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HIGH-RESOLUTION TRACE ELEMENT CHEMISTRY ACROSS THE CRETACEOUS-TERTIARY BOUNDARY IN DENMARK

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ABSTRACT

Closely spaced samples on millimeter scale across the Cretaceous-Tertiary boundary clay in Denmark were analyzed by instrumental neutron activation analysis. The results show a strong correlation between Cr and Ir while Co, Zn, As, Sb and Au are correlated with Fe. The elemental peaks for Ir-Cr and Fe are separated by 6 mm. The Fe peak is found in burrow-fillings at the lowermost part of the boundary clay. Chromite grains extracted from boundry clay in Denmark and New Zealand show a compositional common group. The composition points to an ultrabasic (kimberlitic) origin of the chromites. Tandem accelerator mass spectroscopy demonstrated, that there are no Ir carriers in addition to elemental carbon in the boundary clay from two localities in Denmark.

Keywords: Cretaceous-Tertiary boundary, iridium, trace elements.

RESUMEN

Las arcillas del límite Cretácico-Terciario (K/T) en Dinamarca muestreadas a escala milimétrica se han analizado por activación neutrónica. Los resultados muestran una fuerte correlación entre el Cr y el Ir, mientras que Co, Zn, As, Sb, y Au están correlacionados con el Fe. Las anomalías del Ir-Cr y del Fe están separadas por una distancia de 6 mm en la sección. El pico del Fe se encuentra asociado a rellenos de galerías de origen orgánico en la parte basal de la arcilla. Los granos de cromita extraídos de las arcillas del límite K/T de Dinamarca y de Nueva Zelanda son del mismo grupo composicional, lo que apunta a un origen ultrabásico (kimberlítico) de las cromitas. La espectrometría de masas hecha mediante un acelerador-tamden demostró que no hay portadores de Ir en las arcillas del límite K/T, de las dos localidades danesas estudiadas, aparte del carbono elemental.

Palabras clave: Límite Cretácico-Terciario, Iridio, Elementos traza.

THE LOCALITIES

Only two localities in Denmark are known to be un-affected by Quaternary or earlier tectonic disturbances of the Cretaceous-Tertiary (K/T) boundary (Fig. 1). The first one is situated on Stevns Klint and has earlier been reported to have 185 ng/g Ir as peak value (Hansen *et al.*, 1986). This is about 45 times the commonly reported value of around 4 ng/g (Alvarez *et al.*, 1982). If an integrated Ir deposition is considered the value at Stevns Klint is at least 610 ng/cm^2 as compared to less than 100 ng/cm^2 from most other localities (Kyte *et al.*, 1985; Strong *et al.*, 1987).

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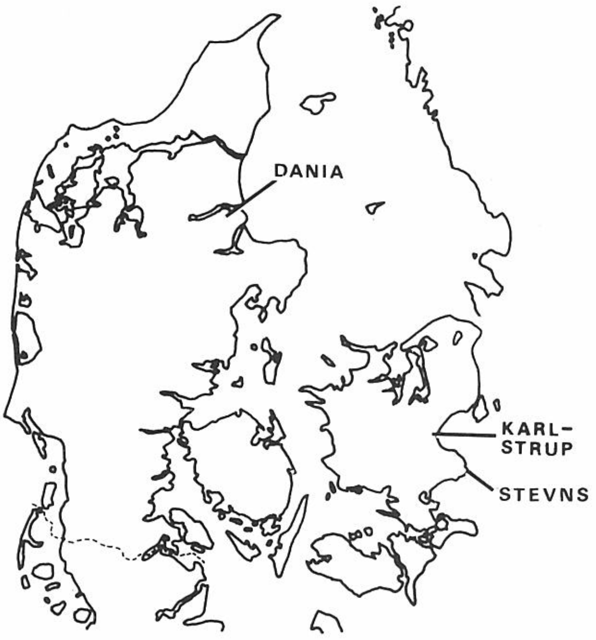

Figure 1. Map of Denmark showing location of localities mentioned in the text.

tektites related to a hypothesized major meteoritic impact (Smit and Romein, 1985).

The other tectonically undisturbed K/T boundary in Denmark is exposed in the now abandoned limestone quarry at Karlstrup situated some 20 km south of Copenhagen. From this locality spherical algae filled by pyrite were reported (Hansen *et al.*, 1986a). The pyrite infill indicates that deposition of the K/T boundary clay at this locality took place in an anaerobic environment. The maximum Ir value found at this latter locality is around 10 ng/g. Thus in the two tectonically undisturbed localities the iridium content is significantly different. The difference was suggested as being due to the difference in depositional environment where Stevns Klint is shallower and receives more air-borne material than does Karlstrup. This is also reflected in the absence in Karlstrup of the grey chalk rich in carbon black, which is well developed at Stevns (Hansen *et al.*, 1987).

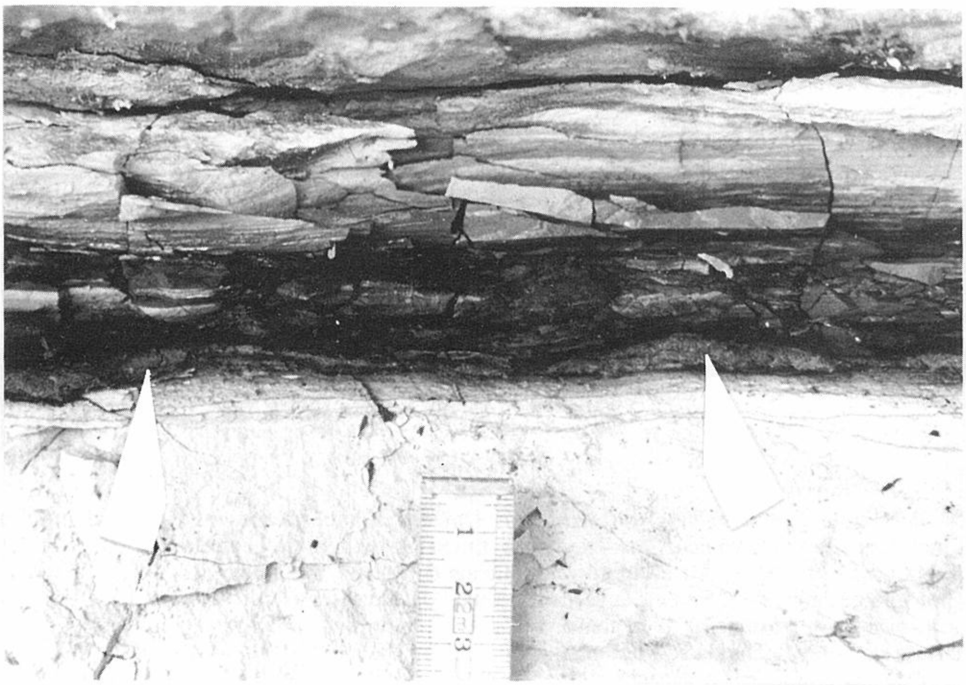

Figure 2. Detail of the undisturbed Cretaceous-Tertiary Fish Clay at Harving, Stevns Klint. At the lower boundary of the black part are seen the compressed rust-colored burrow-fills (arrows). This is where the goethite-filled prasinophyte algae are most common. Higher in the black Fish Clay and above it, in the paler material, are seen numerous compressed, partly filled burrows giving the impression of a laminated deposit. Scale in cm.

The red bottom layer of the Fish Clay (Fig. 2) was pointed out as being a level of compressed, semi-filled burrows containing i.a. spherical algal remains filled with the mineral goethite (Hansen *et al.*, 1986a). The spherules have earlier been explained as diagenetic alteration products after micro-

PYRITES

The Firsh Clay at Stevns Klint has earlier been described as being anaerobic due to its black colour, laminated appearance plus the presence of pyrite. The laminated appearance is due to compressed, partly filled animal burrows (Hansen *et al.*, 1986a) while the black colour is due to the high content of carbon black as well as small charcoal pieces (Hansen *et al.*, 1987). Pyrite appears to be present along with nodules that are commonly found along the boundary between the grey chalk and the Fish Clay. Pyrite nodules have, however, also been observed at the contact between the grey chalk and the Danian bryozoan limestone, leading to the conclusion, that the pyrite nodules formed much later than the time of deposition of the Fish Clay. The trace element chemistry of the nodules as investigated by INAA, shows that they are almost devoid of siderophilic elements including iridium. This is in contrast to the suggestion by Rucklidge *et al.* (1982) that pyrite should be the Ir-carrying phase.

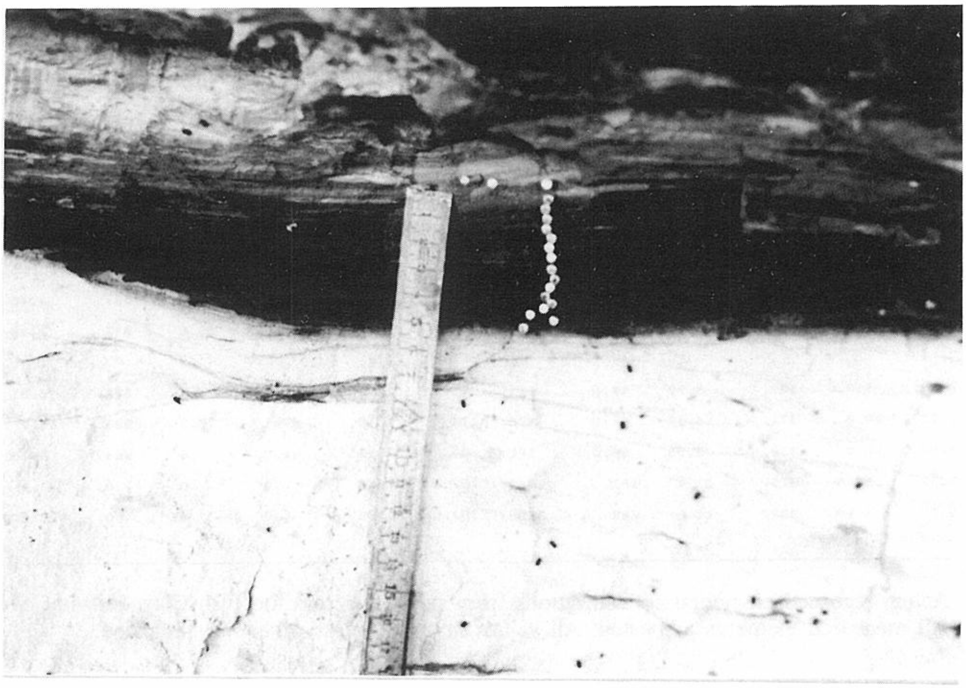

Figure 3. Detail of the undisturbed section across the Fish Clay at Harving, Stevns Klint showing the position of the Al-capsules used for the detailed sampling for INAA. Scale in cm.

Sample level in mm.	Ir	Cr	Fe	Co	Zn	As	Sb	Au
60.0	4	15	5	--	7	--	3	15
59.0	7	19	6	3	7	--	3	11
58.5	6	20	6	3	6	--	3	4
56.5	8	26	8	5	8	--	4	20
50.5	7	26	7	4	7	--	2	10
47.0	8	32	7	4	6	--	3	16
43.0	10	29	5	3	6	--	2	--
39.0	15	34	5	4	6	--	3	6
35.5	24	36	10	9	12	--	9	11
32.0	18	36	7	6	9	--	6	9
28.0	19	41	6	5	7	--	3	8
23.5	29	46	18	15	18	--	19	23
19.5	34	45	20	13	20	26	13	12
16.6	44	54	20	10	19	18	8	22
12.5	50	58	16	11	19	--	8	18
9.5	73	83	22	21	24	25	20	42
7.5	100	100	28	28	30	38	34	51
5.5	93	91	24	24	25	28	27	48
3.5	18	58	90	76	78	82	76	39
1.5	15	54	100	100	100	100	100	100
maximun	185	373	14	238	0.22	302	29.8	55
in	ppb	ppm	%	ppm	%	ppm	ppm	ppb

Table 1. Selected elements from samples across the Fish Clay, Harving, Stevns Klint. All values re-calculated into % of the maximum value.

THE BASAL LAYER

Sampling was made at the undisturbed locality Harvig on Stevns Klint *in situ* by aid of 3 mm diameter aluminium capsules, that were pressed directly into the soft sediment (Fig. 3). Great care was taken to avoid the compressed carbonate burrow-fills. The lowermost samples was, however, deliberately taken in the rust-red basal layer of burrows.

Selected elements from this series is shown in Table 1 while all the measured elements are recorded in Table 2. From these values it is obvious that the elements Ir and Cr are strongly correlated. The remaining elements are all correlated with Fe. These are Co, Zn, As, Sb and Au. The Ir-Cr peak is separated from the Fe-Co-Zn-As-Sb-Au peak by 6 mm. The two elemental peaks are not correlated but represent different time periods and events in the depositional history where the Fe-Co-Zn-As-Sb-Au deposition occurred much later that the Ir-Cr peak (Figs. 4-6).

	Ca %	Sc	Cr	Fe %	Co	Zn	As	Se	Br	Rb	Sr	Sb	Cs	Ba
60.0 mm	30.9	5.12	57.3	.77	100.	154.	.0	.0	.0	.0	1440.	.74	1.05	165.
59.0 mm	30.5	6.15	72.0	.88	7.96	147.	.0	.62	.0	16.5	1510.	.73	.91	301.
58.5 mm	29.2	6.14	75.3	.84	7.57	135.	.0	.41	.0	19.7	1360.	.77	1.02	181.
56.5 mm	21.6	7.69	96.3	1.18	10.7	182.	.0	.0	.0	22.6	1550.	1.05	1.07	340.
50.5 mm	22.4	7.23	96.3	1.18	10.7	152.	.0	.0	.0	25.7	1290.	.68	.89	237.
47.0 mm	22.1	7.42	96.4	1.02	8.50	145.	.0	.60	1.2	29.8	1260.	.79	1.01	199.
43.0 mm	23.2	7.28	109.	.70	7.97	142.	.0	.44	81.6	21.3	1270.	.63	1.00	314.
39.0 mm	19.2	7.88	125.	.77	9.80	145.	.0	1.08	158.	24.3	1200.	.87	.83	315.
35.5 mm	18.3	7.65	133.	1.45	20.9	264.	.0	95.8	117.	15.5	1390.	2.71	.77	290.
32.0 mm	18.3	8.61	134.	1.03	14.4	204.	.0	18.8	73.3	18.5	1420.	1.79	.92	378.
28.0 mm	17.6	7.96	151.	.82	11.9	162.	.0	4.60	144.	16.0	1240.	.93	.92	223.
23.5 mm	14.9	8.88	170.	2.68	36.3	419.	.0	18.6	111.	.0	784.	5.51	.0	160.
19.5 mm	13.8	8.30	167.	2.97	29.7	460.	77.0	41.2	97.7	13.2	1440.	3.98	.62	303.
16.6 mm	12.8	8.88	200.	2.94	24.4	429.	52.9	22.2	148.	18.0	837.	2.41	.77	195.
12.5 mm	12.2	9.25	217.	2.39	26.7	417.	.0	11.3	142.	16.6	812.	2.38	.63	166.
9.5 mm	8.07	9.77	309.	3.27	49.6	551.	75.3	21.1	151.	.0	578.	6.01	.54	178.
7.5 mm	3.22	10.4	373.	4.19	67.0	676.	114.0	18.2	97.1	10.7	521.	10.2	.25	0.
5.5 mm	3.07	10.4	339.	3.56	56.0	570.	85.2	15.3	64.0	.0	464.	8.15	.45	0.
3.5 mm	1.59	9.46	215.	13.4	181.	1760.	247.0	19.4	.0	.0	0.	22.6	.0	341.
1.5 mm	3.78	8.90	202.	14.8	238.	2260.	302.0	19.5	.0	.0	0.	29.8	.0	0.

Table 2. Actual recorded elemental concentrations from samples across the Fish Clay, Harving, Stevns Klint. All measured elements are listed. All values in ppm unless otherwise indicated.

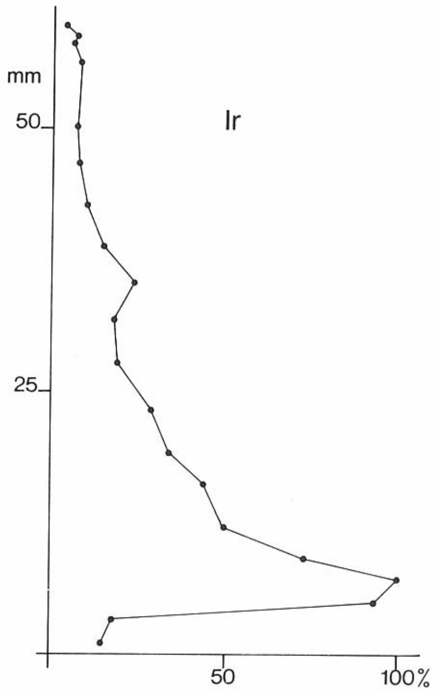

Figure 4. Distribution of iridium across the Fish Clay, Harving, Stevns Klint (see Fig. 3). The zero level is at the lowermost boundary of the black Fish Clay. Values from Table 1. Note that the iridium spike occurs above the bottom of the profile.

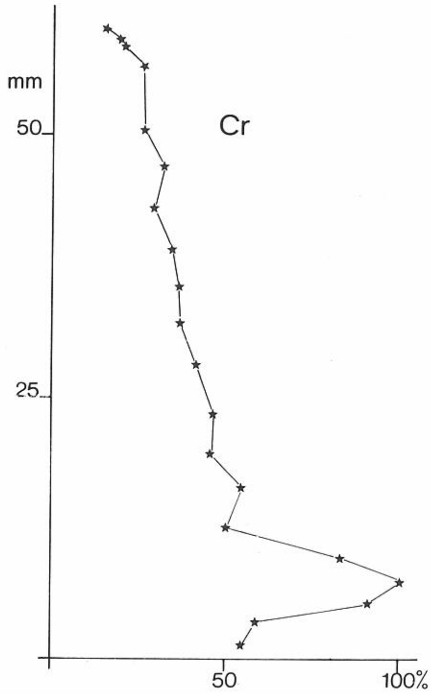

Figure 5. Distribution of chromium across the Fish Clay, Harving, Stevns Klint (see Fig. 3). The zero level is at the lowermost boundary of the black Fish Clay. Values from Table 1. Note that the chromium spike occurs above the bottom of the profile and follows that of the iridium (Fig. 4).

La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Hf	Ta	Ir ppb	Au ppb	Th	
57.1	32.8	23.6	11.5	1.44	1.05	2.87	.39	.78	.26	6.69	8.45	6.03	60.0 mm
61.3	49.7	44.1	12.7	1.83	1.30	2.95	.44	1.12	.22	11.4	6.34	2.84	59.0 mm
52.3	42.6	27.2	11.0	1.54	1.08	2.73	.36	1.20	.24	11.9	2.23	2.68	58.5 mm
97.4	60.8	58.7	18.5	2.59	1.77	4.35	.66	1.60	.23	15.3	11.5	2.74	56.5 mm
81.0	50.5	48.3	14.1	2.16	1.77	4.35	.66	1.34	.18	13.0	15.4	2.74	50.5 mm
59.6	41.4	35.2	11.2	1.58	1.51	3.52	.47	1.51	.19	15.3	9.13	2.56	47.0 mm
66.0	39.9	47.3	12.2	1.67	1.16	2.74	.42	1.40	.23	17.5	.0	3.05	43.0 mm
67.4	42.2	31.6	11.0	1.72	1.22	2.95	.33	1.44	.24	26.9	3.19	2.85	39.0 mm
67.9	45.2	46.4	12.5	1.73	1.12	2.79	.38	1.41	.23	45.2	6.32	2.81	35.5 mm
88.1	55.1	67.2	14.2	2.30	1.55	3.04	.43	1.52	.30	32.9	5.23	3.15	32.0 mm
61.6	39.3	35.5	10.6	1.62	1.14	2.16	.35	1.65	.26	34.9	4.68	2.70	28.0 mm
72.7	34.6	51.0	15.5	1.73	1.23	2.16	.37	1.47	.0	54.0	13.0	4.29	23.5 mm
60.0	44.6	37.6	11.2	1.59	1.03	1.79	.31	1.60	.24	62.6	6.85	3.15	19.5 mm
48.5	28.3	30.2	10.1	1.30	.79	1.83	.32	2.05	.24	80.8	12.10	3.10	16.6 mm
49.5	37.6	39.4	10.9	1.41	1.57	1.30	.21	1.80	.29	93.0	9.92	3.04	12.5 mm
24.1	14.4	12.6	5.69	.72	.50	.76	.15	2.54	.32	135.	23.2	3.21	9.5 mm
12.6	10.2	.0	3.09	.39	.30	.53	.07	3.17	.25	185.	28.6	3.12	7.5 mm
12.1	8.47	.0	2.94	.36	.28	.60	.13	3.00	.29	172.	26.6	3.29	5.5 mm
10.3	8.40	.0	.0	.38	.0	.46	.09	2.35	.42	32.8	21.7	4.45	3.5 mm
32.1	19.5	32.1	6.66	.89	.57	1.31	.19	2.21	.40	27.2	55.9	5.15	1.5 mm

Table 2 (cont.)

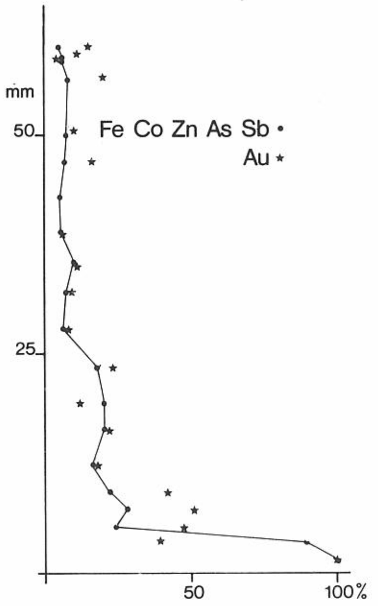

Figure 6. Distribution of iron (cobalt, zinc, arsenic, antimony) and gold across the Fish Clay, Harvig, Stevns Klint (see Fig. 3). The zero level is at the lowermost boundary of the black Fish Clay. Values from Table 1. Note that the iron spike occurs at the bottom of the profile and does *not* correspond to that of iridium and chromium. The gold exhibits a small spike at the level of the iridium and chromium spikes but has its maximum value at the iron spike.

That the horizontal component of all the rusted burrows ends at the same level is a simple consequence of the fact, that organisms adapted to soft sediments do not burrow into harder sediments. Accordingly they all terminate at the transition from the Fish Clay to the underlying grey chalk. At the time of burrowing the Fish Clay was not compacted, and as the width of the burrows (as seen on cleaved pieces) is more than 20 mm, a compaction factor of at least 20 times is evident for the Fish Clay proper. The black Fish Clay has a maximum thickness of around 4 cm at the most. From this follows that the thickness in un-compacted state was 20 × 4 cm = 80 cm. This means that the Fish Clay basins at Stevns Klint, with a depth of 50-80 cm originally were filled by the black sediment, which later through compaction became the black Fish Clay. The black sediment in itself is not dominated by clay minerals, but by the green alga *Botryococcus*.

ELEMENTAL CARBON AND VOLCANISM

Part of the iridium in the boundary clay is situated on elemental carbon (Hansen *et al.*, 1987). The elemental carbon is from isotopic evidence of terrestrial origin and unrelated to meteoritic carbon. It cannot originate from world wide forest fires as indicated by isotopic evidence and the duration of the depositional period of the carbon black-rich interval at Stevns Klint. The suggestion that it could be of volcanic origin therefore becomes relevant (Hansen *et al.*, 1987).

The very strong correlation between chromium and iridium lead us to speculate, whether the kind of volcanism involved could be of ultrabasic nature (i.e. of kimberlitic kind) since this type of volcanoes are known to contain elemental carbon such as carbonados.

The reasoning goes the following way: If the volcanism had been acidic to intermediate, it could have left dissolution-resistant minerals. If, on the other hand, a volcanic outfall was in the form of glass, and if this glass was acidic, we should be able to find the results of the devitrification. One of the obvious things one should meet would be zeolites such as e.g. clinoptilolite as found by Hansen and Andersen (1969) in Paleocene deposits. Devitrification of acidic and intermediate glass often lead to formation of zeolites and sometimes replacement of carbonates. Zeolites are, however, rare at the K/T boundary at Stevns Klint. On the other hand, the boundary clay is in fact not very clay-rich since the main part of the black Fish Clay is composed of the green alga *Botryococcus*. The clay fraction has been showed (Christensen *et al.*, 1973; Rampino and Reynolds, 1983; Kastner, *et al.*, 1984) to be composed of almost pure smectite. Smectites are normally considered the result of devitrification of volcanic material.

If the volcanic ash or glass had a basic or ultrabasic composition the result would be a very early devitrification and alteration. If we assume an ultrabasic composition, heavy minerals of the spinel group such as chromite would have had a very good change of withstanding weathering and therefore be preserved.

CHROMITES

Among the spinel minerals, the chromite is probably the most informative. The composition of chromites is well studied and often gives an indication as to the origin.

We therefore made experiments with acid residues, which, after treatment with hot HCl, were sampled for their magnetic fraction using wet magnetic separation. The extracted fraction was post-treated with HF to dissolve silicates followed by exposure to hot HCl in order to drive out the silica. After cleaning, the magnetic residue was pipetted onto formvar-covered transmission electron microscope grids. They were analyzed in the scanning electron microscope equipped with an energy dispersive X-ray analyzer. By applying the scanning-transmission mode of the microscope, the particles could be analyzed almost without background except for the "bremsstrahlung" from the grains themselves.

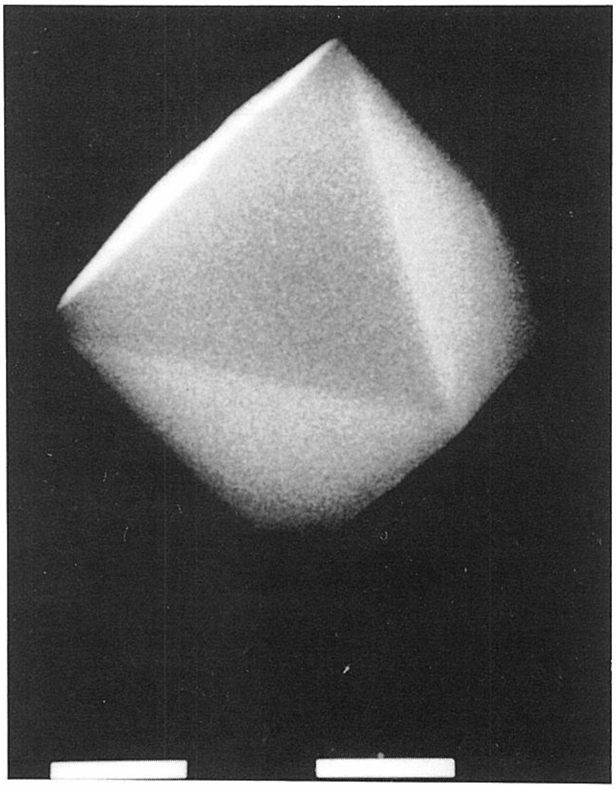

Figure 7. Scanning electron micrograph of a chromium rich chromite octohedron from Woodside Creek, New Zealand. Each scalebar = 1 micron.

It was possible to find a rather high number of chromite grains, not only at Stevns Klint, but also in a sample of the Creaceous-Tertiary boundary clay from Woodside Creek, New Zealand earlier used by Hansen *et al.* (1986a) (Fig. 7). The resultant analytical values are presented in Fig. 8. A local chromite component is present in the New Zealand sample. It is a low chromium –high iron chromite. There is, however, a field common to both New Zealand and Stevns Klint in the rather high chromium range. According to Haggerty (*in* Rumble, 1976) the composition of the common group is indicative of ultrabasic rocks such as kimberlites. The composition indicates, that the chromites could have formed close to the "diamond window".

In addition to the elements iron and chromium, many grains were found to contain 0.5 % Zn. This value is the detection limit of the analytical system used. Some of the grains with less than 0.5 % Zn were analysed in an electron microprobe equipped with crystal spectrometers. The detection limit of the electron microprobe is around 0.02 % Zn in such an analyzing configuration. The analyzed grains with less than 0.5 % Zn were found to have 0.1-0.3 % Zn. We did not find a single grain with Zn-content below 0.1 %.

With the analytical system applied we did not detect elements other than Cr, Fe and Zn.

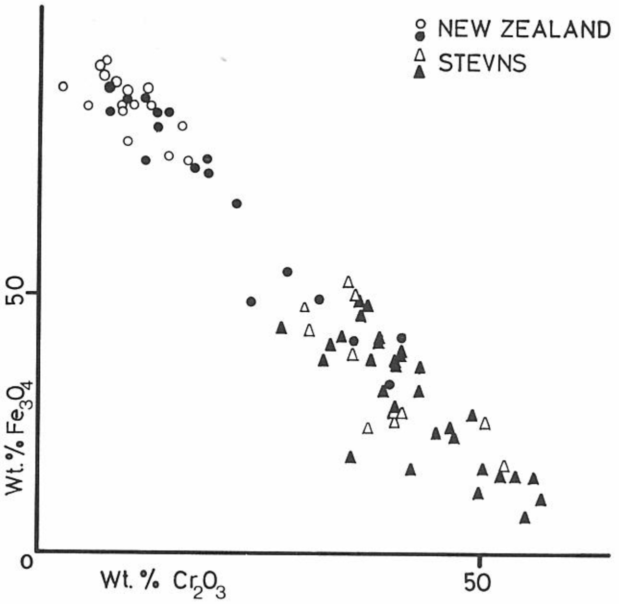

Figure 8. Plot of chromium and iron content of isolated chromite grains from Cretaceous-Tertiary boundary clays from New Zealand and Stevns Klint. Open signatures represent grains with less than 0.5% zinc which is the lower detection limit in the analytical system applied.

TANDEM ACCELERATOR EXPERIMENTS

In 1982 Rucklidge *et al.*, analyzed Fish Clay from Stevns Klint for platinum-group elements by Tandem Accelerator Mass Spectroscopy (TAMS) and found that certain grains contained many times more Pt than the usual clay background. The authors suggested that the Pt-rich grains were generally rich in noble metals and were identical to the ubiquitous pyrite grains found in the Fish Clay.

During the operating phase of the OSIRIS-system (OSIRIS: Oxford Supersensitibe Injector for Radioactive Isotope Separation experiment on the EN-tandem accelerator at Oxford) samples of Fish Clay from Stevns Klint and the Dania Quarry were analyzed.

The performance and analytical techniques of the OSIRIS system is described in Chew *et al.*, (1981, 1984), Chew and Allen (in prep.) and Rasmussen *et al.* (in prep.).

We found that samples of homogenized Fish Clay were poor targets for the Cs-sputter source of the OSIRIS inlet system. The samples were therefore heated to ca. 1000 °C in vacuum in a RF-furnace for a few seconds.

This treatment outgassed and fused the samples and allowed TAMS analysis of the samples by OSIRIS. There is a chance that a noble element such as Os is lost in this process, but we consider it unlikely that the fusion process is able to fractionate Ir from Pt.

Aliquots of the homogenized samples analyzed by TAMS were analyzed by INAA and selected values are shown in Table 3.

In the present paper we shall concentrate on output versus time results from two OSIRIS experiments (Figs. 9-10). Three masses were analyzed namely 193 (Ir), 194 (Pt) and 195 (Pt). In both output curves are seen that particles are encountered which are enriched in Pt only and not in Ir. Estimates of the etching speed in the Cs-sputter ion source suggest that the single grains are in the size range 0.1-10 microns. The total volume of Fish Clay analyzed in Fig. 9 is about 1 cubic millimeter.

OSIRIS standardization was made by adding 3% of a noble metal oxide standard, analyzed by instrumental neutron activation analysis, to a pure CaCO3-powder which was fused in the RF-furnace as described above.

The two localities differ in their content of Ir which is also evident from the output curves (Figs. 9-10). Except for this difference, the two curves are essentially identical with respect to occurrence of sudden higher Pt values obviously corresponding to sputtering of one or more grains.

CONCLUSIONS AND DISCUSSION

In a recent paper Hansen *et al.* (1987) found that Ir at the Cretaceous-Tertiary boundary in Denmark was absorbed primarily onto elemental carbon. They did, however, suggest that an additional Ir-carrier could be present.

With the very good correlation between Ir and Cr found in the sample series analysed from Stevns Klint, chromite appeared to be an obvious candidate

Sample	Sc	Co	Fe %	Zn	Eu	V	Dy	Al %	$CaCo_3$ %	Ir ppb	Ir* ppb	Pt* ppb
Stevns												
KLR3	8.4	18.6	2.7	295	1.4	242	4.95	5.19	47	31	18	30
Dania												
D20	3.8	9.1	10.5	72	0.6	45.1	2.18	1.96	75	1.7	3.2	1.4

Table 3. INAA of aliquots of samples from Stevns Klint and Dania Quarry analyzed by TAMS. All values in ppm unless otherwise indicated. Ir* and Pt* concentrations measured by TAMS.

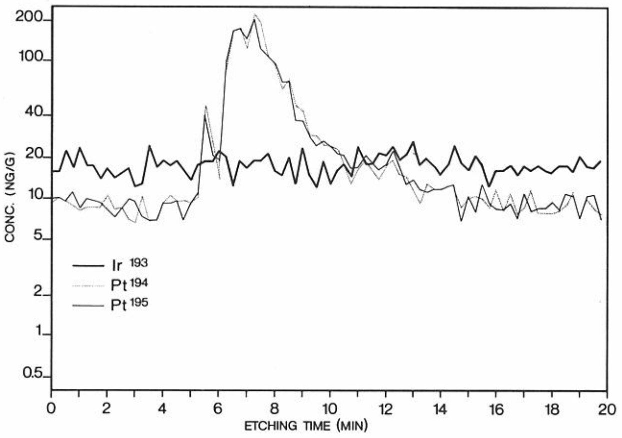

Figure 9. TAMS output versus etching time of black Fish Clay from Stevns Klint. Note that the two spike-forming curves represent masses 194 and 195 (both Pt) while mass 193 (Ir) does not change output level.

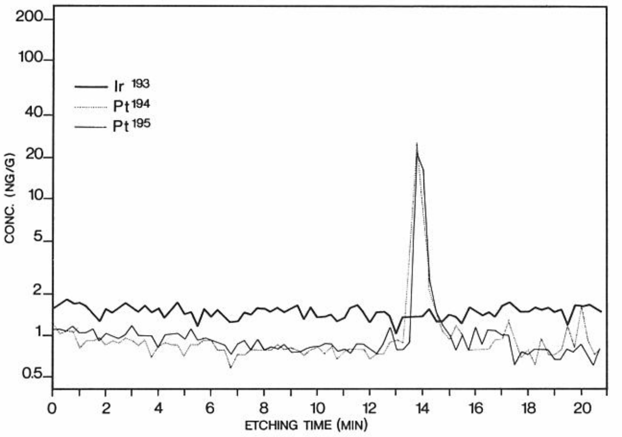

Figure 10. TAMS output versus etching time of brecciated Fish Clay from the Dania Quarry, Like in Fig. 9 the two spikeforming curves represent masses 194 and 195 (Pt) while mass 193 (Ir) does not change level.

for the additional Ir carrier since it is generally known as a noble metal carrier.

Our TAMS experiments do, however, convince us, that there is no additional Ir carrier besides the elemental carbon in the Fish Clay at Stevns Klint and at the Dania Quarry. The output versus time curves demonstrate that scattered grains contain platinum but have no enrichment in iridium.

We believe that the scattered grains found in the TAMS experiment are chromites because of their Pt enrichment. Crocket (*in* Cabri, 1981) reported chromites from ultrabasic rocks that were enriched in Pt but not in Ir.

The relatively high Zn content in the chromites indicates that the grains are of terrestrial origin. The high content of chromium in the chromite group common to boundary clay from New Zealand and Stevns Klint points to an ultrabasic origin of these chromites.

One of the obvious candidates as a source for the Ir at the Cretaceous-Tertiary boundary is the hot-spot volcanism forming the largest known volcanic eruptive complex in Phanerozoic time, namely the Deccan Traps in India (Courtillot *et al.*, 1986).

The hot-spot volcano Kilauea on Hawaii has recently been reported to erupt iridium (Zoller *et al.*, 1983, Olmez *et al.*, 1986). It was suggested that the high fluorine and chlorine content of hot spot eruptions was responsible for the transfer of the iridium from the magma to the surface where compounds like IrF_6 gas was suggested to play a role (Zoller *et al.*, 1983).

This was recently challenged by Wood (1987) who suggested from thermodynamic considerations that such a transfer seemed unlikely.

It may be that the suggested transfer mechanism involving IrF_6 is not correct, but the naked fact remains, that Ir is transported in some gas phase to the outlets of the volcano Kilauea and becomes absorbed to the finest dust fraction. We suggest that a parallel mechanism was active during the eruptions of the Deccan Traps volcanism, and that the magma was depleted in Ir by this process, leading to depletion of Ir in the associated early chromites that were spread globally through the ultrabasic eruptions. The iridium from this process was adsorbed onto the elemental carbon which was produced at the same time.

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