# Global impact-induced $CO_2$ acidification of seawater at the Cretaceous–Paleogene boundary: the conspicuous "impact" layer of the Fish Clay at Højerup (Stevns Klint, Denmark)

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***ABSTRACT*:** The shallow-seawater Cretaceous-Paleogene boundary section at Højerup-Fish Clay consists of a very thin redish biogenic calcite-poor "impact" layer overlain by thick black marl. A similar "impact" layer is found in the corresponding sections at Agost in Spain, El Kef in Tunisia and Woodside Creek in New Zealand. A low biogenic calcite of the "impact" layers at Højerup, Agost, El Kef and Woodside Creek probably reflect both the dissolution of this calcite by the global acidification and a low calcareous plankton production at the Cretaceous-Paleogene boundary. The acidification was created by an increase of $CO_2$ into the atmosphere triggered by the boundary impact. The global acidification of seawater was most likely a very brief event and lasted just several decades.

*KEYWORDS: Cretaceous–Paleogene, Fish Clay, impact layer, global acidification*

# INTRODUCTION

Alvarez et al (1980) explained anomalous Ir in the Cretaceous-Paleogene boundary (KPB) marine clay-rich deposits at three localities Gubbio in Italy, Højerup and Woodside Creek by proposing a late Cretaceous asteroid impact on the Earth. Subsequently, this suggestion was followed by reports of the prominent Ir anomaly in many other marine KPB clay-rich deposits around the world. These KPB deposits worldwide marks one of the most significant impact events in the Phanerozoic and this was probably largely responsible for one of the great extinctions in Earth history.

It has been suggested that the KPB impactor was a carbonaceous chondrite-type body (Kyte 1998; Shukolyukov and Lugmair 1998). Very recently, Trinquier et al. (2006) 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/Cr enrichments of layer IIIB are only consistent with a single impact event of a large extraterrestrial impactor. The use of helium-3 as a constant-flux proxy of sedimentation rate implies deposition of the most shallow-seawater KPB clay-rich beds occurred in about 10 kyr (Mukhopadhyay et al. 2001).

Fish Clay near village of Højerup (hereafter referred as the Fish Clay) is a classic KPB section in Denmark (Fig. 1) and it appears to be a very condensed and incomplete KPB succession (Ekdale and Bromley 1984). The lithology of the Fish Clay has been described by Christensen et al. (1973). The authors distinguished four distinctive layers within this boundary section: a 1-2 cm bottom 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), Fig. 2. Elliott (1993) subdivided unit III into the redish smectite-rich layer IIIA overlain by the black marl layer IIIB, Fig. 2. Very recent lithostratigraphic study indicates that transitional layer II should not be included in the Fish Clay member since it forms the very top of the latest Maastrichtian bryozoan chalk I (Surlyk et al. 2006).

Layers III and IV are here considered to constitute the main part of the Fish Clay. Unit IIIA is underlain by the latest Maastrichtian bryozoan-rich chalk (layers I/II), and unit V is overlain by the Danian Cerithium limestone (layer VI).

Deposition of the Maastrichtian bryozoan-rich chalk occurred in a rather shallow epicontinental sea, but within the euphotic zone, in about 150 m (Bromley 1979), Fig. 3. The Fish Clay probably represents a much shallower depositional environment than this chalk. Together with the Cerithium limestone of earliest Danian age, the Fish Clay forms infillings of small basins between the crests of the latest Maastrichtian bryozoan bioherms (Machalski and Heinberg 2005, and references therein).

The aim of this review to synthesize/reinterpret some of the available data obtained from the experimental studies of the conspicuous redish carbonate-poor smectite-rich layer IIIA in order to support the global acidification of seawater instigated by the KPB impact. For the same purpose and from the same reason, I will briefly reconsider the corresponding data acquired from the experimental studies of the corresponding layers within the prominent KPB sections at Agost, El Kef and Woodside Creek, Fig. 1.

## Layers IIIA and IIIB

IIIA is a thin 2-4 mm layer which is mainly (>90 %) made up from smectite. This layer contains some biogenic non-Maastrichtian calcite (probably reworked) (Wendler and Willems 2002), pyrite- and goethite-rich microspherules (Smit 1999), 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 grains as altered meteorite fragments, which were formed when impact glasses was transformed to smectite. Layer IIIA also contains a very few shocked quartz grains: about 2-3 of every thousand of quartz grains are shocked (Bohor et al. 1985; Schmitz 1992; Miura et al. 1992). However, it is still not unambiguous is their number really anomalous relative to background contents.

Layer IIIB is the smectitic marl containing anomalous Ir (Schmitz 1988), soot (Wolbach et al. 1985) and kerogen (Premović et al. 2000). IIIB is also rich in microspherules but they are much less abundant than in IIIA (Schmitz 1985). The base of IIIB (sublayer IIIBp), enriched in macroscopic pyrite concretions/framboids (Schmitz 1985) makes easy to distinguish the top of IIIA and the base of IIIB, Fig. 2.

## “Impact” layer

In most marine shallow 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. Most researchers are inclined to the view that the “impact” layer was deposited during a global decrease in ocean productivity after the KPB impact (e.g. Arenillas et al. 2006); (2) a 2 to 3-mm goethite-rich “impact” layer at the base of the boundary clay; (3) anomalously high Ir values generally concentrated in the “impact” layer. Unit III of the Fish Clay 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.

In the earliest and most popular scenario of the KPB impact event, the distinct basal (usually redish) 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 boundary clays 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 target rocks ejected into the stratosphere.

Some researchers have expressed their skeptism about the impact-derived interpretation for layer IIIA. For example, Schmitz (1985) consider that this Fe-rich layer represents the boundary between oxic (layers I/II) and anoxic (layer IIIB) formed during early diagenesis; the goethite/pyrite enrichment is due to pyrite precipitation/oxidation, microbial activities, and associated geochemical processes. Glasby and Kunzendorf (1996) consider that layer IIIA just represents the oxidation of pyrite spherules during oxic diagenesis.

Like at Højerup, at Agost, El Kef and Woodside Creek the biogenic calcite ooze of the latest Maastrichtian is also sharply capped by the redish “impact” layer (Schmitz 1988) that passes upward into the marl. The sections at Agost, El Kef and Woodside Creek are among the most continuous and complete marine sections for the KPB transitions, in which the “impact” layer provides an excellent record of the distal ejecta facies related to the KPB impact. In addition, the base of the El Kef section has been officially designated as the boundary global stratotype section and point (GSSP) for the KPB (Cowie et al. 1989). Previous sedimentary studies have also shown that the sections at Agost, El Kef (Ortega-Huertas et al. 2002) and Woodside Creek (Strong 1977) are deposited in marine shallow regions; depths of their deposition are presented in Fig. 3.

The “impact” layers are also found in other continuous and complete shallow-seawater KPB sections in Italy (e.g. at Gubbio and Petriccio), Tunisia (at Elles and Aïn Settara), in Spain (at Caravaca), in France (at Bidart), in Egypt (at Wadi Nukhul) and in New Zealand (at Flaxbourne River), Fig. 1. In addition to the remarkable Ir anomaly, the geochemical/mineralogical markers of the impact event, such as platinium group of elements (PGE), some siderophile metals (especially Ni and Cr), shocked quartz grains, microspherules, Ni-rich spinels are identified in the “impact” layers of the sections at Agost, El Kef and Woodside Creek. Most of these markers are compatible with the idea that these layers are directly related to the KPB impact. Of note, despite lower Ir enrichment in the Flaxbourne River KPB section (21 ppb) compared to Woodside Creek (54-100 ppb) the Flaxbourne section is considered to be more complete (Strong 2000). Stratigraphically the marine shallow “impact” layers correspond to the “impact” layers of the continental KPB sections of the Western Interior of North America described by Pollastro and Bohor (1993). Anomalous Ir, PGE, Ni, Cr, shocked quartz grains and microspherules also occur in these continental layers. The deep sections in the Atlantic and Pacific also show the “impact” layer (e.g. Schulte et al. 2006, and references therein).

## Paleocene-Eocene Thermal Maximum

Very recent study of marine sediments during a period of extreme global warming (about 55 Ma ago) known as the Paleocene-Eocene Thermal Maximum (PETM) demonstrated that the sediments deposited at the start of the PETM show an abrupt transition from carbonate-rich ooze to a clay-rich redish layer in which calcite shells are completely absent. Above this layer, the carbonates gradually begin to reappear about 40-50 kyr and another 40 kyr for the formation of the normal carbonate-rich ooze (Pagani et al. 2006). They estimate that at least about

4,000 Gt of carbon would be required to produce the abrupt change in paleoocean water chemistry during the PETM, including lowering of pH. The PETM period was marked by a rapid rise in greenhouse gases (mainly $CO_2$ and $CH_4$) that heated Earth by roughly 5°C, in less than 10 kyr. The climate warming that lasted about 170 kyr caused widespread changes including mass extinction in the world paleoocean water due to acidification.

## Global acidification of seawater

The KPB event has some general similarities with a catastrophic, transient PETM event. Very early some authors have suggested that an increased atmospheric $pCO_2$ could have taken place at the KPB (e.g. McLean 1978; Emiliani et al. 1981). Hsü and McKenzie (1985) estimated that at the KPB elevated $pCO_2$ levels (about 1140 ppmv) of the atmosphere was up to 3 times greater than modern atmospheric $pCO_2$ levels (about 380 ppmv). Recently, Beerling et al. (2002), using the stomatal density from plant fossils deposited just after the KPB suggested that atmospheric $pCO_2$ may have risen from 300-500 ppmv (the background levels) to at least 2,300 ppmv within 10 kyr of the KPB. Although, this value is considered unreliable (Wilf et al. 2003), other evidence indicates that a significant transitory $pCO_2$ increase of the atmosphere occurred in the earliest Danian (see, e.g. Hollis 2003), and also implicating impact into a limestone-rich target area (O'Keefe and Ahrens 1989; Pope et al. 1997).

The KPB atmosphere would be also additionally degraded by a lower quantity of other acid-forming gases $NO_x$ generated by the impactor passage through the atmosphere (Prinn and Fegley 1987) though chemical effects of $NO_x$ would be only local or regional in scale (Robertson et al. 2004).

A main decline in the calcareous plankton production in seawater biostratigraphically coincides with the KPB in addition to impact evidence at Højerup, Agost, El Kef and Woodside Creek and elsewhere (Fig.1), where the placement of the KPB is unambiguous. The decline probably initiated by various impact-related environmental stresses, including the global acidification of seawater (see below).

The microscopic examination across the Fish Clay shows that abiotic calcite precipitation is only minor contribution to total calcite production (Premović et al. 1993, 2000, 2007). This also shows that the transition from the calcareous

Maastrichtian biogenic ooze (layers I/II) to layer IIIA is extremely abrupt with only small zone of smectite particles below the otherwise sharp base of layer IIIA. Biogenic calcite is abundant in layers I/II (i.e., in the Maastrichtian bryozoan-rich ooze) but it is completely absent in layer IIIA. The concentration profile of biogenic calcite (as $CaCO_3$) across I-V layers is presented in Fig. 4. The concentrations of this calcite are high in layers I/II but decrease sharply in layer IIIA, reaching a minimum. Upward from layer IIIA, the biogenic calcite concentrations increase gradually in layers IIIB, IV and V, having much higher levels.

In theory, much of the impact-derived $CO_2$ in the atmosphere should have been absorbed by the seawater leading to a global decline in seawater pH. This acidification process would trigger massive destruction of calcareous plankton and dissolution of biogenic calcite. For example, Hansen (1990; 1991) suggested that, after the KPB, enhanced atmospheric $CO_2$ in the seawater at Stevns Klint could generate the biogenic calcite-deprived Fish Clay. I suggest, therefore, that the complete deficiency of biogenic calcite in layer IIIA is linked to a large increase in dissolution of biogenic calcite (mainly calcareous plankton shells) caused by the global acidification of seawater and a large decline in calcareous plankton production triggered by the KPB impact. The same is probably true for the "impact" layers at Agost, El Kef and Woodside Creek and for many other "impact" layers of the shallow coastal KPB sections, Fig. 1. The global acidification of seawater was probably created by an increase of $CO_2$ into the atmosphere triggered by the KPB impact. Moreover, according to O'Keefe and Ahrens (1989) dissolution of biogenic calcite from the seawater's euphotic zone could release additional quantities of $CO_2$. The pH of seawater in shallow coastal zones such as Højerup, Agost, El Kef and Woodside Creek (or elsewhere) would be additionally lowered with acid rains especially with their fluvial runoffs and springs from adjacent land areas. However, these rains would have been probably locally neutralized by alkaline rocks and soils (Robertson et al. 2004). Acid rains have been proposed partly to account for destruction of calcareous plankton in oceans at the KPB (e.g. Brett 1992).

The top (3-4 cm) of the Maastrichtian bryozoan ooze chalk (layer II) shows abundant evidence of post-depositional dissolution (Schmitz et al. 1992; 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 base of layer IIIB (sublayer IIIBp), Fig. 2. In my opinion, this dissolution is probably a result of the downward diffusion of the acidified pore seawater at the KPB.

The mass fish mortality at the KPB at Højerup received a considerable attention from Alvarez et al. (1984), inferring that the fish kill is related to the impact that produced the Ir anomaly. Microscopic examination of the Fish Clay show that calcium phosphates (mainly apatite) derived from fish debris (scales, bones and teeth) is abundant in layers I/II but completely absent in layers IIIA/IIIB. The biogenic apatite (as $Ca_3(PO_4)_2$) profile across layers I-V is also shown in Fig. 4. (Note that for the sake of clarity, the $Ca_3(PO_4)_2$ concentrations are multiplied with a factor 5). As biogenic calcite, biogenic apatite reaches a minimum in layer IIIA and it is probably created by the dissolution of this mineral as a result of the global acidification of seawater and the decrease in calcareous plankton production.

## Time scale of the global acidification

Wendler and Willems (2002) consider that unit III represents a fast, continuous sedimentation under decreasing energy. The problem is, however, that during the deposition of layer IIIA sedimentation have probably been extremely condensed by the dissolution of biogenic calcite by the acidified KPB seawater, 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 (Schmitz et al. 1992). 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.

Since the overlying layer IIIB contains a high biogenic calcite (derived mainly from the calcareous dynocysts), about 35 % of the whole rock (Fig. 4), it appears that the global acidification of seawater at the KPB was, in geological terms, a very brief event. Both de-acidification of seawater and a very fast recovery of an initially low biogenic calcite precipitation are indicated by an enormous (ca. $10^4$)

increase in the number of calcareous dynocysts, reaching its maximum just above layer IIIA (Hansen et al. 1986; Wendler and Willems 2002).

Kasting et al. (1986) estimated that the carbonate dissolution in the Fish Clay was brief and lasted approximately 20 yr. Wendler and Willems (2002) proposed that unit III represents 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.

Robin et al. (1991) proposed on the base of the stratigraphic distribution of the Ni-rich spinels in the red layer at El Kef that its deposition time did not exceed an upper limit of 100 yr. This suggestion is strengthened by $^3$He measurements which indicate this limit is of about 60 yr (Mukhopadhyay et al. 2001). On the basis of calculated average sedimentations and estimated age, Arenillas et al. (2002) suggested that the duration of the "impact" layer deposition at El Kef is probably <20 yr assuming the sedimentation rate in the "impact" layer is about 14.9 cm kyr$^{-1}$. Carbon isotope evidence of the Woodside Creek and Flaxbourne sections have found evidence which is consistent with extreme but a short-lived change in $pCO_2$ level in the seawater after the KPB event (Hollander et al. 1993). Considering that the "impact" layers at Højerup, Agost, El Kef and Woodside Creek are of a similar thickness it seems reasonable to suggest that the global acidification of seawater lasted for several decades. Just for comparison, calcareous plankton productivity had not completely recovered for more than 200 kyr after the KPB (Alegret et al. 2004).

The fast global de-acidification of seawater after the KPB impact event was probably due either to a buffering ability of seawater or to an "unknown" acid-neutralizing mechanism which existed in seawater at that time.

## Global warming

The impact-induced release of $CO_2$ would enhance atmospheric greenhouse warming and give a rise to worldwide increase in temperature at the KPB. Kasting et al. (1986) were first who modeled the possible global temperature increase from elevated atmospheric $pCO_2$ following an impact event. Experimental evidence indicates that significant transitory global warming occurred in the earliest Paleogene (Hsü and McKenzie 1985; Rampino and Volk 1988; Stott and Kennett 1990; Caldeira and Rampino, 1990; Wolfe 1990; Sarkar et al. 1992;

Hollander et al. 1993; Brinkhuis et al. 1998; Wilf et al. 2003; Hollis 2003) which might be related to post-impact greenhouse conditions. For example, the isotopic geochemical $\delta O^{18}$ and $\delta C^{13}$ studies of the Caravaca section and other two Spanish sections (Sopelana and Zumaya, Fig. 1.) show a warming of ca. 7-12°C at or just above the KPB (Rampino and Volk 1988). They suggested that the decline in global productivity of calcareous planktons may have also precipitated a severe warming. Caldeira and Rampino (1990), on the other hand, estimated a much lower increase (2°C). Wolfe (1990) estimated a much higher temperature increase (10°C) at the KPB based on botanical data. Sarkar et al. (1992) demonstrated a rapid cooling of 6°C just before the KPB followed by rapid warming (10°C) immediately after it.

Hollander et al. (1993) estimated that the warming of global climate would have persisted for approximately $10^3$ yr after the KPB event during the episode of mass extinction and reduced ocean plankton productivity. Hsü and McKenzie (1985) suggested rapid fluctuations in the overall warming development in the first 50 kyr after the KPB based on oxygen isotopic evidence.

## Time of the global acidification

Many researchers consider that an extraterrestrial impactor (ca. 10 km in diameter) formed the ca. 180 km crater at Chicxulub (Yucatan Peninsula, Mexico, Fig. 1) at KPB. Because the impact target could be a predominantly carbonate-rich marine sedimentary, a massive amount of $CO_2$ (accompanied with lesser $SO_2$) was instantaneously released into the atmosphere. Keller et al. (2003) proposed multiple impact scenario: the first impact (with no Ir anomaly) occurred at Chicxulub in the latest Maastrichtian (ca. 65.3 Ma) associated with major Deccan volcanism; the second impact event (with Ir anomaly) occurred at the KPB (65 Ma); and, the third one in the earliest Danian about 100 kyr after the KPB. There is, however, still a vigorous debate about the plausibility of this scenario. For example, Arenillas et al. (2006) carried out a high resolution planktic foraminiferal biostratigraphical analysis of the KPB sections at the Bochil and Guayal (Mexico, Fig. 1), and correlated to those obtained from the El Kef and Caravaca sections. They concluded that the thick Bochil and Guayal KPB clastic unit are chronostratigraphically equivalent to the El Kef and Caravaca "impact" layers. Their micropaleonological data confirmed that the KPB impact event and the Chicxulub impact event are the same one, contradicting the suggestions by Keller and others that the Chicxulub impact predated the KPB by about 300 kyr. On the other hand, latest multidisciplinary studies (stratigraphy, sedimentology, mineralogy and geochemistry) of the KPB section at Brazos (Texas, Fig. 1) carried out by Keller et al. (2007) strongly, however, support their earlier suggestion. Thus, if the multiple impact scenario is valid then the Ir anomaly at Højerup, Agost, El Kef, Woodside Creek and simultaneous global acidification of seawater are only consistent with the second impact of Keller and others occurring at the KPB.

Opponents of the KPB impact usually suggest that gigantic volcanic eruptions (e.g. Deccan Traps in India) could produce a similar increase in $pCO_2$. Liu and Schmitt (1996) in their search for the signatures of paleoocean changes recorded by the Ce anomalies in marine carbonate sediments, particularly focused on the KPB and epochs before and after the boundary. They did not observe that the pH changes of ocean deep water which could be unambiguously attributed to the immense volcanic increase of $CO_2$ from the Deccan Trap flows. Nevertheless, if the proposed global acidification of seawater at the KPB is real, it took place during an inactive Deccan Trap volcanic phase. In addition, the short duration (a few decades) of this acidification is incompatible with the Deccan Trap volcanism, which lasted over 500 kyr, but it is consistent with the (geologically speaking) instantaneous KPB impact event.

## Conclusions

The “impact” layers of the marine shallow sections at Højerup, Agost, El Kef and Woodside Creek evidently contain a record of the KPB impact and its aftermath which is still well-preserved. A low biogenic calcite content of these four layers probably is a consequence of dissolution caused by the global acidification of seawater and low productivity of calcareous planktons at the KPB. The acidification was generated by a rise of the concentrations of $CO_2$ in the atmosphere instigated by the impact. The global acidification of seawater was most likely a very brief event and lasted just several decades.

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**Fig. 1**. Paleolocations of the marine shallow KPB sections at 1) Højerup, 2) Agost, 3) El Kef, 4) Woodside Creek, 5) Gubbio, 6) Petriccio, 7) Elles, 8) Aïn Settara, 9) Caravaca, 10) Bidart, 11) Wadi Nukhul, 12) Flaxbourne River, 13) Sopelana, 14) Zumaya, 15) Chicxulub, 16) Bochil, 17) Guayal and 18) Brazos.

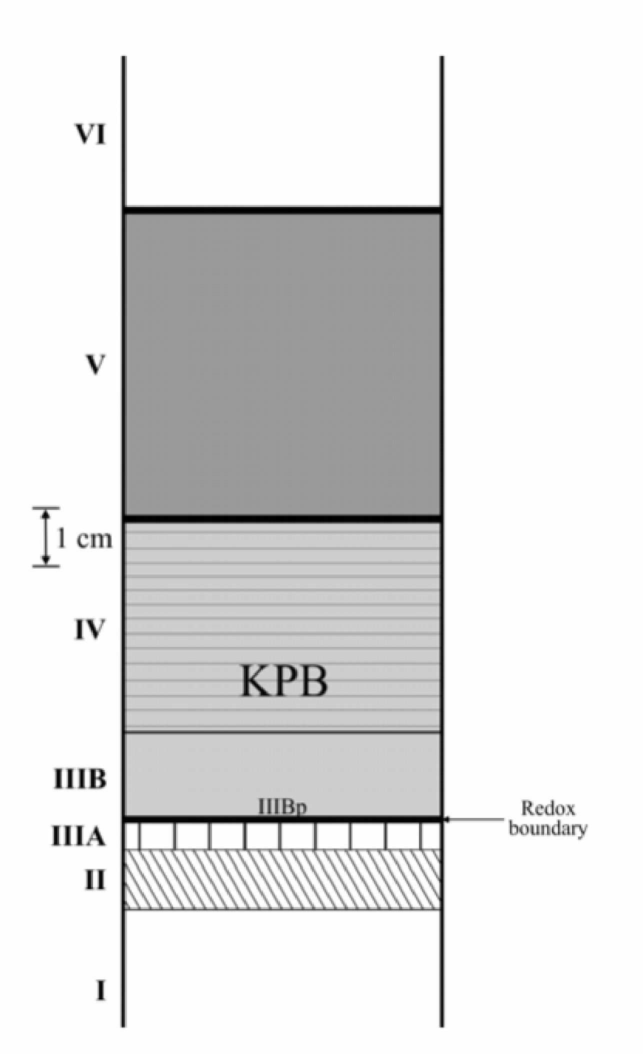

**Fig. 2.** Schematic illustration of the internal layering in a stratigraphic section of the Fish Clay.

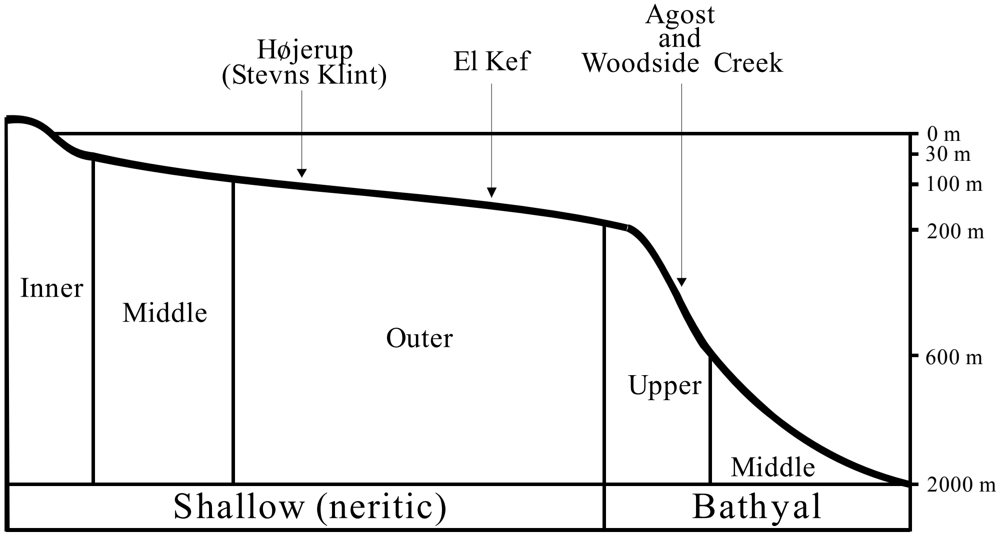

**Fig. 3.** Depth of deposition of the "impact" layers at Højerup, Agost, El Kef and Woodside Creek.

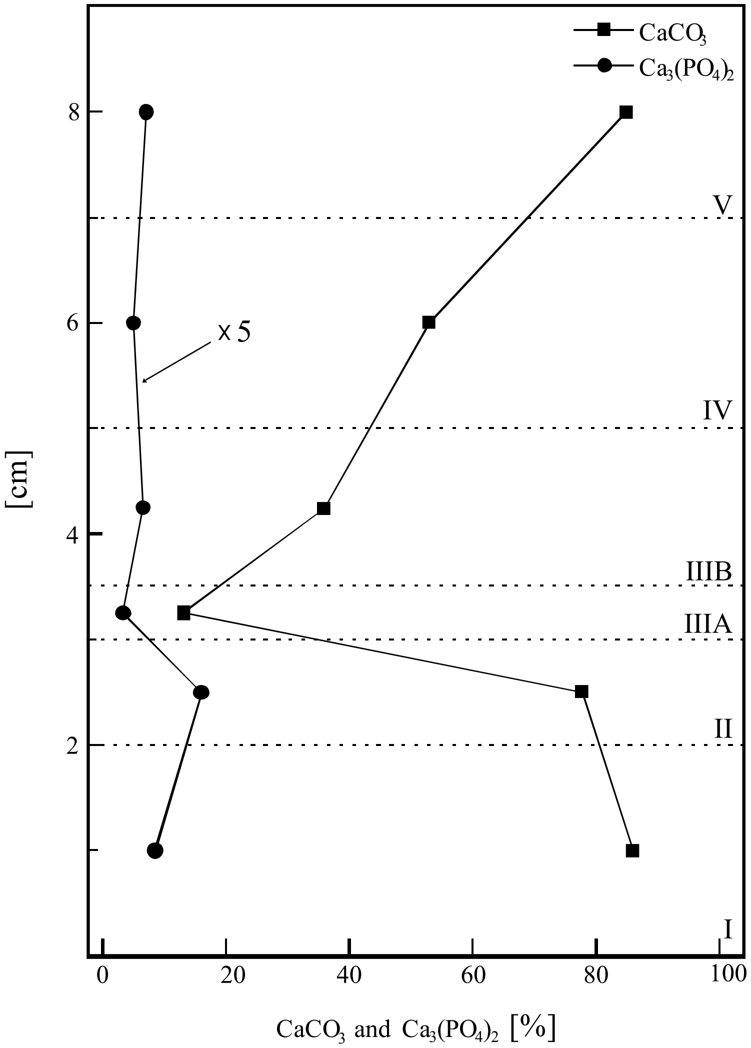

**Fig. 4.** Distribution of biogenic (as $CaCO_3$) and apatite [as $Ca_3(PO_4)_2$] [%] across layers I-V.