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and Luis W. Alvarez

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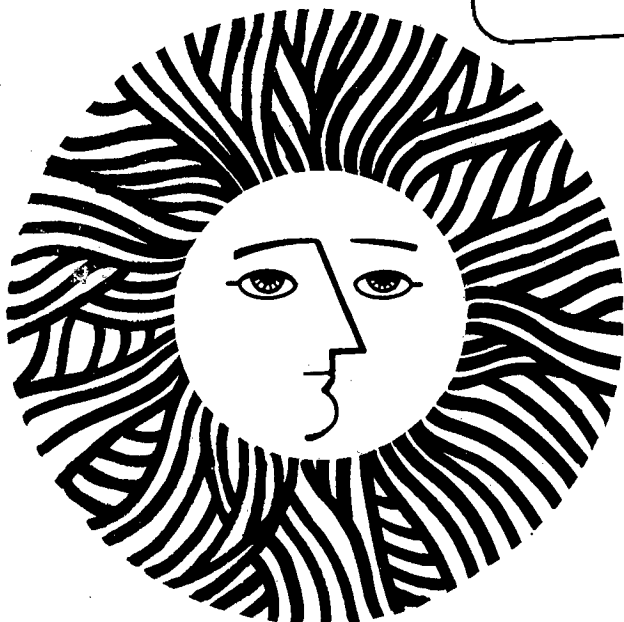
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SYNCHRONOUS WITH TERMINAL EOCENE
EXTINCTIONS

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Abstract

An iridium anomaly has been found in exact coincidence with the known microtektite level in DSDP site 149 in the Caribbean Sea. The maximum Ir abundance was 0.4 ppb and the best value of background for 6 samples not in the microtektite region was 0.00 ± 0.05 ppb. The Ir is probably not in the microtektites but was deposited simultaneously with them. This could occur if the Ir were deposited from a dust cloud resulting from a bolide impact as has been suggested for the anomaly associated with the Cretaceous-Tertiary boundary. Other workers have deduced that the microtektites are part of the North American strewn tektite field which is dated at ~35 m.y. B.P. It has also been found that the microtektite horizon in deep-sea cores is synchronous with the extinction of 5 radiolarian species and is very close to, but probably slightly below, the Eocene-Oligocene boundary as based on various micropaleontological criteria. Mass extinctions also occur in terrestrial mammals at about this time. The Ir anomaly, the tektites and microtektites are all supportive of a major bolide impact ~35 m.y. ago.

Iridium and other siderophile elements depleted in the earth's crust occur in anomalously high concentrations at the same stratigraphic level as the marine micropaleontological extinctions that define the Cretaceous-Tertiary boundary at about 66.7 m.y.B.P. This anomaly has been found worldwide. Published data from six laboratories document 12 sites in marine sediments (1-6) and one site in terrestrial sediments from New Mexico (7) and several other occurrences have been discussed (8). High-precision stratigraphic information from southern Spain demonstrates deposition of the iridium during an interval no longer than about 50 years. (9). Geochemical details of the anomaly indicate that it was caused by impact on the earth of an extraterrestrial object, probably having the composition of a carbonaceous chondrite and a diameter of about 10 km (2,8,10,11). Size-frequency statistics on Apollo objects and known terrestrial impact craters indicate that an impact of this magnitude should occur roughly every 100 m.y. (12), and theoretical calculations of impact dynamics are compatible with this hypothesis (13). Suggested killing mechanisms for an extinction following a bolide impact include suppression of photosynthesis during a period of darkness before settling of the dust injected into the atmosphere by the impact (2), a temperature increase resulting from direct energy coupling to the atmosphere and/or an enhanced greenhouse effect from water vapor transferred from an oceanic impact site to the stratosphere (14), and poisoning by toxic chemicals introduced into ocean and atmosphere by a cometary impacting object (15).

The impact hypothesis for the terminal Cretaceous extinctions suggests that evidence for impact of an extraterrestrial object might be found at the stratigraphic horizons of other mass extinctions. In fact, there is already one case where evidence for an impact is known at, or at least close to such

an extinction. The North American tektites on land, and the associated microtektites studied in sea-bottom cores principally by Glass and his co-workers (16,17), provide direct evidence for a major impact. The strewnfield extends halfway around the earth and contains at least 10^{10} metric tons of impact melt in the form of far-traveled glassy spherules (17). Five radiolarian species die out at the microtektite level (16), but the event occurred about 2 m.y. (18) before the Eocene-Oligocene boundary as defined in the Deep-Sea Drilling Project (DSDP) reports (19). The boundary defined in this way may or may not be synchronous with the major turnover of mammal taxa that defines the Eocene-Oligocene boundary in terrestrial sequences in North America, Europe, and Asia (20), a question beyond the scope of this paper. Dates suggested for the boundary are 32.5 ± 0.9 m.y. (18) and 38.0 m.y. (21). The best value for the fission track and K/Ar ages of North American tektites is of $34.2 \pm .6$ m.y. (18), and the microtektites give fission track ages of 34.6 ± 4.2 m.y. (23).

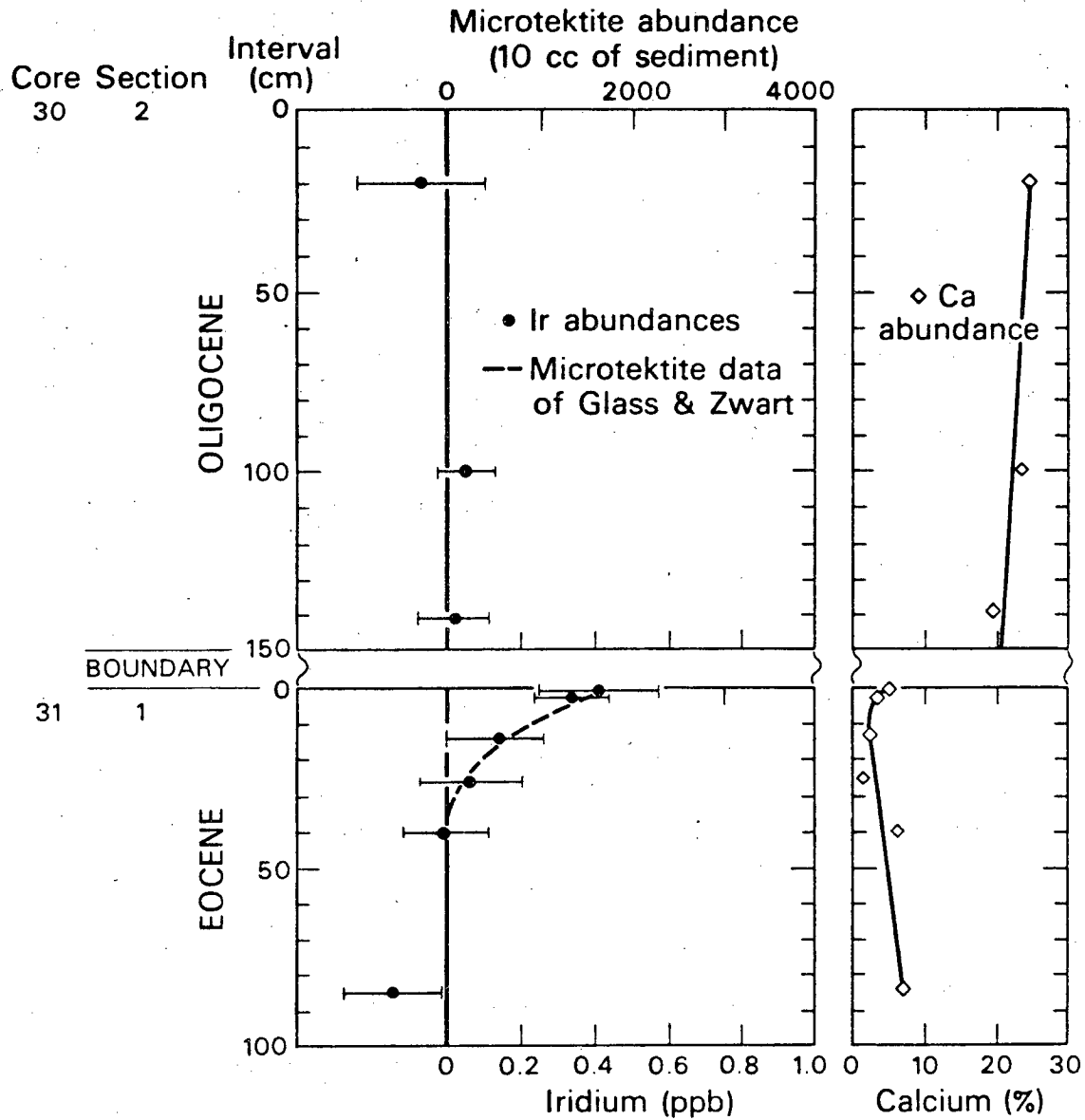
The possible relation between the Eocene-Oligocene extinctions and a major impact has been considered by other workers (17,24). In order to determine whether the impact that produced the North American strewnfield also gave rise to an iridium anomaly, we measured 30 elements by high-precision techniques of neutron activation analysis (NAA) in 9 samples from DSDP site 149 in the eastern Caribbean. A preliminary report on this work, including the recognition of a distinct iridium anomaly, has appeared as an abstract in the program for the October 1981, Snowbird, Utah Conference (25). (A post-deadline paper on the same subject was presented at that conference by R. Ganapathy.)

DSDP site 149 cored a "radiolaria-rich nannoplankton chalk" in the Middle Oligocene of core 30, and a "semi-indurated calcareous-rich radiolarian ooze" in the Upper Eocene of core 31 (19). The basal Oligocene is missing between cores 30 and 31 (19, 26), a gap possibly amounting to 7 m (16). This was

the discovery site for the North American microtektites (27), but unfortunately the peak of microtektite abundance was apparently lost in the unrecovered interval between cores 30 and 31. The microtektite abundance rises rapidly at the top of core 31, but is back to near zero at the base of core 30 (fig. 1). Despite the missing section, this core offered an opportunity to look for an extraterrestrial component. Samples from more complete sites containing microtektites have been obtained, and are being measured.

Table 1 gives the stratigraphic levels and the abundances of selected elements for the 9 samples from cores 30 and 31 of DSDP site 149. Anomalously high iridium levels were found, coinciding with the highest abundance of microtektites, at the top of core 31. The two highest samples in core 31 have Ir concentrations of $.41 \pm .16$ and $.34 \pm .10$ ppb, as a fraction of the whole rock. The next sample below has a value for Ir which appears to follow the trend of the microtektite abundance but which is in fact indistinguishable from zero at the 2 standard deviation level. The other six samples, at levels where microtektites are very rare or absent, are also indistinguishable from zero and have a best value for the iridium abundance of 0.00 ± 0.05 ppb. The principal conclusions of this paper, therefore, are first, that the association of iridium anomalies with major impact events, inferred for the Cretaceous-Tertiary boundary, is strengthened by recognition of an iridium anomaly at a microtektite horizon; second, although not all impacts which produce detectable iridium enrichments are necessarily related to extinctions (28), the association of iridium anomalies with extinctions is strengthened by the synchronous disappearance of 5 species of radiolaria with the appearance of the iridium and microtektite anomalies near the Eocene-Oligocene boundary; and third, that detailed studies of the latest Eocene are needed to determine whether or not the terminal Eocene mass extinction of land mammals is synchronous with the tektite-iridium horizon.

DSDP Site 149 EOCENE-OLIGOCENE GEOCHEMICAL ANOMALIES



XBL 819-1356

Figure 1 Iridium and calcium whole-rock abundances in cores from DSDP Site 149. Error bars in the Ir data are one standard deviation. One standard deviation in the Ca measurements are smaller than the size of the points.

TABLE I
Selected DSDP 149 Chemical Data*

<u>Core</u>	<u>Section</u>	<u>Interval (cm)</u>	<u>Ca (%)</u>	<u>Cr (ppm)</u>	<u>Ni (ppm)</u>	<u>Ir (ppb)</u>
30	2	20-21	25.1 ± .7	27.0 ± 0.9	56 ± 6	<.36 (-.06 ± .18)
30	2	100-101	23.5 ± .8	27.7 ± 0.5	53 ± 6	<.21 (.05 ± .08)
30	2	140-141	19.7 ± .7	34.0 ± 0.5	76 ± 8	<.22 (.02 ± .10)
31	1	1-2	5.4 ± .5	30.4 ± 1.1	86 ± 10	.41 ± .16
31	1	3-4	3.6 ± .5	30.8 ± 1.1	98 ± 10	.34 ± .10
31	1	14-15	2.6 ± .6	32.7 ± 1.1	103 ± 10	<.42 (.14 ± .14)
31	1	26-27	1.2 ± .4	29.7 ± 0.7	93 ± 9	<.34 (.06 ± .14)
31	1	40-41	6.1 ± .6	27.1 ± 0.7	77 ± 8	<.24 (-.01 ± .12)
31	1	84-85	6.9 ± .5	25.3 ± 0.9	75 ± 9	<.26 (-.15 ± .13)

* The indicated precisions of measurement are standard deviations in the counting of gamma rays. Ca was calibrated vs. a CaCO₃ primary standard, Cr and Ni were calibrated vs. a secondary standard, STANDARD POTTERY (38), with abundances of 102 ± 4 and 278 ± 7 ppm respectively (39), and Ir was calibrated vs. a secondary standard, DINO-1 (prepared from the Danish Cretaceous-Tertiary boundary layer) with an Ir abundance of 31.5 ± 0.6 ppb. The accuracies of the measurements are comparable to the precisions. When backgrounds comparable to gamma-ray peak intensities are subtracted, negative differences are sometimes obtained. If the difference is negative or smaller than 2 standard deviations, the sum of 2 standard deviation plus the value (of positive) is given as the upper limit for a 95% confidence level. The differences, expressed in ppb, are also shown in parentheses.

Discovery of the Late Eocene iridium anomaly raises a number of questions for further study, but a few preliminary considerations can be given here.

Of the six Late Eocene samples, the two which definitely contain Ir average 34.5 ppm Cr and 92 ppm Ni, and the other 4 average slightly less. The maximum abundances of these elements which should be due to a separate component in the Ir-rich samples are 8.5 and 29 ppm, respectively, after statistical treatment of the data to provide about a 95% confidence level. Ultramafic rocks contain Ir in even higher abundances than the observed anomaly but estimates of their contribution can be made because of their high Cr and Ni contents. From 126 measurements in ultramafic rocks of Ni and Ir abundances (29, 30, 31) and 24 of Cr and Ir (31), the expected Ni and Cr abundances in the Ir-rich samples due to such an intrusion would average ~48 and 126 ppm respectively, much higher than the observed limits (if no marine fractionation is assumed). If, on the other hand, the intrusive component were due to a chondritic extraterrestrial source, the added Cr and Ni abundances would be ~2 and 7 ppm (32) respectively, consistent with the observed limits.

Meteorite ablation debris is continually accumulating in deep-sea sediments. From Maurrasse's value of 1.6 mm/1000 yr for Late Eocene sedimentation in DSDP site 149 (26) and Barker and Anders' relationship between Ir abundance and sedimentation rate (33), corrected for appropriate densities, the maximum expected Ir concentration would be 0.02 ppb. The observed value is 20 times higher, which agrees with the interpretation of the microtektites as evidence for a single large impact.

Measurements of Ir in the microtektites are in progress, but in the meantime, estimates are useful. If the Os abundance of ≤ 1 ppb in the correlative Bediasite tektites from Texas (34), and the typical Ir/Os ratio of about 1 in chondritic material (35) are combined with the maximum abundance of microtektite mass in core 31, 0.2% (16), the Ir abundance at the top of core

31 would be <0.002 ppb. The much higher values observed indicate that the iridium was not carried primarily by the microtektites. This agrees with the interpretation that tektites are formed from shock-melted target rock, with only a minor contamination by extraterrestrial material.

Even though terrestrial sources of Ir are rare, there are some which can cause serious errors. In a response to three letters to Science (36) concerning the Cretaceous-Tertiary (C-T) boundary, we stated that an Ir anomaly had been found associated with a continental C-T deposit in Montana (37). We subsequently found that this attribution of the anomaly was completely erroneous, and that the Ir was due to the platinum wedding rings worn by a new technician who had prepared the samples for analyses. Platinum used for jewelry contains about 10% Ir, which is used as a hardening agent. If a platinum ring loses 10% of its mass in 30 years, the average loss per minute (if it ends up on a sample) is about two orders of magnitude higher than our sensitivity of measurement. Thus the Ir anomaly measured near the Eocene-Oligocene boundary is comparable to the average amount lost from a platinum ring in ~2 seconds. Tests also demonstrated that gold impurities were introduced into samples if the sample preparer wore a gold wedding ring. Because of a concern for the possibility of Pt, Ir and Au contamination in the handling of deep-sea cores and other material collected in searches for geochemical anomalies, we have discussed these effects with many laboratories and at many meetings and have stressed it here. None of the published results of our group, except for the Montana comment discussed above, were effected by the wedding ring anomalies, and steps have been taken to minimize the possibility of a recurrence in our laboratory.

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