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Cretaceous-Paleogene boundary (KPB) Fish Clay at Højerup (Stevns Klint, Denmark): Ni, Co, and Zn of the black marl

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ABSTRACT

The black marl of the Fish Clay at Højerup is mainly made up of biogenic calcite and cheto-Mg-smectite. We suggest that the formation of the smectite occurred during the latest Maastrichtian (or earlier) and that it represents a short period of rapid redeposition through coastal erosion occurring at the Cretaceous-Paleogene boundary (KPB) sea level lowstand. The smectite of the black marl shows enhanced concentrations of Ni, Co, and Zn. The predominant source of these metals was probably the impact-ejecta fallout deposited on the top of nearby soil which was leached by the impact-induced-acidic surface waters. Most of the content of Ni and Co in the smectite is derived from the chondritic component of the fallout, but the ultimate origin of Zn may have been the impact-target rocks. Incorporation of the metals into the smectite took place during the KPB but before its redeposition at the Fish Clay site. The biogenic calcite-rich fraction of the black marl also shows high concentrations of Ni, Co, and Zn. The ultimate source of the metals was also probably the impact-ejecta fallout on the nearby soil at Stevns Klint. Enrichments of Ni in the biogenic calcite-rich/smectite fractions of the black marl represent the sudden input of the metal into the seawater at the KPB.

KEYWORDS **Geochemistry. Cretaceous-Paleogene boundary. Fish Clay. Nickel. Cobalt. Zinc. Smectite.**

INTRODUCTION

The Fish Clay at Højerup (hereafter referred to as the Fish Clay) belongs to one of the classic KPB deposits at Stevns Klint (Fig. 1; Desor, 1847). Lithology of the Fish Clay, which is of earliest Danian age, was described by Christensen et al. (1973). The authors distinguished four distinctive layers within this boundary section: a 1-2 cm bottoms Maastrichtian grey marl (layer II), a 2-5 cm thick brown-to-black marl (layer III) and grey-to-black marl (layer IV) and the top light-grey marl (layer V), (Figs. 2A and 2B). Layers III and IV are here considered to comprise the main part of the KPB section. There is, however, no sharp boundary between layers III and IV, and it is difficult to distinguish the top of layer III and the base of layer IV. Layer V is overlain by the Danian Cerithium limestone (VI). Recent lithostratigraphic studies have indicated that transitional layer II should not be included in the Fish Clay members since it forms the very top of the latest Maastrichtian bryozoan chalk I (Surlyk et al., 2006). Lithological units of the Fish Clay appear to be remarkably persistent from Bøgeskov in the north to Rødvig in the south; a distance of about 14.5 km. Similar units can also be distinguished in other parts of the world (Schmitz, 1988).

Elliott (1993) subdivided layer III into a red layer IIIA overlain by black marl IIIB, (Figs. 2A and 2B). Layer IIIB (maximum ca. 2-4 cm) contains high Ir levels (Schmitz, 1988; Graup et al., 1992), soot (Wolbach et al., 1985), and kerogen enriched in Cu^{2+}-porphyrins (Premović et al., 2000). Layer IIIB also contains minor amounts of microcrystalline/macroscopic pyrite (FeS$_2$) and goethite derived from weathered/oxidized pyrite (Schmitz, 1985).

Álvarez et al. (1980) first reported an anomalously high Ir concentration (86.7 ppb) in combined layers III/IV; Kastner et al. (1984) explained this enhanced Ir by proposing a late Cretaceous asteroid impact on the Earth. Similar enrichments have been reported in several other prominent shallow-sea KPB sediments from all over the world (e.g., Gilmour and Anders, 1989). It has been also suggested that a late Cretaceous impactor was a (carbonaceous) C1 chondrite-type body (Kyte, 1998; Shukolyukov and Lugmair, 1998; Quitté et al., 2003). A multi-isotopic and trace element investigation by Frei and Frei (2002) of the Fish Clay suggested that platinium group of elements (Ir, Ru, Pt and Os) originated from global input of cosmogenic material into the ocean derived from a likely chondritic impactor. Very recently, Trinquier et al. (2006) have shown that Cr isotopic signature of layer IIIB exhibits an isotopic ratio that would represent mixing of a carbonaceous chondrite of CM2 type with terrestrial material.

The mineralogy of the Fish Clay is comparatively simple, with smectite and authigenic (mainly biogenic) calcite being the principal components. Clay mineralogy studies have indicated that the distinctive cheto Mg-smectite is the predominant clay mineral in the Fish Clay (Rampino and Reynolds, 1983; Kastner et al., 1984; Elliott et al., 1989; Elliott, 1993). Kastner et al. (1984) pointed out that the major element chemistry, mineralogy, and oxygen isotope analyses indicate that III/IV smectite is the alteration product of impact-derived glasses. Bauluz et al. (2000) provided further experimental evidence [scanning electron microscopy (SEM) and transmission electron microscopy (TEM)/analytical electron microscopy (AEM)] that supports this conclusion.

In contrast, Rampino and Reynolds (1983), Hansen et al. (1986), Elliott (1993), and Premović et al. (1993) presented evidence, based on the clay mineralogy and the geochemistry of major and trace elements, that the central part of the Fish Clay (layers III/IV) contains a pure smectite formed by the diagenetic alteration of volcanic ash. Recently, Drits et al. (2004) carried out chemical analysis, solid state nuclear magnetic resonance (NMR) spectroscopy and atomic force microscopy of the IIIB clay fraction. These authors reported that this fraction consists of two phases: a high-smectite phase (70%) composed of 95% smectite and 5% illite, and a low-smectite phase (30%) having 50% illite. According to Drits et al. (2004), these two phases are most likely formed from volcanic

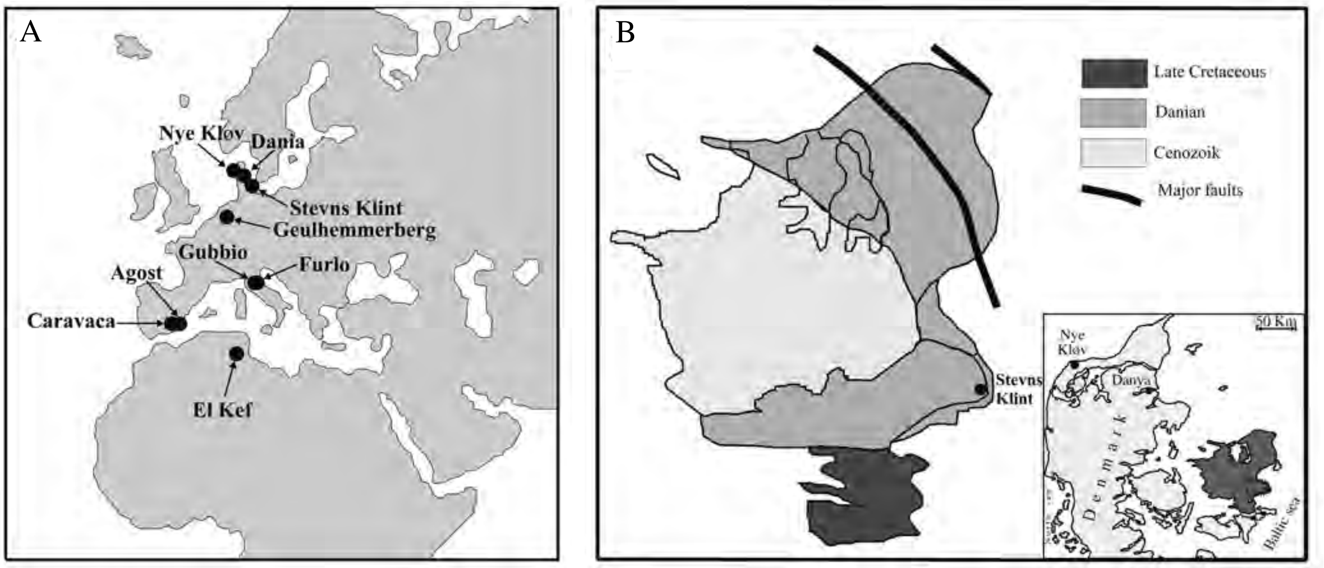


FIGURE 1 **A) Location map showing the KPB site at Stevns Klint in relation to some prominent KPB sites outside of Denmark. B) Simplified geological map of the eastern Denmark (based on Håkansson and Pedersen, 1992) with the location of accessible KPB sections at Nye Kløv and Dania.**

ash. The authors argued that a very small part, if any, of the smectite within the Fish Clay was derived from the impact-ejecta fallout (IEF) containing asteroid/crater target materials.

Apart from Ir, layer IIIB is also enriched in other trace metals including Ni, Co, and Zn (Christensen et al., 1973; Schmitz, 1985, 1988; Schmitz et al., 1988, 1992; Premović et al., 1993, 2000). To date, the question of the origin of the trace metals has not been resolved. Christensen et al. (1973) proposed that these metals concentrated due to an accumulation of mainly terrigenous materials with minor amounts of clay minerals of diagenetic origin. Kyte et al. (1985) analyzed layers IIIA/IIIB for trace metals (in particular siderophiles) and suggested that only layer IIIA (usually referred to as the "impact layer") should be used to estimate the primary IEF of the Álvarez et al. (1980) impact, as trace metals in higher layers arose mainly from the IEF on nearby soil being laterally transported by the surface waters to the sea. Schmitz (1988) proposed that the trace metal precipitation in the Fish Clay was induced by various redox-controlled processes in connection with the decomposition of abundant algal matter. He argued that the concentrated trace metals of layers IIIB/IV precipitated as sulfides from the seawater, though the authors also pointed out that the ultimate origin of some of these metals (e.g., Ir and Ni) may have been an Earth-impacting asteroid. Of note, some researchers (e.g., Bohor, 1990; Zhou et al., 1991; Schmitz, 1992; Evans et al., 1994) considered that anoxic conditions in the small interbiohermal troughs at Højerup may have concentrated trace metals.

Elliott et al. (1989) and Elliott (1993) showed that IIIB smectite is a possible carrier phase of trace metals, including Ni, Co, and Zn. These authors argued that the trace metals originated from the seawater already enriched in them and that the IEF was a source of their enrichments. In contrast, Premović et al. (1993) concluded that most of the trace metals (including Ni and Co) in the IIIB smectite are strictly detrital in character, i.e., having been incorporated into the smectite prior to being deposited at the Fish Clay site.

A very recent study of the trace metal geochemistry, including Ir, Ni, Co, and Zn, associated with the IIIB kerogen indicates that most of these trace metals were originally bound with the humics in oxic soil of the adjacent coastal areas in eastern Denmark (Premović et al., 2007). They concluded that Ir, Ni, Co, and Zn were most likely augmented by the IEF through the leaching by the impact-induced acidic surface waters. Premović et al. (2000, 2007) suggested that the humics were fluvially transferred onto the Fish Clay during the KPB transition.

In this study, Ni, Co, and Zn in the IIIB smectite were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). These metals were chosen primarily because of their distinctive (but relatively simple) geochemical activities and properties. In general, these metals show similar geochemical behaviors in sedimentary environments. Essentially, this paper is complementary to our previous studies (Premović et al., 1993, 2000, 2007) and discusses some geochemical aspects of Ni, Co, and Zn within the IIIB smectite that may be important in understanding of the geochemical/depositional processes that occurred during the sedimentation of the Fish Clay. An understanding of these processes that led to the enrichments of Ni, Co, and Zn within this clay would also shed light on the sequence of sedimentary episodes that led to this enhancement. Although important to the overall understanding of the KPB at Højerup, layer IIIA is not discussed here.

EXPERIMENTAL

Inductively Coupled Plasma-Optical Emission Spectrometry

Ni, Co, and Zn of the whole-rock sample of layer IIIB and its smectite and carbonate fractions were analyzed by

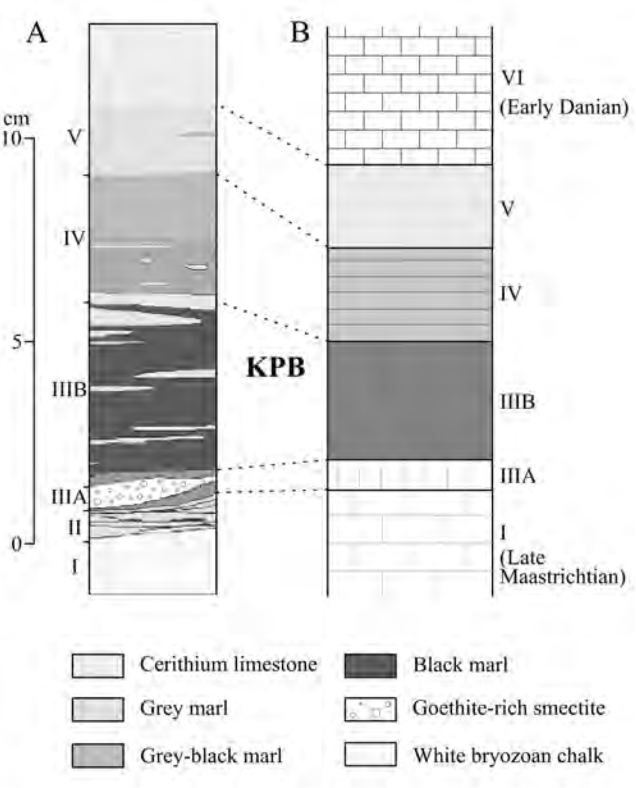


FIGURE 2 **A) Lithology of the Fish Clay (after Surlyk et al., 2006). B) With an oversimplified schematic illustration of the internal layering.**

ICP-OES. A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas. Total uncertainty (including accuracy error) of the analysis ranges from 5% to 20% for Ni, Co, and Zn.

Fourier Transform Infrared (FTIR) Spectrometry

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

Electron Spin Resonance (ESR)

ESR measurements were performed on the finely ground powder of a smectite sample of layer IIIB which was transferred to an ESR quartz tube (4 mm o.d., 3 mm i.d.). Spectra were recorded at 120 K and 4.3 K on a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz. The quantitative measurement of the absolute concentration of paramagnetic Fe^{3+} in IIIB smectite of layer IIIB was carried out by the method described by Balan et al. (2000).

X-Ray Diffraction (XRD)

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

Scanning Electron Microscopy (SEM)/Energy Dispersive Spectrometry (EDS)

All SEM/EDS works were carried out using a Jeol JSM-35 electron microscope equipped with a Tracor TN-2000 energy dispersive X-ray spectrometer. Operating conditions for energy-dispersive analyses were at 25 keV accelerating voltage, 0.1 µA beam current and a beam spot diameter of approximately 3 µm.

Analysis and fractionation

Sample of layer IIIB was collected from an outcrop 200 m south of the old church of Højerup. The rock sample was dried in an oven and carefully ground in an agate mortar. The fractionation procedure was similar to that used by Saxby (1976) and Premović et al. (1993). The major steps in preparing the four fractions are:

1. Powdered rock (48 g) was treated (12 h) with acetate buffer: acetic acid (1 M)/sodium acetate (1 M) solution at pH 5.0 (Lyle et al., 1984) to remove most of the carbonates. The soluble material constitutes the carbonate fraction. Carbonate removal was checked by XRD/FTIR analyses. The soluble portion constitutes the carbonate fraction analyzed for Ni, Co, and Zn by ICP-OES. It appears that the treatment of the sediments with the acetic acid/sodium acetate is the most efficient and simple method for removing carbonates with a minimal damage to the clays present (Cook, 1991).

2. The insoluble residue from (1) was demineralized further by repeated treatment with cold HCl (6 M, room temperature, 12 h). Soluble part constitutes the cold HCl fraction analyzed for Ni, Co, and Zn by ICP-OES. This treatment may remove some minor amounts of Ni, Co, and Zn from smectite.

3. The insoluble residue from (2) was demineralized with boiling HCl (6 M, 80ºC, 12h). The acid-soluble part constitutes the smectite fraction, i.e., the smectite concentrate. Smectite removal was checked by XRD/FTIR analyses. The smectite fraction was analyzed for Ni, Co, and Zn by ICP-OES.

4. The residue constitutes the acid-insoluble fraction. This fraction was also analyzed for Ni, Co, and Zn by ICP-OES.

SEM/EDS analyses on the demineralized fractions also confirm that dissolution was essentially complete and that a good selectivity was obtained at each stage of demineralization.

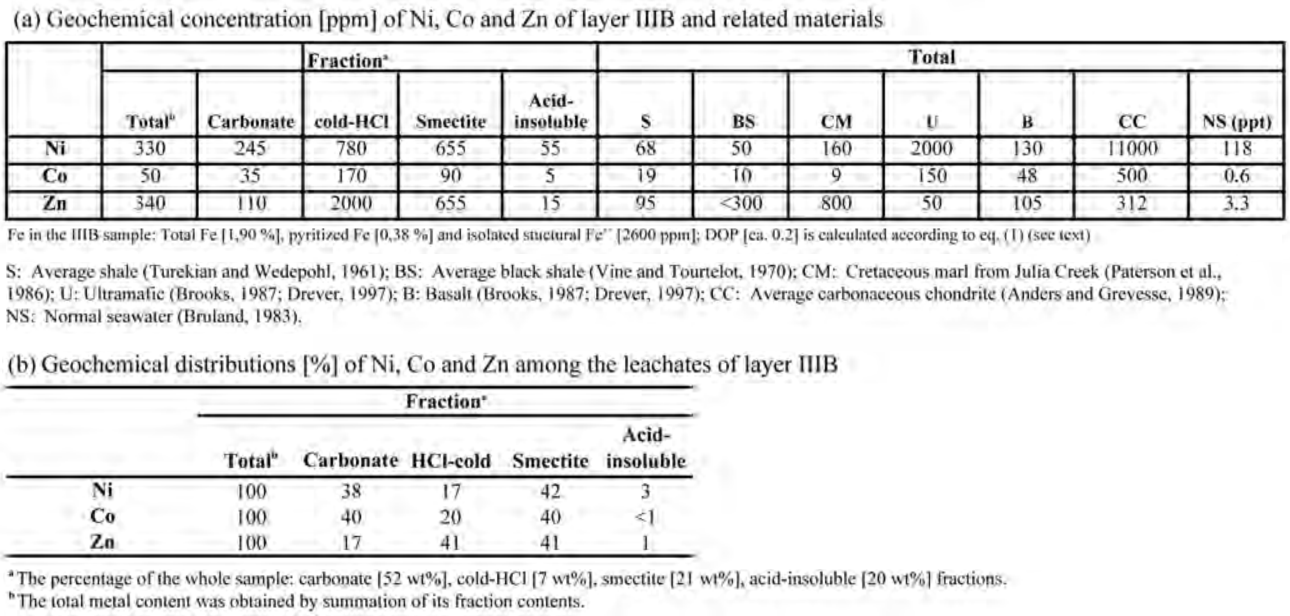
The sequence of leaching steps used was adopted so that Ni, Co, and Zn associated with various parts of would be removed in the following order: (step 1) exchangeable metals, and a fraction of the carbonate-hosted metals; (step 2) the metals primarily associated with metal oxides (including Fe oxides), with carbonates and with monosulfides; and, (step 3) the metals predominantly associated with IIIB smectite.

The analytical results for Ni, Co, and Zn in the carbonate, cold-HCl, smectite and acid-insoluble fractions of layer IIIB are given in Table 1a; the geochemical distribution of Ni, Co, and Zn among these four fractions are presented in Table 1b. XRD mineralogical analyses of these fractions are given in Table 2.

Chemical analysis

Chemical analyses of layer IIIB (whole-rock and its fractions after the each leaching steps) were performed using the most precise gravimetric/titrimetric methods providing the relative standard deviation (RSD) less than 5%. The results are given in Table 3.

TABLE 1 **Geochemical data.**



(a) Geochemical concentration [ppm] of Ni, Co and Zn of layer IIIB and related materials

	Fraction[a]					Total							
	Total[b]	Carbonate	cold-HCl	Smectite	Acid-insoluble	S	BS	CM	U	B	CC	NS (ppt)
Ni	330	245	780	655	55	68	50	160	2000	130	11000	118
Co	50	35	170	90	5	19	10	9	150	48	500	0.6
Zn	340	110	2000	655	15	95	<300	800	50	105	312	3.3

Fe in the IIIB sample: Total Fe [1,90 %], pyritized Fe [0,38 %] and isolated stuctural Fe'' [2600 ppm]; DOP [ca. 0.2] is calculated according to eq. (1) (see text)

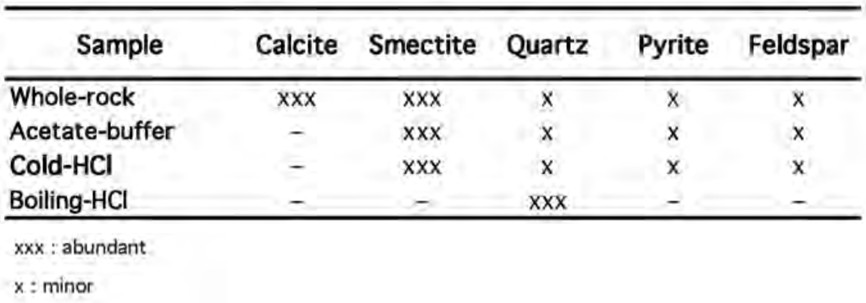
S: Average shale (Turekian and Wedepohl, 1961); BS: Average black shale (Vine and Tourtelot, 1970); CM: Cretaceous marl from Julia Creek (Paterson et al., 1986); U: Ultramafic (Brooks, 1987; Drever, 1997); B: Basalt (Brooks, 1987; Drever, 1997); CC: Average carbonaceous chondrite (Anders and Grevesse, 1989); NS: Normal seawater (Bruland, 1983).

(b) Geochemical distributions [%] of Ni, Co and Zn among the leachates of layer IIIB

	Fraction[a]				
	Total[b]	Carbonate	HCl-cold	Smectite	Acid-insoluble
Ni	100	38	17	42	3
Co	100	40	20	40	<1
Zn	100	17	41	41	1

[a] The percentage of the whole sample: carbonate [52 wt%], cold-HCl [7 wt%], smectite [21 wt%], acid-insoluble [20 wt%] fractions.
[b] The total metal content was obtained by summation of its fraction contents.

TABLE 2 **Mineralogical composition of layer IIIB and its demineralised fractions.**



Sample	Calcite	Smectite	Quartz	Pyrite	Feldspar
Whole-rock	xxx	xxx	x	x	x
Acetate-buffer	–	xxx	x	x	x
Cold-HCl	–	xxx	x	x	x
Boiling-HCl	–	–	xxx	–	–

xxx : abundant

x : minor

TABLE 3 **Amount [wt%] of respective oxides remaining after different leaching steps of layer IIIB.**

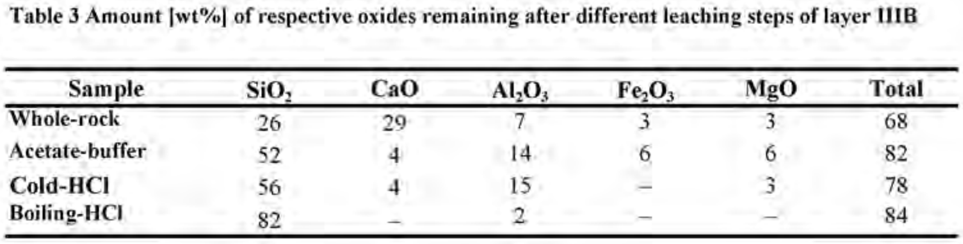


Table 3 Amount [wt%] of respective oxides remaining after different leaching steps of layer IIIB

Sample	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Total
Whole-rock	26	29	7	3	3	68
Acetate-buffer	52	4	14	6	6	82
Cold-HCl	56	4	15	–	3	78
Boiling-HCl	82	–	2	–	–	84

Reactive Fe extraction

This procedure was undertaken by mixing 0.5 g of layer IIIB with 15 mL of a 1 M HCl solution at room temperature for 24 h (Huerta-Díaz and Morse, 1990; Leventhal and Taylor, 1990; Brumbaugh and Arms, 1996). The result is presented in Table 1a.

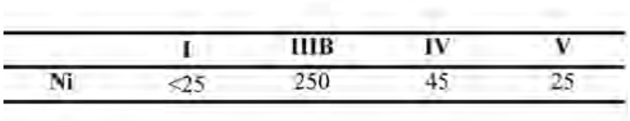
RESULTS

Trace Ni, Co, and Zn in IIIB leachates

Table 1a shows that the concentrations of Ni and Co in layer IIIB are considerably higher than those found in average shales, in average carboniferous shales or even in the well known marine-shallow anoxic shales enriched in trace metals such as the Cretaceous marl (similar to layer IIIB) from Julia Creek (Australia). The concentration of Zn is similar to those of average black shales. The corresponding references are listed in Table 1a.

SEM/EDS analyses show that the carbonate fractions of layers I, II, IIIB, IV, and V contain high levels of calcite almost completely derived from calcareous microbiota. The acetate buffer step removes about 52% of the entire sample of layer IIIB (Table 1b) as a result of the total dissolution of carbonates (Table 2); this fraction contains 38%, 40% and 17% of total Ni, Co, and Zn, respectively (Table 1b). In addition, we analyzed by ICP-OES the Ni content in the carbonate fractions of layers I, IIIB, IV, and V. The results are shown in Table 4 and Fig. 3.

TABLE 4 **Geochemical concentration [ppm] of Ni in the carbonate fraction of layers I, IIIB, IV and V.**



	I	IIIB	IV	V
Ni	<25	250	45	25

We analyzed Ni in the carbonate fraction of a KPB sediment, equivalent to the Fish Clay, from another marine site (about 4 km from the Højerup location) at the southernmost part of Stevns Klint close to Rødvig. We previously analyzed Ni in the carbonate fractions of the KPB deposits at Nye Kløv (ca. 320 km away from Stevns Klint) and Dania (ca. 220 km away) in western Denmark (Premović et al., 1993). For comparison, we determined Ni in the carbonate fractions of the marine-shallow KPB deposits outside Denmark at Caravaca/Agost (Spain), El Kef (Tunisia), Geulhemmerberg (Holland) and Furlo/Gubbio (Italy, Fig. 1). These analytical results are presented in Table 5. Analytical results for Ni in the carbonate fractions (mainly biogenic calcite) of the KPB sections at Rødvig, Nye Kløv/Dania, Agost, El Kef, Geulhemmberg and Furlo/Gubbio show normal background levels of Ni (5-15 ppm) (Table 5). The carbonate fraction of the Caravaca sample is only slightly enriched (70 ppm) in Ni. Table 1a shows that the carbonate fraction (mainly biogenic calcite) of marl from Julia Creek also contains elevated concentrations of Ni, Co, and Zn (Patterson et al., 1986).

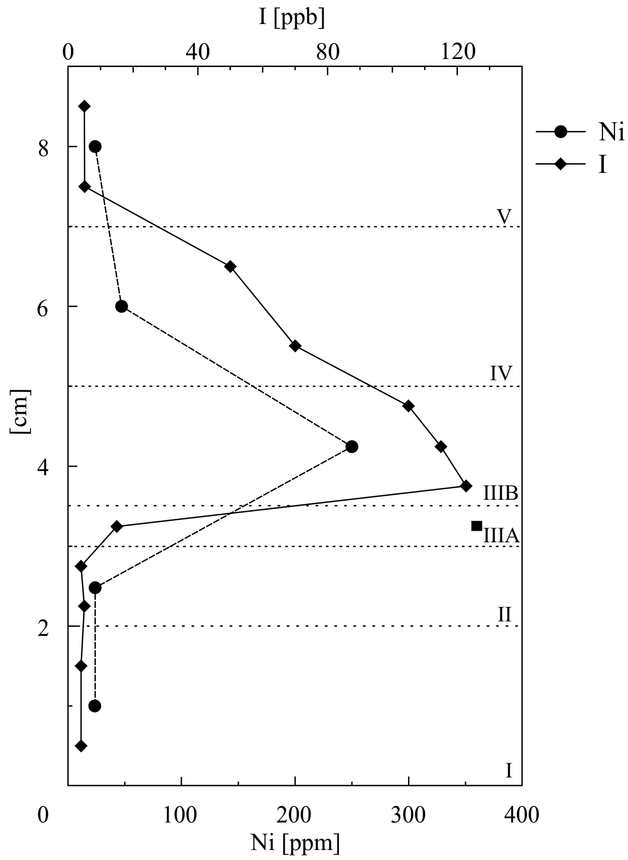
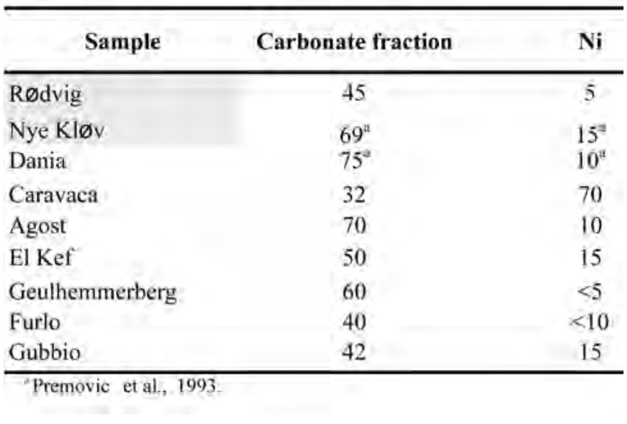


FIGURE 3 **Concentration profiles of Ir (ppb) in the carbonate-free fractions (after Schmitz, 1988) and Ni (ppm) in the carbonate fractions of layers I-V.**

The cold-HCl leaching removes most of metal oxides/sulfides (7 wt% of the whole sample) (Table 1b); this leachate confines 17%, 20% and 41% of Ni, Co, and Zn, respectively (Table 1b). These metals were almost certainly precipitated as oxides/sulfides and/or incorporated into goethite; their minor parts were likely sorbed on the smectite particles (Schmitz, 1985; Schmitz et al., 1988; Premović et al., 1993). What is noteworthy regarding Zn is that its oxide and sulfide are completely soluble in 6 M cold HCl. This may explain the high abundance of Zn (2000 ppm) associated with the cold-HCl leachate (Table 1a).

TABLE 5 **The carbonate fractions and their Ni content (ppm) of the KPB sediments at the Danish Basin and various localities (see Fig. 1 for their locations).**



Sample	Carbonate fraction	Ni
Rødvig	45	5
Nye Kløv	69[a]	15[a]
Dania	75[a]	10[a]
Caravaca	32	70
Agost	70	10
El Kef	50	15
Geulhemmerberg	60	<5
Furlo	40	<10
Gubbio	42	15

[a] Premovic et al., 1993.

The boiling-HCl step dissolves 21% of the entire sample (Table 1b), most of the IIIB smectite (Table 2). About 40% of the total Ni, Co, and Zn is located in this clay (Table 1b). The ICP-OES analysis reveals that the IIIB smectite contains approximately 2.2% Fe; most of this metal is probably present as Fe-oxides adhering to the surfaces of the smectite particles. ESR measurements show that the concentration of isolated structural Fe^{3+} in the IIIB smectite is about 2600 ppm (Table 1a).

Table 1b shows that ≤5% of total Ni, Co, and Zn reside in the acid-insoluble fraction; they are mainly present in the IIIB kerogen (Premović et al., 2007). Thus, only small amounts of Ni, Co, and Zn released from kerogen during the leaching phases contribute to their concentrations in each particular fraction.

Degree of pyritization (DOP)

DOP is defined as the molecular concentration ratio of pyrite Fe (insoluble in cold 1 M HCl) to the total reducible/reactive Fe (soluble in cold 1 M HCl) in the sediment;

$$\mathrm{DOP} = \text{Pyrite Fe}/[\text{Pyrite Fe} + \text{Fe (soluble in 1 M cold HCl)}] \quad (1)$$

The DOP value of layer IIIB (ca. 0.2; Table 1a) is very low and comparable with (wholly or partly) oxygenated depositional environments (Roychoudhury et al., 2003). Note that HCl extraction usually overestimates the amount of pyritized Fe. This is supported by stereomicroscopy/SEM/EDS analyses conducted on the sample of layer IIIB before grinding/leaching, which indicates that pyrite is a very minor constituent.

DISCUSSION

Redeposition/formation of IIIB smectite

According to Christensen et al. (1973), the chalk clast/sand/silt grain sizes indicates that detrital material was mainly deposited during accumulation of layer III and that they were transported over a relatively short distance. The contents of the chalk clasts/sand/silt (Christensen et al., 1973) and detrital kerogen (Premović et al., 2000) in the Fish Clay sharply increases, reaching its maximum in layer III, and then declines upwards more gradually.

Hansen et al. (1992) estimated that the duration of the deposition of the Fish Clay was around 40 kyr. Premović et al. (2000) inferred that layer III was deposited within an interval of about 40 yrs. Wendler and Willems (2002) considered that this layer represents the first decades or centuries of deposition following the KPB impact event and that layer IV characterize a relatively fast but continuous low energy sedimentation. Layers V/VI were deposited more slowly (for 5-15 kyr) (Kastner et al., 1984; Kyte et al., 1985).

The smectite content of the Fish Clay sharply increases reaching its maximum in layer IIIA and then declining gradually through layers IIIB and upwards; the underlying latest Maastrichtian chalk and overlying layers V/VI contain smectite that is indistinguishable from IIIB smectite but in lower amounts (Elliott, 1993). This author also reported that the cheto-Mg-smectite is widespread, probably diachronously, throughout the Danish Basin. Drits et al. (2004) suggested that if the smectite phase throughout layers I-VI is formed from volcanic glass, then this phase arose from the same source and was deposited episodically during a long interval beginning with the late Cretaceous and ending with the early Danian.

Biostratigraphic (Surlyk, 1997; Håkannson and Thomsen, 1999; Wendler and Willems, 2002) and stable isotope (Hart et al., 2004) studies of the microfossil-rich successions of eastern Denmark have indicated a sharp sea level fall at the KPB. As a result of this sea level regression taking place at the KPB, large areas of earlier marine shallow sediments in the Danish Basin were exposed to coastal erosion. We suggest that the IIIB smectite possibly represents a short period of rapid redeposition through coastal erosion occurring during the KPB sea level lowstand. This is in agreement with an earlier suggestion that smectite within layers IIIB/IV represents detritus swept into seawater at Stevns Klint during the seawater regressive events (Schmitz, 1988). Small interbiohermal troughs at Højerup, formed by a series of mounds in the latest Maastrichtian chalks (Hart et al., 2004), provided a suitable platform for accumulation of the IIIB smectite (Premović et al., 2007). Consequently, it appears that its emplacement probably took place between the latest Maastrichtian and earliest Danian, i.e., at the KPB.

Trinquier et al. (2006) estimated that layer IIIB contains about 3.8-6.8% chondritic material. Assuming that the IEF is a mixture containing approximately equal amounts of the impactor and impactite materials (Melosh, 1989), a simple calculation shows that layer IIIB contains about 7.6-13.6% of material directly derived from the IEF. The remainder (ca. 86.4-92.4%) is mainly carbonates and detrital smectite of local provenance.

Low-temperature geochemical processes (diagenesis) of smectite formation from volcanic glasses in common sedimentary environments typically results over 10^5-10^6 yr (Millot, 1970); the same is probably true for the impact-derived glasses, as these theoretically should be similar to usual volcanic glasses. Thus, the formation of the IIIB smectite at the original site almost certainly must have predated the redeposition by at least 10^5-10^6 yr, i.e., this took place during the latest Maastrichtian (66-65 Ma ago) or earlier.

Distribution of cosmogenic Ir (micronuggets?)

Geochemical studies (Tredoux et al., 1989; Graup et al., 1992) have shown that the Ir profile (on a whole rock basis) across the Fish Clay column is characterized by a sharp and anomalous maximum in the base of layer III with a gradual upwards decrease (tailing-off) from its maximum. There is now a little doubt that the anomalous Ir in the Fish Clay originated from an extraterrestrial source.

Schmitz (1988) reported Instrumental Neutron Activation Analysis (INAA) data for Ir in the non-carbonate fractions (smectite concentrate) of the Fish Clay. Based on his results, the concentration profile of Ir across the Fish Clay is presented in Fig. 3. The concentrations of Ir are relatively low in layer IIIA and start to increase sharply, reaching its maximum in layer IIIB. Upwards from this layer, Ir concentrations decrease gradually in layers IV and V, having much lower levels.

Very recently, Premović et al. (2007) reported that the Ir spike coincides precisely with a humic kerogen spike in layer IIIB in time and is equally intense. They suggested that Ir (as "micronuggets"?) associated with humics was probably fluvially transported from the soil on adjacent land and was redeposited in a shallow marine setting at Højerup.

Besides the strongest Ir anomaly in the Fish Clay, Rocchia et al. (1984, 1987) reported that the anomalous concentrations of Ir extend into the underlying latest Maastrichtian bryozoan-rich chalk (layers I/II) and overlying earliest Danian limestone (layer VI), over a thickness of about one meter. Consequently, it appears that terrestrial influx of cosmogenic Ir (as "micronuggets"?) to the seawater at Højerup lasted for, at least, 10 kyr. The origin and nature of the overall vertical distribution of Ir at this location require detailed sedimentological, mineralogical, and geochemical analyses.

Incorporation of Ni, Co, and Zn into IIIB smectite

Three mineralization steps remove almost all Ni, Co, and Zn in IIIB. This portion of the metals forms a so-called reactive fraction and usually refers to the soluble fraction readily available for participitation in various geochemical reactions under normal sedimentary conditions (Huerta-Diaz and Morse, 1990). The incorporation of Ni, Co, and Zn in IIIB smectite could occur either during diagenesis or after it by sorption. Layer IIIB was deposited under strong anoxic conditions, or soon after deposition the conditions became strongly anoxic, which prevailed 65 Ma after its formation (Premović et al., 1993, 2007). This may readily explain its very small ratio of "pyritized" to "oxidized" Fe, i.e., the low DOP value (ca. 0.2), Table 1a.

Table 1b shows that the considerable amounts of total Ni (42%), Co (40%) and Zn (41%) reside in the IIIB smectite. Of course, these fractions of Ni, Co, and Zn were soluble and available for incorporation into this clay; the same is true for internal (structurally isolated) Fe^{3+} ions. Under prolonged anoxic conditions, most of the Ni and Co would be preferentially incorporated into pyrite and Zn would precipitate as insoluble solid sulfides (Huerta-Diaz and Morse, 1990), i.e., the concentrations of their ions in sedimentary solution at equilibrium would be very small. A similar argument applies to internal Fe^{3+} ions, which are unstable with respect of pyrite in anoxic environments (Garrels and Christ, 1965). We may therefore conclude that the enriched association of Ni, Co, Zn, and internal Fe^{3+} with IIIB smectite reflects normal oxic conditions but not strong anoxic conditions. Layer IIIB contains benthic foraminifera (Schmitz et al., 1992) that could not live in an anoxic environment. Consequently, it appears that the IIIB smectite and benthic foraminifera were transferred from the same well-oxygenated submarine site at the same time.

In ordinary (oxygenated) seawater with a pH of about 8, predominant Ni^{2+}, Co^{2+}, and Zn^{2+} ions would be almost solely present. Smectites possess a large specific surface area ($6\text{-}8 \times 10^5$ m^2 kg^{-1}), and a relatively high structural charge (up to 1200 meq kg^{-1}) imparting them with important sorptive properties. It is, therefore, quite possible that metal ions like Ni^{2+}, Co^{2+}, and Zn^{2+} reside in the exchangeable Mg^{2+} interlayer sites of the IIIB cheto-smectite. These positions are excellent coordinating sites that would be very rapidly filled by these metal ions after diagenesis under oxic conditions. Indeed, Rybicka et al. (1995) investigated the adsorption/desorption behavior of Ni and Zn on cheto Mg-smectite (Arizona, USA) under oxygenated conditions, and reported that the adsorbed amounts of Ni and Zn were relatively high (about 40-50%). Therefore, IIIB smectite was open to exchange with the oxygenated seawater that was already enriched in Ni and Zn for tens or even hundreds of thousands of years after formation. This must also be true for Co, which shows a similar geochemical behavior as Ni in sedimentary environments.

Ni, Co, and Zn in smectite: origin

The relatively high concentrations of Ni, Co, and Zn in IIIB smectite (Table 1a) argue against a local volcanic source, such as chemical weathering of volcanic basaltic rocks. The average abundances of Ni, Co, and Zn in basalts (and other volcanic rocks) would necessitate rather drastic concentrations of these metals during weathering; only ultramafic rocks contain significant Ni and Co concentrations but very low Zn (Table 1a).

The distribution patterns of Ni, Co, and Zn in the most prominent shallow-marine KPB deposits throughout the world, including those at Fish Clay, are very similar. These metals are also well correlated with one another and, also, with cosmogenic Ir (e.g., Gilmour and Anders, 1989). It also appears that they have their maxima at about the same stratigraphical level (e.g., Strong et al., 1987; Schmitz, 1988) and that the clays are their dominant carrier phase. This is a consequence of the fact that most Ni, Co, and Zn in the sediments in question have a common global source, a similar geochemical behavior, and they were probably widespread in the near shore marine environments worldwide at the KPB.

The average concentrations of Ni, Co and Zn in C1 chondrites are summarized in Table 1a. The concentrations of Ni and Co within the IIIB smectite is much lower than the average Ni and Co in C1 chondrites; Zn is approximately twice as high as its average content in C1 chondrite. Gilmour and Anders (1989) suggested a chondritic origin of anomalous Ni and Co in the most prominent KPB deposits including the Fish Clay; they also considered the excess of Zn to be crustal in origin. Strong et al. (1987) also concluded that Ni in one of the above mentioned deposits at Flaxbourne River (New Zealand) is mainly of meteoritic origin, but they argued that Co and Zn are probably terrestrial, and primarily crustal.

Erikson and Dickson (1987) carried out mass balance calculations of airborne trace metal influxes to the sea associated with the 10 km diameter chondritic impactor of Álvarez et al. (1980). These calculations showed that the seawater would be enriched by factors of 660 (Ni), 6300 (Co) and 6800 (Zn); assuming that 100% of these metals are dissolved, their concentrations would be ca. 78 ppb (Ni), 3.8 ppb (Co), and 2.2 ppb (Zn). These concentrations are much higher than the average concentrations in normal seawater (Table 1a). However, if the estimate of rapid deposition of layer IIIB (Premović et al., 2000; Wendler and Willems, 2002) is correct, then it seems unlikely that the primary IEF was an adequate source for these metals in the IIIB smectite.

Another, but more abundant, source for Ni, Co, and Zn could be the IEF on nearby soil at Stevns Klint. Indeed, Davenport et al. (1990) estimated that the soil surface after the 10 km-in diameter chondritic impactor of Álvarez et al. (1980) would be covered with the IEF, having Ni between 133-1330 ppm that is much greater than the contemporary average level of Ni (16 ppm) in soil; the IEF would also have Co between 7-70 ppm. It is reasonable, therefore, to assume that a substantial part of the Ni and Co within the IIIB smectite ultimately came from a C1 chondritic component associated with the IEF covering nearby coastal soil.

As pointed out before, an interesting finding in the IIIB smectite is profound Zn enrichment that is higher than the average Zn in C1 chondrite (Table 1a). Simple metal supply calculations suggest that the Zn content of the air fall derived from the 10 km chondritic impactor would be between 4-38 ppm; however, this Zn abundance in the top layers of soil would also necessitate its rather excessive concentration during chemical weathering. Therefore, it seems reasonable to assume that Zn in the IIIB smectite was probably largely provided by the target rocks.

Thus, the soil at Stevns Klint during the KPB may have differed in composition from ordinary soil, perhaps, because of the excess of Ni, Co, and Zn. Consequently, we assume that most of the Ni, Co, and Zn in the IEF on top of this soil was leached by the surface waters acidified by the impact-induced acid rains, as previously hypothesized by Premović et al. (2000, 2007). We offer the following model (Fig. 4) as a first approximation of the processes involved. Most of the IIIB smectite was probably formed from volcanic ash at the original submarine site (a topographic high) before the latest Maastrichtian (Fig. 4A). After immediate settling on nearby soil, the airborne IEF was leached of Ni, Co and Zn by the impact-induced acidic surface waters. These metals were then taken up by smectite before redeposition (Fig. 4B). Smectite enriched in Ni, Co, and Zn were redeposited from the original site to the Fish Clay site, which was a topographic low (Fig. 4C). The redeposition resulted from coastal erosion generated by the sea level fall at the KPB.

Ni, Co, and Zn in biogenic calcite-rich fraction

In an earlier report, Premović et al. (1993) suggested that a substantial proportion of the carbonate minerals in layers III/IV are not authigenic, i.e., they were transported from a well-oxygenated marine site into the Fish Clay. The transfer occurred simultaneously with the redeposition of the smectite. The fact that the bulk of the calcareous microfossils in layers III/IV are reworked/redeposited late Cretaceous/early Paleogene species supports this proposal.

The biogenic calcite-rich fraction of layer IIIB contains relatively high concentrations of Ni, Co, and Zn

(Table 1a). Using similar arguments as above, it is also reasonable to suggest that a major fraction of the Ni, Co, and Zn in the biogenic calcite-rich fraction of layer IIIB is also ultimately due to chemical weathering by the impact-induced acidic surface waters of the IEF on nearby soil. The remarkably regular stratigraphic distributions of Ni in the carbonate fractions of layers I-V (Fig. 3) cannot be due to incidental diagenetic effects, but suggests a significant dependence on an external input. Table 4 and Fig. 3 reveal that the late Maastrichtian biogenic chalk contains background levels of Ni (<25 ppm); a more than 10-fold increase of Ni in the biogenic calcite-rich fraction of layer

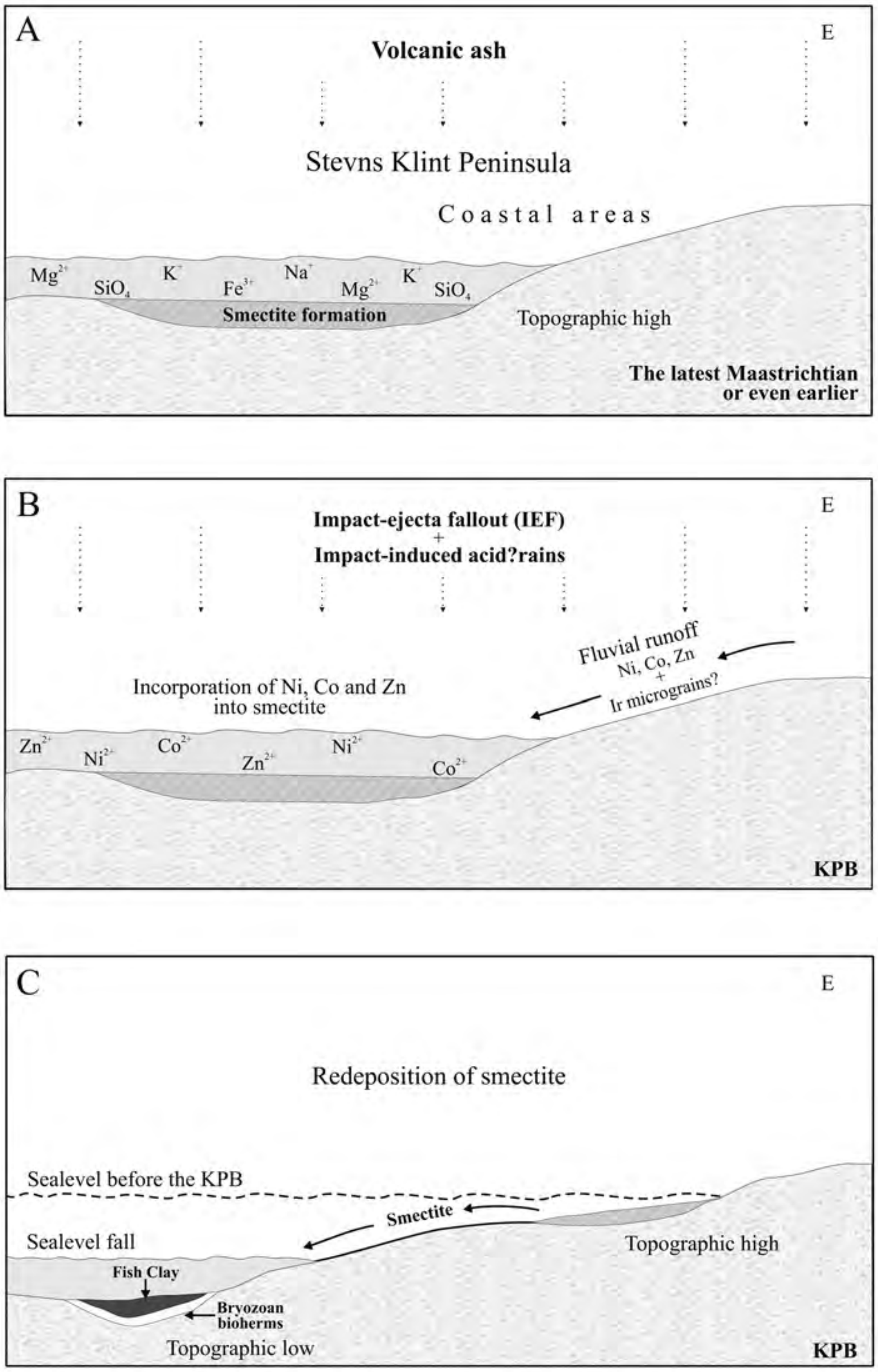


FIGURE 4 | **Proposed model for geochemical relations between the IEF, Ir, Ni, Co, and Zn and the Fish Clay.**

IIIB is consistent with a single rapid introduction of Ni into the seawater at Stevns Klint. The background value of Ni in the same fraction of layer V suggests that after deposition of layers III/IV the influx of Ni into this seawater probably ceased to exist at all.

Layer IIIB contains fewer well-preserved calcareous dinoflagellates (Wendler and Willems, 2002) and poorly preserved calcareous planktic and benthic foraminifera (Schmitz et al., 1992). If most of the Ni, Co, and Zn reside in biogenic calcite, then their calcite shells are most likely their hosts; they could be introduced into the shell structure through inorganically controlled incorporation of their 2+ ions. These ions may substitute for the Ca^{2+} ions in the calcite matrix since they have similar ionic radius and the same charge as Ca^{2+}. Of course, the incorporation could take place only in the ordinary oxygenated seawater already highly enriched in the Ni^{2+}, Co^{2+}, and Zn^{2+} ions. An alternative possibility is that these ions actually occur, instead of in biogenic calcite, in their non-biogenic carbonate minerals that were redeposited simultaneously with the smectite.

We propose that most of the Ni, Co, and Zn in the carbonate fraction of layer IIIB represents biological Ni, Co, and Zn, i.e., the direct biochemical incorporation of the divalent cations into the shells of calcareous microbiota. SEM/EDS analyses, however, show that the KPB sediments near Rødvig, at Nye Kløv and Dania, also contain relatively high levels of biogenic calcite (45-75% of total sample; Table 5). As pointed out earlier, the biogenic calcite-rich fractions contain no enhanced Ni concentrations, contrary to expectations. If the biochemical uptake of calcareous microbiota led to the formation of the shells enriched in Ni in layer IIIB, then it would be strange that the corresponding biogenic materials in the Danish Basin, especially at nearby Rødvig, show no evidence of this activity.

The use of 1 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. Considerable amounts of specifically sorbed Ni, Co, and Zn are solubilized by this buffer solution at pH 5.0 (Hickey and Kitrick, 1984). A previous geochemical study, however, suggested that contamination of this source represents a serious problem only if the trace metal concentrations in the acetate buffer leachate are less than 10 ppm (Boyle et al., 1981). Thus, it is highly unlikely that high Ni in the carbonate fraction of layer IIIB comes from the sorbed Ni on the smectite.

Interestingly, the Ni/Co ratio in the smectite/carbonate fractions of layer IIIB has almost the same value of about 7. This is consistent with the assumption that the same IEF is likely to have been responsible for their Ni and Co enrichments. For comparison, the Ni/Co ratio for ordinary seawater and C1 chondrite is about 197 and 22, respectively (these two values are calculated using the data given in Table 1a). According to Strong et al. (1987), the low Ni/Co ratio (1.1) in the KPB deposit at Flaxbourne River (New Zealand) shows that the Co is largely of terrestrial origin.

The analytical results of the carbonate fractions (containing mainly biogenic calcite) of the prominent KPB sediments outside Denmark at Caravaca/Agosta, El Kef, Geulhemmberg, and Furlo/Gubbio also indicate that these contain normal background levels of Ni (<30 ppm), except the Caravaca sample (70 ppm) (Table 5). It is reasonable to assume that local variables (e.g., physicochemical conditions of sedimentation, sedimentation rate, etc.) may have affected the process of concentrating Ni in their calcite fractions, or may just reflect very local circumstances. It is noteworthy that the oceanic KPB sediment at Blake Nose also shows a profound enrichment of Ni (up to 165 ppm) associated with the biogenic calcite-rich fraction (Premović et al., 2004).

CONCLUSIONS

1. It appears that the cheto Mg-smectite of black marl of the Fish Clay at Højerup (layer IIIB) is detrital in character, most likely having been redeposited from the oxygenated submarine site.
2. The formation of IIIB smectite was most likely completed before the Cretaceous-Paleogene boundary (KPB), probably during the latest Maastrichtian (66-65 Ma ago) or earlier.
3. Geochemical considerations indicate that the impact-ejecta fallout (IEF) from nearby soil was the primary source for the relatively high Ni, Co, and Zn in the IIIB smectite. We suggest that most of Ni and Co was most likely derived from the chondritic component of the IEF, but Zn was mainly derived from the target rocks. Incorporation of Ni, Co, and Zn into the IIIB smectite took place before redeposition at the KPB.
4. The biogenic-calcite rich fraction of layer IIIB is also enriched in trace Ni, Co, and Zn. The ultimate source of these metals was also probably the IEF in nearby soil.
5. Abundant Ni, Co and Zn in the biogenic calcite-rich/smectite fractions of layer IIIB indicate a sudden and high influx of these metals into the seawater at Stevns Klint at the KPB. These metals were probably leached from the IEF by impact-induced acidic waters.

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REFERENCES

Álvarez, L.W., Álvarez, W., Asaro, F., Michel, H.V., 1980. Extraterrestrial cause for the Cretaceous-Tertiary extinction. Science, 208, 1095-1108.

Anders, E., Grevesse, N., 1989. Abundances of the elements: Meteoritic and solar. Geochimica et Cosmochimica Acta, 53, 197-214.

Balan, E., Allard, T., Boizot, B., Morin, G., Muller, J.-P., 2000. Quantitative measurement of paramagnetic Fe^{3+} in kaolinite. Clays and Clay Minerals, 48(4), 439-445.

Bauluz, B., Peacor, D.R., Elliott, W.C., 2000. Coexisting altered glass and Fe-Ni oxides at the Cretaceous-Tertiary boundary, Stevns Klint (Denmark): Direct evidence of meteorite impact. Earth and Planetary Science Letters, 182, 127-136.

Bohor, B.F., 1990. Origin of microlayering in worldwide distributed Ir-rich marine Cretaceous/Tertiary boundary clays (Comment). Geology, 18, 88-89.

Boyle, E.A., Huested, S.S., Jones, S.P., 1981. On the distribution of copper, nickel and cadmium in the surface waters of the North Atlantic and North Pacific Oceans. Journal of Geophysical Research, 86, 8048-8066.

Brooks, R.R., 1987. Serpentine and its vegetation: A multidisciplinary approach. Portland, Dioscorides Press.

Bruland, K.W., 1983. Trace elements in seawater. In: Riley, J.P., Chester, R. (eds.). Chemical Oceanography. London, Academic Press, 157-220.

Brumbaugh, W.G., Arms, J.W., 1996. Quality control considerations for the determination of acid-volatile sulfide and simultaneously extracted metals in sediments. Environmental Toxicology and Chemistry, 15(3), 282-285.

Christensen, L., Fregerslev, S., Simonsen, A., Thiede, J., 1973. Sedimentology and depositional environment of Lower Danian Fish Clay from Stevns Klint, Denmark. Bulletin of the Geological Society of Denmark, 22, 193-212.

Cook, R.J., 1991. A comparison of method for the extraction of smectites from calcareous rocks by acid dissolution techniques. Clay Minerals, 27, 73-80.

Davenport, S.A., Wdowiak, T.J., Jones, D.D., Wdowiak, P., 1990. Chondritic metal toxicity as a seed stock kill mechanism in impact-caused mass extinctions. Geological Society of America Special Paper, 247, 71-76.

Desor, E., 1847. Sur le terrain danien, nouvel étage de la craie. Bulletin de la Société Géologique de France, 4(2), 179-182.

Drever, J.I., 1997. The geochemistry of natural waters: Surface and groundwater environments, 3rd ed, Upper Saddle River, Prentice-Hall Inc.

Drits, V.A., Lindgreen, H., Sakharov, B.A., Jakobsen, H.J., Zviagina, B.B., 2004. The detailed structure and origin of clay minerals at the Cretaceous/Tertiary boundary, Stevns Klint (Denmark). Clay Minerals, 39, 367-390.

Elliott, W.C., 1993. Origin of the Mg-smectite at the Cretaceous/Tertiary (K/T) boundary at Stevns Klint, Denmark. Clays and Clay Minerals, 41, 442-452.

Elliott, W.C., Aronson, Jr. J.L., Millard, H.T., Gierlowski-Kordesch, E., 1989. The origin of the clay minerals at the Cretaceous/Tertiary boundary in Denmark. Geological Society of America Bulletin, 101, 702-710.

Erikson, D.E., Dickson, M., 1987. Global trace-element biogeochemistry at the K/T boundary: Oceanic and biotic response to a hypothetical meteorite impact. Geology, 15, 1014-1017.

Evans, N.J., Gregoire, D.C., Goodfellow, W.D., McInnes, B.I., Miles, N., Veizer, J., 1994. The Cretaceous-Tertiary fireball layer, ejecta layer and coal seam: Platinum group element content and mineralogy of size fractions. Meteoritics, 29, 223-235.

Frei, R., Frei, K.M., 2002. A multi-isotopic and trace element investigation of the Cretaceous–Tertiary boundary layer at Stevns Klint, Denmark - inferences for the origin and nature of siderophile and lithophile element geochemical anomalies. Earth and Planetary Science Letters, 203, 691–708.

Garrels, R.M., Christ, C.L., 1965. Solutions, minerals, and equilibria. New York, Harper and Row, 450 pp.

Gilmour, I., Anders, E., 1989. Cretaceous-Tertiary boundary event. Evidence for a short time scale. Geochimica et Cosmochimica Acta, 53, 503-511.

Graup, G., Palme, H., Spettle, B., 1992. Trace element stratification in the Stevns Klint Cretaceous/Tertiary boundary layers. Lunar Planetary Science, 23, 445-446.

Håkansson, E., Pedersen, S.A.S., 1992. Geologisk kort over den Danske Undergrund (Geological map of Denmark). Varv, Copenhagen.

Håkansson, E., Thomsen, E., 1999. Benthic extinction and recovery patterns at the K/T boundary in shallow water carbonates, Denmark. Palaeogeography, Palaeoclimatology, Palaeoecology, 154(1-2), 67-85.

Hansen, H.J., Rasmussen, K.L., Gwozdz, R., Walaszczyk, K.I., 1992. Time structure of a mass extinction: The Cretaceous-Tertiary boundary (Abstract). Meteoritics, 27, 230.

Hansen, H.J., Gwozdz, R., Hansen, J.M., Bromley, R.G., Rasmussen, K.L., 1986. The diachronous C/T plankton extinction in the Danish basin. Earth Sciences, 8, 382-384.

Hart, M.B., Fiest, S.E., Price, G.D., Leng, M.J., 2004. Reappraisal of the K-T boundary succession at Stevns Klint, Denmark. Journal of the Geological Society, 161, 885-892.

Hickey, M.G., Kitrick, A., 1984. Chemical partioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. Journal of Environmental Quality, 13, 372-376.

Huerta-Diaz, M.A., Morse, J.W., 1990. A quantitative method for determination of trace metal concentrations in sedimentary pyrite. Marine Chemistry, 29, 109-114.

Kastner, M., Asaro, F., Michel, H.V., Alvarez, W., Alvarez, L.W., 1984. The precursor of the Cretaceous/Tertiary boundary clays at Stevns Klint and DSDP Hole 46. Science, 226, 137-143.

Kyte, F.T., 1998. A meteorite from the Cretaceous/Tertiary boundary. Nature, 396, 237-239.

Kyte, F.T., Smit, J., Wasson, J.T., 1985. Siderophile interelement variations in the Cretaceous-Tertiary boundary sediments from Caravaca, Spain. Earth and Planetary Science Letters, 73, 183-195.

Leventhal, J., Taylor, C., 1990. Comparison of methods to determine degree of pyritisation. Geochimica et Cosmochimica Acta, 54, 2621-2625.

Lyle, M., Heath, R.G., Robins, J.M., 1984. Transport and release of transition elements during early diagenesis: sequential leaching of sediments from Manop Sites M. and H. part I. pH 5 acetic acid leach. Geochimica et Cosmochimica Acta, 48, 1705-1715.

Melosh, H.J., 1989. Impact cratering: A geologic process. New York, Oxford University Press.

Millot, G., 1970. Geology of clays. Berlin, Springer-Verlag, 429 pp.

Patterson, J.H., Ramsden, A.R., Dale, L.S., Fardy, J.J., 1986. Geochemistry and mineralogical residences of trace elements in oil shales from Julia Creek, Queensland, Australia. Chemical Geology, 55, 1-16.

Premović, P.I., Todorović, B.Ž., Pavlović, M.S., 2007. Cretaceous-Tertiary boundary Fish Clay at Højerup (Stevns Klint, Denmark): Trace metals. Bulletin de la Société Géologique de France, 178(5), 411-421.

Premović, P.I., Pavlović, N.Z., Pavlović, M.S., Nikolić, N.D., 1993. Physicochemical conditions of sedimentation of the Fish Clay from Stevns Klint, Denmark and its nature: Vanadium and other supportive evidence. Geochimica et Cosmochimica Acta, 57, 1433-1446.

Premović, P.I., Nikolić, N.D., Pavlović, M.S., Panov, K.I., 2004. Geochemistry of the Cretaceous-Tertiary transition boundary at Blake Nose (N. W. Atlantic): Cosmogenic Ni. Journal of Serbian Chemical Society, 69(3), 205-223.

Premović, P.I., Nikolić, N.D., Tonsa, I.R., Pavlović, M.S., Premović, M.P., Dulanović, D.T., 2000. Copper and copper(II) porphyrins of the Cretaceous-Tertiary boundary at Stevns Klint (Denmark). Earth and Planetary Science Letters, 177, 105-118.

Quitté, G., Robin, E., Capmas, F., Levasseur, S., Rocchia, R., Birck, J.L., Allègre, C.J., 2003. Carbonaceous or ordinary chondrite as the impactor at the K/T boundary? Clues from Os, W and Cr isotopes. Lunar and Planetary Science, 34, 1615 pdf.

Rampino, M.R., Reynolds, R.C., 1983. Clay mineralogy of the Cretaceous-Tertiary boundary clay. Science, 219, 495-498.

Rocchia, R., Renard, M., Boclet, D., Bonte, P., 1984. Essai d'évaluation de la transition C-T par l'évolution de l'anomalie en iridium; implications dans la recherche de la cause de la crise biologique. Bulletin de la Société Géologique de France, 26, 1193-1202.

Rocchia, R., Boclet, D., Bonte, P., Devinaeau, J., Jehanno, C., Renard, M., 1987. Comparaison des distributions de l`iridium observées à la limite Crétacé-Tertiaire dans divers sites européens. Memoirs de Societe Geologie de France, 150, 95-103.

Roychoudhury, A.N., Kostka, J.E., Van Cappellan, P., 2003. Pyritization: a palaeoenvironmental and redox proxy reevaluated. Estuarine, Coastral and Shelf Science, 57, 1-11.

Rybicka, E.H., Calmano, W., Breeger, A., 1995. Heavy metals/desorption on competing clay minerals; an experimental study. Applied Clay Science, 9, 369-381.

Saxby, J.D., 1976. Chemical separation and characterization of kerogen from oil shale. In: Yen, T.F., Chilingarian, G.V. (eds.). Oil Shale. Amsterdam, Elsevier, 103-128.

Schmitz, B., 1985. Metal precipitation in the Cretaceous-Tertiary boundary clay at Stevns Klint, Denmark. Geochimica et Cosmochimica Acta, 49, 2361-2370.

Schmitz, B., 1988. Origin of microlayering in worldwide distributed Ir-rich marine Cretaceous/Tertiary boundary clays. Geology, 16, 1068-1072.

Schmitz, B., 1992. Chalcophile elements and Ir in continental Cretaceous-Tertiary boundary clays from the western interior of the USA. Geochimica et Cosmochimica Acta, 56, 1695-1703.

Schmitz, B., Andersson, P., Dahl, J., 1988. Iridium, sulfur isotopes and rare earth elements in the Cretaceous-Tertiary boundary layer at Stevns Klint, Denmark. Geochimica et Cosmochimica Acta, 52, 229-236.

Schmitz, B., Keller, G., Stenvall, O., 1992. Stable isotope changes across the Cretaceous-Tertiary boundary at Stevns Klint, Denmark: arguments for long-term oceanic instability before and after bolide impact event. Palaeogeography, Palaeoclimatology, Palaeoecology, 96, 233-260.

Shukolyukov, A., Lugmair, G.W., 1998. Isotopic evidence for the Cretaceous-Tertiary impactor and its type. Science, 282, 927-930.

Strong, C.P., Brooks, R.R., Wilson, S.M., Reeves, R.D., Orth, C.J., Mao, X.-Y., Quintana, L.R., Anders, E., 1987. A new Cretaceous-Tertiary boundary site at Flaxbourne River, New Zealand: Biostratigraphy and geochemistry. Geochimica et Cosmochimica Acta, 51, 2769-2777.

Surlyk, F., 1997. A cool-water carbonate ramp with bryozoan mounds: Late Cretaceous-Danian of the Danish Basin. In: James, N.P., Clarke, J.A.D. (eds.). Cool-Water Carbonates. Tulsa, SEPM Special Publications, 293-307.

Surlyk, F., Damholt, T., Bjerager, M., 2006. Stevns Klint, Denmark: Uppermost Maastrichtian chalk, Cretaceous–Tertiary boundary, and lower Danian bryozoan mound complex. Bulletin of the Geological Society of Denmark, 54, 1–48.

Tredoux, M., De Wit, M.J., Hart, R.J., Lindsay, N.M., Verhagen, B., Sellschop, J.P.F., 1989. Chemostratigraphy across the Cretaceous-Tertiary boundary and a critical assessment of the iridium anomaly. Journal of Geology, 97, 585-605.

Trinquier, A., Birck, J.-L., Alle'gre, C.J., 2006. The nature of the KT impactor. A ^{54}Cr reappraisal. Earth and Planetary Science Letters, 241, 780–788.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some minor units of the Earth`s crust. Geological Society of America Bulletin, 72, 175-190.

Vine, J.D., Tourtelot, E.B., 1970. Geochemistry of black shale deposits - a summary report. Economic Geology, 65, 253-272.

Wendler, J., Willems, H., 2002. The distribution pattern of calcareous dinoflagellate cysts at the Cretaceous/Tertiary boundary (Fish Clay, Stevns Klint, Denmark)-Implications for our understanding of species selective extinction. In: Koeberl, C., Macleod, K.G. (eds.). Catastrophic Events and Mass Extinctions: Impact and Beyond. Geological Society of America Special Paper, 356, 265-277.

Wolbach, W.S., Lewis, R.S., Anders, E., 1985. Cretaceous extinctions: evidence for wildfires and search for meteoritic material. Science, 230, 167-170.

Zhou, L., Kyte, F.T., Bohor, B.F., 1991. Cretaceous/Tertiary boundary of DSDP Site 596, South Pacific. Geology, 19, 694–697.

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