

# Iridium-bearing Carbon Black at the Cretaceous-Tertiary Boundary

HANS JØRGEN HANSEN, KAARE L. RASMUSSEN, RAJMOND GWOZDZ and H. KUNZENDORF

Hansen, H. J., Rasmussen, K. L., Gwozdz, R. & Kunzendorf, H.: Iridium-bearing carbon black at the Cretaceous-Tertiary boundary. *Bull. geol. Soc. Denmark*, vol. 36, pp. 305–314, Copenhagen, December, 31st, 1987. <https://doi.org/10.37570/bgsd-1988-36-11>

Carbon black has been observed to be the staining agent of the 3.5 m grey chalk underlying the Fish Clay in the Stevns Klint section. We show that carbon black extracted from the grey chalk and Fish Clay has a carbon isotope value significantly different both from the underlying Upper Cretaceous carbon black and from that of Upper Cretaceous charcoal. Carbon black stained bryozoan skeletons in the grey chalk are often seen to encrust on non-stained bryozoan skeletons and *vice versa* in the same stratigraphic level. This indicates that carbon black deposition took place in pulses during the ca. 50,000 year long grey chalk time interval. The carbon black-stained bryozoan skeletons are found to be rich in Ir as well as in other elements, and we demonstrate that the Ir-carrying phase is not a silicate, but rather the carbon black itself. A volcanic origin is suggested for the Ir-bearing carbon black.

*H. J. Hansen and R. Gwozdz, Geological Central Institute, University of Copenhagen, Øster Voldgade 10, DK-1350, Copenhagen, Denmark. K. L. Rasmussen, Geophysical Institute, Haraldsgade 6, DK-2200, Copenhagen, Denmark.  
H. Kunzendorf, Research Establishment Risø, DK-4000, Roskilde, Denmark. June 6th, 1987.*

## Introduction

Carbon black has been observed frequently in the sedimentary column since Devonian time, and is generally interpreted as soot, originating from forest fires or the burning of grassland (Smith et al., 1973, Herring, 1985, Goldberg, 1985). According to Herring (1985) the deposition rate varies rather smoothly between ca. 5  $\mu\text{gC}/\text{cm}^2/\text{y}$  today and ca. 0.001  $\mu\text{gC}/\text{cm}^2/\text{y}$  at the beginning of Tertiary time.

Lately Wolbach et al. (1985) reported large occurrences of carbon black in the boundary clay of three Cretaceous-Tertiary sections. From their measurements Wolbach et al. (1985) estimated a global average carbon black deposition of 21,000  $\mu\text{gC}/\text{cm}^2$  in Fish Clay time, an exceptionally large figure. Wolbach et al. (1985) suggested that a proposed impactor at the end of Cretaceous time (Alvarez et al., 1980, Kyte et al., 1980, Ganapathy, 1980) was responsible for this excessive carbon black deposition by having ignited a world-wide forest fire.

McLean (1985a, 1985b) estimated (following Leavitt, 1982) a present day (predominantly volcanic) background  $\text{CO}_2$  release of 4.1  $10^{12}$  moles/y, corresponding to 9.6  $\mu\text{gC}/\text{cm}^2/\text{y}$ . This is

in excellent agreement with Herring (1985). McLean (1985a, 1985b) furthermore estimated a total  $\text{CO}_2$  release from the Deccan Traps, India, of 5  $10^{17}$  moles, corresponding to some 1,180,000  $\mu\text{gC}/\text{cm}^2$ . The time over which this excess carbon was released was estimated by Besse et al. (1986) to have been less than one My.

In the present work we present evidence for the occurrence of an anomalous carbon black deposition starting already several meters below the Fish Clay in Stevns Klint, and continuing through Fish Clay time. We furthermore present evidence that this anomalous carbon black is Ir-bearing.

## Observations and experimental procedures

Carbon black as well as charcoal in the transitional deposits between the Cretaceous and Tertiary beds in Stevns Klint, Denmark is found to be the agent that stains part of the boundary clay, the Fish Clay, black. We also find carbon black in higher amounts earlier in the stratigraphical sequence at Stevns Klint. The deposition of chalk which is stained by carbon black, starts 3.5 me-

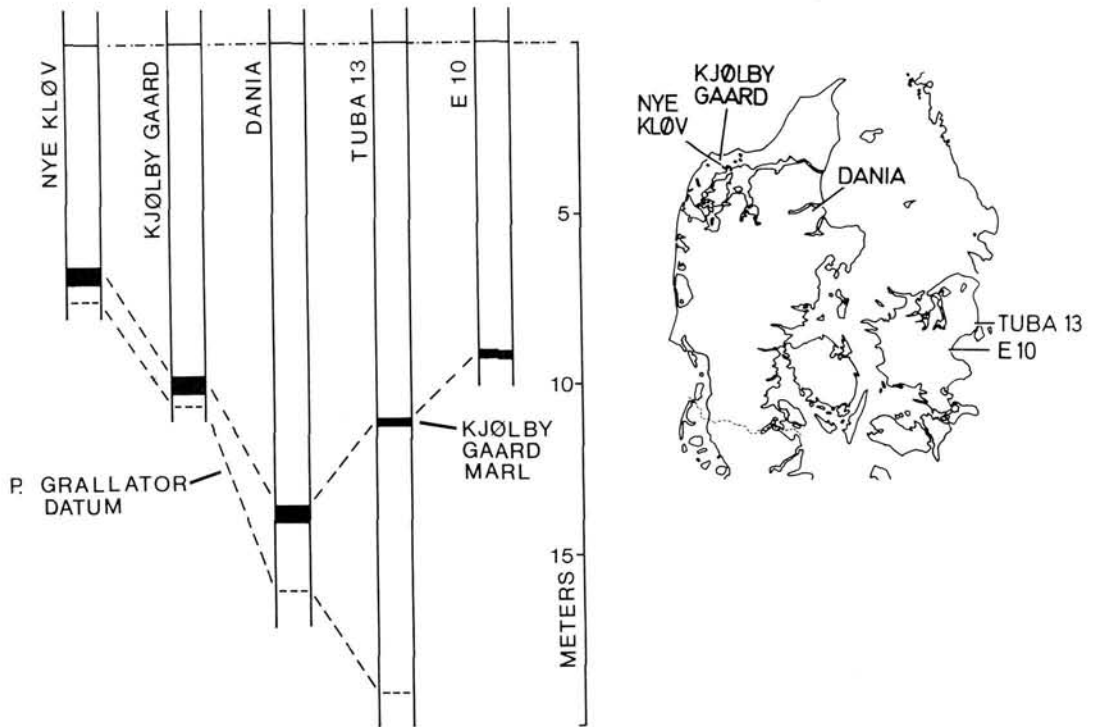


Fig. 1. Thickness of the sedimentary sequence between the Fish Clay and the Kjølbj Gaard Marl, which is ubiquitous throughout the Danish Basin. The localities are shown in order of occurrence from west to east. This relationship is used to estimate an accumulation rate at Stevns Klint, which is situated ca. 30 km south of the drill site of E 10. If we accept a Maastrichtian sedimentation rate of 10 cm/1000 y, and assume that this applies the locality with the thickest interval, namely Dania, we estimate an East Denmark sedimentation rate of 10 m/14 m times 10 cm/1000 y equal 7 cm/1000 y. Also shown is the *Palynodinium grallator* first occurrence in some of the sections.

ters below the onset of the Fish Clay sedimentation. This is seen in the section as the beginning of the grey chalk, coincident with the hardground (Ekdale and Bromley, 1984). The time occupied by this formation is, of course, difficult to estimate precisely. We will try to give a rough estimate.

As an attempt to establish a regional deposition rate we have compared the sediment thickness between the level of the Kjølbj Gaard Marl and the Fish Clay at five Danish localities, spread over some 270 km, as is shown in fig. 1. The maximum Maastrichtian sedimentation rate in Denmark can be estimated as 700 meters divided by 7 My, or 10 cm/1000 y (Stenestad, 1972, Odin, 1982). If we conservatively assume that this rate prevailed at the locality with the highest accumulation rate in fig. 1, namely the 14 meters at the "Dania" quarry, we estimate a sedimentation rate for the East Denmark sections (TUBA 13 and E 10) of ca. 7 cm/1000 y (i.e. 10 m/14 m times

10 cm/1000 y). Accepting this average estimate of the sedimentation rate, we calculate that the 3.5 meters of grey chalk at Stevns Klint represents ca. 50,000 years of sedimentation.

During detailed microscopical examination of



Fig. 2. Collection of carbon black-stained bryozoa from the upper part of the grey chalk at Stevns Klint. Sampling level 4-7 cm below the Fish Clay.

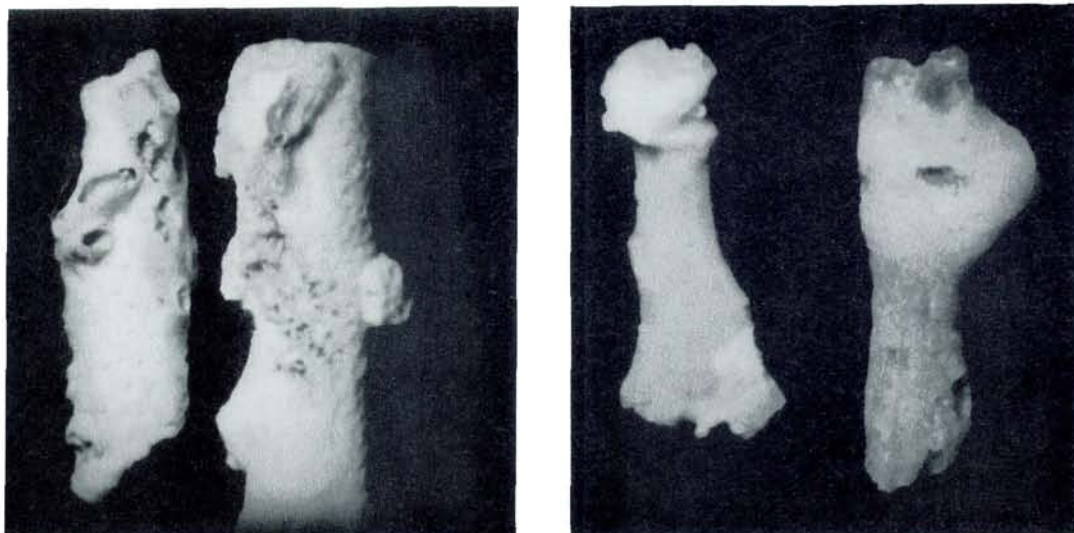


Fig. 3. Encrusting carbon black-stained bryozoa on non-stained bryozoa and *vice versa*.

samples from the grey chalk we found numerous skeletons of carbonate fossils, predominantly bryozoa, that were stained dark grey to almost black by carbon black (fig. 2). We also found a close relationship between black encrusting bryozoa growing directly on white bryozoa, and *vice versa* (fig. 3). Many places in the 3.5 meters of grey chalk the stained and non-stained bryozoa were found right next to each other in the same stratigraphical level.

The find of stained and non-stained fossils allowed us to design an experiment that permits studying the chemical composition of the carbon black without prior chemical treatment. By manual preparation two samples were collected, one of stained bryozoa and one of non-stained white bryozoa. Both samples, each consisting of about ten fragments of bryozoan skeletons, were taken from the same stratigraphical level namely 4–7 cm below the Fish Clay at Stevns Klint. The two samples were analyzed by instrumental neutron activation analysis. The samples were irradiated for 24 hours in a thermal neutron flux of  $3 \cdot 10^{13}$  n/cm<sup>2</sup>/sec, and later counted for gamma rays. The elemental abundances determined are listed in table 1.

We have furthermore extracted pure carbon black samples of milligram size from the white chalk, the grey chalk, and the Fish Clay in order to determine carbon isotopes. The amount of

sediment needed was ca. 4.5 kg of white chalk, 1.0 kg of grey chalk and 0.1 kg of Fish Clay. The samples were dissolved in 30% HCl. The residues were boiled with 30% HCl in order to dissolve

Table 1. Elemental abundances as determined by instrumental neutron activation analysis. Each sample consists of ca. 10 bryozoan skeletons. Both samples have been picked from the same stratigraphic level, 4–7 cm below the bottom of the Fish Clay at Stevns Klint, Denmark.

	Black Bryozoa µg/g	White Bryozoa µg/g
Na	170.	150.
K	150.	130.
Ca	368000.	340000.
Sc	2.22	2.05
Cr	2.9	2.2
Fe	540.	470.
Co	29.	7.8
Zn	25.	13.
As	3.6	1.1
Br	1.5	1.1
Sr	760.	640.
Sb	0.3	0.086
La	5.0	4.7
Ce	3.7	3.4
Nd	9.0	8.5
Sm	0.68	0.68
Eu	0.15	0.14
Yb	0.56	0.51
Lu	0.083	0.077
W	0.12	0.11
Ir	0.00106	0.00054
Au	0.0037	0.0028
Th	0.15	0.11
U	1.3	1.1

Table 2. Delta-C<sup>13</sup> PDB isotopic ratios of carbon black extracted from Stevns Klint, Denmark.

Carbon black from Stevns Klint, Denmark	
	delta 13-C PDB
Fish Clay	-27.35 ± 0.02
Grey chalk	-27.81 ± 0.05
White chalk	-26.62 ± 0.05

dolomite and Fe<sup>+++</sup> containing minerals. The residues were then treated with hot 40% HF followed by hot 30% HCl. In the white chalk and grey chalk samples the residues consisted, at this step in the process, of carbon black and dinocysts. The dinocysts were separated from the carbon black by filtering through a 10 micron nylon filter. The filtrate was checked under the microscope using transmitted light, 1000 times enlargement and phase contrast illumination to ensure the purity of the carbon black concentrate. In the case of the Fish Clay sample, the residuum consisted of carbon black, dinocysts, charcoal and kerogen (probably remnants of the oil-containing green alga *Botryococcus*). The separation of carbon black from the dinocysts and most of the recognizable charcoal was effectively made by the filtration procedure through 10 micron mesh. The smaller kerogen pieces were, however, numerous in the filtered residuum. These kerogen pieces were removed by adding small amounts of H<sub>2</sub>O<sub>2</sub> to the residuum. As could be judged from the light microscopy, the kerogen was more readily oxidized than the carbon black particles. The carbon black concentrates were analyzed for carbon isotopes by mass spectroscopy and the results are shown in table 2. The value obtained from the Fish Clay sample may be too heavy due to possible occurrence of submicroscopic particles of kerogen or charcoal, which have escaped the preparation procedure.

We have also determined carbon isotopic values for an Upper Cretaceous charcoal sample extracted from the Stevns Klint Fish Clay. The charcoal was separated from the remaining components of the acid residue by application of the technique described by Hansen and Gudmundsson (1979). As this technique involves soaking in ethanol, the charcoal residuum was heated under vacuum to 200°C for 20 minutes before mass spectroscopic analysis.

Upper Cretaceous peat coal from the Rognac Limestone, France, was also analyzed for carbon

isotopes after extraction of the humic fraction by dimethylchloride with 10% methanol. Upper Maastrichtian coal from Nûgssuaq, West Greenland, and charcoal from Biarritz, France, were also analyzed. The results are shown in table 3.

## Discussion

### Black bryozoa and carbon isotopes

The fact that stained bryozoa and non-stained bryozoa occur together and actually grow on each other in the same stratigraphic level indicates that the inflow of carbon black to the basin took place in pulses. That a pulsed carbon black deposition has not led to a laminated deposit is probably due to a strong activity of burrowing organisms, the traces of which are also ubiquitous and well preserved in the Stevns Klint section (Ekdale and Bromley 1984).

It is apparent from figure 4 that the carbon black from the grey chalk and the carbon black from the Fish Clay have almost identical delta-C<sup>13</sup> values, while the carbon black extracted from the underlying white chalk has a significantly lower delta-C<sup>13</sup> value, differing by ca. one permille. This suggests to us, that the carbon black of the grey chalk and the Fish Clay are derived from the same source, whereas that of the white chalk is in the range of Upper Cretaceous coal values. The Upper Cretaceous background probably consists of forest fire-derived carbon black and charcoal, which is reflected in the charcoal delta-C<sup>13</sup> values of table 3. Other workers have found comparable Upper Cretaceous coal values. Schimmelmann and DeNiro (1984) found delta-C<sup>13</sup> values between -25.8 and -26.6 permille in York Canyon, New Mexico. The results in Tables 2 and 3 are not consistent with a hypothesis that the carbon black in the Fish Clay should be derived from forest fires, because the delta-C<sup>13</sup> values of the carbon black extracted from the grey chalk and

Table 3. Delta-C<sup>13</sup> PDB isotopic ratios of charcoal extracted from the Upper Maastrichtian section at Stevns Klint, Denmark; Biarritz, France (average of 5 samples); Rognac, France; Nûgssuaq, Greenland.

Charcoal from:	delta 13-C PDB
Stevns Klint, Denmark :	-23.22
Nûgssuaq, Greenland :	-24.92
Rognac, France :	-24.59
Biarritz, France :	-23.58

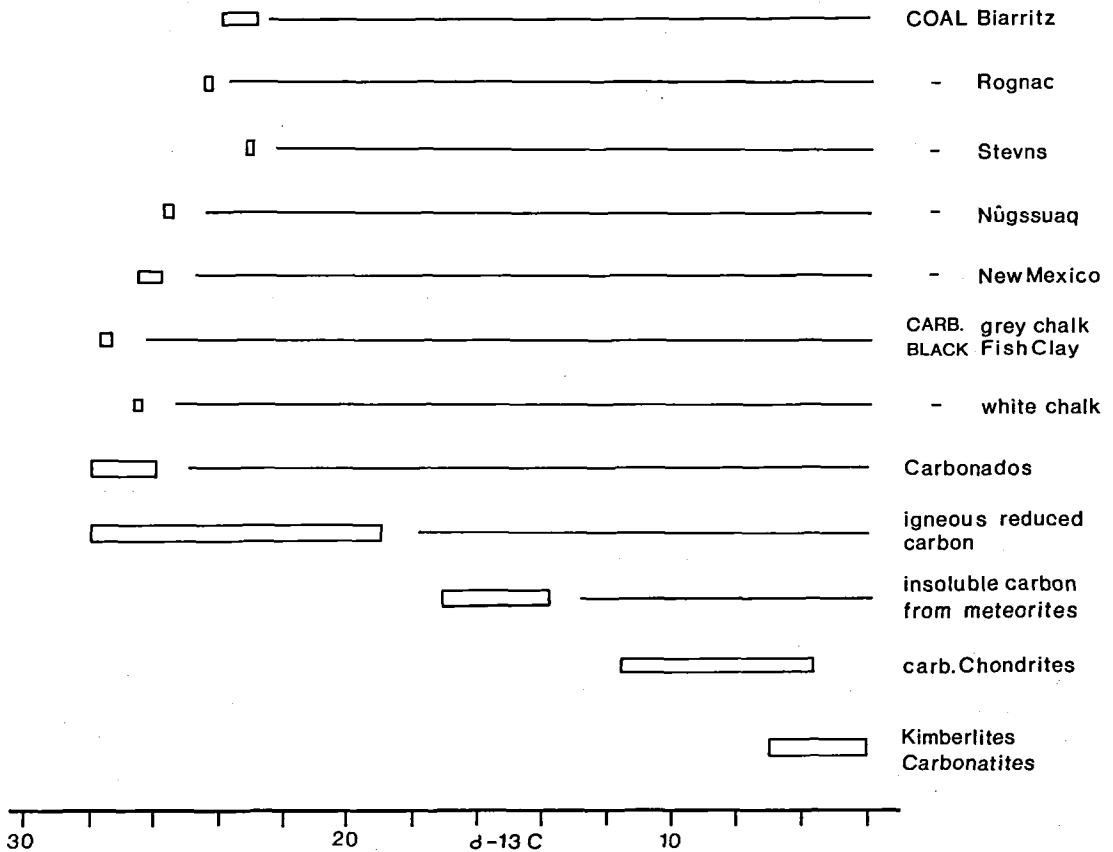


Fig. 4. Delta 13-C PDB of various materials.

Fish Clay (table 2) are 3-4 permille different from the usual Upper Cretaceous charcoal values (table 3).

Both our delta-C<sup>13</sup> measurements and our observations of the inter-related stained and non-stained bryozoan skeletons contradicts the hypothesis suggested by Wolbach et al. (1985), that the origin of the carbon black should be a giant forest fire started by an impacting bolide.

### Ir-bearing Carbon black

In figure 5 we have shown the ratio of elemental abundances between stained bryozoa and non-stained bryozoa as given in table 1. It is evident that the stained bryozoan skeletons are enriched in Ir, Au, Co, Cr, Zn, As, Sb, Br and Th relative to the non-stained ones.

It is an obvious possibility that the enriched elements in the stained bryozoa could be due to a higher content of some hypothetical silicate phase, i.e. that the stained bryozoa incorporated more Ir-bearing silicates than did the white bryozoa. This is, however, not the case, as can be seen when we normalize the abundances of table 1 by a typical lithophile element such as Sc (fig. 6). It is obvious from fig. 6 that the Sc-normalized abundances of Ir, Au, Co, Cr, As, Sb, Br and Th is higher in stained bryozoa than in non-stained bryozoa, and we therefore conclude that the carrier phase for Ir and the other enriched elements is not a silicate.

The fact that As and Sb is enriched in the stained bryozoa could suggest that a sulphide phase (FeS<sub>2</sub>) or strongly adsorbing minerals with Fe<sup>+++</sup> was present in the skeletons. To further investigate this possibility, we dissolved the stained bryozoa, after they had been irradiated

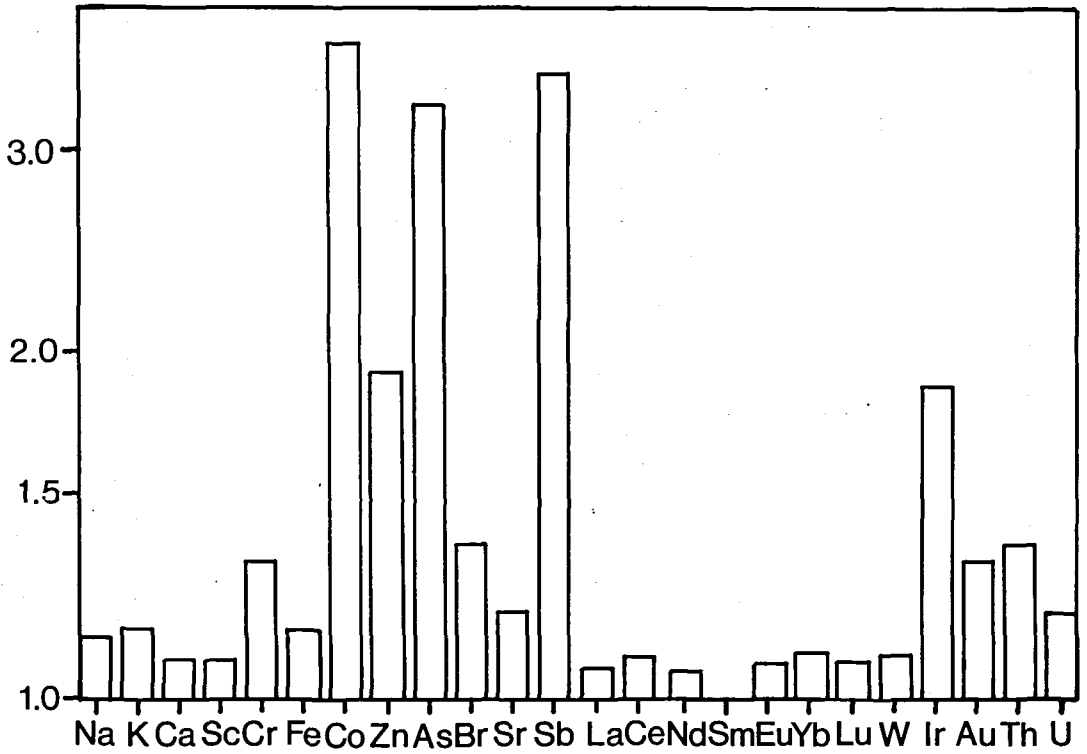


Fig. 5. Elemental abundance ratios between the stained and the non-stained bryozoa. The data shown are the elemental abundances given in table 1.

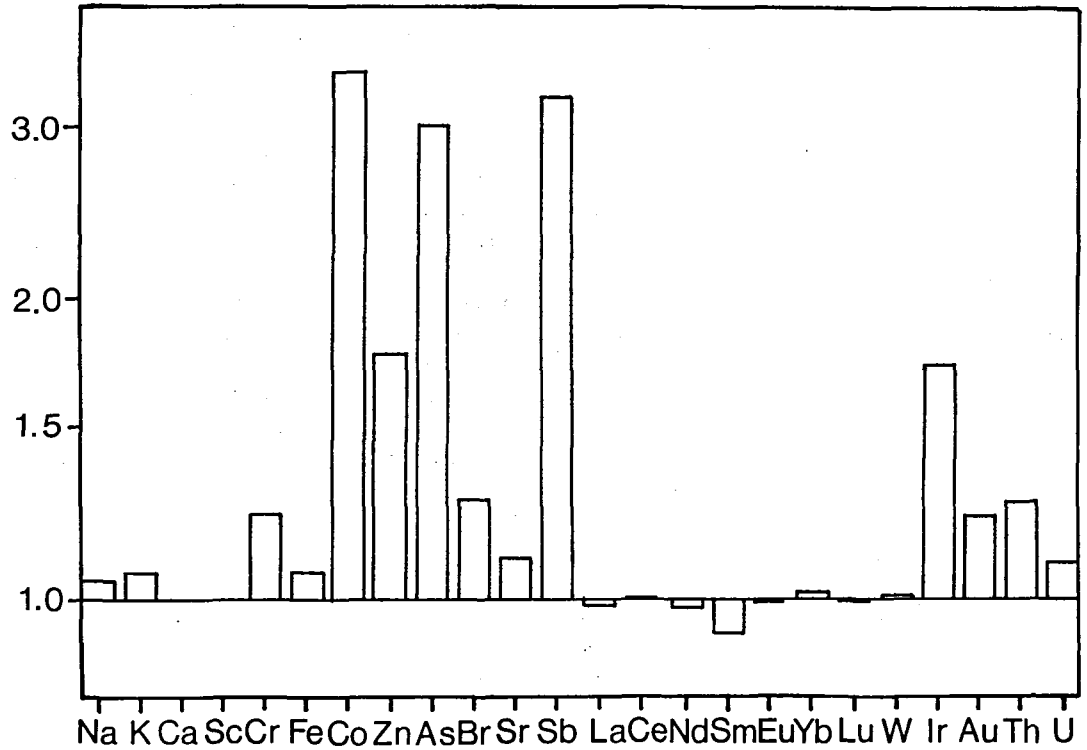


Fig. 6. Scandium-normalized elemental abundance ratios between stained and non-stained bryozoa. Data from table 1.

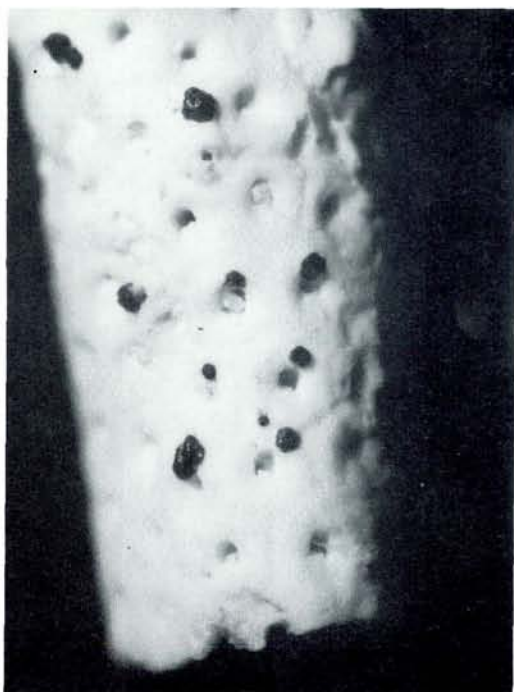


Fig. 7. Bryozoan skeleton with micro-manganese nodules on the surface. Sampling level 1-3 cm below the Fish Clay at Stevns Klint.

and measured by INAA, in 4% acetic acid. After cleaning in 4 baths of 4% acetic acid, the residue of the stained bryozoa were pipetted onto a small platinum disc. The residuum was studied in a scanning electron microscope equipped with an energy dispersive X-ray analyzer.

We found that the most common particles were composed of Fe and very low contents of Si and Cl. The color of these particles as seen under the light microscope is bright red. We interpret this as indicative of a mineral of the goethite/chamosite group. We did not find any sulfides in the residue. In addition to the red grains we found one black rounded particle with a diameter of about 100 microns. The energy dispersive X-ray analyzer detected more than ca. 0.5% wt of Mg, Al, Si, P, Cl, K, Ca, Ti, Mn, Co, Ni and Zn in this nodule. The analysis was not quantified, but the composition is dominated by Mn with smaller amounts of Ca, Co, Ni and Zn. Such manganese micro-nodules are ubiquitous on the surface of bryozoan skeletons in the upper part of the grey chalk (fig. 7). Manganese nodules are known to be rich in various trace elements (Haynes et al.

1985), and the enrichment of Co, Zn, As, Br, Sb and Th in our sample of stained bryozoa can comfortably be explained by a higher content of manganese micro-nodules. The only elements significantly enriched in the stained bryozoa that cannot be accounted for by manganese micro-nodules are Ir, Au and Cr (Haynes et al. 1985).

The abundance pattern of the rare earth elements in the bryozoa are quite similar when normalized to the rare earth elements abundances in either clays (North American Shale, Haskin et al. 1968) or manganese nodules (Fleet 1984, Haynes et al. 1985), so unfortunately no constraints can be placed on the carrying phase for these elements. A negative Ce anomaly is observed as is expected from creatures living in sea water.

The presence of the microscopic manganese nodules, clearly indicate that the conditions on the sea floor at Stevns Klint in grey chalk time were oxidizing. Since we have shown the Ir and Au neither to be situated in a silicate phase nor in manganese micro-nodules, the obvious possibility left is that the Ir sits directly on the carbon black itself. Nothing in our observations is incongruent with this hypothesis.

It should be noted that the carbon black content of the grey chalk is indeed very low and often only causes a medium grey coloration of the bryozoa. It is therefore surprising, that this, obviously small fraction of the skeleton is sufficient to cause an Ir enrichment of a factor of almost two for the "whole rock" bryozoan samples. In order to estimate the amount of carbon black present in the stained bryozoa the following experiment was made. A small sample of carbon black-stained bryozoa were dissolved in 4% acetic acid. The residue was divided into a magnetic and a non-magnetic fraction in a special container made of a 2 cm diameter glass tube that was glued to a cover glass by epoxy glue. Underneath the cover glass a small powerful magnet was placed and the residuum was poured into the container. The sample was stirred by a pipette and the part of the sample that was not kept in the bottom-part close to the magnet was pipetted off and is in the following called the non-magnetic fraction. The non-magnetic and the magnetic residues were pipetted onto pieces of filter paper that were earlier dried for 24 hours under vacuum and weighted on a microgram balance in a dry atmosphere. The papers were allowed to dry lying on

top of disposable nylon surgery brushes so that it would remain with a minimum contact with the substrate ("a fakir mount"). A non-magnetic fraction was studied in the scanning electron microscope and found to be dominated by organic matrices from the dissolved bryozoa. Thus, the measured weight of the carbon black on the filter paper (which prior to weighing was dried in the same way as the paper itself) also includes the weight of the organic matrices.

The measured weight fraction of the non-magnetic residue was 0.16% of the original sample weight. The weight fraction of the magnetic residue was 0.82% of the original sample weight. Assuming an original bulk Ir concentration of 1 ng/g in the stained bryozoa, and taking into account the above reservations, we arrive at a lower limit for the Ir concentration on the carbon black itself of 625 ng/g. We are aware of the possibility, that some unknown Ir carrying component might have become dissolved by the 4% acetic acid and the Ir been transferred to the carbon black, though we find it less likely in view of the very weak acid used in the experiment. Our analysis of isolated carbon black from the Fish Clay which was processed using 30% HCl and 40% HF yielded an Ir abundance of 3,600 ng/g.

We suspect that the Ir adsorbed onto the carbon black could account for much of the Ir present in the grey chalk (< 100 pg/g, according to Kastner et al., 1984), but we consider it unlikely that the Ir carried by carbon black can account for all the Ir in the Fish Clay (the highest Ir abundance reported is 185 ng/g, Hansen et al. 1986). Some additional carrier almost certainly must be present in the boundary clay.

The world-wide occurrence of carbon black at the Cretaceous-Tertiary boundary has been suggested to be the result of forest fires of global extent ignited by a supposed bolide impact (Wolbach et al., 1985). This suggestion is in poor agreement with the occurrence on Stevns Klint of raised carbon black content in the chalk already 3.5 meters below the boundary clay. The signature of the bolide, namely the Ir anomaly, occurs ca. 50,000 years later than the onset of high carbon black deposition.

We believe that the occurrence of carbon black already 3.5 meters below the Fish Clay at Stevns Klint is associated with the fact, that, at the time of deposition, Stevns Klint was situated very near

to the coast. In South Sweden, a series of tectonically controlled blocks were dry land and could, accordingly, collect much of the airborne material being deposited. The grounded airborne material was brought into the basin and deposited close to the coast. This, in connection with the extreme white color of the white chalk itself, makes our observations of the coloration of the grey chalk possible. This scenario is further attested to by the very high Ir concentrations registered in the Stevns Klint Fish Clay as compared to other boundary sections. Accepting a peak Ir abundance of 185 ng/g (Hansen et al. 1986) we calculate an enrichment factor of ca. 45 times over the world average of ca. 4 ng/g. We predict that the early deposited carbon black is present at other boundary sections too, but probably not in the same concentrations as at Stevns Klint unless these sections are also coast near. It should be noted that it will be harder to see the carbon black in a sediment of less white color than that of Stevns Klint.

As to the origin of the carbon black, the carbon isotope values of table 2 indicate that the carbon black is unrelated to meteoritic material (Hoefs, 1980). Instead we find it consistent with an Earthly origin from reduced carbon or carbonados. Carbonados are amorphous lumps of pure carbon associated with kimberlites and diamonds (Hoefs, 1980).

Carbon black has been found as internal coating in vesicles of basaltic deep sea glasses along with CO<sub>2</sub> gas. This has led to the suggestion that the gas at the time of submarine extrusion was CO, which reacted inside the vesicle to form free carbon and CO<sub>2</sub> (Mathez and Delaney, 1981). Crystals of graphite has also been found in close proximity of submarine volcanic vents (Jedwab and Boulègue, 1984). This suggests that a conversion process turning CO into CO<sub>2</sub> and C (graphite) could take place during the eruption.

In view of our present findings, we suggest that the Ir-bearing, isotopically anomalous, carbon black in the grey chalk and the Fish Clay of Stevns Klint was generated during subaerial volcanic eruptions, where exotic volcanic volatiles such as Ir-fluoride (Zoller et al., 1983) were immediately adsorbed to carbon black produced during the event by a mechanism similar to the CO-conversion mechanism (Mathez and Delaney, 1981, Jedwab and Boulègue, 1984).



## Summary

We have extracted carbon black from the grey chalk and Fish Clay at Stevns Klint, Denmark, and shown it to be isotopically distinct from carbon black extracted from the underlying white chalk, the difference being ca. one permille. In the grey chalk, which initiates three and a half meters, or ca. 50,000 years, before the Fish Clay, we have observed numerous occurrences of white bryozoa interconnected with carbon black-stained bryozoa in the same stratigraphic level. The carbon isotopes of the carbon black extracted from the grey chalk is found to be distinctly (3–4 permille) different from Upper Cretaceous charcoal values.

These observations are interpreted as reflecting a pulsed or multistage deposition of carbon black lasting for ca. 50,000 years.

We find our interpretation in contradiction of a bolide ignited world-wide forest fire scenario as the origin of the carbon black at the Cretaceous-Tertiary boundary.

We find that the carbon black-stained bryozoa have a higher Ir-content than the white bryozoa. On the basis of Sc-normalized abundances, we concluded that the Ir-carrying phase is not a silicate, but rather the carbon black itself.

As to the origin of this Ir-rich carbon black we propose a subaerial volcanic eruption mechanism, in which carbon black is formed in large amounts, followed by immediate adsorption of Ir-fluorides onto the carbon black.

**Acknowledgements.** We wish to thank Birte Warming for technical assistance. The work was supported by the Danish National Science Research Council.

Since the senior author of this article is also the editor of the Bulletin of the Geological Society of Denmark, the chairman of the Society has acted as editor of the present paper.

## Dansk sammendrag

Vi har observeret, at sod er det, der giver farve til gråkridtet på Stevns Klint. Sodfarvede bryozoa er i gråkridtet fundet voksende på ufarvede bryozoa og omvendt. Dette fortolker vi som tegn på, at sodaflejregningen foregik i pulser (i modsætning til et konstant nedfald). Længden af tidsrummet for gråkridtets dannelse anslår vi til 50,000 år, og dette kombineret med den pulserende aflejring, tillader os, at afvise den globale skovbrands-hypotese, som er foreslået af Wohlbach et al. 1985. Vi har analyseret farvede og ufarvede bryozoa ved hjælp af instrumentel neutronaktivitetsanalyse og fundet, at de farvede bryozoa er berigede i Ir, Au, Cr, Co, Zn, As, Sb og Th. Vi har observeret hyppig forekomst af mikroskopiske mangan noder

i gråkridtet, og disse kan forklare berigelsen af Co, As, Sb, Zn og Th. Berigelsen af Ir og Au fortolker vi som stammende fra selve soden. Vi forslår, at soden er af vulkansk oprindelse, og at ædelmetallerne ved det vulkanske udbrud har udfældet sig direkte på soden.

## References

- Alvarez L. W., Alvarez W., Asaro, F. and Michel, H. V. 1980: Extraterrestrial cause for the Cretaceous-Tertiary extinction. *Science* 208, 1095–1108.
- Besse, J., Buffetaut, E., Cappetta, H., Courtillot, V., Jaeger, J.-J., Montigny, R., Rana, R. S., Sahni, A., Vandamme, D. and Vianey-Liaud, M. 1986: The Deccan Trapps (India) and Cretaceous-Tertiary boundary events. *Lecture notes in Earth Sciences* 8, 365–370.
- Ekdale, A. A. and Bromley, R. G. 1984: Sedimentology and ichnology of the Cretaceous-Tertiary boundary in Denmark: Implications for the causes of the terminal Cretaceous extinction. *J. Sed. Pet.* 54, 681–703.
- Fleet, A. J. 1984: Aqueous and sedimentary geochemistry of rare earth elements. In *Rare Earth Elements Geochemistry* (Ed. P. Henderson). Elsevier, Amsterdam. 343–373.
- Ganapathy, R. 1980: A major meteorite impact on the earth 65 million years ago: evidence from the Cretaceous-Tertiary boundary clay. *Science* 209, 921–923.
- Goldberg, E. D. 1985: *Black Carbon in the Environment*. John Wiley, New York. 198 pp.
- Hansen, H. J., Gwozdz R., Hansen J. M., Bromley, R. G. and Rasmussen, K. L. 1986: The diachronous CT plankton extinction in the danish basin. *Lecture notes in Earth Sciences* 8, 381–484.
- Hansen, J. M. and Gudmundsson, L. 1979: A method for separating acid-insoluble microfossils from organic debris. *Micropaleontology* 25, 113–117.
- Haskin, L. A., Haskin, M. A., Frey, F. A. and Wildeman, T. R. 1968: Relative and absolute terrestrial abundances of rare earths. In *Origin and distribution of the elements* (Ed. L. H. Ahrens). Pergamon, Oxford. 889–912.
- Haynes, B. W., Law, S. L., Barron, D. C., Kramer, G. W., Maeda, R. and Magyar M. J. 1985: Pacific manganese nodules: Characterization and processing. *Bulletin 679 U.S. Department of the Interior, Bureau of Mines*. 44 pp.
- Herring, J. R. 1985: Charcoal fluxes into sediments of the North Pacific ocean: the Cenozoic record of burning. In *The Carbon cycle and atmospheric CO<sub>2</sub>: Natural variation Archean to present*. (Ed. E. T. Sundquist and W. Broecker), American Geophysical Union: Geophysical Monograph Series 32, 419–442.
- Hoefs, J. 1980: *Stable Isotope Geochemistry*, 2. edition, Springer Verlag, 208 pp.
- Jedwab, J. and Boulègue, J. 1984: Graphite crystals in hydrothermal vents. *Nature* 310, 41–43.
- Kastner, M., Asaro, F., Michel, H. V., Alvarez, W. and Alvarez, L. W. 1984: The precursor of the Cretaceous-Tertiary boundary clays at Stevns Klint, Denmark, and DSDP hole 465A. *Science* 226, 137–143.
- Kyte, F. T., Zhou, Z. and Wasson, J. T. 1980: Siderophile-enriched sediments from the Cretaceous-Tertiary boundary. *Nature* 288, 651–656.
- Leavitt, S. W. 1982: Annual volcanic carbon dioxide emission: an estimate from eruption chronologies. *Environ. Geol.* 4, 15–21.
- Mathez, E. A. and Delaney, J. R. 1981: The nature and distribution of carbon in submarine basalts and peridotite nodules. *Earth Planet. Sci. Lett.* 56, 217–232.
- McLean, D. M. 1985a: Mantle degassing induced dead ocean in the Cretaceous-Tertiary transition. In *The Carbon cycle*

- and atmospheric CO<sub>2</sub>: Natural variation Archean to present. (Ed. E. T. Sundquist and W. Broecker), American Geophysical Union: Geophysical Monograph Series 32, 493-503.
- McLean, D. M. 1985b: Deccan Traps mantle degassing in the terminal Cretaceous marine extinctions. *Cretaceous Research* 6, 235-259.
- Odin, G. S. 1982: The Phanerozoic time scale revisited. *Episodes* 3, 3-9.
- Schimmelmann, A. and DeNiro, M. J. 1984: Elemental and stable isotope variation of organic matter from a terrestrial sequence containing the Cretaceous/Tertiary boundary at York Canyon, New Mexico. *Earth Planet. Sci. Lett.* 68, 392-398.
- Smith, D. M., Griffin, J. J. and Goldberg, E. D. 1973: Elemental carbon in marine sediments: a baseline for burning. *Nature* 241, 268-270.
- Stenestad, E. 1972: Træk af det danske bassins udvikling i øvre Kridt. *Geol. Surv. Denmark, Yearbook* 1971, 63-69.
- Wolbach, W. S., Lewis, R. S. and Anders, E. 1985: Cretaceous extinctions: evidence for wildfires and search for meteoritic material. *Science* 230, 167-170.
- Zoller, W. H., Parrington, J. R. and Kotra, J. M. P. 1983: Iridium enrichment in airborne particles from Kilauea volcano: January 1983. *Science* 222, 1118-1120.