

The Cretaceous-Tertiary boundary Fiskeler at Stevns Klint, Denmark: the geochemistry of the major trace metals

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Trace metals in the four discrete layers of the Cretaceous-Tertiary boundary (Fiskeler) at Stevns Klint (Denmark) are relatively well studied, yet much remains to be learned about them. Therefore, an integrated study of the trace (meteoritic Ir, partly meteoritic Cr/Ni/Co/Au and terrestrial Zn/Cu/La/Ce/Nd/Sm/Eu/Tb/Yb/Ta/Th) metals in the basal black marl of Fiskeler and in its (carbonate, HCl-soluble, smectite, HCl-insoluble, silicate and kerogen) fractions was undertaken. The mineralogy of the marl is comparatively simple, authigenic calcite (mainly derived from planktonic marine algae: coccoliths), detrital Mg-smectite and quartz being the principal components, with lesser amounts of kerogen, Fe³⁺-oxides, pyrite, ilite and feldspar. Selective leaching procedures were used to establish geochemical associations and specific mineralogical locations of the trace metals. The results identified the main locations of the major trace metals (Cr/Ni/Co/Zn/Cu/Ir/Au). They occur mainly in the smectite and, to a lesser extent, in the biogenic calcite (Ni/Co/Zn) and kerogen (Ir/Au). The trace metal data are in accordance with the hypothesis that substantial proportions of Cr/Ni/Co/Zn/Cu/Ir/Au were probably contained in the detrital smectite arriving at the site of the deposition. In a general discussion of the results, a geochemical model describing the incorporation of trace metals in the smectite is presented, based on the weathering/transport of the clay by (impact-induced) acid surface waters and the adsorption of trace metal ions by the smectite particles/colloids in the acidic solution of nearby oxic soil. The distribution/enrichment patterns of Cr/Ni/Co/Zn of the basal black marl and higher Fiskeler layers indicate, on the other hand, that notable proportions of these metals were incorporated into the smectite structure during the formation of the clay. The trace metal data are also considered in light of previously published paleoecological and geochemical information for Fiskeler. It is proposed, for example, that the local (impact-induced) superacid rainfall and wildfires played an important role in providing appropriate humics (*i.e.* appropriate organics of decaying land green plants) having porphyrin structures for the formation of kerogen (enriched with Cu²⁺-porphyrins). In addition, it has been suggested that the biogenic calcite with high Ni is probably a product of

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the metabolic uptake of boundary seawater (enriched with this metal) by the coccoliths. The metal enrichment of the seawater was created by a sudden and high influx of (apparently mainly meteoritic) Ni: airborne and laterally redeposited (by the acid surface/river waters) from a nearby soil. Lastly, the lateral distribution of kerogen (enriched with Cu^{2+} -porphyrins) supports an earlier interpretation presented by Hultenberg^{1,2} that the alleged (Nye Kløv/Dania) boundaries in northwestern Denmark represent erosion and subsequent redeposition of Fiskeler in eastern Denmark.

Keywords: geochemistry, Cretaceous-Tertiary boundary, trace metals, smectite, kerogen.

INTRODUCTION

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

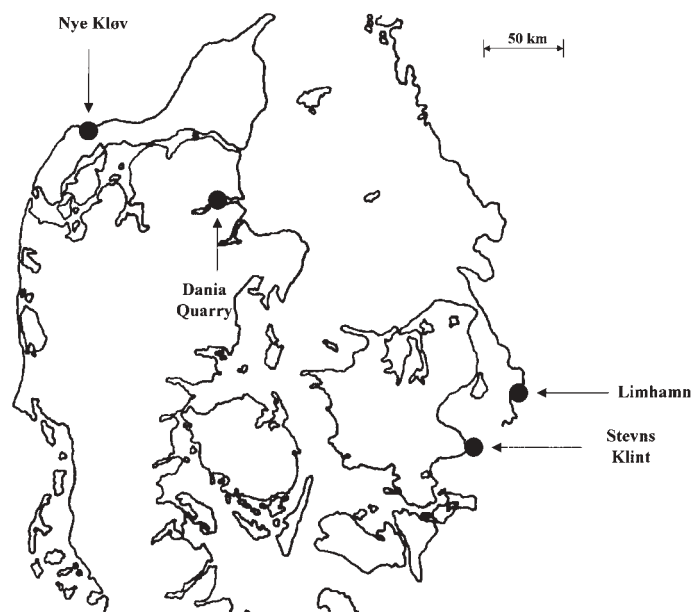


Fig. 1. Location of the samples of the Danish/Swedish boundaries.

Palynological studies of FK by Hultenberg^{1,2} indicate that II was deposited under normal marine conditions and that the base part of III was deposited in a milieu strongly affected by a freshwater influx; whereas the top of III, IV and V were accumulated under a predominant marine influence. He suggested that a local Maastrichtian freshwater agent, a river (hereinafter referred to as the FK river) close to the FK Basin was the source for detritus (including the clay/humics) of the boundary. Clay mineralogy studies indicate that the distinctive

Mg-smectite is the predominant clay mineral in FK.⁴⁻⁶ In general, the high-Mg/low-Al smectites (such as the III smectite) were most likely formed by the alteration of volcanic material.⁷ Elliott *et al.*⁵ and Elliott⁶ presented evidence (based on clay mineralogy and the geochemistries of the major/trace element) that the FK smectite is of volcanic origin and that pyroclastic basaltic volcanism was probably its predominant progenitor. They also reported that Mg-smectite is the predominant clay mineral not only in FK (eastern Denmark), but also at two alleged boundaries (in two outcrop sections: Nye Kløv/Dania) a few hundred kilometers away in northwestern Denmark, Fig. 1, although, in these sections there is no FK but rather an abrupt change from the underlying Maastrichtian sequence to the overlying Danian sequence.⁸ In addition, they found that Mg-smectite is the principal clay mineral in Tertiary marls at the Limhamn Quarry (Sweden), Fig. 1 situated up to 8 meters above the boundary, and also in the bed deposited up to 32 meters below the boundary.

Alvarez *et al.*⁹ reported an anomalous high Ir concentration in FK. To explain the enhanced Ir concentration, the authors proposed a late Cretaceous asteroid impact on the Earth. This proposal was soon followed by reports of Ir enrichments in several other boundaries from all over the world. Kyte *et al.*¹⁰ proposed that only the III/IV layers of FK could be used to estimate the impact fallout (asteroidal matter/target rock). Apart from Ir, FK is enriched in other trace metals: partly meteoritic Cr/Ni/Co and non-meteoritic (terrestrial) V/Cu.^{11,12} Christensen *et al.*³ proposed that these metals concentrated due to an accumulation of mainly terrigenous materials with minor amounts of clay minerals of diagenetic origin. Elliott *et al.*⁵ and Elliott⁶ showed that the III smectite is a possible carrier phase of the trace metals (Cr/Ni/Ir/Au) and the rare earth elements (REE) (La/Ce/Nd/Sm/Eu/Tb/Dy/Yb/Lu). Alternatively, they suggested that the trace metals are associated either with a submicron phase (undetected by X-ray) or with the organic fraction of III.

To date, the question of the origin/nature of Cr/Ni/Co in the III smectite is not resolved. Elliott *et al.*⁵ and Elliott⁶ reported that Danish boundary smectites contained much higher levels of these metals compared with the smectites from the marls from Limhamn Quarry. For this reason, these authors argued that the Cr/Ni/Co in the III smectite originated from the boundary seawater, which was enriched with these metals from the impact-ejecta fallout. Premović *et al.*^{11,12} consider that much of the Cr/Ni/Co (as well as Cu/V) of the III smectite is strictly detrital in character, *i.e.*, having been transported to the site of deposition already contained in the clay. One of our goals in the present work is to discuss further the geochemical properties of the Cr/Ni/Co/Cu associated with the various fractions of III, which support our earlier interpretation.

Geochemical analyses of III revealed that this rock contains up to *ca.* 3 % of insoluble organic matter: kerogen.¹¹⁻¹³ Geochemical extractions performed by Wolbach *et al.*¹⁴ indicate that the III kerogen contains predominantly (>90 %) a highly resistant terrestrial kerogen, a reactive marine kerogen and a minor fraction (<1 %) of elemental carbon (soot/charcoal) particles.

In many previous studies of FK, most attention has been focused on the trace metals present in the inorganic fractions (in particular the smectite), much less regard has been paid to trace metals associated with kerogen. Schmitz *et al.*¹³ reported that kerogen separated from the III/IV kerogen concentrate exhibits enhanced concentrations of Ni/Co/Cu/Ir/Au. Accord-

ing to these authors, trace metal precipitation in FK was induced by various redox-controlled processes in connection with the decomposition of the abundant algal matter. Schmitz¹⁵ argued that the concentrated trace metals of the III/IV sample were precipitated as sulfides from the FK seawater; though the authors, also, pointed out that the ultimate origin of some of these metals (e.g. Ir/Cr/Ni/Co) may have been an Earth-impacting asteroid.

According to Premović *et al.*,¹² the III kerogen represents a mixture of marine kerogen diluted by kerogen derived from the terrigenous humic substances of a nearby organic rich (oxic) soil (hereinafter referred as the FK soil). These authors also proposed a model in which enormous (impact-induced) superacid rainwaters redeposited the humics of the FK topsoil into the FK Basin. The geochemistries of V/Cu imply that the III smectite and the III humics (as the ultimate precursors of the III kerogen) had different sites of formation.¹²

In this study more than sixteen trace metals were determined by AAS, ICP-OES and INAA for the carbonate, HCl-soluble, smectite, HCl-insoluble, silicate and kerogen fractions of III. In order to describe the geochemical characteristics of III and to understand the behavior of trace metals during sedimentation of III, trace metal abundances were compared with each other among all fractions. Essentially, this paper is largely complementary to our earlier studies^{11,12} and discusses broader aspects of the geochemistry of trace metals in the III smectite/kerogen which may be important in understanding the geochemical and paleoecological events that occurred during the KT boundary. Finally, we would like to emphasize that the ultimate terrestrial sources of the III smectite and trace metals associated with the various fractions of III are beyond the scope of this paper, since they had little to do with the geochemical aspects of the boundary.

EXPERIMENTAL

The experimental techniques/methods have already been described earlier.^{11,12,16} The samples were analyzed by AAS/INAA/ICP-OES. Total uncertainties (including accuracy error) of the analyses for the trace metals range from 5 % to 20 %.

Dr. Helle Schummel collected bulk samples of III from an outcrop 200 m south of Højerup Church. A III sample was dried in an oven and carefully ground in an agate mortar. The powdered rock sample (48 g) was treated (12 h) with acetic acid (0.5 M) to remove the carbonates. The soluble portion constitutes the carbonate fraction (analyzed for trace metals by AAS). The insoluble material constitutes the carbonate-free fraction. The carbonate-free fraction was demineralized (2 h) with HCl (6 M, 80 °C, 2 h). This acid solution removes the smectite fraction,¹¹ the soluble portion represents the HCl-soluble fraction. The HCl-soluble/smectite fractions were analyzed for trace metals by INAA/ICP-OES and AAS. The insoluble portion comprises the HCl-insoluble fraction (analyzed for trace metals by INAA/ICP-OES). This part was first demineralized (72 h) with HF (22 M/12 M HCl, 80 °C) and then with boiling HCl (12 M, 12 h). The soluble portion constitutes the silicate fraction (analyzed for trace metals by INAA/ICP-OES). The insoluble (mainly organic) portion was further extracted (Soxhlet, 72 h) for bitumen with benzene: methanol (6:1, v/v). The insoluble part (>99 % of organic fraction) represents the kerogen fraction (analyzed for trace metals by INAA/ICP-OES).

RESULTS AND DISCUSSION

Trace metals and III

The trace metals determined in III may be arbitrarily divided into two groups. For the first (major) group of trace metals Cr/Ni/Co/Zn/Cu/Ir/Au, the contents in the carbonate,

smectite, silicate and kerogen fractions were determined. The analytical results are given in Table Ia. Table Ib shows the distribution [ppm/%] of these metals among the six fractions of III. The results of the analyses given in Table Ia, generally, agree with those already published.^{5,6,11,12,13,15,17} Cr/Ni/Co/Cu/Zn were chosen primarily because of the relatively simple chemistry of their ions in natural waters. In addition, some of these metals show a similar geochemical behaviour in natural waters (*e.g.*, Ni/Co/Zn/Cu). Special focus was given to meteoritic Ir because this metal is probably the best tracer for the identification of the impact material in III; partly meteoritic (Cr/Ni/Co/Au) metals are a mixture derived from terrestrial/meteoritic sources. For the sake of clarity, the results pertaining to the III smectite/kerogen will be discussed separately.

TABLE Ia. Geochemical concentration of the major trace metals among the six (carbonate, HCl-soluble, smectite, HCl-insoluble, silicate and kerogen) fractions of III

Metal		Fraction*						
		Total	Carbonate	HCl-S**	Smectite	HCl-I**	Silicate	Kerogen
Cr	ppm	150	20	630	350	25	15	160
Ni	ppm	355	245	1025	565	55	15	625
Co	ppm	55	35	165	90	5	<5	40
Zn	ppm	310	110	1185	655	15	15	25
Cu	ppm	80	10	280	160	60	15	715
Ir	ppb	40	0	145	80	40	5	500
Au	ppb	25	0	65	35	40	10	475

*The percentage of the whole sample: carbonate [52.0 %], the HCl-soluble fraction [21.0 %], smectite [38±5 %], the HF-insoluble fraction [27.0 %], silicate [25.2 %], kerogen [1.8 %].

**HCl-S (HCl-soluble); HCl-I (HCl-insoluble).

The analytical results (Table Ia) show that the major trace metals in the III smectite are present at levels well above the normal abundance in clays,¹⁸ whereas most of the Cr (89 %)/Ni (60 %)/Co (62 %)/Zn (80 %)/Cu (74 %)/Ir (74 %)/Au (60 %) reside in the III smectite (Table Ib). This is consistent with previous studies on the distribution of these metals in the III smectite.^{5,6,11,12}

For the second group of metals Ta/Th/REE, only information on the silicate/kerogen fractions is available. The analytical results are given in Table IIb (INAA/ICP-OES). These metals/elements were chosen because of their distinctive (but relatively simple) geochemical activities and properties. The results for Cr/Ni/Co/Zn/Cu (Table Ia) and the X-ray diffraction, Fourier transform infrared, electron spin resonance, scanning electron microscopy/microprobe analyses on the demineralized fractions of III confirm 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 pyrite (FeS₂) and insoluble minerals, including some fluorides as artifacts of the kerogen isolation procedure (which precipitate from a solution of aluminosilicate matrix in HF/HCl solution¹⁹).

It is worth mentioning that the results of the geochemical analysis of the III kerogen show that several trace metals (*e.g.*, Cr/Ni/Cu/Ir/Au) occur at relatively high

concentrations (Table Ia) despite the rigorous preparative technique employed. Hence, the results should be regarded as minimum values representing trace metals strongly bound to the III kerogen.

The fluviatile sedimentation model of FK

A plausible (so-called fluviatile) explanation for the succession of the FK depositional settings was offered by Hultenberg.² According to this author, at some time during the deposition of FK, an abrupt increase of the outflow of the FK river occurred, resulting in the formation of the base part of III. A subsequent decrease in the river outflow resulted in the formation of the top of III (and afterward IV/V). The cerithium (VI) limestone (which overlies FK) definitely indicates a return to normal marine sedimentation conditions similar to those of I/II. The chalk I is separated from the upper limestone VI by some < 20 cm of FK (II–V), suggesting that a relatively short period of time (geologically speaking) elapsed between the end of the Maastrichtian chalk-forming stage and the initiation of the Danian limestone deposition.

If Hultenberg's interpretation is accepted as a reasonable working hypothesis, it follows that one of the very first (impact-induced) traumatic effects in the FK area was a huge superacid rainstorm. This storm was probably caused by sudden impact-related atmospheric^{20,21}/climatic anomalies.^{8,22} This rainstorm increased enormously the acidified runoffs (the flash flooding of the FK soil) both of the acid surface waters (streams, creeks) and the FK (probably acidified) river carrying suspended smectite (and other detritus) and terrestrial plant debris (including freshwater algae^{1,2}) into the FK Basin (Fig. 2). This resulted in the first deposition of III (i.e. its base part). At the same time, the impact of fallout settling/local wildfires was also felt, as Ir, kerogen and (associated soot) emerge simultaneously in the layer.

Cu-P and the III humics

According to Premović *et al.*¹² the kerogen isolated from III contains anomalously high levels of Cu (up to 1000 ppm). Their geochemical analyses, also, indicate that Cu in the III kerogen is predominantly (> 90 %) in the form of Cu²⁺-porphyrin (4000 ppm, determined by ESR). In addition, the geochemical evidence presented by these authors indicate that the kerogen Cu²⁺-porphyrins (Cu-P) were not formed *in situ* (i.e., within III) but that they are strictly detrital in character, i.e. they were transported from the nearby FK soil to III. According to several studies,^{23–25} Cu²⁺ chelation by porphyrins is exceedingly rapid (half-lives < 1 s⁻¹) and the rate of the Cu²⁺ incorporation into porphyrins is nearly independent of the nature of the porphyrins themselves. Given that Cu²⁺ is available as such, in H₂O–O₂–CO₂ systems (such as the FK oxic soil water) essentially only at pH < 5¹² and Eh > 0.1,²⁶ we can only surmise that Cu²⁺ chelation must have occurred in the (oxic) FK soil solution under acidic (pH < 5) conditions prior to entering III.

Geochemical analyses show that the carbonate-free fraction of III contains a relatively high content (up to 6 %) of kerogen (enriched with Ir/soot).^{11,12,27} On the contrary, the corresponding fractions of the underlying II/overlying V contain insignificant amounts (≤ 0.1 %) of kerogen. The formation of the humics (which caused an additional acidification of the FK soil) commenced abruptly as a result of the impact and de-

clined more gradually during the III/IV deposition.^{11,12} The simultaneous occurrence of the Ir/soot anomalies is compelling evidence that the formation of the III kerogen (enriched with Cu–P) was due to a geochemical process that was in some way coupled to the asteroid impact. We suggested here that the III humics were derived from the rapid deposition of organic materials derived from decaying land green flora, resulting from local extinction events including superacid rainfall/wildfires. This invites the reasonable conclusion that the probable source of the free porphyrin structures within the humic skeleton was chlorophylls of plant vestiges. Thus, it is reasonable to suggest that III (highly enriched with the smectite, Ir, kerogen with Cu–P and soot) may echo the first geochemical effects of the impact on the FK soil ecosystem. The gradual upward decline of kerogen from its maximum in III is simply a reflection of the decreasing proportion of the detrital humics (brought by the FK river to the FK Basin) relative to the predominant local inorganic detritus + authigenic calcite.

Experimental studies and observations on modern/ancient soils suggest that the FK soil solution in which humic Cu–P was formed was not a normal soil solution. It was probably very rich in Cu and porphyrins and had a lower-than-normal pH (< 4: see below). Specifically, the accumulation of the humic Cu–P in an oxic soil solution requires, however, that those chemical factors governing their formation be exactly right; the content of neither Cu nor free humic porphyrins should be low. The acid surface waters could, however, highly enhance the concentrations of both Cu, by severe leaching of the corresponding source rock, and the humic free porphyrins, by chemical degradation of terrestrial green plants (containing chlorophylls). This would, for certain, facilitate the formation of the humic Cu–P in the FK topsoil. Thus, we suggest that the formation of the III humics (enriched with Cu–P) was probably stimulated by both superacid rainfall/local wildfires.

Weathering and redeposition of the III smectite and the acid surface water

The smectites (*e.g.*, the III clay) are largely derived from volcanic materials and their formation from parent volcanoclastic (or basic igneous) rocks occurred often in a neutral-to-weakly alkaline (pH \geq 7) environment. Abundant volcanogenic smectite in ancient sedimentary rocks of marine origin usually reflects the close presence of an exposed volcanic area. The composition of the smectites (including their trace metal contents) formed from similar volcanic materials can be quite uniform over fairly large areas (*e.g.*, the boundary deposits of Denmark). The smectites can have been transported from their source area to marine or terrestrial basins mainly by rivers (*e.g.*, the FK river). Detrital smectites in marine sedimentary rocks, especially those from the late Cretaceous (*e.g.*, the III smectite), originated mainly from weathering of terrestrial soils/rocks.⁷ These smectites are the most ubiquitous clay minerals encountered in ancient carbonaceous sedimentary rocks of marine origin (*e.g.*, the FK marl), commonly forming 50–80 % of the clay assemblage.

Premović *et al.*¹² proposed that during the KT event the acid surface waters weathered out the III smectite at its original site. The smectite content of FK sharply increases reaching its maximum in the base of III and then declines more gradually through the top of III, IV and V. These features provide supporting evidence of both increased weathering of the III smectite with the advent of superacid rainfall (the base part of III) and decreased weathering with the closing stages (the top of III, IV and V) of the

superacid rain precipitation. This is congruent with the sedimentation model presented by Hultenberg.² Evidently, the weathering processes (caused by the acid surface waters) highly intensified the influx of terrigenous detrital materials (smectite/sand/silt) into the FK Basin (through the FK river). Clearly, such a detrital input could considerably contribute to the high smectite content of III compared with the other FK layers.

Stability of the III smectite in acid surface waters

The stability of the III smectite is the main factor, however, which should be considered in its weathering/redeposition. The stability of the smectite mineral lattices depends on the ability of various ions in the environment either to remain in equilibrium with the clay mineral or to replace the exchangeable ions. The smectites are stable in a neutral-to-weakly alkaline ($\text{pH} \geq 7$) milieu and quite unstable under strong acid ($\text{pH} \leq 6$) conditions. In fact, under acid conditions, H^+ ions replace metallic cations in the smectite structure and the clay mineral tends to become rather unstable.⁷ For example, Ni can be relatively easily stripped from the clays in acid ($\text{pH} < 6$) environments.²⁸ Selective leaching experiments by HCl^{11,13} show that the III smectite is partly or completely decomposed under acid conditions (after several days of chemical treatment). It contains large proportions of Mg/Al, as well as the major trace metals, implying that these metals could have been easily leached from the III smectite by the acid surface waters.^{20,29} We consider that the III smectite (and associated Cr/Ni/Co/Zn/Cu) endured these early geochemical traumas as: (a) the clay sources usually have sufficient carbonate rocks to buffer the acid surface waters and/or (b) the III smectite particles/colloids were suspended in the acid surface waters and the FK soil/river waters for a relatively short time (only a few days or so) which was insufficient for any significant metal leaching/decomposition of the III smectite. It follows that the acid surface waters/FK river were probably suitable chemical agents for weathering/translocation of the III smectite.

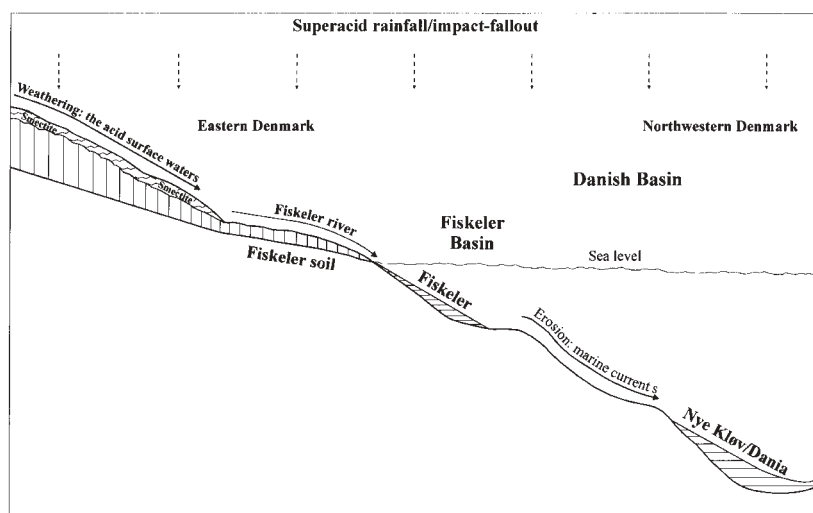


Fig. 2. Proposed model for KT hydrogeochemical relations between the smectite, FK soil and FK (and the Nye Kløv/Dania deposits).

An understanding of the geochemical processes that led to major trace metal enrichment of the III smectite would shed light on the sequence of events that led to the formation of III. Prinn and Fegley²⁰ pointed out that an acid deposition (with a global-average pH of about 1) on a carbonate-deficient source area could mobilize large quantities of trace metals (*e.g.*, Cr/Ni/Co/Zn/Cu) into the surrounding environment (such as the FK soil). Our preferred hypothesis is that the III smectite came from a local source and the clay was removed (from the clay original site) by the acid surface waters. The smectite particles/colloids were then transiently introduced into the FK soil (Fig. 2) which was already aggravated by major (terrestrial/meteoritic) trace metals mobilized (from the corresponding sources) by the same waters. This event was followed by the emplacement (by the acid surface waters) of the III smectite/humics mixture from the FK soil into the FK river, and ultimately to III, Fig. 2. Thus, the III smectite would have had ample opportunity for reactions with major (terrestrial/meteoritic) trace metals while being transported in the acid surface/FK river waters since this material probably underwent several episodes of transport before reaching III. Evidently, the metallation kinetics of the III smectite was quite fast due to the relatively high concentrations of both the smectite (intensely weathered out by the acid surface waters) and dissolved (meteoritic/terrestrial) trace metals (abundantly leached from their sources by these waters).

As mentioned above, the underlying late Maastrichtian (I) and overlying early Danian (V/VI) calcareous beds contain Mg-smectite (which is indistinguishable from the III smectite) but in low amounts. This implies that the influx of the smectite into the basin of the deposition probably began at some time during the late Maastrichtian (before the KT event) and persisted during the early Danian (after the KT event), but at a very low level. It appears likely that the main weathering agent of the smectite (before/after: the superacid rainfall, *i.e.*, the KT event) was ordinary (non-acidic) surface waters and its main redeposition carrier was an ordinary (non-acidified) river.

Cr and the III smectite

The average concentration of Cr in natural waters ranges from: 0.3 ppb (seawater) and 1 ppb (freshwater). Cr exists in natural waters in two main oxidation states Cr³⁺ and Cr⁶⁺.³⁰ The predominant Cr species in natural waters at pH > 3 and for effective metal concentration >1 ppm is insoluble Cr₂O₃; under these conditions the amount of Cr⁶⁺ (as CrO₄²⁻/HCrO₄⁻) is extremely low.³¹ Griffin *et al.*³² determined the effects of the oxidation state and pH on the sorption of Cr by a pure smectite. These researchers found that up to 300 × more Cr³⁺ than Cr⁶⁺ was adsorbed by the smectite. Griffin *et al.*³² pointed out that Cr³⁺ incorporation into the smectite skeleton is, mainly, due to the adsorption of predominantly hydrolyzed species CrOH²⁺. The adsorption isotherms obtained by Griffin *et al.*³² showed that the amount of the Cr³⁺ ions adsorbed (under anoxic conditions and at pH 4) by smectite increases with the equilibrium Cr³⁺ content of the smectite suspension, reaching its saturation (*ca.* 12 × 10⁵ ppm) at an equilibrium Cr³⁺ level of *ca.* 600 ppm. These isotherms also show that the III smectite could only attain its high Cr level (350 ppm, Table Ia) through adsorption of CrOH²⁺ ions at a relatively high equilibrium Cr concentration (>10 ppm) present in the overlying (boundary) seawater. This suggests that adsorption of Cr from the overlying seawater was not the principal

mechanism for the incorporation of this metal into the III smectite unless it is assumed that the Cr content of the water from which the adsorption occurred increased enormously (> 30,000-fold). There is, however, no independent justification for this assumption. Also, geochemical studies indicate that the solubility of Cr^{3+} in aqueous solutions decreases as the solution pH is increased above pH 4, with essentially complete precipitation occurring at pH 5.5.^{33,34} Evidently, very little Cr would be available for adsorption by the III smectite in the strong anoxic sedimentation milieu of III at $\text{pH} \geq 6$.¹¹ Accordingly, most of the Cr within the III smectite structure is detrital, *i.e.*, its incorporation into the III smectite just preceded the clay deposition in III. Consequently, it is reasonable to assume that the Cr within the III smectite structure is largely present as CrOH^{2+} , acquired through adsorption processes in the FK soil and/or fixed during smectite formation.

Extraterrestrial Cr and the III smectite

Very recently, Shukolyukov and Lugmair³⁵ analyzed Cr in the III basal sublayer (*e.g.*, the SK10 sample³⁶) employing a high precision mass spectrometry. According to these researchers, the Cr isotopic composition (the $^{52}\text{Cr}/^{53}\text{Cr}$ ratio: -0.34×10^{-4}) of the sample is different from that (0.04×10^{-4} to -0.04×10^{-4}) of terrestrial sources and indicates an extraterrestrial source: a carbonaceous chondrite-type impactor (the $^{52}\text{Cr}/^{53}\text{Cr}$ ratio: -0.41×10^{-4} (Allende) and -0.43×10^{-4} (Orguella)). Using the above values for the $^{52}\text{Cr}/^{53}\text{Cr}$ ratios, simple arithmetic reveals that >60 % of Cr of SK10 is chondritic. This suggests that a considerable amount of the Cr in the III smectite could be derived from impact fallout, *i.e.*, a meteoritic source, which was adsorbed (as CrOH^{2+}) by the III smectite from the overlying FK soil water. The available data, however, do not permit an evaluation of the amount of chondritic Cr or the amount derived from terrestrial sources in the III smectite. Geochemical studies indicate that Cr in most soils occurs as Cr^{3+} ; its solubility in the presence of soil decreases above pH 2.5, with virtually complete precipitation occurring at about pH 4.5 (Ref. 30 and references therein). Thus, we suggest that incorporation of meteoritic Cr occurred in the FK soil solution at $\text{pH} < 4$. This accords with our hypothesis that the FK soil solution was acidified by the acid surface waters (*i.e.*, ultimately by superacid rainfall).

Ir and the III smectite

The III smectite/kerogen contain Ir as high as 80 ppb/500 ppb (Table Ia), respectively. Schmitz¹⁵ and Schmitz *et al.*¹³ reported that almost 50 % of the total Ir is present in the III/IV kerogen; Elliott *et al.*⁵ reported that Ir is concentrated in the III smectite. The III Ir most likely has the same meteoritic origin as the Ir found in enhanced levels at many KT boundaries all over the world. Ir tends to occur as fine-grained minerals in ancient carbonaceous rocks and it may be erroneously identified as being inorganically or organically associated.³⁷ The fact that Ir resides concomitantly in three fractions of III (Table Ib): the smectite (74 %), the silicate portion (3 %) and the kerogen fraction (22 %) strongly indicates that this metal was once present in the FK natural waters mostly in ionic form, but not as fine-grained minerals. This does not mean, however, that Ir was originally in these waters.

According to the ionic concept, upon impact on the Earth, the meteoritic metals (*e.g.*, Ir/Cr/Ni/Co) would vaporize by the high temperature of the fireball, and would be

converted later to the most stable oxides (*e.g.*, $\text{IrO}_2/\text{Cr}_2\text{O}_3/\text{NiO}/\text{CoO}$ and/or Co_2O_3) by reacting thermally with atmospheric O_2 . The largest part of these oxides would react with S-/N-oxides present in high concentrations in the atmosphere during the KT event,^{20–22,29} generating the corresponding water-soluble nitrates/sulfates. Thus, trace metals derived from the asteroidal component of the impact fallout (*e.g.*, Ir/Cr/Ni/Co) would reach the FK waters largely as the corresponding metal nitrates, sulfates and oxides, which would be readily dissolved. Evidently, the Ir ions would precipitate (as highly insoluble IrS_2 and/or Ir_2S_3) preferentially in the strong anoxic milieu (rich in H_2S) of III, *i.e.* the Ir ions in the strong anoxic III sedimentary solution would not be readily available for incorporation into the III smectite structure. It is more likely that incorporation of Ir into the III smectite structure was an event that just preceded the accumulation of III, *i.e.*, it occurred in the FK soil solution. The impact fallout (and associated meteoritic trace metals) in the FK soil can be interpreted in terms of two kinds of fallout primary/secondary, as defined by Wolbach *et al.*²⁷ In line with their definition, the primary fallout would represent the initial (impact-ejecta) airfall which settled onto the FK soil and the secondary came from lateral transport (by the acid surface waters) of primary fallout (from the nearby topographic highs) into the soil (a topographic low), Fig. 2. Kyte *et al.*³⁶ suggest that only the basal III sublayer (which we did not analyze separately in this study) should be used to estimate primary fallout, as Ir in higher layers/sublayers arose mainly from secondary fallout material laterally transported from other nearby localities. We reason that after the (immediate) deposition of the initial (airborne) fallout into the FK soil, the weathered (secondary) fallout from other localities was laterally transported and mixed (in the soil) with detrital III smectite/humics (containing already some Cr/Ni/Co/Au of terrestrial origin: see below). The swift chemical alteration of the impact fallout by the superacid rainfall, in the transporting acid surface waters and the acidic FK soil solution resulted in the high mobilization of the meteoritic Cr/Ni/Co/Ir/Au which were then rapidly adsorbed by the III smectite particles/colloids and the III humics. In addition, there could have been apparent concentrating mechanisms for both the smectite and trace metals (derived from the impact fallout/terrestrial sources) in the FK soil which did not occur in other boundary soils in Denmark (or elsewhere in Europe). Perhaps regional/local conditions (*e.g.*, topography, the presence of humics *etc.*) were favorable for a swift, efficient and concentrated accumulation of the III smectite and trace metals in the FK soil. Thus, it seems quite likely that lateral transport of meteoritic fractions of Cr/Ni/Co/Ir/Au could contribute to a large extent to the high concentration of these metals in the FK soil.

Au and the III smectite/humics

As Ir, Au belongs to the platinum group of elements and, along with Ir/Cr/Ni/Co, it is concentrated in chondritic meteorites. According to geochemical data reported by Schmitz¹⁵ and Schmitz *et al.*,¹³ almost 50 % of the Au (of the total Au) is present in the III/IV kerogen; the remainder resides in the III/IV smectite. Elliott⁶ reported also relatively high amounts of Au in the III smectite.

Table Ib shows that 60 % of the Au resides in the III smectite (15 ppb); 6 % in the silicate fraction (<5 ppb) and 34 % in the kerogen fraction (10 ppb). Like Ir, Au was also

once present as ionic species. Geochemical studies indicate that Au could be stable in natural waters simply as AuCl_4^- . Considering that Au^{3+} species are stable only in oxic milieu, we suggest that the incorporation of Au (mainly as AuCl_4^-) in the III smectite took place in the oxic solution of Fiskeler soil. In addition, many geochemical studies (*e.g.* Ref. 38) suggest that in oxic soil water (*e.g.* the FK soil solution) Au could be readily chelated by the humics.

TABLE Ib. Geochemical distributions of the major trace metals from selective leaching experiments

Metal		Fraction*						
		Total	Carbonate	HCl-S**	Smectite	HCl-I**	Silicate	Kerogen
Cr	ppm	150	10	135	135	5	<5	<5
	%	100	7	90	89	3	<3	<3
Ni	ppm	355	125	215	215	15	5	10
	%	100	35	61	60	4	<2	<4
Co	ppm	55	20	35	35	<5	<1	<1
	%	100	36	64	62	<1	<1	<1
Zn	ppm	310	55	250	250	5	5	<1
	%	100	17	81	80	2	2	<1
Cu	ppm	80	5	60	60	15	5	10
	%	100	6	75	74	19	6	13
Ir	ppb	40	0	30	30	10	<5	10
	%	100	0	75	74	25	3	22
Au	ppb	25	0	15	15	10	<5	10
	%	100	0	60	60	40	6	34

*The percentage of the whole sample: carbonate [52.0 %], the HCl-soluble fraction [21.0 %], smectite [38±5 %], the HF-insoluble fraction [27.0 %], silicate [25.2 %], kerogen [1.8 %].

**HCl-S (HCl-soluble); HCl-I (HCl-insoluble).

Inorganic detritus of Fiskeler and the acid surface waters

Microscopic inspection of a thin section indicates that II/III/IV contain mostly calcite derived exclusively from calcareous algal plates (coccoliths >95 %).^{11,12} The investigations of FK by Schmitz,^{15,17} Schmitz *et al.*,¹³ and Premović *et al.*^{11,12} revealed that authigenic (biogenic) calcite is a major constituent of II; the high local (inorganic) detritus (and associated low biogenic calcite) begins abruptly with III, in particular with its basal sublayer. Upwards, the amount of detritus is considerably reduced (IV) or cease to exist at all (V/VI). The superacid rainfall would lower the alkalinity of the FK surface seawater so much that many marine calcareous organisms would be dissolved.^{20,29,39} Considering this, it appears very likely that III (especially its base part) was produced by both a temporary loss of the calcareous shells (*i.e.*, the biogenic calcite) and a higher influx of inorganic detrital materials (smectite/silt/sand). Hence, the gradual upward decline of detritus (especially its predominant component: smectite) from its maximum in III is simply a reflection of the increasing proportion of authigenic

(biogenic) calcite relative to detrital materials. We interpret this decline to be related to the progressive decreasing of the acidity of the FK surface seawater (which halted the formation of the biogenic calcite) which resulted from the gradual attenuation of the superacid rain precipitation.

Toxic Ni and the III biogenic calcite

A high proportion (> 50 %) of Ni (245 ppm, Table Ia) resides in the carbonate fraction of III, Table Ib; this value lies within the range of that (300 ppm) reported by Premović *et al.*¹¹ It appears likely that the location of the Ni is in the calcite. The Ni²⁺ ions may substitute the Ca²⁺ ions in the calcite matrix since Ni²⁺ has a similar ionic radius/the same charge as Ca²⁺. The high content of Ni in the biogenic III calcite appears to represent biological Ni, *i.e.*, direct incorporation of Ni²⁺ into the calcareous shells of coccoliths occurred during their metabolic uptake of seawater. In contrast to Ni, the Cr/Co/Zn contents of the III carbonate fraction are comparable with those in calcite (also mainly derived from coccoliths) of II/IV.

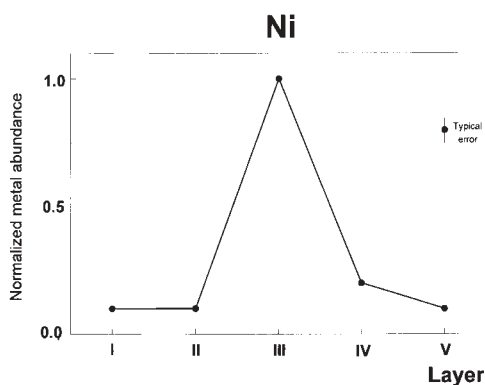


Fig. 3. Distribution of Ni within the carbonate (I, II, III, IV and V) fractions normalized to the metal content of the III carbonate.

Davenport *et al.*⁴⁰ estimated that the top of a boundary soil would be covered with primary fallout, containing Ni that is one or two orders of magnitude greater than the contemporary average level of Ni (16 ppm) in soils. Primary (airfall) fallout Ni (mainly as soluble sulfates, nitrates and oxides: see above) would surely be dissolved in oxic surface seawater; airborne (*i.e.*, asteroidal) Ni covering the FK soil would be readily mobilized by the acid surface waters and laterally transported by the FK river to the surface seawater. Indeed, our geochemical analysis shows that the II carbonate fraction contains less than 20 ppm of Ni and that the carbonate Ni is the highest in III, diminishing upward (IV) and ultimately disappears (V), Fig. 3. The abrupt (and more than tenfold) increase in Ni is consistent with a rapid introduction of (presumably meteoritic) Ni into the FK surface seawater: through both airfall and lateral redeposition. The sharp drop in the carbonate Ni from III to IV/V (Fig. 3) suggests that during the deposition of IV/V the influx of this metal was considerably reduced (IV) and probably ceased to exist at all (V). This implies that the high input of meteoritic Ni lasted for a comparatively short time period, *i.e.*, during the deposition of III (< 40 years¹²), or even shorter. Thus, it seems very likely that Ni within the III biogenic calcite structure is indeed a sharp time marker, representing the sudden airfall of the impact-derived

materials in the FK area. Evidently, the abrupt injection of high amounts of Ni (and other toxic trace metals) into the surface seawater during the deposition of III would be particularly vulnerable to marine flora.^{20,40}

In summary, the superacid rainfall caused a local weathering of the III smectite (at its original site). In addition, as a result of both the high influx of the acid surface/FK river waters and associated toxic trace metals (*e.g.*, Ni), an annihilation of the mainly calcareous organisms occurred in the FK surface seawater. This annihilation halted the formation of biogenic calcite for a short time interval, *i.e.*, during the deposition of III (or even shorter), subsequently followed by marl-forming (IV). The simultaneous occurrence of Ir, kerogen (enriched with Cu–P and soot) and the high carbonate (mainly meteoritic) Ni is strong evidence that III represents a deposit closely linked to the occurrence of the asteroidal impact.

Cr/Ni/Co/Zn/Cu and the III smectite

Considering that the III smectite is a redeposited material,^{5,6,11,12} it may be reasoned that much of its Ni/Co/Zn is either detrital (in the sense of having been brought into the FK Basin already located in the clay structure) or authigenic (in the sense of having been adsorbed by the III smectite from the overlying FK seawater). Geochemical evidence indicate that III was deposited either under strong anoxic conditions or soon after deposition the conditions became strongly anoxic and H₂S was present in both III and the overlying seafloor water.¹¹ Under such conditions, most of the Ni²⁺/Co²⁺/Zn²⁺ would precipitate as insoluble sulfides. In other words, the strong anoxic sedimentation conditions of III were adverse for the adsorption of Ni²⁺/Co²⁺/Zn²⁺ by the smectite. This implies that Ni/Co/Zn in the III smectite are strictly detrital in character. It is worth noting that if the incorporations of Ni/Co/Zn into the III smectite structure occurred in an oxidizing/acidic (pH < 4) milieu of the FK soil solution, then the Ni²⁺/Co²⁺/Zn²⁺ ions would be almost solely present.

Premović *et al.*^{11,12} consider that the Cr/Ni/Co/Cu were placed within the III smectite structure as the corresponding ionic forms (CrOH²⁺/Ni²⁺/Co²⁺/Cu²⁺). A notable fact is that the enrichment/distribution patterns of these metals within the smectite throughout III/IV/V are similar.^{5,6,11,12,13,15,17} This indicates similar geochemical behavior of CrOH²⁺/Ni²⁺/Co²⁺/Zn²⁺ during their chemical interactions with the smectite in the Fiskeler soil solution.

One has to consider timing, the geochemical stage at which the incorporation of the metal in the smectite structure occurred, in order to be able to understand the mechanism by which a particular detrital trace metal was incorporated into the III smectite. A detrital metal of the III smectite can be a primary entity: *i.e.*, a metal present in this clay before the redeposition. For example, V (mainly as VO²⁺) within the III smectite is a primary detrital metal in view of the fact that it was incorporated during the formation of the III smectite.^{11,12} Secondary enrichment of detrital metal could take place during the clay emplacement. Hence, Cu¹², Ir and the meteoritic fractions of Cr/Ni/Co within the III smectite structure are, for certain, secondary detrital metals in view of the fact they were incorporated into the III smectite during the clay redeposition.

In contrast to Ir, the Cr/Ni/Co/Zn/Cu contents of the III smectite are only 1.5 (*e.g.*, Cu) to 3 (*e.g.*, Cr) times higher than those of the II smectite.^{6,12} The II smectite is miner-

alogically identical to that of III (see above) and it is absolutely clear that Cr/Ni/Co/Zn/Cu within its skeleton have absolutely nothing to do with either the impact fallout or the acid surface waters. This fact infers that the greater proportions of these metals were probably incorporated into the II/III smectite during the formation of the clay. It is, therefore, quite possible that some (or a lot) of the partly meteoritic metals (Cr/Ni/Co/Au) are derived from non-impact (or terrestrial) sources. Thus our geochemical model envisages weathering of terrestrial rocks and impact-derived materials in the elevated land around the Fiskeler Basin to be the important provider of both detrital III smectite and (meteoritic/terrestrial) trace metals.

There is also a remote possibility that considerable proportions of the terrestrial fractions of the trace metals (*i.e.*, Cr/Ni/Co/Au) of the III smectite were released from an initially much a larger amount of III smectite. This clay could have been either partly or completely decomposed by the acid surface waters and the liberated metals captured by the III smectite. Trace metal data and mineralogy (Table I) invalidate this hypothesis, as it would involve the decomposition of very large amounts of the original smectite, with consequential changes in the mineralogy; these were not observed.

Cr/Ni/Co/Zn/Cu/Ir and the HCl-insoluble residue of III

Mineralogical analysis indicates that the HCl-insoluble fraction of III is mainly of terrigenous origin and contains predominantly rounded grains of quartz (> 50 %) and illite (mica)/feldspar. The enrichment and distribution patterns of the trace metals associated with the HCl-insoluble fraction of III are presented in Tables Ia, b respectively, and Fig. 4. The results show that the III kerogen fraction contains: > 70 % of Ni (625

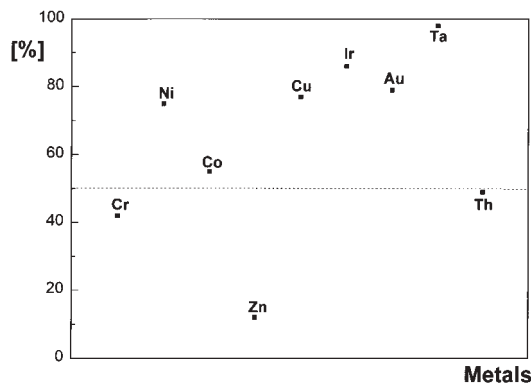


Fig. 4. Distribution of trace metals in the III HCl-insoluble (silicate + kerogen) fractions of III.

ppm)/Cu (715 ppm)/Ir (500 ppb)/Au (475 ppb). The leaching experiments on the III/IV kerogen fraction performed by Schmitz *et al.*¹³ infer that the bulk (*ca.* 99 %) of the Ir resides within the kerogen structure. Tables Ia, b and Fig. 4 also show that *ca.* 50 % of the Cr (160 ppm)/Co (40 ppm) and < 15 % of the Zn (25 ppm) are contained in the III kerogen fraction. The remaining amounts of Cr/Ni/Zn/Cu are associated with the silicate fraction, *i.e.*, mainly within the illite/feldspar. The illite/feldspar minerals are undoubtedly terrestrial and evolved from weathering of the local rocks. Thus, relatively high proportion (15 ppm) of Cr/Ni/Zn/Cu, Table Ia, in the III silicate fraction supports

further our notion that considerable proportions of these metals in III are strictly detrital and arose from terrestrial sources.

Ni/Co/Cu, pyrite and the III humics

FeS₂ is abundant in III and some of Fe³⁺-oxide particles (goethite) may represent oxidized FeS₂.¹⁵ According to Premović *et al.*,¹¹ the III FeS₂ is formed diagenetically under strong reducing conditions and is coupled with a sudden influx of humics during the boundary event. The acid leaching steps remove most of the Fe (> 80 %). This is due to the destruction of the III smectite and the total dissolution of Fe³⁺-oxides. It appears likely that a considerable amount of residual Fe is associated with different forms of FeS₂ within the III kerogen. Ni/Co/Cu may be removed from natural waters in sulfide-rich environments if they were appreciably coprecipitated with another metal sulfide (*e.g.*, FeS₂). Thus, FeS₂ could be an excellent concentrating agent for the trace metals (*i.e.*, Ni/Co/Cu) in the FK seawater. Since it is difficult to separate associated insoluble sulfide minerals (especially FeS₂) from the III kerogen, this may partially or fully account for the important proportions of some sulfide-related trace metals (*e.g.*, Ni/Co/Cu) in the III kerogen fraction. In fact, the III FeS₂ is the host phase for Ni/Cu that are known, also, to have an organic affinity in III.^{12,13} The AAS analyses indicate that the III kerogen contains 2.7 % of Fe. Assuming that all the Fe is bound as FeS₂ (*i.e.*, that the fraction of organic Fe in the III kerogen is small), it can be easily calculated that the III kerogen fraction contains 5.7 % FeS₂ (*i.e.*, 3 % pyritic S). Using the maximum values of Ni (3100 ppm)/Co (250 ppm)/Cu (130 ppm) in FeS₂ associated with the III kerogen fraction¹⁷ and the above value for FeS₂, it can be readily computed that substantial proportions of Ni (>70 %) and Co/Cu (> 90 %) are incorporated into the III kerogen. On the other hand, elemental/electron microprobe analyses indicate that the III kerogen contains a high content of organic S (1.6 %) and a low content of S (> 0.2 %) ascribed to (finely disseminated) FeS₂, embedded into the kerogen skeleton.¹² Considering that INAA shows that the III kerogen fraction contains 4.7 % of S, it can easily be estimated that this fraction contains no or very little non-pyritic (*e.g.*, sulfate) S.

Lastly, the authors accept the conventional view that virtually all the S in the S-rich kerogen was generated during diagenesis of kerogen, when syngenetic S (finely disseminated FeS₂ and organic sulfur forms) were incorporated. Accordingly, we reason that the S enrichment of the III kerogen occurred at the time of FeS₂ formation, *i.e.* during diagenesis of this material in the strong anoxic sedimentation milieu of III.

Premović *et al.*¹² suggested that the III kerogen could have been derived from the humics, which were transported to the FK Basin from a laterally adjacent oxic soil. The acid surface/FK river waters evidently carried a low load of humic particulates into the FK Basin as III contains a relatively low amount of kerogen (1.8 %, Table I). The fact that the III kerogen is enriched with Ni/Cu (Table Ia) implies that these two metals were available for chelation by the III humics during the boundary event. Thus, the FK soil solution must have had a relatively low pH because Ni/Cu are not very soluble at pH > 5.^{12,41} This further reinforces our hypothesis that the FK soil solution was highly acidic.

Rare earth elements and the III humics

The REE comprise an extremely coherent geochemical group. These elements commonly exist in natural waters in the 3+ oxidation state and exhibit very similar geochemical properties. Ce exhibits, however, two possible oxidation states Ce³⁺ and Ce⁴⁺. Oxic seawater is generally depleted in Ce (negative Ce anomaly) because air oxidation removes Ce³⁺ (as CeO₂), and anomalies as strong as 50-fold have been reported.⁴²

TABLE IIa. Geochemical distributions of the major trace metals in the III silicate/kerogen fractions

Metal		Fraction	
		Silicate	Kerogen
Cr	ppm	15	10
	%	58	42
Ni	ppm	15	40
	%	25	75
Co	ppm	<5	<5
	%	45	55
Zn	ppm	15	<5
	%	88	12
Cu	ppm	15	45
	%	23	77
Ir	ppb	5	35
	%	14	86
Au	ppb	10	30
	%	21	79

Schmitz *et al.*¹³ found that the REE pattern in FK is not different from that of the underlying I/overlying VI. According to these authors, the bulk (> 90 %) of the REE of FK reside within the apatite phase, being especially abundant in IV which is highly enriched with these elements. Schmitz *et al.*¹³ also reported the pronounced negative Ce anomalies both of the fish scales and the apatite concentrate. Elliott⁶ found that the III smectite (especially its top part) is most depleted in REE, relative to the North American Average Shale (NASC⁴³). He also reported that the IV smectite is the most enriched in REE (relative to the NASC) of the smectite components in the other FK layers. In addition, the smectite constituents of all FK layers show a negative Ce anomaly. Graup *et al.*⁴⁴ also reported negative Ce anomalies throughout FK.

Eight (La/Ce/Nd/Sm/Eu/Tb/Yb/Lu) of the REE were determined (by INAA) in the HCl-insoluble/silicate/kerogen fractions of III (Table IIb). The distributions of the REE in these fractions are given in Table IIc. The silicate portion contains relatively low concentration of REE (< 5 ppm or relative to the NASC). The REE distribution of the III kerogen fraction relative to the NASC is shown in Fig. 5. Contrary to Ce (derived from seawater) of the fish scales, the apatite concentrate and the smectite, the kerogen III fraction displays

an absence of the negative Ce anomaly. This suggests that the REE within the III kerogen probably originated from a terrestrial source and were originally chelated by the detrital III humics. It is noteworthy that Schmitz *et al.*¹³ similarly reported a lack of a Ce negative anomaly in the HCl-insoluble fraction of the III/IV sample.

TABLE IIb. Geochemical concentrations [ppm] of REE/Ta/Th in the III HCl-insoluble/silicate/kerogen fractions

Metal	Fraction		
	HCl-I*	Silicate	Kerogen
La	5	1	35
Ce	5	1	60
Nd	<5	<5	10
Sm	<1	<1	5
Eu	<1	<1	1
Tb	<1	<1	1
Yb	1	<1	10
Lu	<1	<1	1
Ta	<1	<1	10
Th	1	<1	10

*HCl-I (HCl-insoluble).

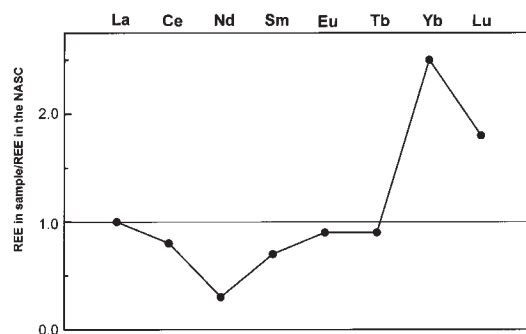


Fig. 5. Distribution of REE in the III kerogen fraction normalized relative to the REE in the NASC.⁴³

Finally, Table IIc show that the bulk (80 %) of Ce is located in the kerogen fraction (60 ppm, Table IIb). The fact that in the highly oxidizing media of the FK soil any available Ce^{3+} would have been removed as CeO_2 at $pH > 3$, the found effective element concentration $> 1 \text{ ppm}^{31}$ additionally supports the high acidity ($pH < 3$) of the milieu of the FK soil solution.

Ta, Th and the III humics

Table IIc/Fig. 4 show that the bulk ($> 90 \%$) of the Ta associated with the HCl-insoluble fraction resides in the III kerogen portion (10 ppm, Table IIb). The predominant Ta species in natural waters at $pH > 5$ and for effective metal concentration $>$

2 ppb is insoluble Ta_2O_3 .³¹ Ta_2O_3 is in equilibrium with TaO_2^+ which predominates in natural waters only at low pH (< 5) values. Thus, we suggest that the bulk of Ta (*i.e.*, TaO_2^+) was chelated initially by the III humics.

TABLE IIc. Geochemical distributions [%] of REE/Ta/Th in the HCl-insoluble/silicate/kerogen fractions

Metal	Fraction		
	HCl-I*	Silicate	Kerogen
La	100	22	78
Ce	100	20	80
Nd	100	<87	>13
Sm	100	35	65
Eu	100	78	22
Tb	100	<87	>13
Yb	100	35	65
Lu	100	<93	>7
Ta	100	<10	>90
Th	100	51	49

*HCl-I (HCl-insoluble).

Table IIc/Fig. 4 show that 50 % of Th in the HCl-insoluble fraction is present in the III kerogen fraction (10 ppm, Table IIb). The predominant Th species at pH > 3 and for effective metal concentration > 2 ppb is insoluble ThO_2 .³¹ ThO_2 is in equilibrium with Th^{2+} , which predominates in natural waters only at pH values lower than 3. Like Ta, the bulk of Th was originally chelated by the III humics.

In conclusion, from the geochemistries of the trace metals associated with the III smectite/kerogen it may be deduced that the pH of the oxic FK soil was less than 3.

Trace metals and the III humics: a final note

Terrestrial humics can either solublize or fix particular trace metals, depending on their state of aggregation. For example, the distinction between fulvic acids, humic acids and humin is based on their aqueous solubility, which is mainly a consequence of their molecular weights. The fulvic acids are soluble in neutral to acidic (pH ≤ 7) milieu and have molecular weights near 1000. The humic acids are soluble only in aqueous alkaline (pH ≥ 7) solution and have molecular weights > 10⁴; and humin (which is very large) is insoluble. Thus, under the acidic (pH < 3) conditions of the FK soil water the III fulvic acids would be soluble and they would chelate particular trace metals to form stable, but soluble complexes. Evidently the acid surface waters would remove these complexes from the FK soil immediately afterwards. Under the same conditions, the III humic acids are insoluble and their presence would result in the fixation of major trace metals (*e.g.*, Cu). Indeed, high levels of both trace metals and Cu (*i.e.*, Cu-P) are only found in humic acids (such as the III humics, *i.e.*, the III kerogen) of a wide variety of or-

ganic-rich soils: recent soils (including peat-soils)^{45–47} and paleosols.⁴⁸ Thus, the III humic acids (enriched with major trace metals/Cu–P) can be regarded as the ultimate precursors of the III kerogen with high contents of the major trace metals/Cu–P.

This can account for the relatively high contents of these metals (*e.g.*, Cu) in the III kerogen. Considering that the III kerogen is a diagenetic product of detrital III humics,¹² it appears likely that most of the kerogen Ni/Co/Cu/Ir/Au/REE/Ta/Th were probably already contained in the detrital humics transported by the FK river into III. The III humics had probably functional (carboxyl, porphyrin *etc.*) groups that were able to chelate these metals before they reached III. Obviously, the acidic FK soil solution could partly remove the trace metals in question from the III smectite and the released metals could be seized by the humics.

Hultenberg's erosional model of the western Denmark deposits

Premović *et al.*¹¹ suggested that the bulk of the smectite of the alleged boundary deposits at the Nye Kløv/Dania locations are, also, of detrital origin. In view of this, the clay was redeposited in the same marine Danish Basin although separated by about 320 km (Stevns Klint-Nye Kløv), 220 km (Stevns Klint-Dania), and 100 km (Nye Kløv-Dania), Fig. 1. Hultenberg^{1,2} claims, on the basis of dinoflagellate biostratigraphy, that the deposition of FK (eastern Denmark) took place several hundred thousands years (*i.e.*, 200,000 y. to 1.5 m. y.) earlier than the deposition of the alleged boundary beds in northwestern Denmark (*e.g.*, Nye Kløv/Dania). In short, he placed the deposits in northwestern Denmark in the uppermost Danian, not in the KT time, *i.e.*, he questioned whether these beds represent a true KT boundary.

According to the speculative sedimentation model presented by Hultenberg,² the alleged boundary deposits in northwestern Denmark represent erosion/subsequent marine redeposition of the true boundary (FK) in eastern Denmark. In accordance with this model, it appears likely that the boundary smectite (brought to the sea mainly by the FK river) was probably extensively eroded/dispersed laterally (at some time after the impact) by marine currents (including impact-induced storm-generated bottom currents) from the marginal zone (close to the FK river delta) to the central deeper parts of the Danish Basin in northwestern Denmark, Fig. 2

The kerogen Cu–P and erosion of the boundary in eastern Denmark

It has been suggested that the III humic Cu–P were largely derived from the plant chlorophylls of an oxic soil.¹² The humic (*i.e.*, kerogen) Cu–P are rare and atypical for ancient sedimentary rocks of marine origin.¹² According to Baker and Louda,⁴⁹ Cu–P were probably derived from enhanced weathering of terrestrial organic accumulations and they are reliable markers for oxidized terrestrial organic matter (such as the III humics) redeposited in a marine environment (*e.g.*, the FK Basin). In all these cases, the humic Cu–P 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 with Cu–P) could be formed simultaneously during the short time period (geologically speaking) of the KT event in both eastern and northwestern Denmark in soils widely separated from each other by > 300 km (FK-Nye Kløv) and > 200 km

(FK-Dania), Fig. 1. The Nye Kløv/Dania rocks (on a carbonate-free basis) contain a much lower concentration ($< 0.1\%$) of kerogen (enriched with Cu–P) compared with the corresponding fraction of III.^{1,2} For this reason, we suggest that the humics (highly enriched with Cu–P) of eastern Denmark were eroded and subsequently translocated by marine currents in deeper parts of the Danish Basin (northwestern Denmark), Fig. 2. This could be an explanation for the lower contents of kerogen (enriched with Cu–P) of the Nye Kløv/Dania rocks compared to FK.^{1,2} Hultenberg² presented a similar interpretation for the low content of Ir in the (Nye Kløv/Dania) rocks in northwestern Denmark. Obviously, redeposition of the humics occurred after the KT event, supporting a diachronicity between FK and the alleged boundary deposits (such as Nye Kløv/Dania) in northwestern Denmark, proposed by Hultenberg.^{1,2}

CONCLUSIONS

1. The grey-to-black marl III of the Danian FK (an impact-fallout-bearing boundary exposed at Stevns Klint, Denmark) is a sedimentary layer exceptionally well-suited for the study of geochemical and paleoecological effects of the KT asteroidal impact.

2. The main carrier of the major trace metals is the III smectite. The geochemistries of the III smectite/humics and associated trace metals infer that these metals are strictly detrital in character, having been transported to III.

3. The III smectite adsorbed most of the meteoritic Ir and important proportions of the terrestrial/meteoritic Cr/Ni/Co/Zn/Cu/Au during its transient existence in the FK soil; the remainder being incorporated during the formation of the clay.

4. The geochemistries of Cr/Ni/Cu/REE/Ta/Th indicate that the FK soil was highly acidic ($\text{pH} < 3$).

5. We interpret the high/abrupt increase of (presumably meteoritic Ni) in the III authigenic (biogenic) calcite as resulting from the asteroidal impact and associated impact-related superacid rainfall.

6. The porphyrin structures of the III kerogen Cu–P were probably derived from the chlorophylls of decaying green land flora. The decay was caused by impact related extinction effects: superacid rainfall/local wildfires.

7. The simultaneous occurrence of Ir, kerogen enriched with Cu–P and soot, as well as biogenic calcite enriched with Ni is strong evidence that III represents the FK layer coupled closely with the asteroidal impact.

8. The lateral distribution of the kerogen Cu–P implies that the alleged boundary deposits in northwestern Denmark, (the Nye Kløv/Dania sedimentary rocks), were formed by erosion/emplacement of FK in eastern Denmark by marine currents, as proposed by Hultenberg.^{1,2}

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ИЗВОД

КРЕДА-ТЕРЦИЈАР ГРАНИЧНИ СЛОЈ РИБЉЕ ГЛИНЕ СА ЛОКАЛИТЕТА STEVNS KLINT, ДАНСКА: ГЕОХЕМИЈА ТРАГОВА МЕТАЛА

ПАВЛЕ И. ПРЕМОВИЋ, НИКОЛА Д. НИКОЛИЋ, МИРЈАНА С. ПАВЛОВИЋ*, БРАТИСЛАВ Ж. ТОДОРОВИЋ, ДРАГАН М. ЂОРЂЕВИЋ, РУЖИЦА С. НИКОЛИЋ, ЛИЛИЈАНА ЛОПЕЗ** и САЛВАДОР ЛО МОНАКО**

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Трагови метала у четири слоја кредо-терцијар (КТ) граничног слоја Рибља глина (Fiskeler) са локалитета Stevns Klint (Данска) релативно су добро проучени, али је ипак остало још нејасноћа. Из тог разлога, урађена је детаљна студија трагова метала (метеоритског Ir, делимично метеоритских Cr/Ni/Co/Au и земаљских Zn/Cu/La/Ce/Nd/Sm/Eu/Tb/Yb/Ta/Th) у основном црном лапорцу Рибља глина и његовим фракцијама (карбонатној, HCl-растворној, смектитној, HCl-нерастворној, силикатној и керогенској). Минералогичка овог лапорца је доста једноставна; аутигени калцит (углавном формиран од планктонских морских алги: коколита), детритални Mg-смектит и кварц су главне компоненте, са малим количинама керогена, Fe³⁺-оксида, пирита, илита и фелдспата. Коришћен је поступак селективног раздвајања да би се утврдили основне геохемијске асоцијације и места налажења трагова метала у присутним минералима. Резултати откривају основна места уградње трагова главних метала (Cr/Ni/Co/Zn/Cu/Ir/Au). Они се јављају углавном у смектиту, а мањим делом у биогеном калциту (Ni/Co/Zn) и керогену (Ir/Au). Подаци о траговима метала су у сагласности са хипотезом да је значајан део Cr/Ni/Co/Zn/Cu/Ir/Au који је доспео на место таложења вероватно већ био садржан у детриталном смектиту. У општој дискусији резултата, дат је геохемијски модел који описује уградњу трагова метала у смектиту, заснованом на распадању/транспорту глине киселим површинским водама (проузрокованим астероидним ударом) и адсорпцијом јона трагова метала смектитним честицама/колоидима у киселом раствору околног земљишта које је садржало кисеоник. С друге стране, примери расподеле/обогаћења основног црног лапорца и виших слојева Рибље глине Cr/Ni/Co/Zn указују да су значајне количине ових метала биле уграђене у смектитне структуре у току формирања глине. Подаци о траговима метала су такође разматрани у светлу претходно публикованих палеоеколошких и геохемијских радова за Рибљу глину. Предложено је, на пример, да су локалне суперкиселе кише (проузроковане ударом астероида) и масовни пожари одиграли важну улогу у обезбеђивању одговарајућих хумичних материјала (нпр. одговарајуће органске материје из распаднутих копнених зелених биљака) са порфиринским структурама за формирање керогена (обогаћеног Cu²⁺-порфиринима). Поред тога, предложено је да је биогени калцит са високим садржајем Ni вероватно производ метаболичког концентрисања из КТ морске воде (обогаћене овим металом) од стране коколита. До овог обогаћења дошло је због наглог и високог прилива Ni (углавном метеоритског) а који је био такође делом транспортован до КТ мора киселим

површинским/речним водама са оближњег земљишта. Најзад, латерална расподела керогена (обогаћеног Cu^{2+} -порфиринима) је сагласна са ранијим тумачењима датим од Хултенберга.^{1,2} Сагласно овом аутору гранични слојеви (Nyе Kløv/Dania) у северозападној Данској су настали ерозијом и каснијом редепозицијом Рибље глине из источне Данске.

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REFERENCES

1. S. U. Hultenberg, *J. Micropalaeontol.* **5** (1986) 37
2. S. U. Hultenberg, *J. Micropalaeontol.* **6** (1987) 35
3. L. Christensen, S. Fregerslev, A. Simonsen, J. Thiede, *Bull. Geol. Soc. Denmark* **22** (1973) 193
4. M. R. Rampino, R. C. Reynolds, *Science* **219** (1983) 495
5. W. C. Elliott, J. L. Aronson Jr., H. T. Millard, E. Gierlowski-Kordesch, *Geol. Soc. Am. Bull.* **101** (1989) 702
6. W. C. Elliott, *Clays Clay Miner.* **41** (1993) 442
7. G. Millot, *Geology of Clays*, Sprenger-Verlag, New York, 1970, Chap. 5, p. 80
8. A. A. Ekdale, R. G. Bromley, *J. Sediment. Petrol.* **54** (1984) 681
9. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208** (1980) 1095
10. F. T. Kyte, Z. Zhou, J. T. Wasson, *Nature* **288** (1980) 651
11. P. I. Premović, N. Z. Pavlović, M. S. Pavlović, N. D. Nikolić, *Geochim. Cosmochim. Acta* **57** (1993) 1433
12. 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
13. B. Schmitz, P. Andersson, J. Dahl, *Geochim. Cosmochim. Acta* **52** (1988) 229
14. W. Wolbach, R. Lewis, E. Anders, *Science* **230** (1985) 167
15. B. Schmitz, *Geology* **16** (1988) 1068
16. S. Lo Mónaco, L. López, G. Garban, A. Lira, A. Rojas, *Rev. Latinoam. Geoquim. Org.* **3** (1997) 43
17. B. Schmitz, *Geochim. Cosmochim. Acta* **49** (1985) 2361
18. K. H. Wedepohl, *Handbook of Geochemistry*, Springer Verlag, Berlin, 1969
19. J. D. Saxby, in *Oil Shale*, T. F. Yen, G. V. Chilingarian, Eds., Elsevier, Amsterdam, 1976, p. 103
20. R. G. Prinn, B. Fegley, *Earth Planet. Sci. Lett.* **83** (1987) 1
21. H. Sigurdsson, S. D'Hondt, S. Carey, *Earth Planet. Sci. Lett.* **109** (1992) 543
22. K. O. Pope, K. H. Baines, A. C. Ocampo, B. A. Ivanov, *Earth Planet. Sci. Lett.* **128** (1994) 719
23. J. G. Erdman, J. W. Walter, W. E. Hanson, *Reprints Div. Pet. Chem. Am. Chem. Soc.* **2** (1957) 259
24. G. Cole, H. F. Shaw, *Clay Miner.* **18** (1983) 239
25. P. P. Zelmer, E. H. Mann, *Org. Geochem.* **5** (1983) 43
26. R. M. Garrels, C. L. Christ, *Solutions, Minerals, and Equilibria*, Harper and Row, New York, 1965, p. 450
27. W. S. Wolbach, I. Gilmour, E. Anders, C. J. Orth, R. R. Brooks, *Nature* **334** (1988) 665
28. S. P. McGrath, S. Smith, in *Heavy Metals in Soils*, B. J. Alloway Ed., Wiley, New York, 1990, p. 125
29. R. Brett, *Geochim. Cosmochim. Acta* **56** (1992) 3603
30. F. C. Richard, A. C. M. Bourg, *Water Res.* **25** (1991) 807
31. D. G. Brookins, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, 1988, p. 176
32. R. A. Griffin, A. K. Au, R. R. Frost, *J. Environ. Sci. Health A* **12** (1977) 431
33. R. J. Bartlett, J. M. Kimble, *J. Environ. Qual.* **5** (1976) 379
34. R. J. Bartlett, B. R. James, in *Chromium in the Natural and Human Environments*, J. O. Nriagu, E. Nierboor Eds., Soils, Wiley, New York, 1988, p. 267
35. A. Shukolyukov, G. W. Lugmair, *Science* **282** (1998) 927
36. F. T. Kyte, J. Smit, J. T. Wasson, *Earth Planet. Sci. Lett.* **73** (1985) 183

37. B. Schmitz, F. Asaro, H. V. Michel, H. R. Thierstein, B. T. Huber, in: *Proceedings of the Ocean Drilling Program, Scientific Results* **119** (1991) 719
38. V. I. Fedoseyeva, N. F. Fedoseyev, G. V. Zvonareva, *Geokhimlya* **22** (1985) 1386
39. J. S. Lewis, G. H. Watkins, H. Hartman, R. G. Prinn, *Geol. Soc. Am. Spec. Pap.* **190** (1982) 215
40. S. A. Davenport, T. J. Wdowiak, D. D. Jones, P. Wdowiak, *Geol. Soc. Am. Spec. Pap.* **247** (1990) 71
41. D. J. Swaine, in *Nickel in the Environment*, J. O. Nriagu Ed., Wiley, New York, 1980, p. 67
42. H. J. W. de Baar, *Ph. D. Thesis*, WHOI/MIT Joint Program in Oceanography, WHOI Tech. Rept. 83-45, 1983
43. L. P. Gromet, R. F. Dymmer, L. A. Haskin, R. L. Korotev, *Geochim. Cosmochim. Acta* **48** (1984) 2469
44. G. Graup, H. Palme, B. Spettle, *Lunar Planet. Sci* **XXIII** (1992) 445
45. B. A. Goodman, M. V. Cheshire, *J. Soil Sci.* **27** (1976) 337
46. M. V. Cheshire, M. I. Berrow, B. A. Goodman, C. M. Mundie, *Geochim. Cosmochim. Acta* **41** (1977) 1131
47. A. L. Abdul-Halim, J. C. Evans, C. C. Rowlands, J. H. Thomas, *Geochim. Cosmochim. Acta* **45** (1981) 481
48. N. Senesi, G. Calderoni, *Org. Geochem.* **13** (1988) 1145
49. E. W. Baker, J. W. Louda, in *Advances in Organic Geochemistry* 1983, P. A. Schenck, J. W. de Leeuw, G. W. M. Lijmbach, Eds., *Org. Geochem.* **6**, Pergamon Press, Oxford, 1984, p. 183.

Errata

In the Information regarding the 40th Anniversary of the Institute of Chemistry, Technology and Metallurgy in Belgrade, printed in the Journal of the Serbian Chemical Society, Vol. 66. No. 9(2001) on the inside of the cover page the following corrections should be made:

1. Instead of: 1985 Prince M. Obrenović... , should be 1859 Prince M. Obrenović...
2. Instead of: 1982 when King Mihajlo III... , should be 1882 when King Mihajlo III...
3. Instead of: 1987 when the Serbian Chemical Society... , should be 1897 when the Serbian Chemical Society...