The conspicuous red "impact" layer of the Fish Clay at Højerup (Stevns Klint, Denmark)

© 2009 г. Pavle I. Premović
Laboratory for Geochemistry, Cosmochemistry and Astrochemistry, University of Nis,
P.O. Box 224, 18000 Nis, Serbia
e-mail: asteroid.pavle@yahoo.com
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The marine Cretaceous–Paleogene boundary (KPB) section at Højerup-Fish Clay consists of a very thin red smectite-rich carbonate-poor ("impact") layer overlain by a thick black marl. Similar red layers are found in the KPB sections at Agost in Spain and El Kef in Tunisia.
Smectite of the red layer of the KPB section at Højerup is probably detrital and redeposited from adjacent coastal or marine areas. This clay mineral is likely mixed with a small amount of smectite derived from impact glasses. Most of the microspherules and nano-size glasses of the red layer at Højerup are probably detrital and simultaneously redeposited with smectite. The deposition of the red layer occurred for several decades to a century at most.

INTRODUCTION

There seems a wide consensus among researchers that anomalous Ir (and other siderophile metals) in the marine KPB sediments 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 [1]. The use of helium-3 as a constant-flux proxy of sedimentation rate implies deposition of the most marine KPB sediments worldwide occurred within about 10 kyr [2].

In the earliest scenario of the KPB impact event, the distinct red 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) of the KPB sections worldwide was created by thousands of cubic kilometers of the impact ejecta dispersed globally. Accordingly, ejecta fallout originated from an impact plume of a vaporized impactor and impactite (target) material ejected into the stratosphere.

Fish Clay near village of Højerup (hereafter referred as the Fish Clay) is a classic KPB section at Stevns Klint, (Fig. 1). The lithology of the Fish Clay has been described by Christensen et al. [3] and Surlyk et al. [4]. The authors distinguished three distinctive layers within this boundary section: 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), (Fig. 2a). Layers III and IV are here considered to constitute the main part of the KPB section at Højerup. Elliott [5] subdivided layer III into the red "impact" layer IIIA overlain by the black marl layer IIIB, (Figs. 2a/b). Layer IIIA is underlain with a Maastrichtian bryozoan-rich chalk (I/II) and unit V is overlain by the Danian Cerithium limestone (VI).

The aim of this paper in to synthesize/reinterpret some of the available data and observations obtained from the experimental studies of the carbonate-poor smectite-rich layer IIIA of the Fish Clay. I will also briefly reconsider the data and observations acquired from the experimental studies of the "impact" layers within the prominent KPB sections at Agost and El Kef, (Fig. 1).

Layers IIIA and IIIB

Layer IIIA is a thin 2–4 mm layer which is mainly (>90%) made up from cheto-smectite. This layer contains some (biogenic?) non-Maastrichtian carbonate (probably reworked) [6], pyrite- (FeS_2-) and goethite-rich microspherules [7], altered nano-size Si-rich glasses and nano-size goethite grains [8, 9] enriched in Ni and Zn [8]. Bauluz et al. [8] interpreted the goethite grains as altered meteorite fragments, which were formed when impact glass was transformed to smectite. The "impact" layer IIIA also contains a very few shocked quartz grains: about 2–3 of every thousand of quartz grains are shocked [10–12]. However, it is still not unambiguous is their number really anomalous relative to background contents.

Layer IIIB is the smectitic black marl containing anomalous Ir [13], soot [14] with the adsorbed the airborne polycyclic aromatic hydrocarbons [15] and humic kerogen enriched in Cu^{2+}-porphyrins [16]. Layer IIIB contains also microspherules (mainly enriched in FeS_2) but they are much less abundant than in IIIA [17]. Layer IIIA also differs from layer IIIB by the excellent preservation of microspherules in the sediment matrix. The base of IIIB (sublayer IIIBp), enriched in macroscopic (up to 5 cm) FeS_2 concretions/framboids [17], makes easy to distinguish the top of IIIA and the base of IIIB, (Fig. 2b).

Graup et al. [18] 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),

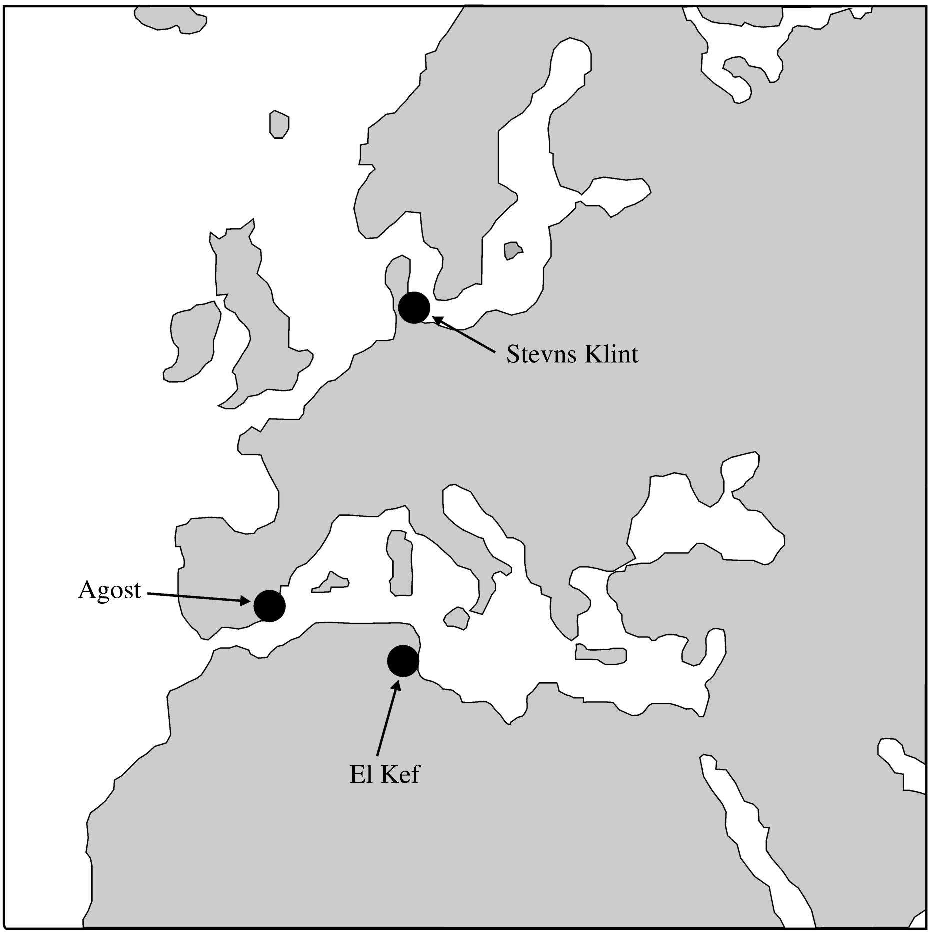

Fig. 1. Paleolocations of the marine KPB sections with the red layers at Højerup, Agost and El Kef .

(Fig. 2b). These larger spherules are deeply incorporated into the smectite matrix and they are enriched in Fe (as FeS_2 and/or goethite) [17, 18].

Recently, Trinquier et al. [19] have shown that Cr isotopic signature of layer IIIB exhibits an isotopic ratio which would represent a mixing of a carbonaceous chondrite of CM2 type with terrestrial material. An important result of their study is that Cr isotopic signatures and Ir and Cr enrichments of layer IIIB are only consistent with a single impact event of a large extraterrestrial impactor. Ac-cording to Mukhopadhyay et al. [2], helium-3 isotopic data for the KPB section at El Kef are also more consistent with an impact of a lone asteroid or a comet.

Like at Højerup, at Agost and El Kef the biogenic calcite ooze of the latest Maastrichtian is also sharply capped by the smectite-rich "impact" layer [13] that passes upward into smectite-rich marl. Previous sedimentary studies have shown that the Fish Clay [20] and KPB sections at Agost and El Kef [21] are deposited in marine near-coastal areas; depths of their deposition are presented in Fig. 3. 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 at the KPB.

Marine KPB "impact" layer

In most marine 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 2 to 3-mm goethite-rich red "impact" layer at the base of the boundary clay; and, (3) anomalously high Ir values generally concentrated in the "impact" layer. The red "impact" layer is present in all complete KPB sections worldwide [7]; this layer is generally considered as marking the KPB. Layer IIIA bears many similarities to the record at these sections except, that Ir is enriched in the base of the overlying smectite-rich marl IIIB not in the underlying "impact" layer IIIA.

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

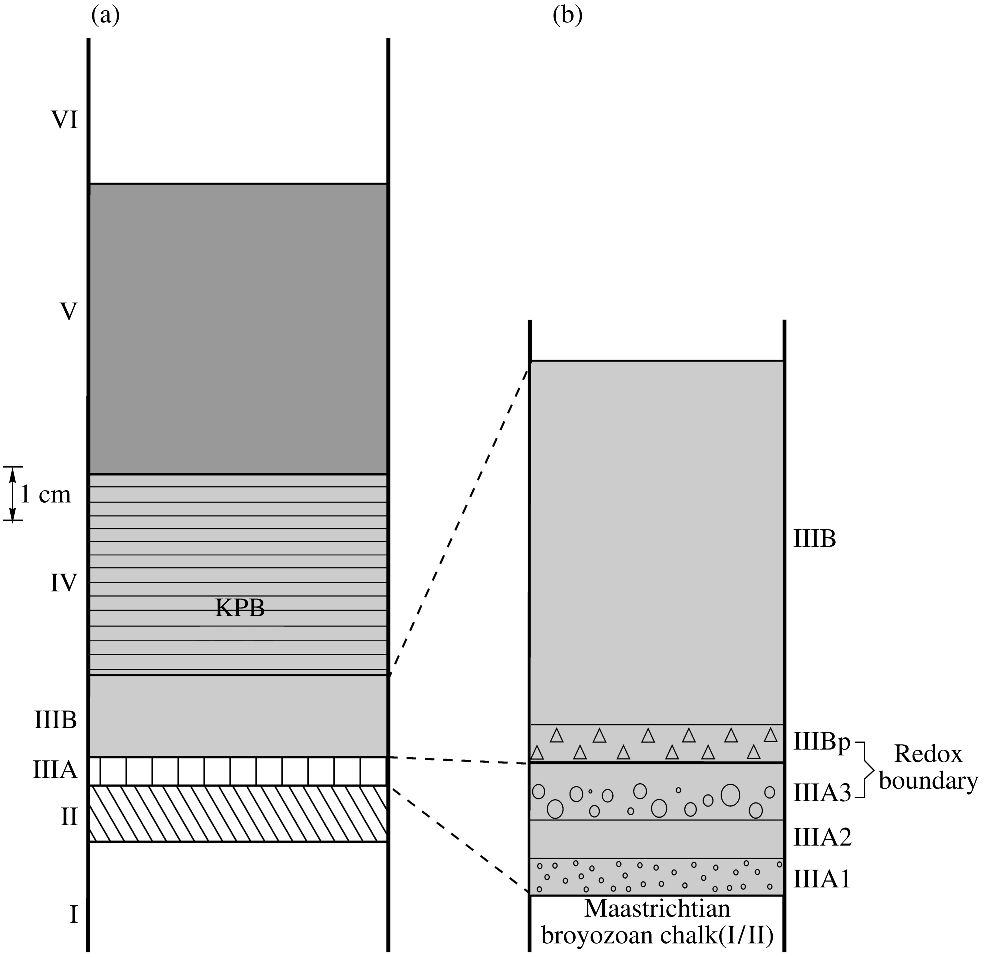

Fig. 2. Schematic illustration of the internal layering in: (a) a stratigraphic section of the Fish Clay and (b) layer III.

section has been officially designated as the boundary global stratotype section and point (GSSP) for the KPB [22].

Detrital smectite

The smectite contents of the Fish Clay sharply increases reaching a maximum in layer IIIA (>90% of the whole rock) and then declines gradually through layers IIIB and IV [5, 16]. The underlying latest Maastrichtian layers I/II and overlying early Danian layer VI contain smectite but in much lower amounts [5], indicating that the influx of smectite began probably at some time during the latest Cretaceous and persisted during the earliest Danian, but at a lower level.

The clay mineralogy studies indicate that the distinctive cheto-Mg-smectite is the predominant clay mineral in layers IIIA/IIIB [5, 8]. Most researchers [e.g., 3, 5, 23–25] 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. [26] 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 Maastrictian layers I/II and earliest Danian layer VI. Electron microscopic studies carried out by Bauluz et al. [8] revealed that smectite of layer IIIA contains the distinctive mineralogical/geochemical signatures linked

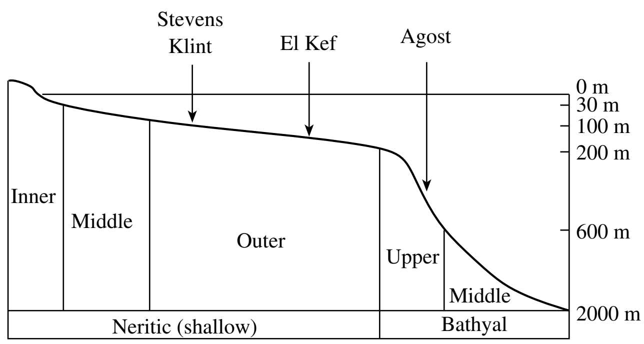

Fig. 3. Depth of deposition of the KPB "impact" layers at Højerup, Agost and El Kef.

directly to the impact glasses. In the earliest and most popular scenario of the KPB impact event, the distinct "impact" layer of the KPB sections worldwide (such as layer IIIA) was deposited for less than a year [27]. Consequently, smectite of layer IIIA would be authigenic and derived mostly from the impact glasses.

Drits et al. [28] carried out chemical analysis, solid state NMR spectroscopy and atomic force microscopy of IIIB smectite and they concluded that this mineral is probably formed from glassy volcanic ash and that a very small part, if any, of it was derived from the impact glasses.

Trinquier et al. [19] 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 [29], 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.

Very recently, Premovic et al. [30] suggested that smectite of layer III represents a short period of rapid 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 [31, 32].

Ortega-Huertas et al. [21] on the basis of mineralogical and chemical composition data inferred 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 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 [33] and the second one is that detrital smectites are inherited from the erosion of soils developed in surrounding areas. Ortega-Huertas et al. [21] proposed that smectites of the "impact" layers at Agost and El Kef may be partially related to impact glasses.

In brief, the major part of smectites of the "impact" layers at Højerup, Agost and El Kef are probably detrital. However, I do not exclude the possibility of a small proportion of these smectites being made up of impact-derived glasses.

Deposition of layer IIIA

Wendler and Willems [6] proposed that layers IIIA/IIIB represent the first decades or centuries following the KPB impact event; Premovic et al. [16] 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, i.e., a considerable thickness may be missing from the record [34]. A simple calculation shows that the maximum thickness of layer IIIA in the absence of dissolution, using the assumed carbonate content of 90%, would be about 2–3 cm at most.

The thickness of layer IIIA is 2–3 mm which would imply duration of about 10–35 yr of its deposition, using the sedimentation rate (10–20 cm per 1000 yr) of Bromley [20]. However, the overall sedimentation rate of Bromley [20] 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 2–3 mm, the accumulation rate must be implausible low, say about 1–3% of the deposition rate of the underlying Maastrichtian bryozoan chalk (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.

Mukhopadhyay et al. [2] estimated that the deposition interval of 50–60 cm- thick KPB section at El Kef is about 11.3 kyr. Robin et al. [35] 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 [2]. 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 at most.

The well-oxygenated sedimentation conditions

Layer IIIB was deposited under strongly reducing conditions and these conditions prevailed 65 Ma after its formation [30]. 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 [9] and goethite-rich microspherules [13]. In general, goethite occurs in sedimentary environment under oxidizing conditions with redox potential Eh > +0.15 V [36]. 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 [16, 25, 30] 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 and hematite in the "impact" layer at Agost [37, 38] and abundant goethite in the "impact" layer at El Kef [35] indicate that these two layers were also probably formed under well-oxygenated seafloor conditions.

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	[17]
Goethite-rich	5500	–	6900	690	n.d.	»
IIIA	1440	195	–	–	15	[13]

n.d. – not detected.

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 impactite and impactor in the ejecta plume. However, some researchers have expressed their skeptism about this interpretation. For example, Hallam [39] suggested that the KPB microspherules probably represent all the possible sources: sedimentary, volcanic and extraterrestrial (i.e., micrometeorites usually found in marine sediments).

Layer IIIA contains hundreds of FeS_2- and goethite-rich microspherules per cubic centimeter deeply incorporated into the smectite matrix [7] assembling about 10% of the layer [13]. Such high concentrations of these spherules are quite rare in sedimentary rocks [40]. Hansen et al. [41] proposed microspherules in layer IIIA are infilling of prasinophyte algae. Schmitz [13] claimed that these spherules are authigenic and were produced through pseudomorphic replacement of FeS_2-rich biogenic spherules. However, Smit [7] argued that microspherules of layer IIIA are generated by the KPB impact and they were diagenetically altered to goethite-rich spherules. At Agost [38, 42] and El Kef [43] the abundant microspherules are made up of either K-feldspar or goethite.

Schmitz [17] reasoned that the goethite-rich microspherules of layer IIIA were originally FeS_2-rich and that during weathering their FeS_2 was partly or wholly oxidized to goethite. In general, sedimentary goethitic microspherules are considered to be a result of pseudomorphic replacement of FeS_2-rich spherules [40].

Morse [44] 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, Co and Zn (Table) 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 coastal sediments [45].

Sternbeck et al. [46] have pointed out that Ni, Cu and Zn are usually not released into seawater during the post-depositional pyritization of marine sediments. I, therefore, suggest the following hypothesis for the geochemical evolution of the pyritic microspherules: 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. 2b). This is expected because at shallower depths, such as at Stevns Klint, Fig. 3, pyritization may readily take place close to the O_2-H_2S interface, sublayers IIIA3 and IIIBp (redox boundary), (Fig. 2b).

As pointed out, Graup et al. [18] reported that small goethite-rich spherules (mainly ca. 100 μm in diameter) and large FeS_2-/goethite- rich spherules (125–800 μm in diameter) show different stratigraphic distribution: sublayer IIIA1 vs. sublayer IIIA3, (Fig. 2b). Such bimodal distribution of microspherules indicates that a differential size grading occurred during their deposition at Højerup. As far as I am aware, the different stratigraphic distributions of microspherules with the size grading have not been observed in the “impact” layers at Agost and El Kef in any marine KPB “impact” layer worldwide.

Distribution of Ir

Ir in ancient sedimentary rocks originates from extraterrestrial, volcanic and continental weathering sources, and these rocks contain approximately 20 ppb of Ir. This metal, together with Ni, is one of the siderophile trace metals that is invariably enriched in the deposits 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 [18, 47–49] 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 [13] also reported the INAA data for Ir in the carbonate-free phase of layers I–V. (Of note, 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. 4. The concentrations of Ir are relatively low (15 ppb) in layer IIIA and start to increase sharply, reaching its maximum in layer IIIB. Upward from this layer, Ir concentrations decrease gradually in layers IV and V, having much lower levels. 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 its goethite-rich microspherules (Table) [17].

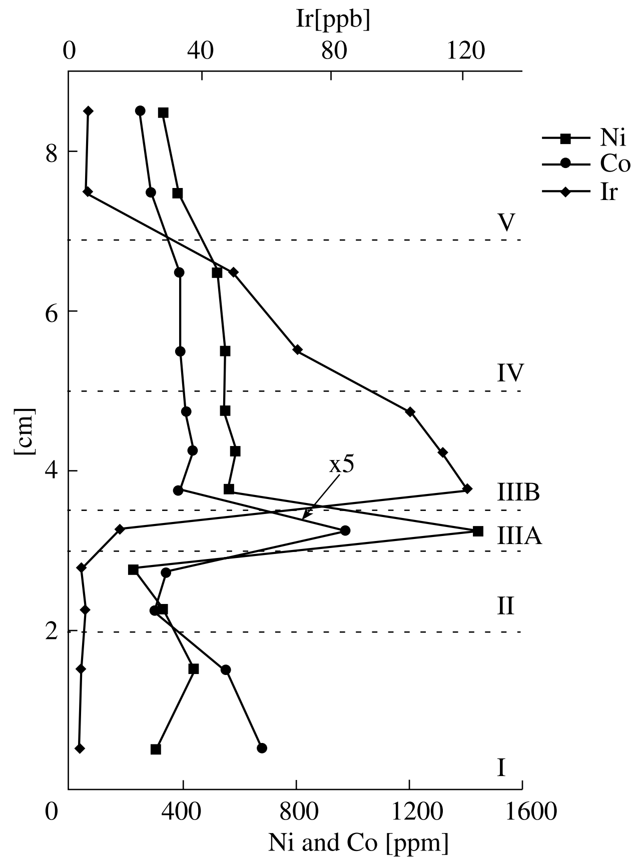

Fig. 4. Distribution of Ni, Co (ppm) and Ir (ppb) of the carbonate-free fractions of layers I–V [13].

This implies that the microspherules cannot be a possible carrier of Ir in the carbonate-free phase of layer IIIA.

Very recently, Premovic et al. [30] reported that the Ir spike coincides precisely with a humic kerogen spike of layer IIIB in time and is equally intense. However, the association of Ir with this kerogen is not necessary chemical and it could be just physical because micron-size Ir-bearing grains are associated with an acid-insoluble residue, which mainly consists of kerogen [50]. This is supported by a finding of Schuraytz et al. [51] 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". Premovic et al. [30] suggested that the humic substances (the kerogen precursors) and Ir were probably fluvially transported from the soil on adjacent land and redeposited in a shallow marine basin at Højerup.

Besides the strongest Ir anomaly in layer IIIB, Rocchia et al. [48, 52] reported that the anomalous concentration of Ir is not limited to the Fish Clay but extends into the underlying latest Maastrichtian bryozoan-rich chalk (I/II) and overlying earliest Danian limestone (layer VI), over a thickness of about one meter. Consequently, it appears that the terrestrial influx of cosmogenic Ir (as "micronuggets"?) to the Fish Clay lasted for, at least, 10 kyr. The Ir maximum in the KPB sections at Agost and El Kef is located in their "impact" layers but the 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 [35]. In contrast, layers IIIB and IV contain >95% of the total Ir influx.

Ni and Co and ejecta fallout

Schmitz [13] 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. 4 as concentration profiles vs. stratigraphic height. (Note, 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 [17] also reported that FeS_2- and goethite-rich (>125 μm) microspherules of layer IIIA contain the relatively high concentrations of Ni and Co (Table). 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.

Kyte et al. [53] analyzed layer IIIB for siderophiles, including Ni and Co, suggesting that these metals are derived from the primary fallout of the Chicxulub impact. Schmitz [13] proposed that the concentrated trace metals in layers IIIA and 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 [5] argued that trace metals in smectite of layers IIIA and IIIB originated from ejecta fallout which accumulated directly on the seafloor. Very recently, Premovic et al. [30] 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. I 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. 13, 54, 55]. Consequently, I assume that Ni and Co in these layers were probably 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.

Detrital glasses and microspherules

Observations made by scanning/transmission/analytical electron microscopies of the KPB "impact" layer at Højerup [8] have revealed the occurrence of nanometer-sized Si-rich glasses which are partially altered to cheto-smectite. Bauluz et al. also reported that these glasses are compositionally similar to the KPB Si-rich impact glasses from Haiti. These authors concluded that the glasses found at Højerup were a component of ejecta fallout generated by the KPB impact. As far as I am aware the glasses are not detected in the KPB sections at Agost and El Kef.

As layer IIIA was most likely accumulated over several decades, most of its glasses were probably redeposited simultaneously with smectite. This is supported by the abundance of the glasses throughout the Fish Clay [8] indicating that there was their continuous contribution over considerable time period. I also tentatively conclude that the microspherules are also probably detrital since they are intimately associated with smectite throughout layers IIIA and IIIB [8]. As pointed out earlier, these two layers spanned at least a time interval of a few decades.

CONCLUSIONS

1. The red "impact" layer IIIA of the KPB sections at Højerup evidently contains a record of the KPB impact and its aftermath which is still well-preserved.
2. IIIA smectite is probably mainly detrital and redeposited from adjacent coastal and/or marine areas.
3. The deposition of layer IIIA occurred for several decades up to a century at most.
4. Layer IIIA is formed under the well oxygenated conditions.
5. The goethite-/FeS_2-rich microspherules of layer IIIA were initially enriched in Fe-oxides which were replaced by goethite or FeS_2 during early diagenesis.
6. Ni, Co and Ir of layer IIIA were sourced by the chondritic component of ejecta fallout settled the nearby coastal soil.
7. Most of the microspherules and glasses of layer IIIA are also probably detrital and simultaneously redeposited with the smectite.

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