985] analyzed layers IIIA and IIIB for trace metals in particular siderophiles and suggested that only IIIA referred to usually as the "impact layer" is a sole representative of the primary impact fallout in the Fish Clay. They also proposed that these metals in the overlying layers mainly arose from the fallout on the nearby land. This fallout was leached from its trace metals by the impact-induced acid surface waters [Kyte *et al.*, 1985].

Ni, Co and Zn in the IIIB kerogen: chondritic vs. terrestrial origin

The distribution patterns of Ni, Co and Zn in most marine K–P strata throughout the world are very similar and these metals are well correlated with cosmogenic Ir and also with one another [Gilmour and Anders, 1989]. Because of the similar Ir, Ni, Co and Zn contests, comparable mechanisms are likely to have been responsible for their enrichments, including their common origin and similar behaviour during diagenesis of the K–P boundary strata worldwide. We assume that a major fraction of Ni, Co and Zn in the IIIB kerogen represents the impact fallout. The concentrations of Ni and Co within the IIIB kerogen are much lower than their average concentrations in C1 chondrites (table I). Davenport *et al.* [1900] estimated that the top of soil after the impact event would be covered with fallout material with Ni content that is one or two orders of magnitude larger than the contemporary average level of Ni (16 ppm) in soils [Nriagu, 1980]. According to these authors, the impact infall would have the concentrations of chondritic Ni and Co between 133-1330 ppm and 7-70 ppm, respectively. It is reasonable, therefore, to assume that most of the Ni and Co within the IIIB kerogen ultimately came from a C1 chondritic component associated with the impact-ejecta fallout covering coastal soil. Gilmour and Anders [1989] suggested a chondritic origin of anomalous Ni and Co in the most prominent K–P section including the Fish Clay. Strong *et al.* [1987] also concluded that Ni in one of these boundary sections at Flaxbourne River, New Zealand, is mainly of meteoritic origin but they argued that Co is mainly terrestrial.

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. Simple metal supply calculations suggest that the Zn content of the airfall derived from the impactor would be 4-38 ppm. This suggests that the Zn in the IIIB kerogen could be augmented by chondritic volatiles of the impactor. Gilmour and Anders [1989] considered that the excess of Zn in the above mentioned boundary sections is of marine origin. Strong *et al.* [1987] suggested that Zn in the K–P boundary deposit at Flaxbourne River was derived from crustal rocks. We suggest that high Zn in the IIIB kerogen is probably primarily sourced by the chondritic and non-chondritic (target rock) material of the impact fallout.

Cr in the IIIB kerogen

As pointed out earlier, most of Cr resides within the IIIB kerogen since very little of this metal is located in FeS_2. Cr is one of the metals that is invariably enriched in the impact-related K–P boundary strata together with Ir and it is also well-correlated with Ni, Co and Zn. Consequently, Cr should be one of the most important indicators of cosmogenic material in the K–P sections worldwide. This implies that a considerable amount of Cr in the IIIB kerogen could be derived from the chondritic component of the impact fallout. Indeed, average Cr concentrations in C1 chondrites are about 2700 ppm and this is probably adequate to explain its high value of 158 ppm in the IIIB kerogen (table I). Cr exists in natural waters and sediments in two main oxidation states, Cr (III) and Cr (VI). Predominant Cr (III) form in natural oxic or anoxic waters at pH > 4 is insoluble, hydrous and/or amorphous Cr_2O_3; under these conditions the Cr^{6+} ion (as and) is in extremely low concentration [Bartlett and James, 1988]. In addition, complexation Cr (VI) and humics in the solution of coastal soil would be negligible because this ion could be quickly reduced to Cr (III) by these substances.

Cr^{3+} is usually restricted to natural acid waters since its solubility in aqueous solution decreases as the solution pH is raised above pH 4, with essentially complete precipitation mainly as Cr_2O_3, occurring at pH 5.5 [Bartlett and James, 1988]. The solution of coastal soil at this pH may contain Cr^{3+}, however, because of its formation of complexes with humic substances. Evidently, very little of the Cr would be available for chelation by humics in the strongly anoxic seawater of layer IIIB at pH 6–7. Thus, most of the Cr was doubtless incorporated into terrigenous humic substances in the oxic coastal soil.

Rai *et al.* [1987] reported that Cr^{3+} forms hydroxy complexes in soil solution, including $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$. Because Cr is not known to form sulfides [Brookins, 1988], and because of the stability field of solid $Cr(OH)_3$ and Cr_2O_3, it is likely that most of the Cr complexed with humics in coastal soil was largely present as $Cr(OH)_2^+$ and/or $CrOH^{2+}$, acquired through the complexation processes. Soil humic complexes of Cr^{3+} formed at pH < 5.5 may remain stable even after the pH was raised to neutrality [Bartlett and Kimble, 1976]. This implies that Cr^{3+}-humics complexes formed in coastal soil would be even stable in the seawater after their transfer.

Ir, Au and the IIIB kerogen

The IIIB kerogen contains high Ir (500 ppb) and Au (475 ppb) and 25% Ir and 40% Au of the total metal reside in this fraction (table I). About 50 % of the total Ir and Au flux in the Fish Clay is hosted by the IIIB and IV kerogen [Schmitz *et al.*, 1988]. Ir and Au of the IIIB kerogen most likely have the same meteoritic origin as they are found in enhanced levels at many K–P boundaries all over the world.

In general, Ir and Au are associated with bio-organic matter in marine and continental sediments [Evans *et al.*, 1993]. It also appears that humics probably played an important role in concentrating Ir in layer IIIB [Schmitz *et al.*, 1988]. However, the Ir would precipitate as highly insoluble IrS_2 and/or Ir_2S_3 like Fe, Ni, Co and Zn [Brookins, 1988] preferentially in the anoxic environment of layer IIIB. Thus, Ir ions would not be readily available for complexation with humics in the anoxic environment of layer IIIB. It is more likely that this process was an event that just preceded the accumulation of layer IIIB, i.e. it occurred in the oxic humics-rich coastal soil. It is, therefore, possible that a part of the Ir inventory of the IIIB kerogen results from a geochemical enrichment of humics in coastal soil. If true, then it implies that a portion of the Ir anomaly in layer IIIB came through geologically speaking instantaneous influx of humics to the seawater. This suggestion is in line with previous estimates of fast deposition of layer IIIB on decadal or centennial time scale [Premović *et al.*, 2000; Wendler and Willems, 2002].

Au, Ir, Ni, Co and Cr are concentrated in chondritic meteorites and Au is one of the most reliable indicators for extraterrestrial contribution to the K–P boundary strata [Lichte *et al.*, 2000]. Many geochemical studies suggest that Au can be readily chelated by humics in oxic soil and that this metal could be stable in natural, oxygenated waters merely as Au^{3+} complexes [e.g. Fedoseyeva *et al.*, 1985]. We suggest that the complexation of Au^{3+} and humics probably took place in coastal soil.

Keller *et al.* [2002] presented evidence for multiple impacts during the K–P transition. The first impact with no Ir anomaly occurred at Chicxulub in the latest Maastrichtian (ca. 65.3 Ma). This impact coincided with major Deccan volcanism. The second impact event with the Ir anomaly occurred at the K–P boundary (65 Ma), and the third one in the early Danian about 100 ky after the K–P boundary. It is, therefore, possible that the Ir anomaly in the IIIB kerogen reflects the second earliest Danian impact event. If we assume that anomalous Ir, Au, Ni, Co, Cr and Zn in this kerogen arose from the same impact fallout, then it is likely that their incorporation into humics occurred at the K–P boundary. It seems also reasonable to assume that the IIIB kerogen represents a short period of rapid redeposition of these humics occurring at the K–P boundary.

Pb and the IIIB kerogen

It is most likely that most of Pb resides in the IIIB kerogen where the concentration of Pb is almost 6 times higher than its mean abundance in C1 chondrites (table I). If Pb originated from the chondritic component of the impact fallout it would necessitate rather drastic concentration of the metal during the weathering/leaching of the impact fallout, and so it seems likely that Pb arose from a terrestrial source. Indeed, geochemical studies of Pb in layer IIIB strongly indicate that this metal is probably of terrestrial origin [Dia *et al.*, 1989; Frei and Frei, 2002]. We suggest that this Pb came from the rock(s) exposed in the coastal areas. The predominant species of Pb in coastal soil could, therefore, be the complexes of Pb^{2+} ions with humics.

REE of the IIIB kerogen

REE have been used as proxy indicators for reconstructing Eh and pH conditions of ancient sedimentary environments [Lui *et al.*, 1988]. Except Ce, REE in natural waters commonly occur in the 3+ oxidation state and exhibit very similar geochemical properties [Brookins, 1988]. Layers IIIB and IV contain relatively high concentrations of REE and the bulk of (> 90 %) of the total rare earths resides in the apatite phase [Schmitz *et al.*, 1988]. These authors concluded that most of these elements precipitated from the seawater at Stevns Klint.

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; Gromet *et al.*, 1984] but highly enriched in REE relative to C1 chondrites (table I; fig. 4). It seems improbable, therefore, that C1 chondritic sources have made an important contribution to the REE in the IIIB kerogen.

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 [Elderfield *et al.*, 1981; Elderfield and Greaves, 1982; de Baar *et al.*, 1983, 1985; Sholkovitz *et al.*, 1994; Dubinin, 2004]. 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 [de Baar *et al.*, 1985] and an absence of a Ce anomaly [Turner *et al.*, 1981].

The IIIB kerogen displays a flat pattern with zero Ce and Eu anomalies (table I; fig. 4), indicating that its REE, probably, did not originate from the seawater. It is rather likely, therefore, that this kerogen (i.e. humics in coastal soil) must have inherited 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 [Verplanck *et al.*, 1999]. Thus, we suggest that ultimately the REE of the IIIB kerogen were perhaps sourced by the 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 [Hoyle *et al.*, 1984; Goldstein and Jacobsen, 1988; Sholkovitz *et al.*, 1992; Tang and Johannesson, 2003], and these types of complexes dominate in acid surface waters enriched in humics [Dubinin, 2004]. It is thus rather likely that REE were initially complexed with humics in coastal soil.

We offer a model as a first approximation to the geochemical processes involved (fig. 3). We suggest that chondritic Ir, Au, Ni, Co, Cr and chondritic and non-chondritic Zn were leached from the 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. Trace metals and REE were then chelated by humics of coastal soil and this uptake occurred rapidly during early diagenesis. Local conditions such as topography (e.g. highlands *vs.* lowlands) were perhaps favourable for efficient and concentrated accumulation of trace 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).

A final hypothesis: A short-term sea-level fall at the K–P boundary?

It appears that the deposition of layer IIIB occurred in low-salinity or even brackish water conditions [Hart *et al.*, 2004] considerable closer to shore line than the underlying latest Maastrichtian chalk. This could imply a more significant input of fresh water compatible with a short-term lowering of sea-level during this deposition. According to Wendler and Willems [2002], the dramatic reduction in

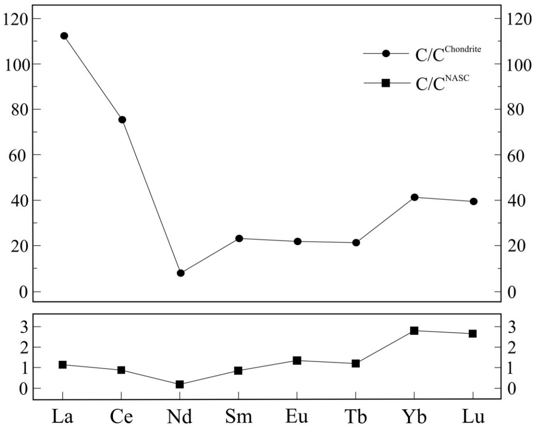

FIG. 4. – Distribution of REE in IIIB kerogen normalized relative to REE in the NASC (■) [Gromet *et al.*, 1984] and chondrite (●) [Anders and Grevesse, 1989].

FIG. 4. – *Distribution de REE dans le IIIB kerogen normalisé au REE dans le NASC (■) [Gromet* et al., *1984] et chondrite (●) [Anders et Grevesse, 1989].*

number of calcareous dinoflagellate cysts belonging to the Pithonelloideae assemblage in layer IIIB infers a short-term sea-level fall. The abundant presence of poorly sorted sand and silt, terrigenous quartz grains [Christensen *et al.*, 1973], the grain size distribution [Christensen *et al.*, 1973; Wendler and Willems, 2002], high content of detrital smectite and humic kerogen [Premović *et al.*, 1993, 2000] indicate that most of material in layer IIIB was probably transported to the site of the deposition of the Fish Clay during a temporary sea-level fall. The sizes of chalk clasts, sand and silt grains indicate this transportation occurred over a relatively short distance [Christensen *et al.*, 1973]. Therefore, the most plausible explanation for the abrupt increase of smectites and humics in layer IIIB is a temporary fall in sea-level in the Danish Basin. The same interpretation is given by Elliott (1993) discussing the source of smectite within the Fish Clay succession.

The humic (i.e. kerogen) Cu^{2+}- porphyrins are rare and atypical for ancient sedimentary rocks of marine origin [Premović *et al.*, 2000]. In general, Cu^{2+}- porphyrins are derived from enhanced weathering of terrestrial organic accumulations and are reliable markers for oxidized terrestrial organic matter redeposited in the marine environment [Baker and Louda, 1983]. In all these cases, the humic Cu^{2+}-porphyrins are generally solitary or sporadic occurrences and are found confined to relatively small soil or sedimentary areas. It seems, therefore, implausible that the humics enriched in Cu^{2+}- porphyrins of the IIIB kerogen were formed simultaneously during the (geologically speaking) short time period of the K–P event in both eastern and northwestern Denmark in soils widely separated from each other (fig. 1A).

The bulk of the smectite of the K–P boundary deposits at the Nye Kløv and Dania locations is also of detrital origin [Premović *et al.*, 1993]. According to the sedimentation model hypothesized by these authors, the boundary deposits in northwestern Denmark represent erosion and subsequent redeposition of the Fish Clay of eastern Denmark. It therefore appears that the K–P boundary strata at Nye Kløv and Dania could have been formed by the redeposition of smectite and the humics from their original sites (i.e. their points of formation) in the eastern part of the Danish Basin. This redeposition could also be attributed to the above mentioned short-term sea-level fall. In general, while sediments were eroded in shallow marine areas during sea-level falls the eroded sedimentary material should collect in adjacent deeper portions of the basins. We may further speculate that the sea-level fall during the K–P boundary could be linked to an eustatic low, or to tectonically or even climatically induced changes somehow triggered by the K–P impact. A study of spatial patterns of the K–P event reveals that an eustatic low is inferred in some 67% of all marginal/shallow-marine K–P strata, while in 33% of the sections no evidence for a regression is evident or even a sea-level rise is suggested [Kiessling and Claeys, 2000]. Therefore, we tentatively assumed that the K–P sea-level fall in the Danish Basin may be of eustatic rather than of regional tectonic or climatic origin.

CONCLUSIONS

Humics (mainly humic acids) in coastal soil can be regarded as the progenitor of the IIIB kerogen [Premović *et al.*, 2000]. From the geochemistry of trace metals (Ir, Au, Ni, Co, Cr, Zn and Pb) and REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) associated with the IIIB kerogen, we may deduce that most of the trace metals and rare earths were originally bound with these humics in an acidic (pH probably 4.5-6.5) and oxic soil of the adjacent coastal areas in eastern Denmark. Apparently, chondritic Ir, Au, Ni, Co, Cr and chondritic and non-chondritic Zn were 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, phenolic and porphyrin groups were able to chelate trace metals 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 already enriched in Cu^{2+}-porphyrins and soot, trace metals and REE were fluvially transferred onto the Fish Clay during the K–P boundary transition.

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