J. Serb. Chem. Soc. 71 (6) 639–659 (2006) UDC 550.4:549.263+553.551(489)
JSCS–3458 *Original scientific paper*

Geochemistry of Ni in the Cretaceous-Tertiary succession Fiskeler (Fish Clay) at Stevns Klint (Denmark): cheto-smectite of the black marl

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(Received 26 May 2005)

Abstract: The Cretaceus-Tertiary (KT) boundary at Stevns Klint (the Højerup succession), Fiskeler, consists of a thin red clay layer overlain by a thick one of black marl. These two layers are made up mainly from cheto-smectite and biogenic calcite. The black marl shows an enhanced concentration of Ni (655 ppm) within its smectite fraction. Additionally, its carbonate fraction also shows an enhanced concentration of Ni (245 ppm). It is reasoned that these enrichments represent a sudden and rapid input of high amounts of Ni into the late Cretaceus seawater at Stevns Klint. The ultimate source of Ni in both the carbonate and smectite fractions of the black marl was probably impact fallout, produced by the KT asteroidal impact, deposited on the nearby soil and leached by the (acid) surface waters. The geochemistry of the Ni supports the hypothesis that the smectite of this marl most likely has a local (marine or terrestrial) provenance and was probably redeposited, after its formation, from the original site to its present location at the KT boundary.

Keywords: geochemistry, Ni, Cretaceous-Tertiary, Fiskeler, smectite, black marl.

INTRODUCTION

Fiskeler of the Højerup succession (hereafter FK) is a classic KT boundary at Stevns Klint. The lithology of FK has been described by Christensen *et al.*[1] The authors distiguished four distinct layers within this boundary: the bottom layer II (Maastrichtian grey marl: 1–2 cm thick), the middle layers III (brown-to-black marl: *ca.* 2 cm thick) and IV (grey to black marl: 3–5 cm thick) and the top layer V (light-grey marl: 5–7 cm thick), Fig. 1. II is underlain by Maastrichtian chalk (I), and V is overlan by Danian cerithium limestone (VI). (The zero level of this Figure

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doi: 10.2298/JSC0606639P

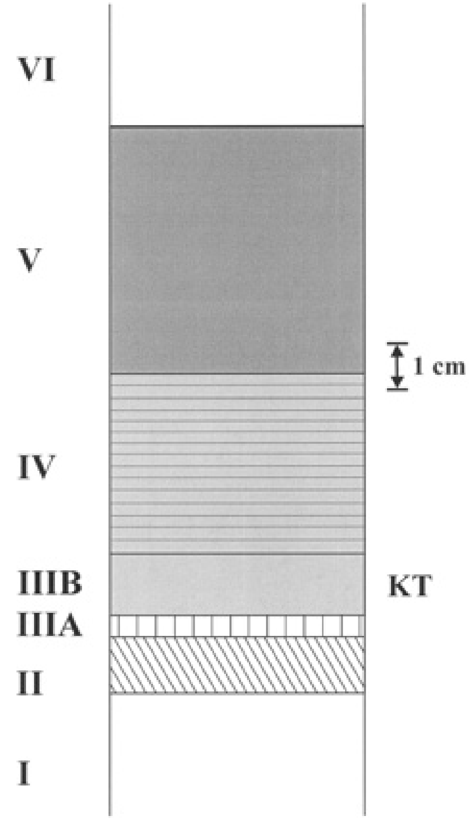

Fig. 1. Schematic illustration of the internal layering in a stratigraphic section of FK.

is defined as the interface between bed I below and bed II immediately above it). Elliott[2] subdivided layer III into the red layer IIIA (which was not analyzed in this study) which is overlain by the black marl layer IIIB, Fig. 1. IIIA is a thin (0.3–0.5 cm) layer with a high content spherules.[3] The IIIB layer is black marl containing high Ir,[4,5] kerogen enriched with Cu^{2+}-porphyrins,[6] and a small amount of macroscopic pyrite (FeS_2).[3] The base of IIIB is also rich in spherules but they are much less abundant then in IIIA.[3] Layers IIIA/B and IV are here considered to constitute the main part of the KT boundary section at Stevns Klint. There is, however, no sharp boundary between IIIB and the IV, which makes it difficult to distinguish the top of IIIB and the base of IV.

Alvarez *et al.*[7] were the first to report an anomalously high Ir concentration in FK. To explain this enhanced Ir concentration the authors proposed a late Cretaceous asteroid impact on the Earth. According to current pedagogy, this impact occurred at the Chicxulub location (Yucatan Peninsula, Mexico), Fig. 2. This proposal was soon followed by reports of Ir enrichments in several other boundaries from all over the world. FK contains also other platinum elements,[8] shocked quartz grains,[9] soot[10] and non-altered/altered impact-derived glass shards and meteoritic

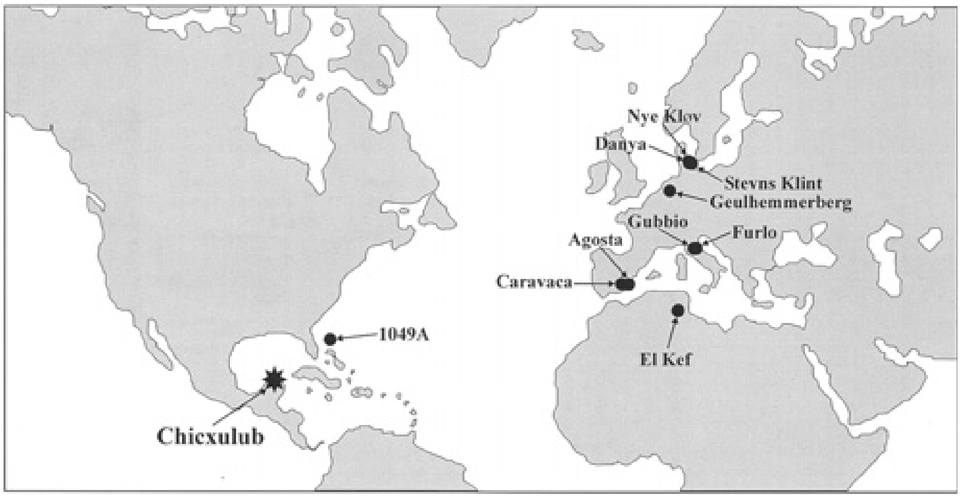

Fig. 2. Location map showing the KT site at Stevns Klint in relation to other prominent KT sites world-wide.

fragments.[11] It has been also suggested that the late Cretaceous impactor was a (carbonaceous) Cl chondrite-type body.[12]

The X-ray diffraction analyses of FK by Rampino and Reynolds[13] indicate that the central part of FK (III/IV) contains pure smectite, which is relatively abundant and of local derivation, formed by the diagenetic alternation of glassy volcanic ash. In contrast, Kastner *et al.*[14] concluded that the major element chemistry, mineralogy and oxygen isotope analyses indicate that the smectite of III/IV is an alteration product of the impact-derived glasses. Premović *et al.*[6,15] suggested that most of the IIIB smectite is detrital and ultimately derived from a local volcanoclastic source. In contrast, Bauluz *et al.*[11] provided experimental evidence [scanning electron microscopy (SEM) and transmission electron microscopy (TEM)/analytical electron microscopy (AEM)] that the smectite in FK is a direct product of impact glasess.[11] In addition, they reported the presence of impact glasses and altered smectite throughout the FK sequence (from II to IV), suggesting that there was a continuous contribution of these glasses to FK over a considerable time. Very recently, Drits *et al.*[16] carried out chemical analysis, solid state NMR spectroscopy and atomic force microscopy of the clay fraction of IIIB. These authors reported that this fraction consists of two phases: a high-smectite phase (70 %) having 95 % smectite and 5 % illite and a low-smectite phase (30 %) having 50 % illite. According to Drits *et al.*[16] these two phases are probably formed from volcanic ash. These authors argued that a very small part, if any, of the smectite within the FK column was derived from asteroidal impact fallout.

Apart from Ir, IIIB is also enriched in Ni.[1,3,4,6,15,17] To date, the question of the origin of these metals in IIIB smectite has not been resolved. Christensen *et al.*[1] proposed that these metals concentrated due to an accumulation of mainly terrigenous materials with minor amounts of clay minerals of diagenetic origin. Schmitz[4] proposed that trace metal precipitation in FK was induced by various redox-controlled processes in connection with the decomposition of the abundant algal matter. He argued that the concentrated trace metals of the IIIB and IV samples precipitated as sulfides from the seawater at Stevns Klint; although the authors, also pointed out that the ultimate origin of some of these metals (*e.g.* Ni) may have been an Earth-impacting asteroid. Elliot[2] and Elliott *et al.*[18] showed that IIIB smectite is a possible carrier phase of trace metals (including Ni). These authors argued that trace metals in IIIB smectite originated from seawater enriched with this metal from the impact fallout. Premović *et al.*[6,15] considered that a lot of the trace metals (including Ni) in IIIB smectite are strictly detrital in character, *i.e.*, they were incorporated into the smectite structure prior to being deposited at the FK site.

In this study Ni in IIIB smectite was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Ni was chosen primarily because of its distinct (but relatively simple) geochemical activities and properties. Essentially, this paper is complementary to previous studies[6,15] and discusses the broader geochemical aspect of Ni within IIIB smectite,[*] which may be important in understanding the geochemical and depositional processes which occurred during the sedimentation of FK. An understanding of these processes which led to the enrichment of Ni within this clay would also shed light on the sequence of sedimentary episodes which led to this enhancement.

EXPERIMENTAL

Inductively Coupled Plasma-Optical Emission Spectrometry

Ni of the whole-rock IIIB sample and its fractions was analyzed by ICP-OES. A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas.

Fourier Transform Infrared (FTIR) Spectrometry

Rock samples were finely powdered and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). The spectra were recorded at room temperature using a Bomem (Hartman & Braun) MB-100 spectrometer set to result in an underformed spectra.

Electron Spin Resonance (ESR)

ESR measurements were performed on the finely ground powders of the rock samples which were transferred to an ESR quartz tube (4 mm o.d., 3 mm i.d.). The spectra were recorded on a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz.

X-Ray Diffraction (XRD)

XRD analyses of the whole rock and their carbonate-free, smectite and silicate fractions were performed using a Philips diffractometer (PW 1050/25) equipped with a proportional counter and discriminator, using Ni-filtered Cu radiation at 40 kV and 20 mA.

Energy Dispersive Spectrometry (EDS)

All EDS analyses were obtained with a Jeol JSM-35 electron microscope equipped with a Tracor TN-2000 energy dispersive X-ray spectrometer. The operating conditions for the en-

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[*] The origin of IIIB smectite is outside the scope of this paper.

ergy-dispersive analyses were 25 keV accelerating voltage, 0.1 μA beam current, and a beam spot diameter of approximately 3 μm.

Analysis and fractionation

Dr. Helle Schummel collected bulk samples of IIIB from an outcrop 200 m south of Højerup Church. The rock sample was dried in an oven and carefully ground in an agate mortar. The fractionation procedure was similar to that used by Premović *et al.*[15] and Saxby.[19] The major steps in preparing the four fractions were:

1. Powdered rock (48 g) was treated (12 h) with an acetate buffer solution, acetic acid (1 M)/sodium acetate (1 M), of pH 5.0[20] to remove most of the carbonates. Carbonate removal was checked by X-ray and Fourier transform infrared (FTIR) analyses. The soluble portion constituted the carbonate fraction (analyzed for Ni by ICP-OES). It appears that the treatment of the sediments with the acetate buffer solution is the most efficient and simple method for removing carbonates with a minimal damage to the clay present.[21]

2. The insoluble residue from (1) above was demineralized further by repeated treatment with cold HCl (6 M, room temperature, 12 h). The soluble part constituted the cold-HCl fraction (analyzed for Ni by ICP-OES).

3. The insoluble residue from (2) was demineralized with boiling HCl (6 M, 80 °C, 12 h). This treatment removed most of the soluble silicates. The acid-soluble part constituted the smectite fraction (*i.e.*, the smectite concentrate). Smectite removal was checked by X-ray/FTIR analyses. The smectite fraction was analyzed for Ni by ICP-OES. The insoluble residue constituted the HCl-insoluble fraction, containing acid-insoluble silicates (*ca.* 90 %), kerogen (*ca.* 10 %) and FeS_2 (< 2 %). This fraction was analyzed for Ni by ICP-OES.

The ESR, XRD, SEM and EDS analyses of the demineralized fractions of IIIB also confirmed that the dissolution was eseentially complete and that a good selectivity was obtained at each stage of demineralization.

RESULTS

Ni within IIIB in the carbonate, cold-HCl, smectite and acid-insoluble fractions of IIIB were determined and the analytical results are given in Table I. The standard deviations for Ni in each fraction are on average 5 % with a maximum of 20 %. The distribution of Ni among the four fractions of the IIIB sample is shown in Table I. The Ni content of the carbonate fractions of layers I, II, IV and V were also determined by ICP-OES. The distribution of Ni in this fraction across FK is presented in Fig. 3. For comparison, the Ni contents of the carbonate and the carbonate-free (smectite concentrate) fraction of a KT succession (equivalent to FK) at another marine site (about 4 km from the Højerup location) at the southernmost part of Stevns Klint close to Rødvig were also determined.

TABLE I. Geochemical concentrations and geochemical distributions of Ni (from selective leaching experiments) among the carbonate, cold-HCl, smectite and acid insoluble fractions of IIIB

Fraction	Sediment ±5 wt %	Ni/ppm[a]	Ni/ppm[b]	Total Ni/%
Carbonate	52	245	125	38
Cold-HCl	7	780	55	17
Smectite	21	655	140	42
Acid insoluble	20	55	10	3
Sediment	100	330	330	100

[a]Geochemical concentration. [b]Geochemical distribution

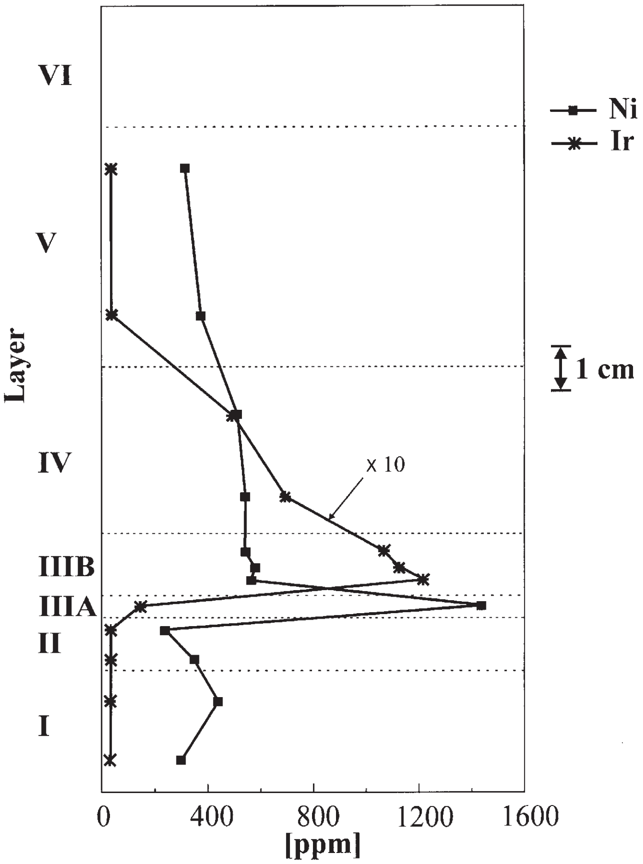

Fig. 3. The distribution of Ni and Ir across FK.

TABLE II. The carbonate fractions (± 5 wt %) and their Ni content (± 5 ppm) of KT boundaries at various localities world-wide (see Fig. 2 for the locations of these deposits)

Sample	Paleorange ±300 km[a]	Carbonate fraction	Ni
Rødvig	12000	45	5
Nye Kløv	12000	53	15[b]
Dania	12000	70	10[b]
Caravaca	9750	32	70
Agosta	9750	70	10
El Kef	11000	50	15
Geulhemmerberg	11500	60	<5
Furlo	11750	40	<10
Gubbio	11750	42	15
1049A	2000	29	165

[a] Approximate distance from the impact site at Chicxulub. [b] Premović *et al.*[15]

Analysis for Ni in the carbonate fractions of other marine KT desposits, at Caravaca/Agosta (Spain), El Keef (Tunisia), Geulhemmerberg (Holland) and Furlo/Gubbio (Italy), was also carried out, Fig. 2. These analytical results are presented in Table II.

PREVIOUS STUDIES OF IIIA/IIIB AND THE RELEVANT INTERPRETATIONS

Origin and nature of IIIA

The origin of IIIA is still controversial. Kyte *et al.*[22] analyzed IIIA sample for trace metals (in particular siderophiles) employing instrumental/radiochemical neutron activation analyses. They suggested that only IIIA should be used to estimate primary ejecta falout of the KT asteroid impact, as trace metals in the higher layers arose mainly from secondary fallout material, laterally transported from nearby localities on land. Kyte *et al.*[22] reasoned that only IIIA (usually referred to as the impact layer, magic layer or fireball layer) is the sole representative of the original impact fallout. In contrast to Kyte *et al,*[23] Schmitz[4] concluded that the major element composition of IIIA indicate that this layer is made up of locally derived clays. He also argued that pore solutions bearing trace metals (mainly Ni) migrated upwards from the slightly oxidized chalks beds into the highly anoxic environment of IIIB.

Premović *et al.*[6] inferred that IIIB was deposited near-shore in shallow seawater within an interval only a few tens of years (about 40 years of sedimentation) or even much less. Wendler and Willems[24] considered that IIIA/B represent the first decades or centuries following the KT impact event and that IV characterizes a relatively fast but continuous low energy sedimentation. Thus, IIIA/B were probably deposited relatively quickly on the seafloor. The problem is, however, that during the formation of IIIA, sedimentation may have been extremely condensed, attributed to the biogenic dissolution of calcite and a significant time may have elapsed between the formation of IIIA and IIIB.[25]

Ni and Ir of IIIA spherules.

Schmitz[3] and Graup *et al.*[5] reported that IIIA contains spherules which vary in size from 0.125 m to 800 mm in diameter and are similar in appearance to those in KT successions worldwide. Schmitz[3] found that these spherules make up about 10 wt % of IIIA and they are its original constituents. IIIA spherules are either wholly pyritic or are partly to fully weathered to geothite.[3–5] These spherules are highly enriched with Ni (5000 ppm)[3] and Ir (up to 17 ppb).[27] It is highly likely that the Ni and Ir in the IIIA spherules were not primary constituents but that they were introduced into their structure during their diagenetic alternaton. The source of Ni in the spherules was probably interstial pore seawater already enriched with this metal.

Schmitz[4] reported ICP-OES data for trace metals in the carbonate-free fractions (mainly the clay concentrates) in more-closely spaced samples accross FK. The clay fraction of I, II, IV, V and VI appears to be the major carrier of these trace metals; their carbonate component is essentially a dilutant which lowers the trace metals concentrations. The Ni data (based on Schmitz's results) are shown as concentration profile *vs.* stratigraphic height in Fig. 3. This Figure shows that the Ni values reach a profound peak concentration of about 1440 ppm in IIIA. A simple calculation indicates that less than one third of the total Ni content in IIIA can be attributed to the spherules. The remaining metal is probably associated with its smectite.

Ir accross FK.

Schmitz[4] also reported INAA data for Ir (on a carbonate-free basis) within the FK column. Based on these results, the concentration profile of this metal across FK is also presented in Fig. 3. The Ir values reach a profound peak concentration of 140 ppb in the base of IIIB. Upwards from this level, the Ir concentration decrease gradually, indicating a single external input of this metal to FK. Note that the Ir concentration in the carbonate-free fraction (the smectite concentrate: Table I) of IIIB are by a factor of 7–8 higher than in the same fraction of IIIA.

Geochemical studies[5,7,28,29] show that the Ir profile (on a whole rock basis) across the FK columns is characterized by a sharp concentration peak in the base of IIIB with an upwards gradual decrease (tailing-off) from its maximum. IIIB/IV contain $>$ 90 % of the total Ir influx within FK. Similarly, these two layers contain $>$ 90 % of the total Ni influx, though its concentration maxima is in IIIA. These results indicate that the accumulation of Ni and Ir may be attributed to the same geochemical event.

Schmitz[4] reasoned that humics at Stevns Klint probably played an important role in concentrating Ir in IIIB. The author reported that about 50 % of the total Ir flux in FK is hosted by IIIB kerogen. This may reflect a strong association of Ir and humics (IIIB kerogen precursor) at Stevns Klint. It appears that Ir has a high affinity for humics in natural waters. For example, Anbar *et al.*[30] found that a large amount of humics in river water enters the Baltic Sea, and about 75 % of the riverine Ir accumulates in the nearshore (brackish) waters similar to that of Stevns Klint. Thus, it is possible that a significant part of Ir inventory in IIIB resulted from a geochemical process which occured in the nearby soil (enriched with humics) of Stevns Klint. If this is correct then it infers that a considerable portion of the Ir anomaly of IIIB came through, geologically speaking, an instantaneous addition of humics (enriched with Cu^{2+} porphyrins) from the nearby soil. This suggestion is in line with the estimate of fast deposition of IIIB by Premović *et al.*[6] and Wendler and Willems.[24]

An interesting finding is the absence of kerogen in the nearby KT succession (equivalent to FK) at Rødvig, indicating that this KT section formed under oxic sedimentary conditions. The ICP-OES analysis show, however, that the smectite concentrate of this section is relatively enriched with Ni (930 ppm) and Ir (10 ppb) (unpublished results).

An important fact illustrated in Fig. 3 is that the clay-rich fractions (the smectite concentrate) of the underlying I/II and overlying IV/V layers are also relatively enriched with Ni, indicating that postdeposit redistribution of this metal probably occurred. The fact that the Ir enrichment, also, extends, to a certain extent, up to V infers that this, apparently chondritic, metal probably also underwent this process. This conclusion is consistent with than made by Wells *et al.*[31] that Ir enrichment in IIIB kerogen probably occurred after deposition as a result of Ir redistribution within this layer.

DISCUSSION

Ni within IIIB

The concentration of Ni in IIIB (Table I) is mostly greater than in average shales,[32] in average carboniferous shales[33] and even in shales known to be enriched with trace metals, such as the Julia Creek carboniferous marl.[34] The distribution of Ni within the IIIB fractions, is given in Table I. It can also be seen from this Table that the acetate buffer step removes about 52 % of the entire IIIB sample, containing 38 % of the total Ni. As stated earlier, this is mainly a result of the total dissolution of carbonates. The cold HCl leaching removes most of the metal oxides/sulfides (7 % of the whole IIIB sample). The Ni (17 % of the total Ni) within IIIB removed by cold HCl is likely sorbed on the carbonate/smectite particles or precipitated as oxides/sulfides. In addition, a significant part of this removable metal may also be incorporated into the structure of Fe-oxides, mainly goethite (α-FeOOH) and ferrihydrite (Fe_2O_3 x $0.5H_2O$). The boiling HCl step disolves most of smectite and monosulfides [chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and pyrrhotite (Fe_{1-x} S], but not disulfides such as FeS_2. A minor amount of Ni (3 % of the total Ni) resides in the acid insoluble fractions (kerogen + FeS_2).

Ni within IIIB smectite

The analytical results in Table I show that considerable amounts of total Ni (42 %) resides in the IIIB smectite. Smectites possess a large specific surface area (6–8 x 10^5 m^2 kg^{-1}) and a relatively high structural charge (up to 1200 meq kg^{-1}) imparting them with important sorptive properties. It is quite possible, therefore, that Ni^{2+} ions reside in the exchangeable Mg^{2+} interlayer sites within the IIIB smectite. These positions are excellent coordinating sites within the smectite structures which would be very rapidly filled by these ions during/after diagenesis. Indeed, Rybicka *et al.*[35] invetigated the adsorption/desorption behavior of Ni on cheto-smectite (Arizona, USA). Ni was about 40–50 % sorbed. It is, therefore, concluded that IIIA/B cheto-smectite was open to exchange (during and after its diagenesis) with the seawater which was already enriched with Ni, *i.e.*, this clay could behave as a sink for Ni if this metal was present in the seawater of Stevns Klint. The experimentally demonstrated ability of cheto-smectite to fix Ni in a few days from solution[35] suggests, however, the feasibility of continued accumulatiion of this metal from seawater enriched with this metal for tens or even hundreds of thousands of years. This is especially true for IIIA since this layer is extremely thin and composed almost completely of cheto-smectite. These characteristics would highly facilitate the exchange of Ni in smectite with interstial pore seawaters. This must also be true for IIIB, as this layer is, also, rather thin (up to 2 cm).

Ni and the nearby soil

The average concentration of Ni in normal seawater is very low in comparison with its content in IIIB smectite, *i.e.,* 118 ppt (Ni).[36] If the above assumptions of fast deposition of IIIB[6,24] are correct then it seems unlikely that normal seawater itself could have been an adequate source for this metal in IIIB smectite. It is more likely that the overlying seawater already enriched with this metal contributed mostly to the Ni in IIIB smectite.

Erickson and Dickson[37] carried out mass balance calculations of the influence of trace metal to the surface seawater associated with the Alvarez *et al.*[7] chondritic impactor. These calculations showed that this water would be enriched by a factor of 660 (Ni). Assuming that 100 % of this metal was dissolved, this concentration in the surface seawater would be *ca.* 78 ppb (Ni). A simple metal supply calculation suggests that this source would not be an adequate supply of Ni. Therefore, a source with a higher concentration of this metal must be searched for. For this reason, an inference on a land source of Ni is needed. Thus, this metal in IIIB smectite is probably the detrital component originating from the nearby soil. However, it is unlikely that an ordinary soil would be adequate to explain the elevated values of this metal and a considerably abundant source is clearly required to explain its enrichment.

Recently, Frei and Frei[38] carried out a multi-isotopic/trace elements study of FK. According to these authors, the sudden changes in the Sr, Pb and Nd isotope compositions/ratios of this boundary indicate enhanced, acid-rain induced continental (local?) weathering input to the seawater at Stevns Klint. The same conclusion was obtained independently by Premović *et al.*[6] from a study of Cu and Cu^{2+}-porphyrins within IIIB. Under these acidic and oxic conditions, Ni would be highly soluble[39] and readily traanslocated by the surface waters. Hence, the seawater at Stevns Klint may have differed in composition from ordinary seawater, perhaps because of extensive acidrain weathering (leaching) of source rock(s) enriched with Ni on land. In addition, there could have been apparent concentrating mechanisms for Ni in the soil at Stevns Klint. Perhaps regional/local conditions (*e. g.* topography, *etc.*) were, also, favorable for an efficient and concentrated accumulation of this metal.

The many studies of the KT events indicate that acid rain(s) at the KT boundary could have been generated by the Alvarez *et al.*[7] impactor. The vast amount of mainly SO_2 generated by such an impact would be globally dispersed and quickly converted into H_2SO_4 aerosols, which would act as nucleation sites for acid rains. On the other hand, opponents of the Alvarez *et al.*[7] impact usually suggest that gigantic volcanic eruptions (*e.g.* Deccan Traps in India) could produce similar acid ranifalls.

The Ir anomaly has been found at more than 80 KT boundary successions throughout the world.[40] Most of these successions were deposited in a nearshore marine environment similar to that of Stevns Klint. In the most prominent of the marine successions, Ni has a maxima at the same stratigraphical level: in a 1–2 mm thick reddish layer like IIIA.[4,41] This is a consequence of the fact that this metal has a common origin and a similar behavior during diagenesis. This argus against a local source of Ni, *e.g.*, acid surface waters leaching the terristrial rocks on the nearby land.

As Ir is a highly compatible metal, the only sources for it in the prominent KT successions are either deep mantle or asteroidal in-fall. The fact that the only large scale volcanic activity at the KT time, Deccan Traps, shows low amounts (< 35 ppt) of Ir in its predominant thoeliitic basalts (99 %) indicates an asteroidal source.[42,43] In addition, geochronological dating of these basalts by these authors shows that the occurrence of their pulse was well before (about 4 millions years) the KT boundary. Thus, if the Ir anomaly in the KT successions worldwide originated from impact fallout then Ni is probably derived from the same source. This conclusion is consistent with most literature concerning their enrichments in the KT succession worldwide. It appears that the clay fraction of these beds is the dominant carrier phase of Ni. For this reason, it can be tentatively hypothesized that most of Ni within the IIIB smectite ultimately came from fallout (enriched with this trace metal), generated by a late Cretaceous impact, covering the nearby oxic soil at Stevns Klint. Indeed, Davenport *et al.*[44*] estimated that, after the Alvarez *et al.*[7] impact, the top soil would have been covered with the primary fallout, and have a Ni content one or two order of magnitude greater than the contemporary average level of Ni in soils (16 ppm).

The concentration of Ni within IIIB smectite is *ca*. 655 ppm (Table I) and much lower then the average Ni concentration in Cl chondrites (11,000 ppm).[45] Thus, assuming that the concerned metal was supplied by the impact falloutt, the excess of Ni in the seawater of Stevns Klint was probably derived from a Cl chondritic component associated with this material, as originally suggested by Elliot *et al.*[18] It is noteworthy that Gilmour and Anders[46] suggested a chondritic origin of anomalous Ni in eleven of the most prominent marine KT successions, including FK.

Anoxic vs. *oxic conditions of the formation of IIIB smectite*

It is almost certain that seawater already enriched with Ni predominently contributed to this metal in IIIB. This enrichment process could have occured either during diagenesis of afterwards by sorption. Unlike the oxic conditions that prevailed during the sedimentation of I/II/V/VI, geochemical evidence indicates that

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[*] According to these authors, the impact infall would have a Ni concentration of between 133–1330 ppm.

IIIB (and most of IV) was deposited either under strong anoxic conditions or the conditions became strongly anoxic soon after deposition and H_2S was present in both IIIB and the immediate overlying seawater.[15] Let us consider whether the incorporation of Ni in an anoxic sedimentary environment can account for its abundances in IIIB smectite.

Schmitz[3] suggested that the abundant presence of the FeS_2 concretions enclosed within IIIB indicates that strong reducing conditions still prevail in IIIB 65 Ma after its formation. Under these conditions most of the Ni would be preferentially incorporated into FeS_2.[47] In this way, the anoxic IIIB would act as a sink for this metal. In other words, strong anoxic conditions would be adverse for the incorporation of Ni into IIIB smectite from the overlying seawater. Table I shows that $\leq$ 5 % of the total Ni resides in the acid-insoluble fraction of IIIB, which contains mainly HCl-insoluble silicates (mainly illites/quartz) and kerogen. The fact that FeS_2 is predominantly associated with this fraction indicates that a rather a low proportion of the total Ni is incorporated into the pyritic component of IIIB. Indeed, most of the Ni of the HCl-insoluble fraction of IIIB resides in kerogen.[48]

In contrast to an anoxic environment, if the incorporation of Ni into IIIB smectite occurred in an ordinary (oxic) seawater (with a normal pH of about 8) then predominantly free Ni^{2+} ions would be present in this water. Hence, it may be concluded that the enriched association of Ni in IIIB smectite does not reflect anoxic but oxic conditions. This means that the diagenetic and/or postdiagenetic incorporation of Ni into IIIB smectite had to occur in an oxic sedimentary environment. (This must also be valid for IIIA). This conclusion is further supported by the following:

(1) Our geochemical analysis showed that IIIB smectite contains about 4 % of Fe (unpublished results). EDS Examination revealed that there is also an abundance of (external) Fe oxide-rich particles (probably goethite/ferrihydrite grains) associated with IIIB smectite. Moreover, an ESR investigation[49] showed that smectite IIIB contains a relatively high (internal) amount of Fe^{3+} incorporated into the smectite structure. These findings are consistent with the formation of IIIB smectite in an oxic environment as (internal or external) Fe^{3+} and Fe^{2+} (and their oxides) are unstable with respect of FeS_2 in anoxic environments.[49] The presence of minor amounts of goethite/ferrihydrite in IIIB could be due to the oxidation of various forms of FeS_2 by air O_2 during (postdiagenetic) weathering lasting 65 Ma.

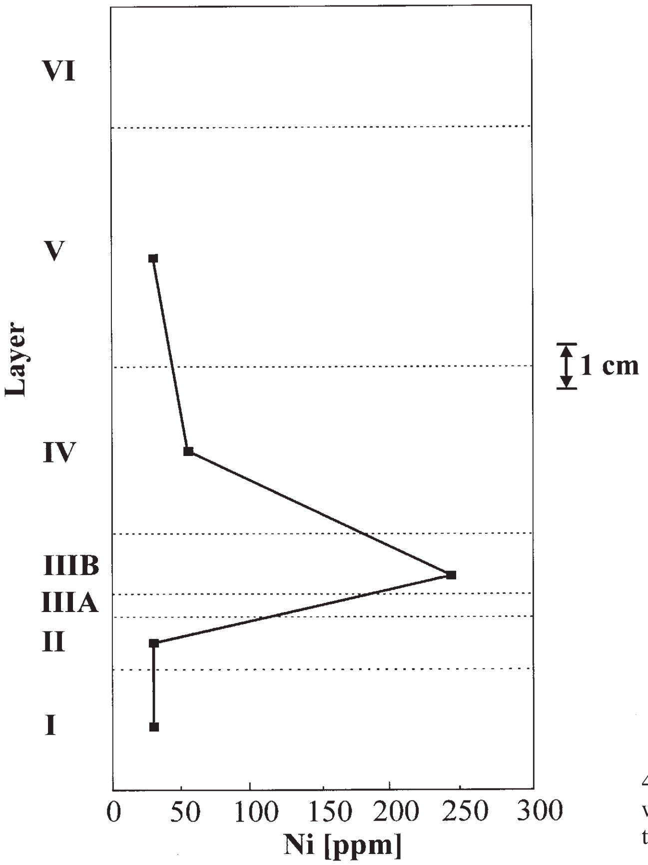
(2) The Cr/V ratio has been used as a paleoenvironmental indicator of sedimentation (Jones and Manning[50] and references therein). Values of V/Cr $\geq$ 4 are thought to represent suboxic/anoxic sedimentation conditions. Values $\leq$ 4 are indicative of slightly oxidizing (dysoxic) conditions, with values $\leq$ 2 suggesting oxic conditions within the sediment. The V/Cr ratios of IIIB smectite is 0.5 (V and Cr concentrations of this clay are taken from the work published by Premović *et al.*[15]) indicating an oxygenated (or ordinary) marine environment. The fact that the aver-

age Re/Mo ratio in IIIB (> 1.2×10^{-2}) (unpublished results) is high with respect to ordinary seawater (3.6×10^{-3}) supports this conclusion.

As pointed out earlier, smectite within IIIA are highly enriched with Ni. This layer was, probably, deposited under oxic conditions, which is supported by the relatively high content (*ca*. 10 %) of nanophase goethite associated with IIIA,[11,51] and by the absence of kerogen in IIIB. According to Krumbein and Garrels,[52] this mineral occurs in sedimentary environment under oxidizing conditions with a redox potential Eh > +0.15 V.

Ni within the biogenic calcite of IIIB

Considering now Ni in the carbonate fraction (mainly biogenic calcite) of the FK layers, the concentration of Ni (245 ppm, Table I) in this fraction of IIIB is anomalous when compared with the average Ni concentration (7 ppm) found in marine calcareous rocks.[53] This is consistent with the earlier suggestion that the seawater of Stevns Klint may have been abundantly enriched in Ni. The distribution of Ni across the FK column shows that the calcite fraction of II contains less



4. The distribution of Ni (ppm) within the carbonate fractions of the layers I, II, III, IV and V.

than 20 ppm of Ni and the concentration of this metal is the highest in IIIB, diminishing upward (IV) and ultimately disappearing (V), Fig. 4. Both the more than five fold increase of Ni in IIIB calcite and the more than five fold decrease in IV calcite are consistent with a single and rapid introduction of Ni into the seawater. The background value of Ni in the calcite fraction of V suggests that after deposition of III/IV, the influx of Ni from the nearby land probably ceased completely.

Ni associated with the calcite component of IIIB may reside in biogenic calcite. If this is a case then this Ni represents biological Ni, *i.e.*, the direct incorporation of Ni^{2+} ions into the shells of calcareous microbiota which occurred during their metabolic uptake of surface seawater already enriched with these ions. Indeed, the Ni^{2+} ions may substitute Ca^{2+} ions in the calcite matrix since Ni^{2+} has a similar ionic radius/the same charge as Ca^{2+}. Combined chemical and FTIR/XRD/SEM/EDS analyses showed that the KT succession near Rødvig also contains a relatively high calcite (about 45 %) mainly derived from calcareous microbiota. The ICP-OES analysis showed, however, that this calcite, contrary to expectations, contains no enhanced concentration of Ni (5 ppm, Table II), compared to the background. If the metabolic activity of calcareous microbiota led to the formation of calcite shells enriched with Ni in IIIB then it is rather strange that the corresponding biogenic material at Rødvig showed no evidence at all of this activity.

An alternative possibility is that the Ni actually occurs in another phase. Apparently the use of 1.0 M sodium acetate is an established method for the dissolution of sedimentary carbonates. However, the effect of this reagent is not limited to carbonate dissolution. A considerable amount of specifically sorbed Ni may be solubilized at pH 5.0.[54] A previous geochemical study, however, suggested that contamination of this source represents a serious problem only if the Ni concentration in the acetate buffer leachate are less than 10 ppm.[55]

Regardles of whether the abundant association of Ni with the carbonate fraction of IIIB is best explained by biogenic or sorbed Ni, it seems very likely that the Ni within this fraction is indeed a sharp time marker, representing a sudden airfall of the impact fallout in the Stevns Klint area. Marine calcerous microbiota would, of couse, be particularly vunerable to a abrupt injection of high amounts of Ni into the seawater at Stevns Klint.[37,44,56] Therefore, the annihilation of calcereous microbiota during KT in the seawater of Stevns Klint may also be attributed to the poisoning effects of Ni. Considering the long scale of the Ni residence time (90,000 y) toxicosis of this metal could have been far more substantial than other environmental effects (including acid rainfall, inhibition of photosynthesis, drop of temperature and greenhouse effects) induced by either an asteroidal impact or a volcanic emission.

In contrast to FK, the carbonate part (mainly biogenic calcite) of the KT boundary sections at Nye Kløv (*ca*. 320 km away from Stevns Klint) and Dania (*ca*. 220 km) in western Denmark (Fig. 5.) contain Ni (≤ 15 ppm) comparable with

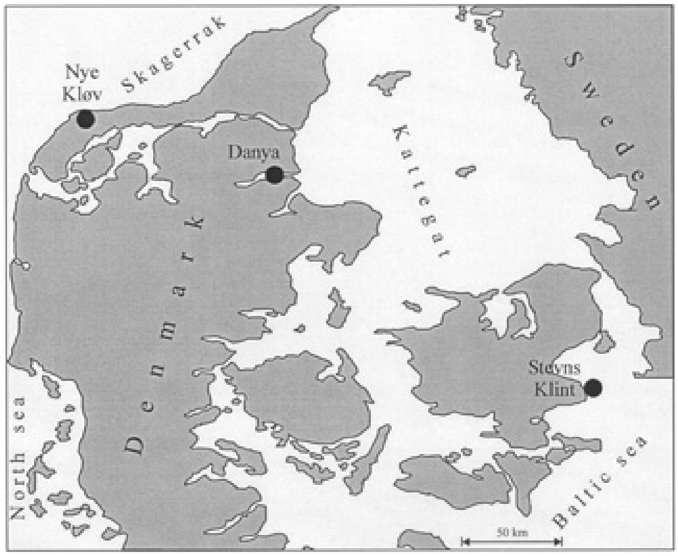


Fig. 5. Location of the samples of the Danish boundaries.

their background levels.[15] The analytical results of the carbonate fractions (mainly biogenic calcite) of the other prominent KT boundaries worldwide (Caravaca/Agosta, El Kef, Geulhemmberg and Furlo/Gubio, Fig. 2) also indicate that these components contain normal background amounts of Ni (≤ 15 ppm), except the Caravaca simple (70 ppm), Table II. It is resonable to assume that local variables [*e.g.,* physicochemical conditions of sedimentation (especially Eh/pH), sedimentation rate, *etc*.] may have affected the process of concentrating Ni in their calcite fractions. It is also noteworthy that the oceanic KT boundary section at Blake Nose (site 1049A, hole A, core 17X, section 2) also shows a profound enrichment of Ni (up to 165 ppm, Table II) associated with the carbonate fraction (mainly biogenic calcite).[57]

The redeposition of IIIB smectite

Drits *et al.*[16] consider two alternatives as likely for the origin of cheto-type smectite within FK. One possibility is that this clay was formed from volcanic glasses then it was deposited at Stevns Klint periodically during a long time from the late Maastrichtian to the early Danian. The second possibility is that the clay is a detrital mineral of volcanic origin that was formed before the KT boundary and then redeposited from its original site to Stevns Klint. The last alternative is in line with the conclusion of Premovic *et al.*[15]

In general, marine KT successions worldwide are depositionally complex and mainly affected by erosion and subsequent redeposition. The variable tickness of the KT successions at different sites of Stevns Klint implies that the material was accumulated on a highly irregular seaflor. Indeed, the sedimentary features of III/IV are more consistent with deposition from several mass-flow events.[1–3,5,18,38,58–61] This is indicated by the abundant presence of (poorly sorted) sand/silt grains,[1] reworked late Maastrichtian fossils and chalks, and rounded grains of terrigenous quartz in IIIB.[11,25,59,61] According to Christensen *et al.*[1] the sand/silt grain size distribution indicates that detrital material was deposited during the accumulation of IIIB. Moreover, the sizes of chalk clasts and sand/silt grains indicate transportation over a relatively short distance.

The most plausible scenario is that IIIB smectite (already enriched with Ni and Ir) was eroded from an original nearby oxic (marine or terristrial) site (a topographic high) onto the FK site (a topographic low). (This must also be true, to some extent, for IIIA/IV smectite). This interpretation is in accordance with the second alternative of Drits *et al.*[16] Thus, the present results/rationalization endorse our earlier contention that IIIB smectite is, probably, detrital in origin.[6,15] As pointed out earlier, the KT succession close to Rødvig is also enriched with Ni but contains no kerogen. It is possible that smectite IIIB was redeposited from this or a similar nearby marine site to FK. Simultaneously with the emplacement of IIIB smectite, terrigenous humics (enriched with Cu^{2+}-porphyrins/Ir) were laterally transported from the nearby oxic soil to FK. This resulted in the formation of IIIB within the FK succession.

There is also support for the detrial model of IIIB smectite in the few non-bioturbated KT sequences: El Kef (Tunisia), Caravaca and Agosta (Spain). Previous studies have shown that these boundary successions are also characterized by deposition of a detrital clay (mainly smectite) layer on top of a mm thin red layer similar to IIIA. This smectite is inherited from the erosion of soils of the nearby areas and/or are derived from an alteration of volcanoclastic rocks.[62] Detrital smectites in marine sedimentary rocks, especially those from the late Cretaceous (*e.g.* the IIIB smectite), originated mainly from the weathering of terristrial soils/rocks.[63] These smectites are the most ubiquitous clay minerals encountered in ancient carbonaceous sedimentary rocks of marine origin (*e.g.* IIIB marl), commonly forming 50–80 % of the clay assemblage. Abundant volcanogenic smectite in ancient sedimentary rocks of marine origin usually reflects the close proximity of an exposed volcanic area. The composition of the smectites formed from similar volcanic materials can be quite uniform over fairly large areas (*e.g.* the KT deposits of the Danish basin).

It the scenario of redeposition is accepted as a reasonable working hypothesis, it follows that the lateral transport of IIIB smectite occurred a long time after the settling of the volcanic glasses on the seafloor of the original site as their diagenetic alteration into smectite should have lasted over a 10^5–10^6 y timescale.[64] Consequently, probably about 10^5–10^6 y elapsed between the settling of the volcanic glasses at the original site and the redeposition of IIIB smectite to FK. The formation of this smectite from the volcanic glasses could, therefore, have been completed before the KT boundary event at about the time of the Chicxulub impact.

Thus, the setting of the volcanic glasses at the original site and the redeposition IIIB smectite to the FK site probably represent two sedimentary events separated by a time interval long enough for the diagenetic transformation of these glasses into smectite.

The smectite content of FK sharply increaases, reaching its maximum in IIIA and then gradually declining through IIIB and IV. As pointed out before, the underlying late Maastrichtian (I) and overlying early Danian (V/VI) layers contain smectite which is indistinguishable from IIIB smectite but in smaller amounts. This implies that the influx of clays into the FK deposition basin probably began at some time during the late Maastrichtian and persisted during the early Danian, but at a lower level. This is compatible with a suggestion of Schmitz[4] that the smectite within the FK succession represents a detritus swept into the seawater at Stevns Klint during the major seawater regressive events of the late Cretaceous.

Several studies have suggested that the beds of the impact glasses in Haiti were probably produced by the Chicxulub impact, thus about $3x10^5$ y prior to the KT boundary (Keller *et al.*[65] and references therein). If IIIA contains the impact spherule glasses similar to those from Haiti, in the sense of Balauz *et al.*,[11] the direct settling of these spherules on the nearshore seafloor of Stevns Klint must therefore have, predated the KT boundary by, say, ca. 3×10^5 y. In view of this it is suggested that the formation of IIIB smectite at its original site probably occurred during the latest Maastrichtian or the earliest Danian.

The redeposition of IIIB: the sea-level fall vs. *impact*

FK contains a very condensed and incomplete KT succession and belongs to the P0 foraminiferal zone of the earliest Danian.[66,67] As pointed out earlier, the biostratigraphic section at Stevns Klint indicates a sharp fall of the sea-level at the KT boundary.[68] It is possible that the redeposition of IIIB smectite from its original site to the present FK location took place during or shortly after the KT boundary, *i.e.*, during the sea-level lowstand at the KT boundary. Thus, FK may represent a short period of rapid erosion related to the KT impact during this sea-level fall. This fall could also have caused the simultaneous lateral transport of humics (enriched with Cu-porphyrins/Ir) from the nearby soil to the FK site. An alternative is that the impact at the KT boundary triggered some turbulence of the local terristrial/marine environments of Stevns Klint, instigating simultaneously the redeposition of IIIB smectite and the transport of these humics to the FK location.

In contrast to FK, Nye Kløv shows every indicattion of being temporarily a complete KT section characterized by a complete set of biostratigraphic zones.[66] This boundary is also marked by a few centimeters thick marl enriched with cheto-smectite. Recently, Premović[69] showed that this (biostratigraphically true) KT boundary could have been formed by the coeval redeposition of smectite and humics (enriched with Cu^{2+} porphyrins) from their original sites in the eastern part of the Danish Basin. Consequently, an erosion induced either by a sharp sea-level fall or an impact-induced turbulence could readily translocate these materials even to the Nye Kløv site. In general, while sediments (*e.g.* FK) are eroded in shallow areas during sea-level falls, the eroded sedimentary material should collect in adjacent deeper portions of the basins (*e.g.* Nye Kløv). If the second possibility is correct then the impact that created this turbulence was either a relatively small impact that occurred in the close vicinity of Stevns Klint or a distant, but large impact one. The fact that the KT boundary event is worldwide marked by an Ir anomaly (and with other extraterrestrial signals) supports the large impact.

Very recently, Keller *et al.*[65] presented evidence for multiple impacts during the KT transition. The first impact (with no Ir anomaly) occurred at Chicxulub in the late Maastrichtian (*ca*. 65.3 Ma). This impact coincided with major Deccan volcanism. The second impact event (with Ir anomaly) occurred at the KT boundary (65 Ma) and the third one in the early Danian about 100 ky after the KT boundary. It is also possible that the Ir anomaly in IIIB represents a second early Danian impact event.[65] Consequently, the anomalous Ir in IIIB is related to the second KT impact at the KT boundary. This would suggest that the source of IIIB smectite and the source of Ir and Ni in IIIB must be different. Thus, if the Ni in this clay arose from the impact fallout, as does its anomalous Ir, then it is likely that their incorporation into IIIB smectite occurred at the KT boundary. The same is true for the association of Ir, Cu, Cu^{2+}-porphyrins and soot with IIIB kerogen,[6] *i.e.*, with humics in the nearby soil of Stevns Klint.

CONCLUSIONS

1. The main carriers of Ni in the IIIB black marl are biogenic calcite and cheto-smectite.
2. Most of Ni within IIIB smectite ultimately came from a nearby oxic soil.
3. The impact-derived fallout on the elevated land around Stevns Klint was probably an important source of Ni.
4. Marine calcareous planktic biota could have been vulnerable to the abrupt injection of high amounst of Ni into the surface KT seawater of Stevns Klint.
5. The geochemistry of IIIB smectite and the associated Ni indicates that this clay is strictly detrital in character, having been redeposited from the nearby marine site of its formation to its present site.
6. Both the redeposition of smectite IIIB and the incorporation of Ni into IIIA/B smectite occurred before the early Danian, *i.e.*, before the KT boundary event.

Acknowledgement: Dr. Helle Schummel (the Højerup sample) and Tove Damholt (the Rødvig sample), to whom our thanks go, collected the FK samples at Stevns Klint used in this work. We thank also the staf of the Laboratoire de Minéralogie et Cristallographie de Paris (LMCP) and the Instituto de Ciencias de la Tierra (ICT), Caracas, without whose help this paper would not have appeared. We are also indebted to LMCP/ICT for the use of their laboratory/instrumental facilities.

Funding support from le Ministère Français de l'Education Nationale, de l'Enseignement Supèrieur et de la Recherche to P. I. P. for his stay at LMPC, Université Pierre et Marie Curie (Paris), is gratefully acknowledged. P. I. P. also acknowledges financial support, which was provided by the Programa Catedra y Consejo de Estudios de Postgrado, for his pleasurable/fruitful stay at ICT (Universidad Central de Venezuela, Caracas). The Ministry of Science and Technology of Serbia (project 142069) financially supported in part this work.

ИЗВОД

ГЕОХЕМИЈА Ni У КРЕДА-ТЕРЦИЈАР НАЛАЗИШТУ FISKELER (FISH CLAY) ИЗ STEVENS KLINT-а (ДАНСКА): CHETO-СМЕКТИТ ЦРНОГ ЛАПОРЦА

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Гранични слој креда-терцијара (KT) Fiskeler из Stevns Klint-a (Højerup налазиште), састоји се од танког црвеног глиненог слоја прекривеног танким црним лапорцем. Ова два слоја се већином састоје од cheto-типа смектита и биогеног калцита. Црни лапорац показује повећану концентрацију Ni (655 ppm) у смектитној фракцији. Уз то, и његова карбонатна фракција показује повећану концентрацију Ni (245 ppm). Сматра се да је ово повећање настало због наглог и брзог прилива велике количине Ni у морску воду касне креде Stevns Klint-a. Основни извор Ni и у карбонатној и у смектитној фракцији црног лапорца је, вероватно, материјал, настао KT астероидним ударом, сталожен у околном земљишту па испран (киселим) површинским водама. Геохемија Ni потврђује претпоставку да је смектит овог лапорца већином локалног (морског или копненог) порекла и да је вероватно поново сталожен после његовог формирања, са изворног места на његову садашњу локацију KT граничног слоја.

(Примљено 26. маја 2005)

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