Reports

A Major Meteorite Impact on the Earth 65 Million Years Ago: Evidence from the Cretaceous-Tertiary Boundary Clay

Abstract. *Evidence for a major meteorite impact on the earth 65 million years ago is shown by the presence of meteoritic debris in the "fish clay" from Denmark representing the Cretaceous-Tertiary boundary. Noble metals (iridium, osmium, gold, platinum, rhenium, ruthenium, palladium, nickel, and cobalt), which are sensitive indicators of meteorites and are normally depleted on the terrestrial surface by factors of 10^4 to 10^2 relative to cosmic abundances, are enriched in this boundary clay by factors of 5 to 100 over the expected abundances. With the exception of rhenium, all the enriched noble metals in the clay are present in cosmic proportions, indicating that the impacting celestial body had not undergone gross chemical differentiation. The major extinction of life on the earth at the end of the Cretaceous Period may be related to the meteorite impact.*

The sudden disappearance of more than 70 percent of all living species on land and in the ocean 65 million years ago, at the end of the Cretaceous Period, is a major event in the history of the earth. Such an extinction has not been seen in any other geologic period. Hypotheses proposed to explain the terminal Cretaceous extinction include (i) spillover of the Arctic Ocean, causing a severe change in the earth's climate, (ii) magnetic reversal, (iii) radiation from a recent supernova, and (iv) meteorite impact. A recent review summarizes current thinking on the extinction and provides many references (*1*).

I became interested in this subject after reading in a local newspaper and a popular scientific weekly (*2*) about a revival of the supernova hypothesis to explain findings by the Alvarez group of a high iridium content in the boundary clay layer separating the Cretaceous and Tertiary periods in Italy. A more recent article mentioned that the Alvarez group now believe the high Ir content was caused by the impact of an asteroid. I decided to investigate this problem by measuring the abundances of all the noble metals in the Cretaceous-Tertiary boundary clay, for the following reason. The noble metals are quite unfractionated from each other in most meteorites, and they occur in cosmic proportions. Therefore, if the observed excess of Ir in the boundary clay extends to all other noble metals in cosmic proportions, the presence of undifferentiated extraterrestrial material in the boundary clay is strongly indicated. However, if the excess of Ir is unaccompanied by excesses of the other noble metals, the high Ir concentration must be attributed to terrestrial processes. Noble metals are severely depleted in terrestrial and lunar surface rocks relative to cosmic abundances; the depletion factors range from 10^5 (Ir) to 10^3 (Ni). That noble metals are sensitive indicators for the detection and characterization of meteoritic material on the surface of the earth and the moon has been amply demonstrated over the past decade (*3*).

Two specimens of "fish clay" from the Cretaceous-Tertiary boundary layer in Denmark were obtained for this investigation. The specimens, grayish brown in color, had small amounts of white $CaCO_3$ inclusions. No attempt was made to separate these white inclusions from the clay. The specimens were crushed gently to yield 1- to 5-mm chips. Five samples ranging in weight from 65 to 243 mg, along with several standards of known elemental content, were irradiated with thermal neutrons for 1 week at a flux of 1×10^{14} sec^{-1} cm^{-2}. Iridium and cobalt were determined nondestructively in all the samples by gamma-ray counting. The remaining elements were determined by gamma-ray counting after extensive radiochemical purification. When it was realized that the five samples had comparable Ir and Co contents, only the two largest ones (~ 208 and ~ 243 mg) were radiochemically purified. The Ir and Co abundances in the five samples and in a sample of pelagic clay from the Pacific Ocean are shown in Table 1. The uniformity of the abundance data for samples 1 to 5 indicates that there is no large-scale inhomogeneity in the specimens. The high Ir content of the fish clay confirms the findings reported by the Alvarez group (*2*).

Table 1. Abundances of Ir and Co in five samples of fish clay representing the Cretaceous-Tertiary boundary in Denmark. Samples represent randomly selected chips from two 3-g pieces. Uncertainties represent 2σ counting statistics (σ is the standard deviation). Abbreviations: ppb, parts per billion; ppm, parts per million.

Sample	Co (ppm)	Ir (ppb)
1	37 ± 1	58 ± 12
2	41 ± 2	69 ± 15
3	49 ± 2	69 ± 12
4	38 ± 1	47 ± 9
5	46 ± 1	55 ± 6
Pelagic clay*		0.8 ± 1.2†

*From mid-Pacific Ocean at a depth of 5 km. †(*8*).

Table 2 lists the abundances of all the noble metals from samples 4 and 5. For comparison, the abundances of noble metals in C1 chondrites (primitive, chemically undifferentiated meteorites that best represent the solar system or cosmic abundance of all nonvolatile chemical elements) (*4*) and in Columbia River Basalt are also listed.

Figure 1 shows the abundances of the noble metals in the two clay specimens relative to C1 chondrites. All these elements are present in the boundary clay at levels well above those normally seen in such terrestrial materials as continental basalts, oceanic basalts, and pelagic clay. Also indicated in Fig. 1 are the relative abundances of the noble metals in Columbia River Basalt BCR-1, a continental basalt that has been extensively analyzed for trace elements (*5*). In the boundary clay, Ir, Os, and Pd are enriched by factors of more than three orders of magnitude; Au, Ni, and Re are enriched by factors of 15, 30, and 60; only Co appears at the same level as in the basalt. Not only are the enriched elements more abundant in the boundary clay, but their abundance pattern roughly matches the chondritic pattern, as evidenced by the flat distribution. Eight of nine noble metals are present in the boundary clay in roughly chondritic proportions. The contents of meteoritic material in the two clay specimens would be 6.5 ± 2.7 and 7.9 ± 3.8 percent if the impacting body had a composition similar to that of C1 chondrites.

Since the close resemblance between the abundance patterns of noble metals in the clay and in primitive meteorites is the most direct evidence for the presence of meteoritic debris in the Cretaceous-Tertiary boundary layer, it is important to ask whether such a pattern could be

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Table 2. Abundances of noble metals in two samples of fish clay representing the Cretacious-Tertiary boundary in Denmark. Uncertainties represent 2σ counting statistics.

Element	Sample 4 (207.8 mg)	Sample 5 (243.4 mg)	C1 chondrites (*4*)	Columbia River Basalt (*5*)
Ir (ppb)	47 ± 9	55 ± 6	514	0.0011 to 0.012
Os (ppb)	40 ± 1	49 ± 2	480	≤ 0.01
Au (ppb)	8.8 ± 0.2	12.3 ± 0.2	152	0.35 to 1.33
Pt (ppb)	24 ± 5	17 ± 6	900	
Ni (ppm)	310 ± 45	322 ± 35	10,300	7.3 to 13
Co (ppm)	38 ± 1	46 ± 1	483	28 to 38
Pd (ppb)	45 ± 8	53 ± 8	460	≤ 0.03
Re (ppb)	35 ± 1	59 ± 1	35	0.64 to 1.06
Ru (ppb)*	37 ± 28, 39		690	

*Ruthenium was determined only in sample 1; see (*19*) for details.

established by terrestrial processes. I have already shown that these elements occur at very low concentrations in major terrestrial materials. Further, the terrestrial abundance pattern (see rectangles in Fig. 1) is essentially noncosmic or nonmeteoritic. Although ultramafic rocks of possible upper mantle origin have average Ir and Os contents of 3 ppb, their Ni contents are around 2000 ppm (*6*). Let us now consider an alternative hypothesis, namely that an abundance pattern such as that observed in the clay could be generated by weathering of ores containing noble metals. Noble metals are often found in Cu-Ni sulfide and MoS_2 ores, where their presence is due to a combination of isomorphism and accommodation in the crystal lattice related to ionic radii. The MoS_2 ore contains Re, and braggite is (Pt,Pd,Ni)S. The abundance pattern found in the Strathcona Mine ores from Sudbury, Canada, for Ru, Os, Ir, Pd, and Au is decidedly noncosmic (*7*). The footwall chalcopyrite has the following composition relative to C1 chondrites: Ir, 2×10^{-3}; Os, 1×10^{-2}; Au, 3×10^{-1}; Pd, 20; and Ru, 2×10^{-2}. The footwall pyrrhotite has essentially the same composition, but the hanging wall pyrrhotite has Ir, 1×10^{-1}; Os, 5×10^{-2}; Au, 3×10^{-1}; Pd, 1.5×10^{-1}; and Ru, 1×10^{-1}. However, high concentrations of the major ore minerals or the characteristic isomorphic constituents such as Mo, Ni, Ag, As, and Se are not found in the boundary clay (*8*). The finding of high Ir in the Cretaceous-Tertiary boundary clay from New Zealand (*9*), Italy, Denmark, and Spain (*10*) suggests that the excess noble metals are not confined to a single geographic site. Consequently, local enrichment is unlikely.

A major anomaly in the noble metal distribution in the boundary clay is the abundance of Re, which is enriched ~ 15 times above the level expected by comparison with other noble metals. Although Re in terrestrial basalts is enriched over Ir or Os, the highest Re content in any oceanic and continental basalt is still below 2 ppb (*11*). Unlike other noble metals, Re can easily go into solution as soluble perrhenate. Perhaps 90 percent of the Re is terrestrial, since Re has been observed to concentrate in bituminous sediments, especially sulfur-bearing oozes and sediments of high organic content (*12*). The anomalous behavior of Re may be better understood when more boundary clay samples from different parts of the world are analyzed.

It should be pointed out that the abundance pattern of noble metals in the boundary clay does not exactly match that in C1 chondrites. The structure observed in the abundance pattern could be due to (i) an actual difference in the chemical composition of the impacting body, or (ii) postimpact processes such as volatilization and weathering. Most iron meteorites (with the exception of group I irons) show highly variable and noncosmic elemental ratios. The relatively flat abundance pattern in Fig. 1 suggests that the impacting body was a stony meteorite, probably of the chondritic group. There are subtle differences in the relative proportions of refractory noble metals (Ir, Os) and moderately volatile noble metals (Au, Pd, Ni) among the chondrites. However, it is difficult to say which class of chondrites matches the extraterrestrial material in the boundary clay, mainly becuase of the uncertainty in assessing the extent of postimpact processes. The Ni deficiency may be due to aqueous alteration, since Pd is not depleted to the same extent as Ni in the boundary clay, while these elements vary proportionately among the different classes of chondrites. Large-scale depletion of Ni and Au has been observed in some meteoritic silicate spherules from Pacific Ocean sediments (*3*). For Pt, part of the problem may lie with its reported abundance in C1 chondrites, which varies by a factor of 3. Since the meteoritic debris mixed with clay remained in the ocean bottom for a long time, it is remarkable that the chemical imprint left by the meteorite is not totally obliterated.

The isotopic ratio of ^{184}Os and ^{190}Os in the fish clay was also measured by neutron activation (*13*). Because different supernovas presumably produce different $^{184}Os/^{190}Os$ ratios, a distinctive ratio in the fish clay might imply a supernova source. Anomalies as high as 300 percent have been reported for elements such as uranium in certain meteorites (*14*). However, the $^{184}Os/^{190}Os$ ratio in the clay was identical to terrestrial and meteoritic values within the counting statistical error, 1.2 ± 3.4 percent (*15*). Hence, there is no evidence for material from a nearby supernova in the Cretaceous-Tertiary boundary clay.

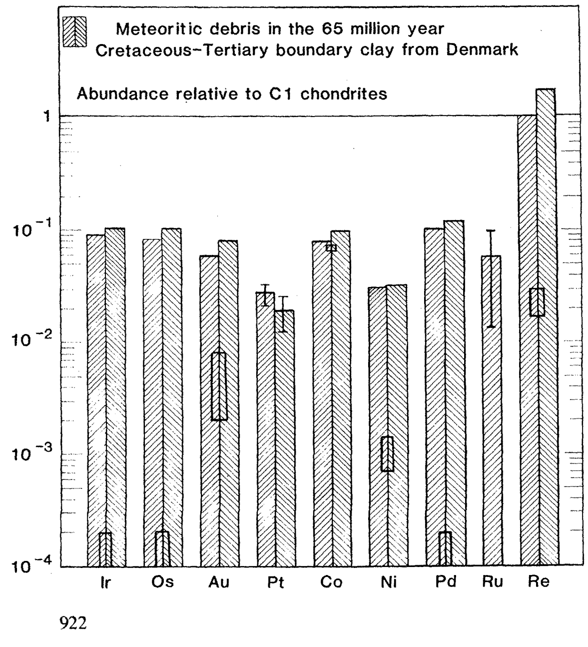

Fig. 1. Not only are the noble metals more abundant in the Cretaceous-Tertiary boundary clay than in terrestrial basalts, but the abundance pattern of the enriched elements matches the chondritic or cosmic pattern, as evidenced by the flat distribution. The meteoritic debris in the boundary clay is of the order of 7 to 8 percent, if the impacting body had a composition similar to that of C1 carbonaceous chondrites. The rectangles over the histograms represent Columbia River Basalt.

I have presented evidence for the presence in the Cretaceous-Tertiary boundary clay of debris from a major meteorite impact on the earth 65 million years ago. If the observed 7 to 8 percent meteoritic debris was uniformly distributed globally within the 2 cm of boundary clay, I infer that the meteorite that struck the earth was 11 km in diameter and weighed 2500 billion tons (*16*). Perhaps this meteorite impact was largely responsible for the catastrophe at the end of the Cretaceous Period. If the eruption of the Tamboro volcano in the Dutch East Indies (Indonesia) caused the year 1816 to be "without a summer" in the New England states and caused famine and epidemic in Bengal (*17*), it is conceivable that a combination of primary and secondary effects stemming from the impact of a giant meteorite could have had devastating effects on life on this planet. Further studies on the worldwide distribution of meteoritic debris in the boundary layers of different geological periods should help us better understand the role played by the impact of celestial bodies on the evolution of life on the earth (*18*).

R. GANAPATHY

Research Laboratory,
J. T. Baker Chemical Company,
Phillipsburg, New Jersey 08865

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5. I have included only reliable neutron activation data for this compilation. For example, the Pd content of BCR-1 by other methods is given as less than 4 ppb, in contrast to ≤ 0.03 ppb by neutron activation. Although the Pt content of BCR-1 is given as less than 10 ppb, I believe the actual value is several orders of magnitude lower than this. Neutron activation data were taken from: R. R. Keays, R. Ganapathy, J. C. Laul, U. Krähenbühl, J. W. Morgan, *Anal. Chim. Acta* **72**, 1 (1974); R. Wolf, G. R. Richter, A. B. Woodrow, E. Anders, *Geochim. Cosmochim. Acta* **44**, 711 (1980).
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13. By measuring the activity ratio of ^{185}Os to ^{191}Os in the fish clay and terrestrial Os samples, one can establish whether ^{184}Os/^{190}Os in the fish clay is different from the solar system value. It was shown earlier that this ratio in terrestrial and meteoritic Os is the same within 2 percent [L. Grossman and R. Ganapathy, *Eos* **57**, 278 (1976)]. A value of -0.1 ± 0.4 percent was reported by H. Takahashi, H. Higuchi, J. Gros, J. W. Morgan, and E. Anders [*Proc. Natl. Acad. Sci. U.S.A.* **73**, 4253 (1976)].
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15. It should be pointed out that a much more sensitive test for supernova debris would be to measure "live" ^{129}I (half-life, 17 million years) in this sample. There exist very sensitive methods to detect low amounts of ^{129}I through a combination of neutron activation and mass spectrometry [R. V. Ballad, D. W. Holman, E. W. Hennecke, J. E. Johnson, O. K. Manuel, L. M. Nicholson, *Health Phys.* **30**, 345 (1976)].
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19. Ruthenium was determined only in sample 1 and toward the end of this investigation, to check whether the meteoritic pattern seen in other elements holds for Ru also. The Ru content was calculated through the ^{97}Ru and ^{103}Ru isotopes. Since ^{97}Ru had appreciably decayed, a value of 37 ± 28 ppb was obtained. Ruthenium-103 is produced from Ru as well as from U in the sample. The U content was 1 ppm. Applying a correction for the fission contribution ($174 \pm 8 - 135 \pm 14$), a value of 39 ppb for Ru was obtained.
20. I thank a number of individuals who contributed to the successful completion of this work: S. Gartner for the prompt dispatch of samples and for stimulating conversation; A. Meyer and coworkers at the University of Missouri–Columbia reactor for their efficiency and enthusiasm; J. Harris, J. Horvath, J. Bayda, and J. Volkert at J. T. Baker Chemical Company for assistance; H. Kaufman, T. Hurley, and A. J. Barnard for encouragement; J. Larimer and S. Larimer for many hours of conversation on the terminal Cretaceous Period; and J. W. Morgan for many helpful suggestions.

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Sulfur Dioxide Emissions from La Soufriere Volcano, St. Vincent, West Indies

Abstract. *During the steady-state period of activity of La Soufriere Volcano in 1979, the mass emissions of sulfur dioxide into the troposphere amounted to a mean value of 339 ± 126 metric tons per day. This value is similar to the sulfur dioxide emissions of other Central American volcanoes but less than those measured at Mount Etna, an exceptionally strong volcanic source of sulfur dioxide.*

The eruption of La Soufriere Volcano on the island of St. Vincent during April and May 1979 consisted of at least seven major events, which provided spectacular injections of volcanic material into the stratosphere (*1*). The heights for some of these injected clouds of ash were in excess of 18 km (*2*). The eruptions provided another opportunity to assess the importance of volcanic activity in the Western Hemisphere with respect to the loading of tropospheric SO_2.

During the latter stages of the eruption, a team from the Canadian Atmospheric Environment Service was sent to St. Vincent, and profiling of the SO_2 emissions was carried out over the first week in May 1979. The profiling was accomplished by means of boat transects of the volcanic plume (pathlength about 9 km) between Chateaubelair Island and Devolet Point off the west coast of St. Vincent (Fig. 1). A Barringer correlation spectrometer (COSPEC) was used in a vertically pointing mode to measure the total overhead burden of SO_2 along the transect. Since the COSPEC is an integrating remote sensor, it measures not the concentration of SO_2 per se but rather the burden, or the product of the concentration and the pathlength (in parts per million–meters), of all overhead SO_2. In other words, the COSPEC would measure the same signal if the total concentration of SO_2 were compressed into a 1-m layer and its concentration were measured in parts per million (volume to volume). Use of the COSPEC for estimating volcanic emissions of SO_2 is becoming standard (*3*–*5*), and this technique provides reliable volcanic SO_2 mass fluxes with a minimum of risk to the researcher.

The results of transects of the plume on 4 May 1979 are shown in Fig. 2. The COSPEC signal (calibrated from internal SO_2 cells) is plotted on the vertical axis, and the horizontal axis shows the crosswind distance from the Eulerian average center of gravity of the plume. The profiles in Fig. 2 are displayed in the orthogonal plane to the plume axis. The Eulerian average is a ground-referenced ensemble average of the measurements taken during a day. During this study, the ash loading in the steady-state plume from La Soufriere was not of a level to significantly deplete the incoming solar radiation (as indicated by the instrumental automatic gain control). On the basis of past experience with industrial plumes, we estimate that the SO_2 burden from this plume was well within the linear region of COSPEC response. Table 1 gives the plume dispersion results in terms of plume bearing and spread at the