The conspicuous redish “impact” layer of the Fish Clay at Højerup (Stevns Klint, Denmark)

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Key words. – Cretaceous-Paleogene boundary, Fish Clay, impact layer, smectite, microspherules, nano-size glasses.

Abstract. – The marine shallow Cretaceous–Paleogene boundary (KPB) section at Højerup-Fish Clay consists of a very thin redish smectite-rich carbonate-poor (“impact”) layer overlain by a thick black marl. Similar redish layers are found in the shallow seawater KPB sections at Agost in Spain and El Kef. The deposition of the “impact” layers at Højerup, Agost and El Kef occurred simultaneously and for several decades to a century at most. Smectites of the “impact” layers of the KPB sections at these three locations are probably detrital and redeposited from adjacent coastal areas. Conceivably, a small part of these smectites is authigenic and derived from the nano-size glasses. The microspherules and nano-size glasses of the “impact” layer at Højerup are likely reworked and redeposited at or near the KPB simultaneously with smectite.

La couche "d'impact" rouge notable de la Fish Clay à Højerup (Stevns Klint, le Danemark)

Mots clés. - Frontière Crétacé-Paléogène, Fish Clay, la couche “d'impact”, smectite, micropetites spheres, verres de nano-taille.

Résumé. – La section Crétacé-Paléogène marine de la frontière (KPB) a Højerup -Fish Clay se compose couche rouge carbonate-pauvre smectite-riche (“impact”) recouverte par une marne sombre épaisse. Des couches semblables de rouge sont trouvées dans les sections peu profondes de l'eau de mer KPB à Agost en Espagne et El Kef en Tunisie. Le dépôt du “impact” pose chez Højerup, Agost et El Kef se sont produits simultanément et pendant plusieurs décennies à un siecle au plus. Smectites des couches de “ impact” des sections de KPB à ces trois endroits probablement détritiques et redeposited des secteurs côtiers adjacents. Peut-ętre, une petite partie de ces smectites est authigène et dérivée des verres de nano-taille. Les micropetites sphères et les verres de nano-taille de la couche de “ impact” chez Højerup sont probablement retravaillés et redéposés simultanément avec smectite à ou près du KPB.

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INTRODUCTION

There seems a wide consensus among researchers that anomalous Ir (and other siderophile metals) in the marine shallow KPB sections worldwide is a result of an Earth impacting event at the late Cretaceous period. It has been suggested that the KPB impactor was a carbonaceous chondrite-type body [Shukolyukov and Lugmair, 1998]. The use of helium-3 as a constant-flux proxy of sedimentation rate implies deposition of the KPB sections occurred in about 10 kyr [Mukhopadhyay *et al.*, 2001].

In most shallow-seawater KPB sections, the boundary clay is easily identified based on one or more of the following: (1) a lithology break from the latest Maastrichtian chalk abundant in calcareous microfossils to a thin layer of clay-rich deposit (boundary clay) extremely poor in calcareous microfossils; (2) a distinct redish 2 to 3-mm goethite-rich layer (known as the "impact layer" a term coined by B. F. Bohor and G. A. Izett, the “fireball layer” by A. R Hildebrand and W. V. Boynton and the “ejecta layer” by J. Smit) at the base of the boundary clay; and, (3) anomalously high Ir values generally concentrated in the “impact” layer. The redish “impact” layers are present in all complete and continuous KPB sections worldwide [Smit, 1999]; this layer is generally consider marking the KPB. In the earliest and most popular scenario of the KPB impact event, the “impact” layer of the KPB sections worldwide was created by thousands of cubic kilometers of the impact ejecta dispersed globally and deposited quite quickly for less than a year [Wolbach *et al.*, 1988]. Accordingly, ejecta fallout originated from an impact plume of a vaporized impactor and impactite material ejected into the stratosphere.

Fish Clay (of earliest Danian [Surlyk *et al.*, 2006]) near village of Højerup (hereafter referred as the Fish Clay) is a classic KPB section at Stevns Klint (eastern

Denmark) (figs. 1a/b). The lithology of the Fish Clay has been described by Christensen *et al.* [1973] and Surlyk *et al.* [2006] (fig. 2a). The authors distinguished three distinctive layers within this boundary section: the 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-d). Layers III and IV are here considered to constitute the main part of the KPB section at Højerup. Similar internal layering has been observed in the other shallow-sea KPB deposits worldwide [Romein and Smit, 1981; Schmitz, 1988]. Elliott [1993] subdivided layer III into the redish "impact" layer IIIA overlain by the black marl layer IIIB (figs. 2b-d). Layer IIIA is underlain with a Maastrichtian bryozoan-rich chalk (I/II) and unit V is overlain by the Danian Cerithium limestone (VI). According to Wendler and Willems [2002], layers IIIA/IIIB represent a fast, continuous sedimentation under decreasing energy.

The aim of this paper to review/synthesize/reinterpret some of the available data and observations obtained from the studies of the "impact" layer IIIA. We will also briefly reconsider the data and observations acquired from the studies of the "impact" layers within the prominent KPB sections at Agost and El Kef (fig. 1a). The KPB sections at Agost and El Kef are among the most continuous and complete marine records known across the KPB. In addition, the base of the El Kef boundary section has been officially designated as the boundary global stratotype section and point (GSSP) for the KPB [Cowie *et al.*, 1989].

Layers IIIA and IIIB

Layer IIIA is a thin 2-4 mm layer (fig. 2d shows the thickness of layer IIIA) which is mainly made up from smectite (figs. 3a-d). This layer bears many similarities to the record at the marine-shallow KPB sections except, that Ir is enriched in the base of the overlying smectite-rich marl IIIB not in the underlying “impact” layer IIIA [Schmitz, 1988]. Well-preserved goethite-rich microspherules in the smectite matrix (fig. 3a) are relatively abundant in layer IIIA; some of them having irregular shape possibly from fragmentation (figs. 3a/b). Only a few FeS_2-rich microspherules are found in this layer [Hansen *et al.*, 1986]. Layer IIIA also contains altered nano-size Si-rich glasses and nano-size goethite grains [Bauluz *et al.*, 2000; Wdowiak *et al.*, 2001] enriched in Ni and Zn [Bauluz *et al.*, 2000]. Bauluz *et al.* [2000] interpreted the goethite nano-grains as altered meteorite fragments, which were formed when impact glasses was transformed to smectite. However, meteoritic Ni-rich spinels are not found in layer IIIA or layer IIIB. Disseminated gypsum ($CaSO_4$) and/or anhydrite ($CaSO_4 \times 2H_2O$) (fig. 3b) is relatively common. A very few shocked quartz grains are also identified, about 2-3 of every thousand of quartz grains are shocked [Bohor *et al.*, 1985; Miura *et al.*, 1992; Schmitz, 1992]. However, it is still not unambiguous is their number really anomalous relative to background contents. Most of non-shocked quartz grains are terrigenous in origin. The base of layer IIIA is in sharp contact with layer II.

Layer IIIB is the smectitic/illititic black marl [Drits *et al.*, 2004] containing anomalous Ir [Schmitz, 1988], soot [Wolbach *et al.*, 1985] with the adsorbed the airborne polycyclic aromatic hydrocarbons [Venkatesan and Dahl, 1989] and humic kerogen enriched in Cu^{2+}-porphyrins [Premović *et al.*, 2000]. Layer IIIB contains also microspherules (mainly enriched in FeS_2) but they are much less abundant than in IIIA [Schmitz, 1985]. The base of IIIB (sublayer IIIBp), enriched in macroscopic FeS_2 concretions [Schmitz, 1985] and framboids (fig. 3c), makes easy to distinguish the top of IIIA and the base of IIIB (figs. 2b/c). Layer IIIB contains also biogenic calcite of the late Maastrichtian/early Danian age probably reworked/redeposited.

Graup *et al.* [1992] performed a high resolution microstratigraphy of layer IIIA on the mm scale and actually they recognized four sublayers: a basal “hard clay” IIIA1 which contains the smaller (ca. 100 μm in diameter) goethitic spherules, immediately above is a “soft” yellow clay IIIA2 covered by a gray clay IIIA3 abundant with larger spherules (between about 125-800 μm in diameter) (fig. 2c). These larger spherules enriched in goethite or partly in FeS_2 are deeply incorporated into the smectite matrix [Schmitz, 1985; Graup *et al.*, 1992].

Like at Højerup, at Agost and El Kef the biogenic calcite ooze of the latest Maastrichtian is also sharply capped by the 2-3 mm-thick smectite-rich “impact” layer [Schmitz, 1988] that passes upward into smectite-rich marl. Previous sedimentary studies have shown that the Fish Clay [Bromley, 1979] and KPB sections at Agost and El Kef [Ortega-Huertas *et al.*, 2002] are deposited in marine near-coastal areas; depths of their deposition are presented in fig. 4. The presence of humic kerogen in IIIB and its absence in the KPB sections at Agost and El Kef highlights a specific local sedimentary and geochemical environment at Højerup.

The conspicuous redish “impact” layer is also found in other continuous and complete shallow-seawater KPB sections in Italy (e.g., at Gubbio/Petriccio), Tunisia (at Elles/Aïn Settara), in Spain (at Caravaca), in France (at Bidart), in Egypt (at Wadi Nukhul) and in New Zealand (at Woodside Creek and Flaxbourne River). The global occurrence of the thin ca. 2-3 mm-thick “impact” layers consistent with a general notion that their formation was probably simultaneous and it is linked to a single abrupt and brief event on a global scale at the KPB such as the asteroidal impact.

Deposition interval of layer IIIA

All previous studies of the Fish Clay have assumed that layer IIIA is associated with a KPB impact at Chicxulub [see, for example, Bauluz *et al.*, 2000]. Wendler and Willems [2002] proposed that layers IIIA/IIIB represent the first decades or centuries following the KPB impact event; Premović *et al.* [2000] suggested that layer IIIB was deposited for about 40 yr or even much less. The problem is, however, that during the deposition of layer IIIA sedimentation have probably been extremely condensed by the dissolution of carbonates (mainly biogenic calcite), and a significant time may have elapsed between the beginning and end of the deposition of layer IIIA [Schmitz *et al.*, 1992]. Kasting *et al.* [1986] estimated that the carbonate dissolution in the Fish Clay was brief and lasted approximately 20 yr.

The top (3-4 cm) of the Maastrichtian bryozoan ooze chalk (layer II) shows abundant evidence of post-depositional dissolution [Ekdale and Bromley, 1984; Smit and van Kempen, 1986; Schmitz *et al.,* 1992; Rasmussen *et al.,* 2005; Surlyk *et al.,* 2006]. Schmitz *et al.* [1992] suggested that this dissolution may have taken place in the seawater and on the seafloor shortly before deposition of layer IIIA. Smit [1999] consider that most of the dissolution of layer II has diagenetic character created by leaching of sulfuric acid produced by oxidation of the abundant FeS_2 concretions/framboids in the sublayer IIIBp (fig. 2c).

The thickness of layer IIIA (2-4 mm) which would imply the duration of about 10-35 yr of its deposition, using the sedimentation rate (10-20 cm per 1000 yr) of Bromley [1979]. However, the overall sedimentation rate of Bromley [1979] is determined of over several meters of the underlying Maastrichtian bryozoan chalk and may not be quite appropriate to a smaller scale of layer IIIA. A minimum sedimentation rate could probably be 1-2 cm per 1000 yr, implying that a maximum duration of several hundreds of years for the deposition of layer IIIA. If the deposition of layer IIIA occurred for 1000 yr, to keep layer IIIA at its observed thickness of about 2-4 mm, the accumulation rate must be implausible low, say about 1-4 % of the deposition rate of the underlying Maastrichtian bryozoan chalk (layers I/II). Besides, the deposition on a millennial time scale would highly reduce the already small amount of impact markers in layer IIIA by the dilution as a result of the continuous influx of detrital smectite (see next section).

Hansen *et al.* [1992] estimated that duration of the deposition of the Fish Clay was around 40 kyr. Mukhopadhyay *et al.* [2001] estimated that the deposition interval of 50-60 cm- thick KPB section at El Kef is about 11.3 kyr. Robin *et al.* [1991] proposed on the base of the stratigraphic distribution of the Ni-rich spinels in the “impact” layer at El Kef that its deposition time did not exceed an upper limit of 100 yr. This suggestion is strengthened by helium-3 measurements which indicate this limit is of about 60 yr [Mukhopadhyay *et al.*, 2001]. Considering that the “impact” layers at Højerup, Agost and El Kef are of similar thickness it seems reasonable to suggest that their deposition occurred for several decades up to a century; the same is probably true for the other “impact” layers worldwide.

Detrital smectite

The clay mineralogy studies indicate that the distinctive cheto-Mg-smectite is the predominant clay mineral in layers IIIA/IIIB [Elliott, 1993; Bauluz *et al.*, 2000]. Most researchers [e.g., Christensen *et al.*, 1973; Rampino and Reynolds, 1983; Hansen *et al.*, 1988; Elliott, 1993; Premović *et al.*, 1993] consider the clay mineralogy and geochemistry indicate that smectite of layer IIIB is detrital and of local derivation formed by the diagenetic alteration of volcanic ash. In contrast, Kastner *et al.* [1984]

concluded that the major element geochemistry, mineralogy and oxygen isotope analyses indicate that smectite of combined layers III and IV is formed authigenically by alteration of the impact-derived glasses. They also found that this smectite differs from the smectite in the latest Maastrichtian layers I/II and earliest Danian layer VI. Recent electron microscopic studies carried out by Bauluz *et al.* [2000] have revealed that smectite of layers IIIA/IIIB contain the distinctive mineralogical/geochemical signatures linked directly to the impact glasses.

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

Elliott [1993] reported that the cheto-Mg-smectite is widespread, probably diachronously, throughout the Danish Basin and was deposited as a result of a marine regression. He also proposed that the underlying latest Maastrichtian chalk and overlying layers V/VI contain smectite which is indistinguishable from IIIB smectite but in lower amounts. The smectite content of the Fish Clay sharply increases reaching its maximum in layer IIIA and then declines gradually through layers IIIB/IV [Elliott, 1993; Premović *et al.,* 2000]. Premović *et al.* [2007, 2008] suggested that smectite of layer IIIB probably represents a rapid submarine redeposition through coastal erosion due to the KPB sealevel lowstand. Small interbiohermal troughs at Højerup provided a suitable platform for the accumulation of smectite. These structures were formed by a series of bryozoan mounds in the latest Maastrichtian chalks [Surlyk, 1997; Hart *et al.*, 2004]. This implies that the influx of smectite into the Fish Clay began probably at some time during the latest Maastrichtian and persisted during the earliest Danian, but at a lower level.

If the hypothesis of the up-to-year formation of the "impact" layer IIIA from the ejecta fallout is valid, then most of its smectite would be derived from the impact glasses. As layer IIIA was most likely accumulated on a decennial scale, most of its smectite was also detrital and redeposited from submarine areas.

Drits *et al.* [2004] carried out chemical analysis, solid state NMR spectroscopy and atomic force microscopy of smectite/illite in layer IIIB. A simple calculation, based on their data, shows that IIIB layer contains ca. 81.5 % of smectite and 18.5 % of illite. Drits *et al.* [2004] concluded that these two clay minerals are probably formed from glassy volcanic ash and that a very small part, if any, of it was derived from the impact glasses. They also reasoned 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 time interval beginning with the late Cretaceous and ending with the early Danian.

Low-temperature geochemical process (early diagenesis) of the smectite formation from volcanic glasses in common sedimentary environments typically results from 10^5-10^6 of years [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 smectite almost certainly must have predated the deposition of layers IIIA/IIIB by at least 10^5-10^6 y. Therefore, we suggest that the formation of smectite at the original site probably took place during the latest Maastrichtian (66-65 Ma ago) or earlier.

Ortega-Huertas *et al.* [2002] on the basis mineralogical and chemical composition data proposed that the boundary smectites at Agost and El Kef are detrital. They reported that in these two sections there is no indication of changing sources and/or sedimentary and diagenetic processes from the latest Maastrichtian to earliest Danian; and, that there are no depositional changes in the smectite assemblage across these two sections. Two hypotheses are proposed to explain abundance of smectites in the KPB sections at Agost and El Kef. The first one is the alteration of volcanic rocks [Ortega-Huertas *et al.*, 1995] and the second one is that detrital smectites are inherited from the erosion of soils developed in surrounding areas. Ortega-Huertas *et al.* [2002] proposed that smectites of the "impact" layers at Agost and El Kef may be only partially related to impact glasses. This view is consistent with their apparent deposition on a decennial scale.

The well-oxygenated sedimentation conditions

Layer IIIB was deposited under strongly reducing conditions and these conditions prevailed 65 Ma after its formation [Premović *et al.*, 2007]. In contrast, the deposition of layer IIIA probably occurred under well-oxygenated conditions. This is supported by its relatively high content (ca. 10 %) of authigenic nano-phase goethite [Bauluz *et al.*, 2000; Wdowiak *et al.*, 2001] and goethite-rich microspherules. In general, goethite occurs in sedimentary environment under oxidizing conditions with redox potential Eh >+0.15 V [Krumbein and Garrels, 1952]. Thus, the well-oxygenated conditions in layer IIIA preceded the stagnant conditions that occurred during formation of the anoxic layer IIIB. The sudden and sharp emergence of FeS_2 concretions/framboids, humic kerogen and soot in layer IIIB [Premović *et al.*, 1993, 2000, 2007] likely reflects the major swift and abrupt change from well-oxygenated to anoxic conditions on the seafloor at Højerup at the KPB.

The abundant presence of goethite/hematite in the “impact” layer at Agost [Diaz-Martínez *et al.*, 2002; Molina *et al.*, 2005] and abundant goethite in the “impact” layer at El Kef [Robin *et al.*, 1991] indicate that these two layers were also probably formed under well-oxygenated seafloor conditions.

Goethite-rich microspherules

Petrological, mineralogical, and geochemical criteria suggest that microspherules in the KPB sections worldwide are similar and originated from the same impact. These spherules are widely believed to represent the impact vapor condensates and melt droplets formed from a mixture of impactor and impactite in the ejecta plume. However, some researchers have expressed their skeptism about this interpretation. For example, Hallam [1987] suggested that the microspherules in the KPB sections worldwide represent all the possible sources: sedimentary, volcanic and extraterrestrial (i.e., micrometeorites usually found in marine sedimentary rocks).

Layer IIIA contains hundreds of predominantly goethite-rich microspherules per cubic centimeter deeply incorporated into the smectite matrix [Smit, 1999], assembling about 10 % of the layer [Schmitz, 1988]. Such high concentrations of the microspherules are quite rare in sedimentary rocks [Vallentyne, 1963]. Hansen *et al.* [1986] proposed that goethite-rich microspherules in layer IIIA are infilling of prasinophyte algae. Schmitz [1985] suggested that these microspherules were originally FeS_2-rich and that during weathering their FeS_2 was partly or wholly oxidized to goethite [Schmitz, 1985]. He also suggested that the FeS_2-rich microspherules are authigenic and were produced through pseudomorphic replacement of FeS_2-rich biogenic microspherules [Schmitz, 1988]. However, Smit [1999] argued that goethtite-rich microspherules of layer IIIA are generated by the KPB impact and they were diagenetically altered to goethite-rich microspherules. At Agost [Martınez-Ruiz *et al*., 1992, 1997; Molina *et al*., 2005] and El Kef [Ortega-Huertas *et al*., 1998] the abundant microspherules are made up of either K-feldspar or goethite. Martinez-Ruiz *et al*. [1992, 1997] suggested that the goethite-rich microspherules were originally FeS_2-rich and later were oxidized to goethite/hematite. In general, sedimentary goethitic microspherules are considered to be a result of pseudomorphic replacement of FeS_2-rich spherules [Vallentyne, 1963].

Morse [1994] has, however, shown that up to 99 % of FeS_2 can be oxidized within 1 day of exposure to well-oxygenated seawater and most of trace elements such as Ni, Cu and Zn are released into surrounding seawater during this process. Thus, if the goethitic microspherules of layer IIIA enriched in Ni, Cu and Zn (table 1) were originally authigenic FeS_2-rich microspherules oxidized by weathering then most of pyritic Ni, Cu and Zn would be released during this process. On the other hand, goethite and other Fe oxides are well-known inorganic scavengers that control trace metal mobility and distribution within marine coastal sediments [Forstern *et al.*, 1976].

Sternbeck *et al.* [2000] have pointed out that Ni, Cu and Zn are usually not released into seawater during the postdepositional pyritization of marine sediments. We, therefore, suggest the following hypothesis for the geochemical evolution of the pyritic microspherules of layer IIIA: a pore solution enriched in H_2S has diffused downsection from the overlying highly anoxic layer IIIB and reacted partially or wholly with the originally Fe oxide-rich microspherules of the uppermost part of layer IIIA (sublayer IIIA3) (fig. 2c). This is expected because at shallower seawater depths, such as at

Stevns Klint, pyritization may readily take place close to the O_2 (sublayer IIIA3) -H_2S (sublayer IIIBp) interface (redox boundary) (fig. 2c).

The thickest known ocean accumulation of the impact microspherules is about 17 cm (Blake Nose, southern Pacific) derived from the Chicxulub impact. This site was about 2000 km from the impact crater at the time of impact [Martinez-Ruiz *et al.*, 2002]. The aggregate thickness of microspherules of layer IIIA is estimated to be 0.2-0.4 cm since they make up ca. 10 % of a layer of 2-4 cm. This value is consistent with a proposal that these microspherules probably originated from the Chicxulub impact, which was ca. 10,200 km at the KPB far from Stevns Klint [Morgan *et al.*, 2006].

Distribution of Ir

Ir in ancient sedimentary rocks originates from extraterrestrial, volcanic and continental weathering sources, and these rocks contain approximately 20 ppt of Ir. This metal, together with Ni, is one of the siderophile trace metals that is invariably enriched in the ancient sedimentary rocks related to the impacts of the extraterrestrial impactors. There is now a little doubt that anomalous Ir in the Fish Clay originated from an extraterrestrial source.

Geochemical studies [Alvarez *et al.*, 1980; Rocchia *et al.*, 1987; Tredoux *et al.*, 1989; Graup *et al.*, 1992] show that the Ir profile (on a whole rock basis) across the Fish Clay column is characterized with a sharp maximum in the base of layer IIIB with an upward gradual decrease (tailing-off) from its maximum. Schmitz [1988] also reported the INAA data for Ir in the carbonate-free phase of layers I-V. (Ir in these layers is wholly located in this phase). Based on his results, the concentration profile of Ir (on a carbonate-free basis) across these layers is presented in fig. 5. The concentrations of Ir are relatively low (ca. 5 ppb) in layers I/II and start to increase sharply (up to 15 ppb) in layer IIIA, reaching its maximum (ca. 125 ppb) in layer IIIB. Upward from this layer, Ir concentrations decrease gradually in layer IV and in layer V returned to about the latest Maastrichtian (layers I/II) values. A relatively low concentration of Ir (9 ppb) is found in the FeS_2-rich microspherules of layer IIIA but this metal is not detected in their goethite-rich counterparts (table 1). These two findings imply that the microspherules cannot be a possible carrier of Ir in layer IIIA.

Very recently, Premović *et al.* [2007] reported that the Ir spike coincides precisely with a humic kerogen spike of layer IIIB in time and is equally intense. Premović *et al.* [2007] suggested that the humic substances (the kerogen precursors) and Ir were probably fluvially and simultaneously transported from the soil on adjacent land and redeposited in a shallow marine basin at Højerup. The association of Ir with the IIIB humic kerogen is not necessary chemical and it could be just physical because micron-size Ir-bearing grains are associated with an acid-insoluble residue [Ping *et al.*, 1991], which mainly consists of kerogen [Premović *et al.*, 2007]. This is supported by a finding of Schuraytz *et al.* [1997] who reported that the lowest mass split (100±40 ng Ir) of a sample of the Fish Clay contains only three ca. 30 μm-diameter Ir-rich "nuggets".

Besides the strongest Ir anomaly in layer IIIB, the relatively anomalous concentrations of Ir extends into the underlying layer II and overlying layer V, over a thickness of about three centimeters, fig. 5. Consequently, it appears that the terrestrial influx of cosmogenic Ir (as "micronuggets"?) to the Fish Clay lasted for, at least, a few decades. The Ir maximum in the KPB sections at Agost and El Kef is located in their "impact" layers but the relative Ir anomaly at these two sites also trails several tens of centimeters above and below the KPB section. For example, the "impact" layer of El Kef only contains 5-10 % of the total Ir influx but more than 40 % of this influx is associated with the latest Maastrichtian chalk [Robin *et al.*, 1991]. In contrast, layers IIIB and IV contain >95 % of the total Ir influx.

Ni and Co and ejecta fallout

Schmitz [1988] reported ICP-OES data for Ni and Co (on a carbonate-free basis) in more-closely spaced samples across the layers I-V. Based on these results, Ni and Co are shown in fig. 5 as concentration profiles *vs.* stratigraphic height. (For the sake of clarity, Co concentrations are multiplied with a factor 5). This figure shows that both metals reach their profound maxima in the carbonate-free fraction of layer IIIA. Schmitz [1985] also reported that FeS_2- and goethite-rich (>125 μm) microspherules of layer IIIA contain the relatively high concentrations of Ni and Co (table 1). A simple calculation, however, shows that these spherules at most could account for only <15 % of these two metals in the carbonate-free phase of layer IIIA.

Ni and Co in the marine-shallow KPB beds are considered to be mostly cosmogenic in origin. Kyte *et al.* [1985] analyzed layer IIIB for siderophiles, including Ni and Co, suggesting that these metals are derived from the primary fallout of the Chicxulub impact. Schmitz [1988] proposed that the concentrated trace metals in layers IIIA/IIIB have precipitated from the seawater and that the precipitation was probably induced by the redox-controlled processes. He also pointed out that the ultimate origin of some of these metals (e.g. Ni) may have been an Earth-impacting asteroid. Elliott [1993] argued that trace metals in smectite of layers IIIA/IIIB originated from ejecta fallout which accumulated directly on the seafloor. Very recently, Premović *et al.* [2007] suggested that the predominant source of Ni and Co in layer IIIB was probably ejecta fallout deposited on the top of nearby coastal soil which was leached by impact-induced acid? surface waters. They also proposed that most of Ni and Co is derived from chondritic component of the fallout. We may hypothesize that the same source is probably responsible for anomalous Ni and Co of layer IIIA.

It appears that the KPB sections at Agost and El Kef have their maxima of Ni and Co at about the same stratigraphical level as the Fish Clay, i.e., in their “impact” layer [e.g. Strong *et al.*, 1987; Schmitz, 1988; Gilmour and Anders, 1989]. Consequently, we assume that Ni and Co in these layers were conceivably also originated from chondritic component of ejecta fallout deposited on nearby adjacent land area(s). In order to confirm this hypothesis, detailed mineralogical and geochemical analyses of each of these sections are necessary.

Impact glasses, microspherules and detrital smectite

As pointed out before, the formation of layers IIIA/IIIB probably occurred at the KPB. It is likely that the incorporation of goethite-rich microspherules and nano-size glasses into these layers occurred prior to their lithification/cementation. Now a question is: are these microspherules and glasses authigenic or reworked/redeposited?

The stratigraphic context of layers IIIA/IIIB suggests it was deposited below wave-base in a low energy environment. Reworked/redeposited and relatively abundant late Maastrichtian coccoliths *Arkhangelskiella cymboformis* (fig. 3d) that went extinct at the KPB, calcareous dynocysts [Wendler and Willems, 2002] and other transported debris [Christensen *et al.,* 1973; Premović *et al.,* 1993; Wendler and Willems, 2002] are present throughout layers IIIA/IIIB, implying that their microspherules are reworked/redeposited at or near the KPB from earlier original submarine deposit. These two processes probably occurred simultaneously with smectite redeposition. Indeed, the spherules are intimately associated (cemented) with detrital smectite throughout layers IIIA/IIIB, and even found in layers V/VI [Hansen *et al*., 1986], i.e., throughout the Fish

Clay. As pointed out earlier, these layers probably spanned a time interval of a few tens thousands years.

Goethite-rich microspherules are also present across the Danish Basin; these were found in the KPB boundary sediments at four localities Nye Kløv, Kjølby Gaard, Dania and Karlstrup separated from Højerup by about 200-300 km [Hansen *et al*., 1986]. It is likely that the microspherules at these four sites were also reworked/redeposited at the same time as those at Højerup.

The abundant presence of goethite-rich microspherules throughout Danish Basin and, at Agost and El Kef indicates that these are probably originally deposited at about the same time in all these localities and derived from the same impact-ejecta fallout of Chicxulub. Indeed, it would be unlikely for the goethite-rich microspherules in these KPB sediments to have more than one origin. Additionally, we may hypothesize that the goethite-rich microspherules at Agost and El Kef were probably reworked/redeposited along with smectite as they are also intimately associated with detrital material.

As pointed out before, Graup *et al.* [1992] reported that small goethite-rich spherules (mainly ca. 100 μm in diameter) and large goethite-/FeS_2-rich spherules (125-800 μm in diameter) show different stratigraphic distribution: sublayer IIIA1 vs. sublayer IIIA3 (fig. 2c). Such bimodal distribution of microspherules indicates that a differential size grading occurred during their reworking/redeposition. As far as we are aware, the different stratigraphic distributions of microspherules with the size grading have not been observed in the "impact" layers at Agost and El Kef and in any other marine shallow KPB "impact" layers worldwide.

Observations made by scanning/transmission/analytical electron microscopies of the KPB "impact" layer at Højerup have revealed the occurrence of nanometer-sized Si-rich glasses which are partially altered to cheto-Mg-smectite [Bauluz *et al.*, 2000]. These authors concluded that the glasses at are compositionally similar to the Si-rich KPB impact glasses from Haiti and they are relics of original ejecta fallout generated by the KPB impact. As far as we are aware, the nano-size glasses are not detected in other four KPB deposits of the Danish Basin and, in the KPB sediments at Agost and El Kef.

As layer IIIA was most likely accumulated over several decades up to a century, its nano-size glasses are also probably reworked/redeposited. Indeed, these glasses are present also throughout the Fish Clay [Bauluz *et al.*, 2000] indicating that there was their continuous contribution over considerable time period, say, for at least 1 kyr. Fig. 6 illustrates the above described depositional model for detrital smectite, enriched in cosmogenic Ni, Co and Ir (micrograins?), reworked/redeposited goethite-rich microspherules and nano-size glasses at Højerup.

CONCLUSIONS

The conspicuous redish “impact” layers at Højerup, Agost and El Kef evidently contain a record of the KPB impact and its aftermath which is still well-preserved. Their deposition occurred simultaneously and for several decades up to a century at most. The major part of smectites in the “impact” layers at these three sites is probably detrital in origin, not excluding the possibility that a small proportion of these smectites being made up of impact-derived nano-size glasses. The “impact” layers in question are formed under the well-oxygenated conditions. Ni, Co and Ir (micrograins?) of the “impact” layers at at Højerup, Agost and El Kef were probably sourced by the chondritic component of ejecta fallout settled on the nearby coastal soil.

The predominant goethite-/minor FeS_2-rich microspherules of layer IIIA were initially enriched in Fe-oxides which were replaced by goethite or FeS_2 during early diagenesis. These microspherules and nano-size glasses of layer IIIA are probably reworked/redeposited at or near the KPB at the same time with smectite.

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TABLE 1. Trace metals contents (ppm) of the >125 μm spherules and the carbonate-free fraction of layer IIIA.

Spherules/ Layer	Ni	Co	Zn	Cu	Ir (ppb)	References
FeS_2-rich	3100	-	3400	220	9	Schmitz, 1985
Goethite-rich	5500	-	6900	690	n.d.	Schmitz, 1985
IIIA	1440	195	-	-	15	Schmitz, 1988

n.d. - not detected.

FIGURE CAPTIONS

FIG. 1. (a) Paleolocations of the marine-shallow KPB sections with the reddish layers at Højerup, Agost and El Kef; (b) geological map of eastern Denmark, [modified after Håkansson and Pedersen, 1992] with the location of Stevns Klint.

FIG. 2. (a) Lithostratigraphic profile of the KPB formation at Højerup [modified after Surlyk, 1979]; schematic illustration of: (b) a stratigraphic section of the Fish Clay and (c) layer III; and, (d) the thickness of layer IIIA.

FIG. 3. SEM photographs of thin section of layer IIIA: showing (a) goethite-rich spherules deeply incorporated into smectite matrix; (b) with a gypsum or anhydrite grain; (c) framboidal FeS_2; and, (d) relatively abundant late Maastrichtian coccoliths: *Arkhangelskiella cymboformis*.

FIG. 4. Depth of deposition of the "impact" layers at Højerup, Agost and El Kef.

FIG. 5. Distribution of Ni, Co (ppm) and Ir (ppb) of the carbonate-free fractions of layers I-V [after Schmitz, 1988].

FIG. 6. Proposed depositional model for detrital smectite, enriched in cosmogenic Ni, Co, and Ir (micrograins?), reworked/redeposited goethite-microspherules and nano-glases at Højerup.

LÉGENDES

FIG. 1. (a) Les paléoendroits des sections KPB peu-profond marines avec les couches rouges à Højerup, Agost et El Kef; (b) la carte géologique du Danemark de l´est [modifié après Håkansson et Pedersen, 1992] avec l'endroit de Stevns Klint;

FIG. 2. (a) Le profil de lithostratigraphic de la formation au KPB à Højerup [modifié après Surlyk, 1979]; l'illustration schématique de : (b) une section stratigraphic de Fish Clay et (c) la couche III; et, (d) l'épaisseur de couche IIIA.

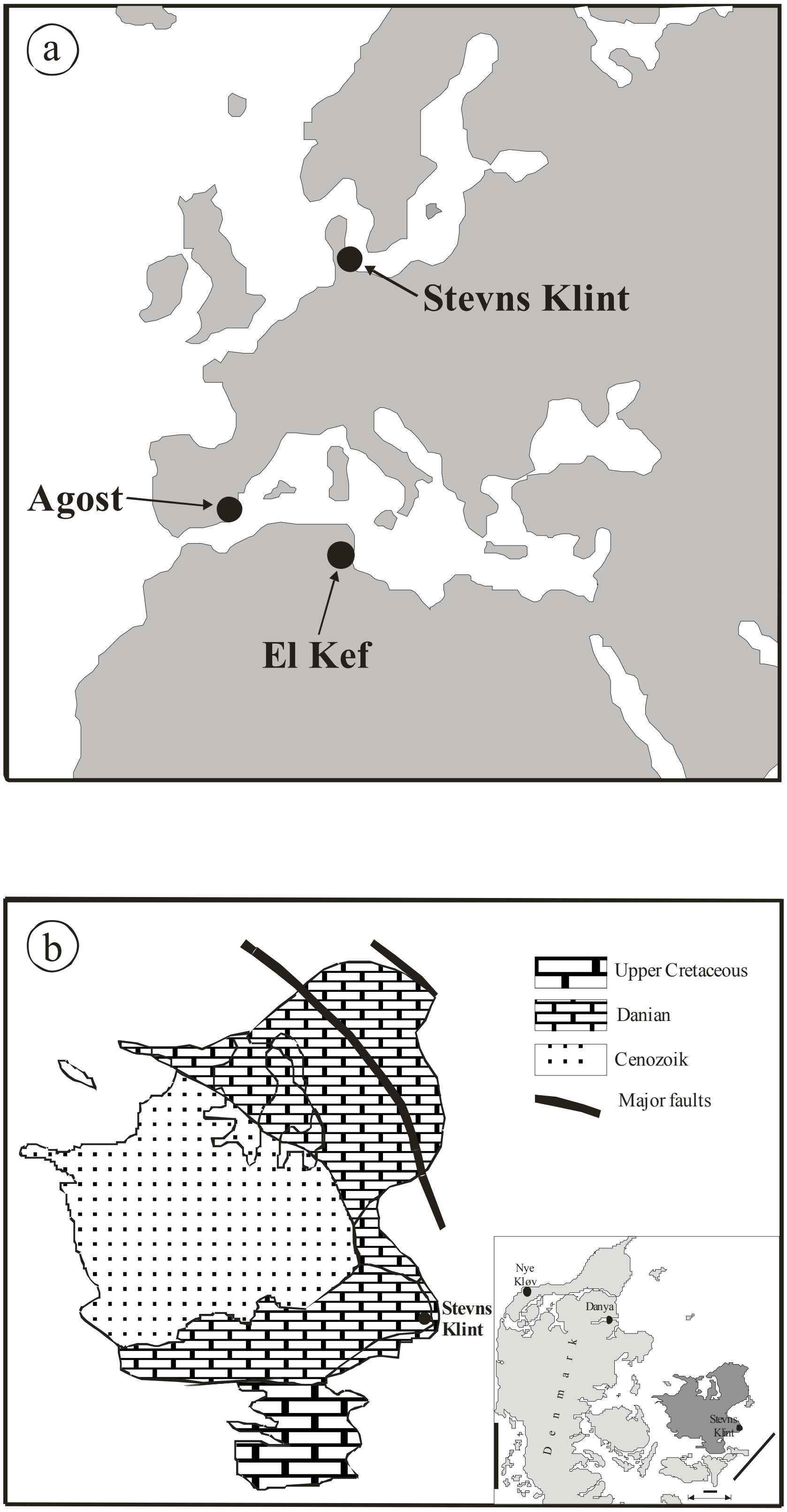
FIG. 3. Les photographies de SEM de section fine de couche IIIA: (a) les petites sphères goethite-riches se constituaient profondément en société commerciale dans la matrice smectite; (b) avec un gypse ou un grain anhydrite; (c) FeS_2 framboide; et, (d) en retard Maastrchtian coccoliths: *Arkhangelskiella cymboformis*.

FIG. 4. La profondeur de déposition des couches "d'impact" à Højerup, Agost et El Kef.

FIG. 5. Distribution of Ni, Co (ppm) et Ir (ppb) des fractions sans carbonate de couches I-V [après Schmitz, 1988].

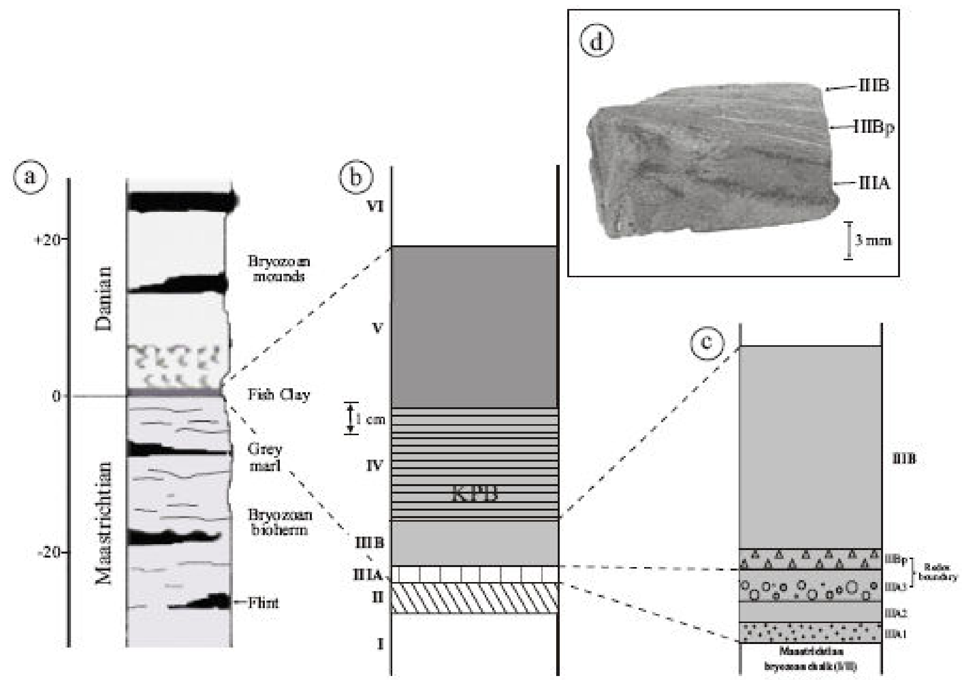
FIG. 6. Proposé modèle de depositional pour smectite détritique, enrichi avec Ni, Co cosmogenic et Ir (les micrograins?), les goethite-micropetites-sphères retravaillé/redéposé et nano-glases à Højerup.

FIGURE 1.



a
Stevns Klint
Agost
El Kef
b
Upper Cretaceous
Danian
Cenozoik
Major faults
Stevns Klint
Nye Kløv
Danya
Denmark
Stevns Klint

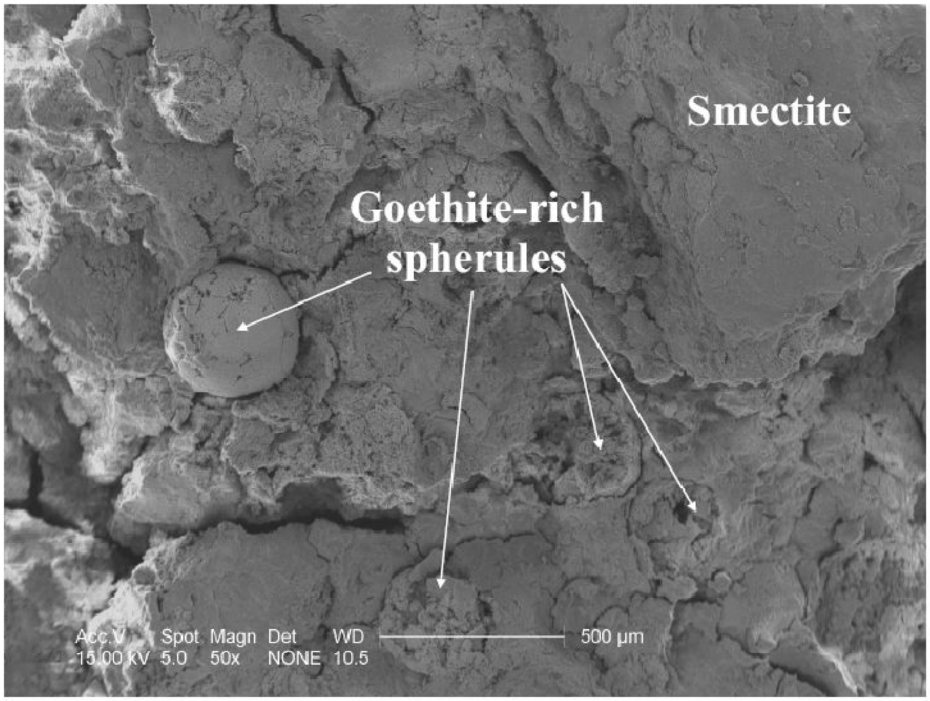
FIGURE 2.



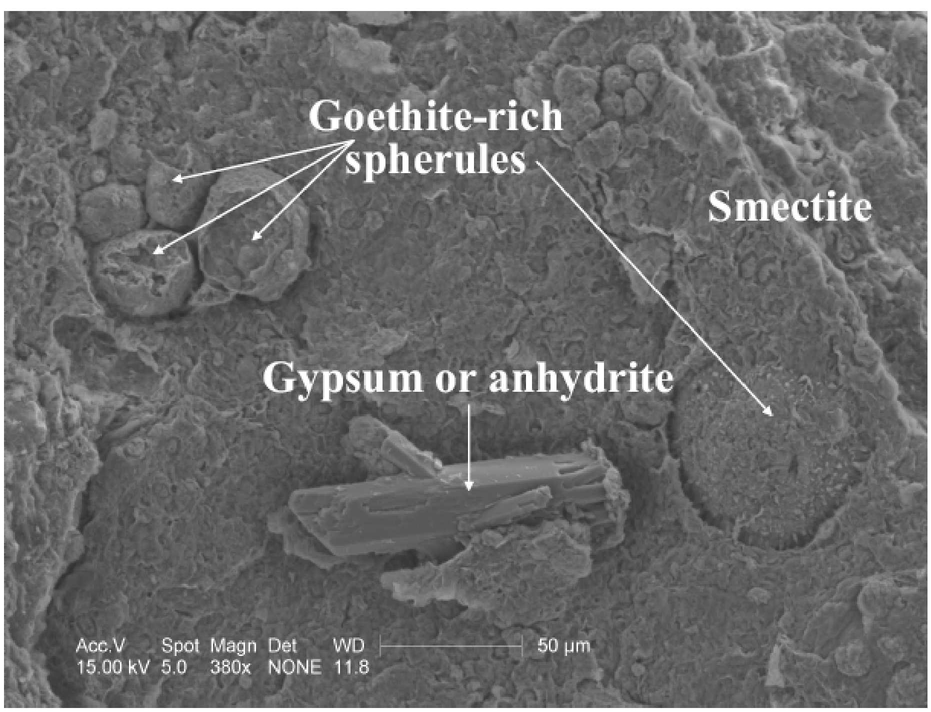
a
+20
0
-20
Danian
Maastrichtian
Bryozoan mounds
Fish Clay
Grey marl
Bryozoan bioherm
Flint
b
VI
V
1 cm
IV
KPB
III B
III A
II
I
c
IIIB
d
IIIB
IIIBp
IIIA
3 mm

FIGURE 3.

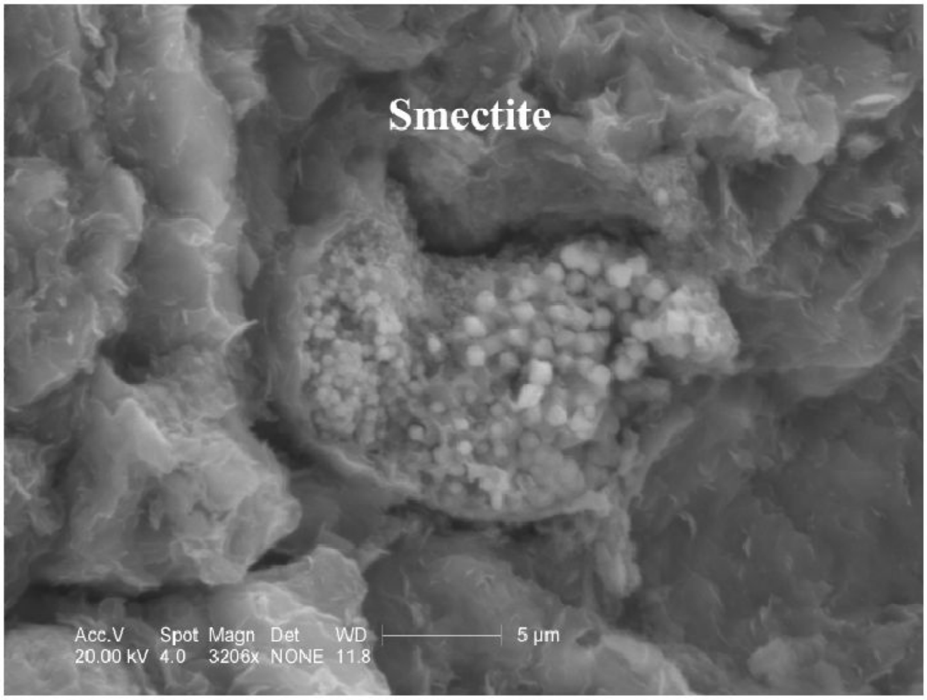
a)


Smectite
Goethite-rich spherules
Acc.V Spot Magn Det WD 500 µm
15.00 kV 5.0 50x NONE 10.5

b)


Goethite-rich spherules
Smectite
Gypsum or anhydrite
Acc.V Spot Magn Det WD 50 µm
15.00 kV 5.0 380x NONE 11.8

c)


Smectite
Acc.V Spot Magn Det WD 5 µm
20.00 kV 4.0 3206x NONE 11.8

d)


Smectite
Acc.V Spot Magn Det WD 5 µm
20.00 kV 4.0 5000x NONE 11.4

FIGURE 4.

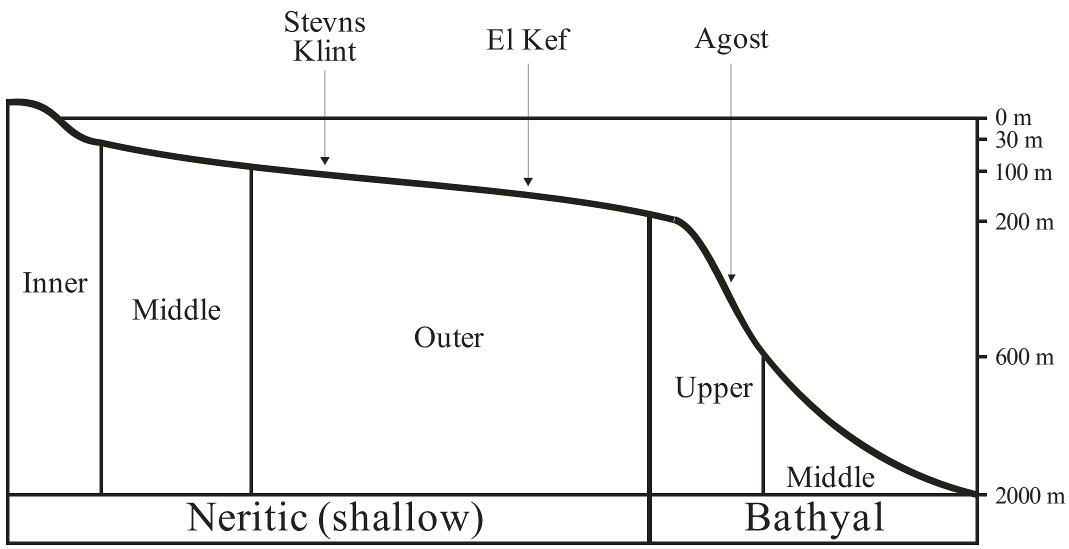
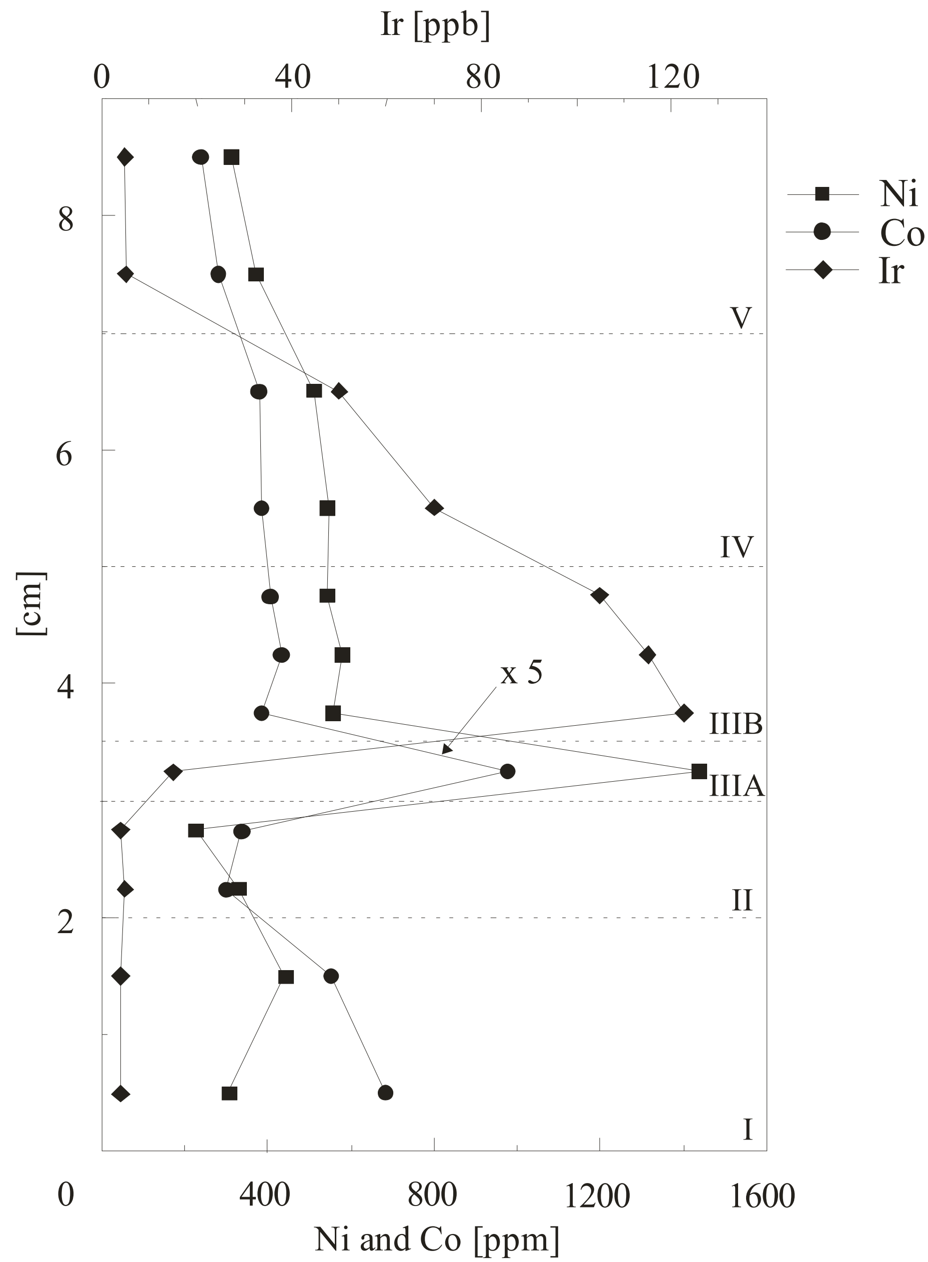
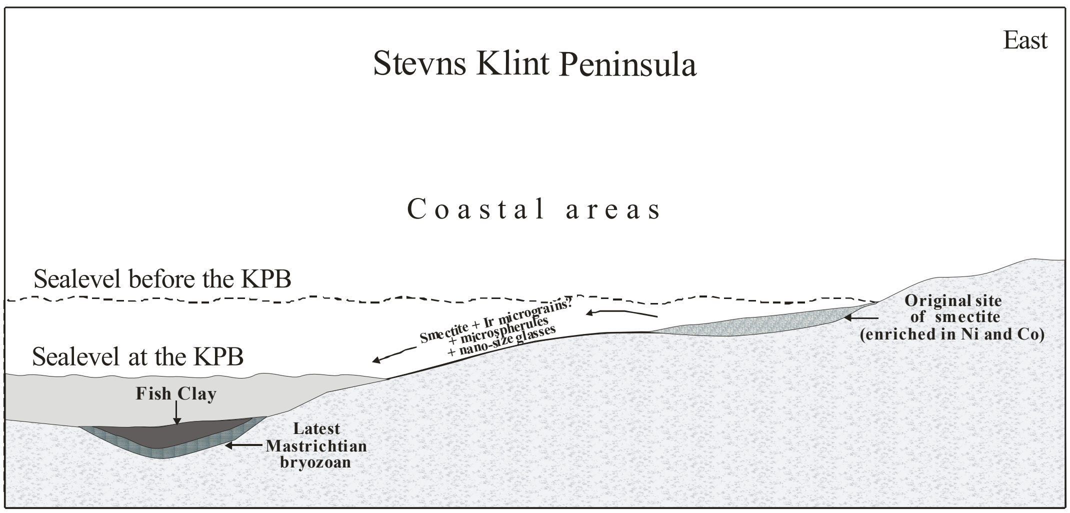

Stevns Klint
El Kef
Agost
0 m
30 m
100 m
200 m
600 m
2000 m
Inner
Middle
Outer
Upper
Middle
Neritic (shallow)
Bathyal

FIGURE 5.



Ir [ppb]
0
40
80
120
Ni
Co
Ir
8
6
4
2
[cm]
V
IV
IIIB
IIIA
II
I
x 5
0
400
800
1200
1600
Ni and Co [ppm]

FIGURE 6.


East
Stevns Klint Peninsula
Coastal areas
Sealevel before the KPB
Sealevel at the KPB
Smectite + Ir micrograins?
+ microspherules
+ nano-size glasses
Original site
of smectite
(enriched in Ni and Co)
Fish Clay
Latest
Mastrichtian
bryozoan