Reports

Osmium-187/Osmium-186 in Manganese Nodules and the Cretaceous-Tertiary Boundary

Abstract. As a result of the radioactive decay of rhenium-187 (4.6×10^{10} years) the osmium-187/osmium-186 ratio changes in planetary systems as a function of time and the rhenium-187/osmium-186 ratio. For a value of the rhenium-187/osmium-186 ratio of about 3.2, typical of meteorites and the earth's mantle, the present-day osmium-187/osmium-186 ratio is about 1. The earth's continental crust has an estimated rhenium-187/osmium-186 ratio of about 400, so that for a mean age of the continent of 2×10^9 years, a present-day osmium-187/osmium-186 ratio of about 400 so that for a mean age of the sepected. Marine manganese nodules show values (6 to 8.4) compatible with this expectation if allowance for a 25 percent mantle osmium supply to the oceans is allowed. The Cretaceous-Tertiary boundary iridium-rich layer in the marine section at Stevns Klint, Denmark, yields an osmium-187/osmium-186 ratio of 1.65, and the one in a continental section in the Raton Basin, Colorado, is 1.29. The simplest explanation is that these represent osmium imprints of predominantly meteoritic origin.

One of the most creative ideas regarding the cause of the many paleontologic extinctions at the Cretaceous-Tertiary boundary is the one put forward by Alvarez *et al.* (1) invoking the impact of a large asteroid or comet with the earth. Their hypothesis grew out of the observation of an unusual chemical signature, specifically a high iridium concentration, at the Cretaceous-Tertiary boundary at Gubbio, Italy. This signature has since been discovered in other marine as well as continental sections bracketing the Cretaceous-Tertiary boundary.

Although this unusual chemical imprint was a compelling enough reason for many people to believe in the existence of an event of worldwide proportions with effects on the evolution of life on the earth, others held that the aqueous geochemistry of trace elements was too poorly known to rule out purely indigenous terrestrial processes for the concentration of these elements. These issues, among others, were aired at a conference on "Large body impacts and terrestrial evolution: Geological, climatological, and biological implications" at Snowbird, Utah, in October 1981, and many of the papers were subsequently published (2).

The search for an independent test of the impact hypothesis centered around the identification of diagnostic isotopic signatures. Recent work with 87 Sr/ 86 Sr, 143 Nd/ 144 Nd, and δ^{18} O (3, 4) could be used to help define the type of terraine and events related to the alleged impact, but the results themselves do not provide

unequivocal certification of an impact. The ¹⁸⁷Os/¹⁸⁶Os ratio in the boundary layers enriched in iridium (and osmium, since osmium generally follows iridium in both meteoritical and terrestrial systems) provides a signature that can be used to test the hypothesis directly (5). The decay of 187 Re (half-life, 4.6×10^{10} years) increases the ¹⁸⁷Os/¹⁸⁶Os ratio over time in proportion to the ¹⁸⁷Re/ ¹⁸⁶Os ratio in the system. Meteorites and the mantle of the earth have an ¹⁸⁷Re/ ¹⁸⁶Os ratio of about 3.2 (6–9), yielding a contemporary ¹⁸⁷Os/¹⁸⁶Os ratio of about 1. Osmium is considerably depleted relative to rhenium in the earth's crust to the extent that the ¹⁸⁷Re/¹⁸⁶Os ratio is about 400. For an average age of the crust of about 2×10^9 years the contemporary average $^{187}\text{Os}/^{186}\text{Os}$ ratio would be around 10. Clearly a marked distinction between cosmic or mantle osmium and crustal osmium should be discernible on the basis of the $^{187}\text{Os}/^{186}\text{Os}$ ratio.

In order to use this diagnostic isotopic ratio for marine systems, the case for the imprint of the continental ratio on seawater has to be made. If the layers rich in Ir (and Os) were derived by geochemical concentration of seawater-dissolved metals, the ¹⁸⁷Os/¹⁸⁶Os of seawater would be seen. A possible complication of this unique test is that the ¹⁸⁷Os/¹⁸⁶Os ratio in seawater is a function not only of the continental supply of osmium but also of the supply from recently derived mantle rocks and the ambient cosmic dust flux. The relative importance of each of these sources had to be ascertained before the ¹⁸⁷Os/¹⁸⁶Os test could be considered a diagnostic one for Cretaceous-Tertiary boundary material. The test we suggested (5) was the examination of contemporary marine manganese nodules for the ¹⁸⁷Os/¹⁸⁶Os ratio. Manganese nodules are produced by slow chemical precipitation of iron and manganese oxides from seawater with attendant coprecipitation of a number of elements including osmium. Should the ratio be uniquely imprinted by old continental crust, then the test would stand. Our strategy therefore was to analyze a number of marine manganese nodules throughout the oceans for ¹⁸⁷Os/¹⁸⁶Os and, on establishing the value of this ratio, proceed to the task of evaluating the source of osmium in the Stevns Klint, Denmark, marine Cretaceous-Tertiary boundary layer. We then compared these results with a measurement in a

Table 1. Osmium-187/osmium-186 ratios in manganese nodules and Cretaceous-Tertiary boundary samples.

| Sample | Location | Approximate water depth (m) | ¹⁸⁷ Os/ ¹⁸⁶ Os* |
|--|-------------------------|--------------------------------------|---|
| Ма | anganese nodules | | · · · · · · · · · · · · · · · · · · · |
| North Atlantic | 0 | | |
| V19-D11 | 38°04'N, 60°13'W | 2900 | 8.09 ± 0.06 |
| V27-D11 | 42°19.9′N, 27°00.3′W | 2900 | 7.97 ± 0.11 |
| South Atlantic, RC16-D10 | 28°25'S, 40°45'W | 4400 | 6.68 ± 0.10 |
| Antarctic, E11-USC-887 | East Pacific sector | 4500 | 8.38 ± 0.19 |
| Indian, RC14-D5 | 19°13.9'S, 61°01.3'E | 3200 | 8.33 ± 0.09 |
| North Pacific, A47-16 | 9°02.3'N, 151°11.4'W | 5000 | 7.65 ± 0.07 |
| South Pacific, Challenger Station 276 | 13°28'S, 149°30'W | 5000 | 5.95 ± 0.18 |
| Cretaceo | us-Tertiary boundaries† | | |
| Stevns Klint fish clay, Denmark | | | |
| Sample from F. T. Kyte | | | 1.660 ± 0.027 |
| Sample from S. Gartner | | | 1.654 ± 0.004 |
| Raton Basin-Starkville South, Colorado |) | | |
| Sample from C. J. Orth | | | $1.29 \hspace{0.2cm} \pm \hspace{0.2cm} 0.04$ |
| kM + 0 + 0 | 1.6 1 1 | | |

*Mean $\pm 2\sigma$ error. \dagger One-gram samples were used for analysis.

continental sediment iridium-rich boundary layer from the Raton Basin in southern Colorado.

Manganese nodules. Seven nodules were chosen from a number of different collections so that the major oceanic areas were represented. The procedure for separating osmium and determining the ¹⁸⁷Os/¹⁸⁶Os ratio with the ion probe has already been described to a large extent (6, 7). The specific modification for manganese nodules is that dissolution of only the authigenic component was effected by the reduction and dissolution of the iron and manganese oxides with oxalic acid. The blank was ≤ 0.05 ng, which is negligible since more than 1 ng of osmium was extracted for analysis. Considering the anticipated low concentrations of osmium (1 to 10 ppb) in manganese nodules (10), about 10 g was used for each measurement. All the chemical separations were made at Yale and the measurements were made on the MIT-Brown-Harvard Consortium Cameca IMS-3f ion probe. The details of the procedure will be published elsewhere.

Our results are shown in Table 1. The overwhelming result is that all the ¹⁸⁷Os/ ¹⁸⁶Os ratios are high (between 6 and 8.4), indicating a dominant continental crust imprint. Two other observations of importance are: (i) the ratios are lower than predicted for a ¹⁸⁷Re/¹⁸⁶Os crustal ratio of 400 and a mean age of 2×10^9 years and (ii) the variations show strong regional trends, which implies a short residence time for osmium (< 100 years?) and the presence of mantle (or possibly cosmic dust) sources in the oceanic signature or significant crustal source variability.

Our interpretation of the manganese nodule data is that the continental and mantle sources are both seen but the continental signature dominates. This certifies the use of the ¹⁸⁷Os/¹⁸⁶Os ratio as a diagnostic indicator of crustal versus episodic cosmic (or possibly mantle) source of osmium at the enriched layers found at a number of Cretaceous-Tertiary boundaries.

Stevns Klint boundary layer. One of the highest iridium (and osmium) concentrations at the Cretaceous-Tertiary boundary was found at Stevns Klint, Denmark (11, 12). We decided to make our first measurement on this sample. We obtained separate samples from S. Gartner of Texas A & M University and F. Kyte of the University of California, Los Angeles, and the results in Table 1 are from multiple runs (also made at MIT) on these samples. The average value of 1.65 is clearly much lower than the expected crustal value and is closest Table 2. Rhenium/osmium ratios in meteoritic materials and in the Stevns Klint fish clay.

| Type of material | Re/Os (atom ratio) | Ref- erence |
|---------------------|---|----------------|
| Chondrites | en en alle en | |
| Ordinary | 0.089 ± 0.007 | (9) |
| Enstatite, type A | 0.089 ± 0.011 | (9) |
| Enstatite, type B | 0.093 ± 0.007 | (9) |
| Carbonaceous | 0.071 ± 0.008 | (17) |
| IIA iron meteorites | 0.13, 0.22 | (7) |
| Pallasites | | |
| Average of | 0.109 ± 0.04 | (18) |
| "main group" | | |
| High value | 0.45 | (18) |
| (Dora) | | |
| Stevns Klint fish | 0.30, 0.20, | (12) |
| clay | 0.19 | |
| | 1.0 | (11) |
| | | |

to the meteoritic value of about 1. What then are the possible interpretations of this result? We can think of three options.

1) The $^{187}Os/^{186}Os$ ratio is the result of an oceanic imprint of a supply with a higher ratio of mantle-derived to continental crust-derived material at the end of the Cretaceous than at present. This hypothesis can be tested by using the ⁸⁷Sr/⁸⁶Sr secular trend in the oceans as recorded in calcareous tests of marine organisms. The oceanic ⁸⁷Sr/⁸⁶Sr ratio has been increasing since the beginning of the Mesozoic, the highest value being found at the present time. The contributors to the oceanic ⁸⁷Sr/⁸⁶Sr signal are strontium from limestone weathering, continental silicate ("granitic") weathering, and marine basalt alteration (hightemperature "weathering" mainly at the spreading centers). Brass (13) calculated the relative proportions of the granitic component relative to the basaltic component as a function of time necessary to yield the observed change in the isotope ratio. At the Cretaceous-Tertiary boundary the active processing of strontium through the oceans required 30 percent of the strontium from granite and 70 percent from oceanic basalt, whereas at present it is 75 percent from granite and 25 percent from oceanic basalt.

If we assume that osmium moves through the system in tandem with strontium and the mobilizable Os and Sr are each equally available in the two sources, then we can estimate the present-day continental ¹⁸⁷Os/¹⁸⁶Os ratio from the manganese nodule data. Using the mean ¹⁸⁷Os/¹⁸⁶Os ratio of manganese nodules so far analyzed (7.6, Table 1) and assuming the basaltic contribution has the mantle ¹⁸⁷Os/¹⁸⁶Os value of 1, then for a 3:1 granite-to-basalt ratio of supply at present the ¹⁸⁷Os/¹⁸⁶Os for the granite continental supply is 9.8. If this continental ¹⁸⁷Os/¹⁸⁶Os ratio is the same for the late Cretaceous, then the 30 percent granite–70 percent basalt source at that time would yield an average value for the Cretaceous seas of 3.6, which is more than twice what we observe at Stevns Klint. If, however, the oceanic basaltic Os influence on seawater at the end of the Cretaceous was 93 percent and the continental 7 percent, the value of 1.65 could be attained.

2) The observed ¹⁸⁷Os/¹⁸⁶Os ratio of 1.65 is due to a volcanic event. The Os/ Ni ratio observed at the Stevns Klint boundary is larger (10^{-4}) than the ratio observed in basaltic rocks (10^{-6}) . (Chondrites and most iron meteorites have a ratio of about 10^{-4} although most of the pallasites have about 10^{-6} .) This would require a volcano with a considerable preferential concentration of Os over Ni in the eruptive material to provide the ratio observed at Stevns Klint. Zoller et al. (14) have observed a large enrichment of Ir as well as Se, Hg, Cd, In, and other elements in atmospheric particulate samples collected at the Mauna Loa Observatory (Hawaii) at the time of the January 1983 eruption of tholeiitic lava at Kilauea. Volatilization of elements at times of volcanic eruption has been known for some time, but this is the first report for Ir. None has been found in recent eruptions at Mount St. Helens or El Chichón (14), which are associated with viscous, silica-rich magmas.

The magnitude of Ir supply to the atmosphere from contemporary eruptions is very small and most of it is removed close to the site of eruption as the result of cooling and condensation. If, however, a large enough event occurred in the past capable of supplying the needed quantities of Ir and Os to sites remote from the volcano, it is conceivable that a volcanic imprint resembling a meteoritic impact could be recorded. In our view such events would be less likely than meteorite impacts. Although explosive volcanism clearly leaves its mark in the geologic record, such events are generally associated with silica-rich effusions and not with the tholeiitic outpourings typical of Hawaii.

3) The $^{187}Os/^{186}Os$ ratio represents the debris from a collision of a large asteroid or cometary body. On the face of it, this appears to be the most attractive hypothesis. Yet there are problems here as well. The $^{187}Os/^{186}Os$ ratio is higher than any yet observed in meteorites (7, 8). The highest value for a IIA iron meteorite is 1.4, compared to the observed value at Stevns Klint of 1.65. Can the Stevns Klint high value be due to crustal contamination?

It has been estimated that 21 percent of the mass of the high-Ir boundary layer

at Stevns Klint is of extraterrestrial origin if the projectile was a C-1 chondrite component (12). With this constraint the dilution of the projectile osmium with crustal osmium would not change the ¹⁸⁷Os/¹⁸⁶Os more than 1 percent. This is not enough to raise the ¹⁸⁷Os/¹⁸⁶Os ratio to the value observed at Stevns Klint. An upper limit of possible contamination of a chondritic projectile osmium with crustal osmium can be set from the calculations of O'Keefe and Ahrens (15). They determined that a 10-km-diameter body would yield a mass of rock or water ejected at the time of collision equal to 10 to 100 times the mass of the projectile. A 100-to-1 dilution of crust to chondritic projectile would increase the ¹⁸⁷Os/¹⁸⁶Os ratio by 10 percent over the value in the chondritic projectile. The value of 1.65 is outside this limit. Therefore, we believe that the high ratio cannot be explained by simple dilution of projectile material with target material.

There are reliable data on the Re/Os ratio of meteorites which can be referred to a present-day ¹⁸⁷Os/¹⁸⁶Os ratio on the assumption of a common initial ¹⁸⁷Os/ ¹⁸⁶Os value and age for all the meteorites. Under these assumptions an ¹⁸⁷Os/ ¹⁸⁶Os ratio of 1.65 would require an Re/ Os element ratio of about 0.30. Table 2, constructed from high-quality data, shows the range of values observed in a number of meteoritic classes. None of the chondritic classes, including carbonaceous chondrites, has an Re/Os ratio that comes close to that required for the alleged cosmic projectile. Iron meteorites and pallasites are higher than the chondrites in their Re/Os ratios, and a few even have sufficiently high values to suggest that the alleged cosmic projectile responsible for the imprint at Stevns Klint ought to belong to this class of objects. Perhaps fortuitously, the reported Re/Os ratios of the boundary clay bracket the value required to yield the observed ¹⁸⁷Os/¹⁸⁶Os ratio (Table 2).

Raton Basin. We also measured the ¹⁸⁷Os/¹⁸⁶Os ratio in an Ir-enriched layer from a nonmarine section in the Raton Basin (Colorado). The high-Ir layer is found at the base of a coal seam which, on the basis of pollen stratigraphy, has been inferred to be at the Cretaceous-Tertiary boundary (16). We received a sample of the material with the highest Ir concentration found at the Starkville South locality, south of Trinidad, Colorado, from C. J. Orth and analyzed it with the ion probe at Paris. The ¹⁸⁷Os/ ¹⁸⁶Os ratio is 1.29 ± 0.04 .

This value is significantly lower than the Stevns Klint ratio. If we argue that crust-derived osmium is not a major contaminant at either of these sites, then clearly they represent projectiles or events of different composition. The ¹⁸⁷Os/¹⁸⁶Os ratios 1.29 and 1.65 are incompatible with chondrites and imply an iron meteorite projectile if we accept the impact hypothesis as the most probably one.

Conclusions. We conclude that the simplest interpretation of the Stevns Klint and Raton Basin evidence is that the layers high in Ir (and Os) are of meteoritic origin. Contamination with continental crust-derived osmium is small, if only simple mixing of our estimated crustal ¹⁸⁷Os/¹⁸⁶Os value is used. If no contamination by a crustal ¹⁸⁷Osenriched source has occurred, then the projectiles cannot be any of the contemporary chondritic classes but may be of iron meteorite affinity. The difference in ¹⁸⁷Os/¹⁸⁶Os between the marine Stevns Klint and nonmarine Raton Basin samples is significant and implies that either different meteorites were involved, or that there have been different amounts of crustal osmium contamination, by unspecified processes, of the meteoritic projectile material at the two sites.

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Computer Simulations of the Belousov-Zhabotinsky Reaction

Abstract. Morphological features of the two-dimensional Belousov-Zhabotinsky reaction were modeled with an algorithm involving only two simple parameters, one describing the productivity of the reaction on a local scale length and the other characterizing the delay or quiescent time after the localized reaction. Self-organizing wavelike structures, including single- and multiarmed spirals, were most easily generated.

While investigating the range of spatial structures produced by varying the parameters of a self-propagating star formation algorithm (1), we found that some of the resulting patterns resemble those found in autocatalytic chemical reactions described in 1958 by Belousov and in 1964 by Zhabotinsky (2) and more recently by Winfree (3) and others (4, 5). The most striking feature of the chemical reaction is the spontaneous appearance of globally coherent structures developing from so-called local oscillators. Although these patterns have been ascribed to symmetry-breaking instabilities caused by diffusion in systems involving more than two variables (6), little more than asymptotic analysis of the rate equations has been performed (7), and the role of the putative local oscillator or echo waves (8) is in dispute. An introduction to the general analytic theory of such autocatalytic reactions can be found in Cohen et al. (9), Tyson (8), and Nicolis and Prigogine (4), while a more popular discussion of the spiral-producing reactions is given by Winfree (10). The simplicity of our simulations suggests that, while the underlying physics may be very complex, the macroscopic manifestations are easy to understand and model.

The chemical experiments (3) show that the following structures can arise. If externally activated (by, say, a hot probe), a single point in the otherwise homogeneous chemical mixture gives rise to an expanding ring of activity. If internally activated (as by a contaminant), the point gives rise to periodic structures of concentric, wavelike rings. However, when a single shell is sheared across its diameter, the end points produce oppositely winding one-armed spi-