

## 39. DISTRIBUTION OF IRIIDIUM AND OTHER ELEMENTS NEAR THE CRETACEOUS/TERTIARY BOUNDARY IN HOLE 465A: PRELIMINARY RESULTS<sup>1</sup>

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### INTRODUCTION

Very significant enhancements of the element iridium have been observed in association with the Cretaceous/Tertiary boundary in marine sediments laid down 65 m.y. ago and subsequently uplifted above the ocean's surface. If our hypothesis for the origin of the iridium and the cause of the Cretaceous/Tertiary life extinctions (the asteroid-impact theory) (Alvarez et al., 1980) is correct, the Ir anomaly should be associated with the Cretaceous/Tertiary boundary region wherever it is intact. The present work was undertaken to search for the Ir anomaly in a deep-sea-drilling core, in order to check this aspect of the asteroid-impact theory.

### CORE DESCRIPTIONS

Basal Tertiary (Paleocene) sediments have been identified 144 cm below the top of Section 3 of Core 3 from Deep Sea Drilling Project Hole 465A, and Cretaceous sediments were identified 2 cm lower (Site 465 report, this volume). The Cretaceous just below the 144-cm level has been described as very white. The region above is a darker white and has dark blobs described as mainly pyrite. Fifty centimeters below the top of Section 3, the color is very white again. There are streaks of the very white material which intrude into the region above the 144-cm level. The edges of these streaks are sometimes flecked with the dark material.

### SAMPLING

Nine samples which bracket the expected Cretaceous/Tertiary boundary region were obtained. Seven of these contained only light-colored components, but two also contained the dark blobs. In the latter two samples, the light and dark fractions were manually separated with forceps. Both fractions were studied. The positions in the core of the 11 samples used in this study are identified in Table 1.

### MEASUREMENTS

All samples were measured by high-precision methods of neutron-activation analysis (Perlman and Asaro, 1969). Most elements were calibrated against the "Standard Pottery" multi-element standard (Perlman and

Table 1. Concordance of sample names.

DSDP Designation	NAA Sample Name	NAA Pill Name
465A-3-3, 80-82 cm	DSEA-14	2005-M
98-100 cm	-15	-N
112-114 cm	-16	-O
118-120 cm	-21	-T
141-143 cm	-19	-R
144-146 cm	-17	-P
3-4, 2 cm	-11	-H
10-12 cm	-12	-J
20-22 cm	-13	-K
Separated pyrite-containing fractions		
3-3, 118-120	-20	-S
141-143	-18	-Q

Asaro, 1971). Chlorine and calcium were calibrated against primary standards, and Ir was standardized against a carefully calibrated sample of the Danish Cretaceous/Tertiary boundary layer at Stevns Klint. The data are shown in Tables 2 through 5. The listed errors are 1-sigma values of the statistical uncertainties in counting gamma rays. The precision of measurements is about equal to these errors. Corrections have been made for all known gamma-ray interferences. The accuracies should be close to the precisions for those elements measured against primary standards or "Standard Pottery"; in the latter instance, the accuracies may be determined more closely by coupling the precisions with the uncertainties in the element abundances in "Standard Pottery" (Perlman and Asaro, 1971). Several elements (Ag, Br, Cu, Mg, Se, and Zn) were calibrated against flux monitors and contain about 10% additional uncertainty.

### CONCLUSIONS

A large enrichment of Ir was found in the region of the Cretaceous/Tertiary boundary, as predicted by the asteroid-impact theory. The Ir enrichment is distributed over ~40 cm of core and is associated both with black blobs and (predominantly) with the light-colored fraction.

The light-colored fraction between 100 and 144 cm below the top of Section 3 is principally CaCO<sub>3</sub>, but probably contains significant amounts of clay, which may contribute to its gray color. The total estimated clay in this region is roughly 9 g/cm<sup>2</sup>, about seven times

<sup>1</sup> Initial Reports of the Deep Sea Drilling Project, Volume 62.

Table 2. Major-element, bromine, and strontium abundances.

Sample	Ca Expressed as CaCO <sub>3</sub> <sup>a</sup> (%)	Al Expressed as Al <sub>2</sub> O <sub>3</sub> (%)	Cl (%)	Na (%) after 0.556 of Cl Abundance Removed <sup>b</sup> (%)	Mg <sup>c</sup> (%)	Fe (%)	Br (ppm)	Residual Br after 0.0034 of Cl Abundance Removed <sup>d</sup> (ppm)	Sr (ppm)
2005-M	92.4 ± 2.2	0.22 ± 0.05	0.850 ± 0.030	0.054 ± 0.018	< 0.6	0.068 ± 0.001	32.8 ± 1.3	< 7	1271 ± 127
-N	92.4 ± 2.2	0.65 ± 0.08	1.274 ± 0.035	0.111 ± 0.020	< 1.4	0.3164 ± 0.0032	52.3 ± 1.6	8.7 ± 2.0	1023 ± 111
-O	85.4 ± 2.5	1.67 ± 0.13	1.488 ± 0.038	0.244 ± 0.022	< 1.2	0.542 ± 0.005	56.7 ± 1.7	< 10	852 ± 100
-T	89.4 ± 2.2	1.34 ± 0.11	1.020 ± 0.032	0.202 ± 0.019	< 0.9	0.3404 ± 0.0035	37.0 ± 1.4	< 6	858 ± 100
-R	86.9 ± 2.0	2.28 ± 0.07	0.878 ± 0.031	0.225 ± 0.018	< 1.25	0.453 ± 0.005	31.9 ± 1.4	< 5	921 ± 104
-P	96.9 ± 2.5	0.25 ± 0.13	1.001 ± 0.032	0.049 ± 0.019	< 1.4	0.044 ± 0.001	37.7 ± 1.3	< 7	939 ± 100
-H	94 ± 4	< 4	2.12 ± 0.05	< 0.06	< 2.3	0.025 ± 0.001	71.9 ± 1.6	< 5	1029 ± 110
-J	98 ± 4	< 6	2.14 ± 0.07	< 0.11	< 1.9	0.026 ± 0.001	75.0 ± 1.7	< 8	982 ± 108
-K	99.9 ± 1.8	0.323 ± 0.031	0.699 ± 0.028	0.039 ± 0.017	< 1.1	0.048 ± 0.001	22.9 ± 1.1	< 3	965 ± 99
Separated pyrite-containing fraction									
-S	4.5 ± 1.6	9.01 ± 0.22	3.17 ± 0.05	0.84 ± 0.03	2.9 ± 0.8	11.2 ± 0.1	105.2 ± 3.6	< 8	< 650
-Q	13.2 ± 1.4	8.47 ± 0.13	2.66 ± 0.12	0.87 ± 0.07	3.2 ± 0.7	9.56 ± 0.11	89.9 ± 3.5	< 11	< 640

<sup>a</sup> Sea water contributions of 0.2% and 0.1% were subtracted from the CaCO<sub>3</sub> abundances in samples 2005-S and 2005-Q, respectively.

<sup>b</sup> In sea water the Na/Cl ratio is given as 0.556.

<sup>c</sup> Sea water contributions of 0.2% were subtracted from the Mg abundances in samples 2005-S and 2005-Q.

<sup>d</sup> In sea water the Br/Cl ratio is given as 0.0034.

Table 3. Rare-earth, barium, and scandium abundances (ppm).

Sample	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Ba	Sc
2005-M	21.57 ± 0.38	2.98 ± 0.10	16.9 ± 0.6	3.256 ± 0.033	0.856 ± 0.011	0.628 ± 0.015	4.55 ± 0.07	2.734 ± 0.027	0.353 ± 0.007	1167 ± 15	2.054 ± 0.021
-N	26.2 ± 0.4	4.75 ± 0.11	21.6 ± 0.7	4.09 ± 0.04	1.081 ± 0.013	0.768 ± 0.018	5.28 ± 0.08	3.164 ± 0.032	0.397 ± 0.009	1605 ± 20	2.968 ± 0.030
-O	27.5 ± 0.5	6.48 ± 0.14	23.2 ± 0.7	4.60 ± 0.05	1.209 ± 0.013	0.847 ± 0.020	5.83 ± 0.09	2.962 ± 0.030	0.371 ± 0.009	1335 ± 19	4.78 ± 0.05
-T	24.3 ± 0.4	5.64 ± 0.13	21.3 ± 0.7	3.98 ± 0.04	1.056 ± 0.013	0.748 ± 0.018	5.10 ± 0.08	2.832 ± 0.028	0.372 ± 0.009	1196 ± 18	3.567 ± 0.036
-R	13.58 ± 0.35	4.17 ± 0.13	10.8 ± 0.6	2.171 ± 0.022	0.552 ± 0.009	0.433 ± 0.014	2.90 ± 0.07	1.672 ± 0.022	0.213 ± 0.007	565 ± 13	4.81 ± 0.05
-P	13.84 ± 0.33	2.25 ± 0.09	11.2 ± 0.5	2.176 ± 0.022	0.564 ± 0.009	0.410 ± 0.012	2.99 ± 0.06	1.818 ± 0.020	0.231 ± 0.006	659 ± 12	1.215 ± 0.012
-H	13.10 ± 0.37	1.91 ± 0.09	10.5 ± 0.5	1.925 ± 0.019	0.502 ± 0.008	0.347 ± 0.012	2.62 ± 0.07	1.705 ± 0.020	0.211 ± 0.006	518 ± 12	0.970 ± 0.010
-J	14.15 ± 0.38	2.09 ± 0.09	11.1 ± 0.5	2.132 ± 0.021	0.558 ± 0.008	0.394 ± 0.012	2.72 ± 0.07	1.787 ± 0.020	0.221 ± 0.006	538 ± 12	1.046 ± 0.010
-K	13.66 ± 0.30	2.01 ± 0.09	11.1 ± 0.5	2.09 ± 0.021	0.542 ± 0.008	0.418 ± 0.011	2.86 ± 0.06	1.763 ± 0.018	0.225 ± 0.006	594 ± 10	1.162 ± 0.012
Separated pyrite-containing fraction											
-S	4.07 ± 0.7	1.56 ± 0.19	—	0.766 ± 0.010	0.19 ± 0.09	0.127 ± 0.009	1.03 ± 0.20	—	0.035 ± 0.015	151 ± 6	—
-Q	6.0 ± 0.7	2.29 ± 0.21	—	1.065 ± 0.011	0.34 ± 0.09	0.180 ± 0.027	1.41 ± 0.16	—	0.070 ± 0.015	245 ± 24	—

Table 4. Abundances (ppm) of elements enhanced by over a factor of 100 in the pyrite-containing fractions, relative to the Cretaceous calcareous samples.

Sample	As	Cr	Co	Cu <sup>a</sup>	Mo	Ni	Sb	Ta	Zn <sup>a</sup>
2005-M	< 2.4	2.23 ± 0.30	0.55 ± 0.05	< 50	< 0.7	3.93 ± 0.17	< 0.07	0.0133 ± 0.0022	11.2 ± 1.8
-N	< 3.5	9.5 ± 0.4	4.51 ± 0.12	< 64	< 1.6	19.14 ± 0.55	0.23 ± 0.04	0.0200 ± 0.0026	18.5 ± 2.2
-O	6.4 ± 1.1	39.1 ± 0.6	2.79 ± 0.10	69 ± 22	1.7 ± 0.5	54.7 ± 1.2	0.67 ± 0.07	0.0628 ± 0.0029	57.7 ± 2.8
-T	< 4.4	22.5 ± 0.5	1.96 ± 0.08	< 78	< 1.7	33.1 ± 0.8	0.59 ± 0.06	0.0393 ± 0.0026	36.1 ± 2.5
-R	5.4 ± 0.9	68.8 ± 0.8	8.44 ± 0.17	< 87	3.3 ± 0.4	64.9 ± 1.3	0.78 ± 0.08	0.0779 ± 0.0028	45.7 ± 2.9
-P	2.3 ± 0.8	2.97 ± 0.25	0.56 ± 0.04	< 47	< 1.0	4.09 ± 0.17	< 0.07	0.0054 ± 0.0020	14.6 ± 1.5
-H	< 2.7	1.00 ± 0.23	0.38 ± 0.04	—	< 0.5	4.19 ± 0.14	0.28 ± 0.04	0.0065 ± 0.0022	10.4 ± 1.4
-J	< 2.0	1.44 ± 0.24	0.51 ± 0.04	—	< 0.8	4.33 ± 0.16	0.077 ± 0.023	0.0099 ± 0.0023	6.0 ± 1.3
-K	< 2.3	2.82 ± 0.25	0.56 ± 0.04	< 37	< 0.8	5.00 ± 0.16	0.088 ± 0.028	0.0057 ± 0.0018	7.9 ± 1.4
Separated pyrite-containing fraction									
-S	111 ± 4	393 ± 6	402 ± 4	954 ± 56	40.7 ± 2.7	1722 ± 39	16.3 ± 0.8	0.592 ± 0.006	~ 10 <sup>3</sup>
-Q	99 ± 4	388 ± 4	310.7 ± 3.3	756 ± 51	98 ± 6	1322 ± 32	18.1 ± 0.9	0.594 ± 0.008	~ 8 × 10 <sup>2</sup>

<sup>a</sup> Flux monitors were used in calibration; there is a systematic uncertainty of 10–20% for each element.

Table 5. Abundances (ppm) of other elements enhanced by over a factor of 10 in the pyrite-containing fractions relative to the Cretaceous calcareous samples.

Sample	Ag <sup>a</sup>	Ir (ppb)	Mn	Se <sup>a</sup>	Th	U	V
2005-M	<0.8	0.78 ± 0.09	147.7 ± 3.0	<0.5	0.096 ± 0.013	0.117 ± 0.015	<25
-N	<0.8	3.70 ± 0.27	224 ± 4	<0.5	0.341 ± 0.029	0.197 ± 0.018	<20
-O	<1.3	9.86 ± 0.48	210 ± 4	<0.6	1.053 ± 0.035	0.286 ± 0.020	<51
-T	<1.3	5.77 ± 0.36	190.1 ± 3.8	<0.4	0.618 ± 0.032	0.192 ± 0.018	<23
-R	<1.2	3.03 ± 0.14	243 ± 5	<0.4	1.801 ± 0.030	0.165 ± 0.016	<32
-P	<0.6	0.70 ± 0.07	123.7 ± 2.5	<0.5	0.090 ± 0.010	0.101 ± 0.014	40 ± 13
-H	<0.6	0.26 ± 0.05	118.1 ± 2.4	<0.4	0.066 ± 0.009	0.078 ± 0.017	—
-J	<0.5	0.39 ± 0.08	126.8 ± 2.5	<0.3	0.067 ± 0.010	0.084 ± 0.017	—
-K	<0.8	0.55 ± 0.08	121.8 ± 2.4	<0.5	0.098 ± 0.010	0.100 ± 0.013	<20
Separated pyrite-containing fraction							
-S	5.0 ± 1.0	10.2 ± 0.8	2146 ± 43	6.58 ± 0.17	2.286 ± 0.023	0.726 ± 0.040	112 ± 23
-Q	3.5 ± 1.0	14.5 ± 0.9	1406 ± 28	4.5 ± 0.5	3.13 ± 0.07	0.829 ± 0.039	129 ± 17

<sup>a</sup> Flux monitors were used in the calibration; there is a systematic uncertainty of 10–20% for each element.

as much as in the Danish (Stevns Klint) or Italian (Gubbio) Cretaceous/Tertiary boundary layers. Although many elements have roughly the same ratios in the light-colored fraction, they do differ somewhat, especially in Ir. The total Ir enrichment is about 520 ng/cm<sup>2</sup>—about 6.5 times the Danish value, and about 35 times the Italian value.

There are very significant Ce depletions in the Cretaceous samples and the Tertiary sample from ~80 cm below the top of Section 3. In the region between 100 and 144 cm below the top of Section 3, the Ce depletion is not as great. This suggests a rare-earth component from a source other than sea water.

The two studied dark blobs probably are principally aluminum magnesium silicate (clay). They have abundant iron, and (from other work) they probably contain pyrite; the maximum abundance of pyrite in these blobs is about 25%. The two blobs are very enriched in a number of elements which form insoluble sulfides, but they are not identical in composition: the abundance of Mo, for example, differs by a factor of two in the two samples. Rare-earth abundances are very low in the dark

blobs; this may in part be because of incompletely separated light-colored material (which contains higher abundances of rare earths). There is excess Ce in these rare-earth patterns over the amount expected from the Sm abundance and the Ce/Sm ratio in the Cretaceous calcareous fraction.

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