Reports

An Iridium Abundance Anomaly at the Palynological Cretaceous-Tertiary Boundary in Northern New Mexico

Abstract. *An iridium abundance anomaly, with concentrations up to 5000 parts per trillion over a background level of 4 to 20 parts per trillion, has been located in sedimentary rocks laid down under freshwater swamp conditions in the Raton Basin of northeastern New Mexico. The anomaly occurs at the base of a coal bed, at the same stratigraphic position at which several well-known species of Cretaceous-age pollen became extinct.*

The discovery by Alvarez *et al.* (*1*) of iridium abundance anomalies at the planktonic Cretaceous-Tertiary (K-T) boundary in uplifted marine sedimentary rocks at sites in Europe and New Zealand and the hypothesis proposed by these authors, that the anomaly could have been produced by impact of a large extraterrestrial body, have generated renewed interest in the possible causes of the great extinction that marks the end of the Cretaceous Period (about 65 million years ago). Further evidence for a platinum-group metals anomaly at the marine K-T boundary has been reported by Smit and Hertogen (*2*) and by Ganapathy (*3*). All the discoveries made thus far have occurred in pelagic sediments. The possibility of marine enrichment processes, such as bottom current activity (*4*) and precipitation of siderophiles in response to alteration of the geochemical environment by the massive extinction of marine organisms (*5*), is considered to have weakened the asteroid impact argument.

We report here the observation of a strong Ir abundance anomaly at the palynological K-T boundary at a location in the Raton Basin of northeastern New Mexico and southeastern Colorado. Three factors influenced the choice of the Raton Basin for our search: (i) it is a large structural basin in which nearly continuous deposition occurred from late Cretaceous to late Paleocene times; (ii) the Raton Formation, which contains K-T boundary zone rocks, was deposited under freshwater conditions; and (iii) the approximate location of the K-T boundary had been established palynologically from past coal explorations and geologic studies.

In the Raton Basin, the stratigraphic succession from the final regression of the Cretaceous epeiric sea up through the K-T boundary zone consists of the Trinidad Sandstone deposited along the eastward-advancing strandline of the sea, followed by the coal-bearing back-beach swamps and deltas of the Vermejo Formation, which in turn is overlain by the basal conglomeratic sandstone of the Raton Formation. Overlying this basal sandstone unit the formation comprises a lower zone that consists mostly of thin to thick beds of fine- to coarse-grained sandstone alternating with beds of mudstone, siltstone, and thin coal (the palynological K-T boundary lies in this zone), and an upper zone that is similar except for the local occurrence of minable thick coal beds.

In 1966 the Kaiser Steel Corporation cored a test hole from the upper zone of the Raton Formation down to the Trinidad Sandstone at a site in York Canyon, about 50 km west of Raton, New Mexico. Tschudy analyzed samples from the numerous coal beds of the lower zone for pollen assemblages and established the palynological K-T boundary within a 3-m interval between two of the coal beds about 80 m above the base of the Raton Formation (*6*, *7*). No vertebrate fossils have been reported in these strata. Deposition of this zone occurred continuously in quiet freshwater swamps and meandering streams, a relatively favorable stratigraphic environment in which an Ir anomaly might be preserved.

Unfortunately, the original cores were not saved, and at the close of 1980 we drilled and cored at a new location about 150 m south of the 1966 site. Starting at a depth of 243 m, 30 m of core was taken with essentially 100 percent recovery. Samples of the thin coal and carbonaceous shale beds were analyzed for pollen assemblages, and continuous samples from the crucial 10-m section judged

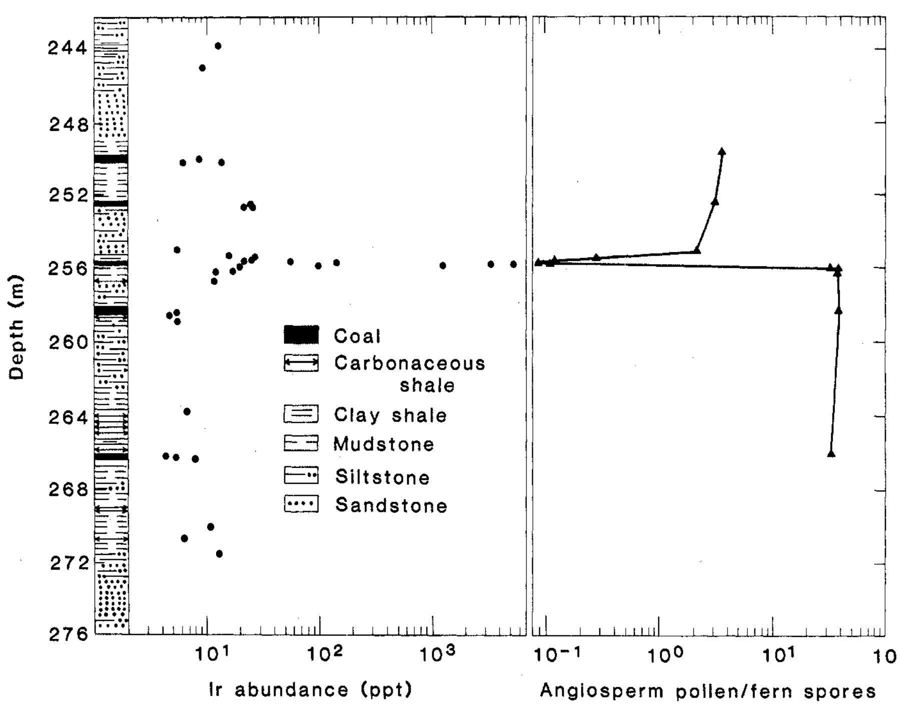

Fig. 1. Iridium abundances (circles) and ratios of angiosperm pollen to fern spores (triangles) as a function of core depth and lithology. The plotted Ir abundances in parts per trillion (parts per 10^{12}) are derived from radiochemically separated samples. The curve through the pollen data is drawn to guide the eye.

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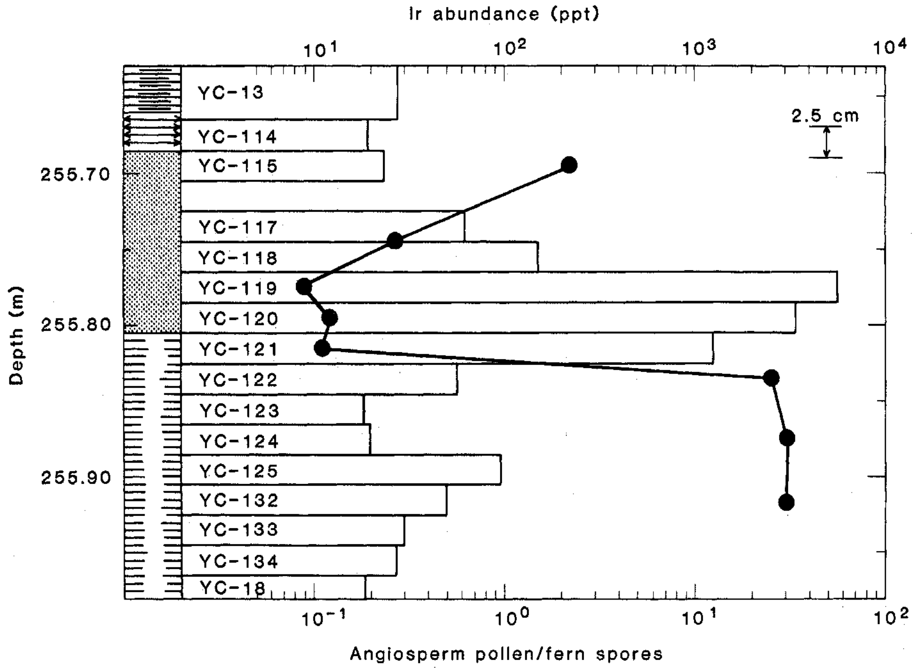

Fig. 2. Expanded view of the data of Fig. 1 in the vicinity of the Ir anomaly and the pollen break. The Ir abundances are given by the histogram and the angiosperm pollen/fern spore ratios by the circles. The curve is drawn to guide the eye. The lithologic symbols are the same as in Fig. 1 except for coal, which is shown by stipple.

to contain the boundary were analyzed for Ir and other trace elements by neutron activation followed by gamma-ray spectrum analysis. Preliminary results from the pollen analysis, based primarily on the disappearance of the Cretaceous marker pollen *Proteacidites*, reestablished the palynological K-T boundary at the same stratigraphic level, within a 1-m interval between a coal bed centered at a depth of 255.7 m and a carbonaceous shale at 256.7 m. Following observation of an Ir peak by gamma-ray spectrum analysis of the gross neutron-irradiated samples, we reexamined this region of the core in greater detail, taking 2.5-cm samples for pollen analysis and for neutron activation analysis; the latter included radiochemical purification of the Ir (*8*), which increases the sensitivity by about two orders of magnitude.

The palynological results showed an abrupt extinction of the pollen taxa *Proteacidites*, *"Tilia" wodehouseii* Anderson, *Gunnera*, and *Trichopeltinites* at the mudstone (sample YC-121) in contact with the base of the coal bed. In contrast, *Ulmipollenites* and as many as 10 to 15 other species did not become extinct. Samples immediately above YC-121 exhibit a notable increase in fern spores, in contrast to the sparse representation of angiosperm (flowering plant) pollen.

The radiochemical Ir data are plotted in Fig. 1, together with the ratios of angiosperm pollen to fern spores; the region of primary interest is displayed in expanded form in Fig. 2. We note that the Ir "spike" coincides with an abrupt drop in the angiosperm pollen/fern spore ratio in the figures. The ratio recovers to about one-tenth of its previous value in the succeeding sediments. We note also that the Ir peak occurs near the base of the coal and at its contact with the underlying mudstone, and that very little clay or other finely divided mineral matter occurs in the coal at the Ir anomaly. If we adopt a simple fallout picture based on the asteroid impact reasoning of Alvarez *et al.* (*1*) for their Gubbio (Italy) section, we would expect a 1- to 5-cm layer of finely divided country rock accompanying the Ir; we do not find it. A related concern following from the occurrence of the concentration spike in a coal bed is that Ir may have been concentrated by some chemical process associated with formation or transformation of the coal. We have attempted to deal with this possibility by careful examination of the other coal beds in the core, plus selected coals in the upper Raton Formation and in the older Vermejo Formation. From these analyses, including some shown in Fig. 1, we have observed no other Ir anomalies to date.

In addition to the Ir data plotted in Fig. 1 (representing only radiochemically separated samples), about 100 other samples from throughout the core were irradiated and analyzed for Ir by high-resolution gamma-ray assay of the whole rock. We have not observed Ir in any of these samples above our sensitivity level of about 500 ppt in coal and 700 ppt in claystone.

The zone of the correlation of the Ir abundance spike with the change in the pollen assemblages contains a stratigraphic complication. Examination of the core at the position of the Ir anomaly revealed a structural irregularity: a slickensided shear surface dipping about 40° from the horizontal at the coal-on-mudstone interface, indicating a small amount of slumping or faulting. Disturbances of this kind are not uncommon in coal sequences where a mixture of soft coal and mud deposits with lenses of sand results in displacement of strata during compaction. The importance of the shear cannot be established by examination of a core from a single hole, but the possibility of missing strata in the core does not alter the significance of the occurrence of the Ir anomaly at the palynological K-T boundary. We are currently searching in other areas of the Raton Basin to try to locate the K-T boundary in undisturbed horizontal bedding.

We have made a few measurements of platinum concentrations in samples that include the Ir anomaly, using neutron activation and radiochemical purification techniques. We observed an atom ratio Pt/Ir = 3 ± 1 at the Ir peak. Other trace elements enriched by a factor of 2 or 3 over their concentrations in samples from above and below the anomaly include Cl, Sc, Ti, V, Cr, Mn, Co, and Zn. The concentrations of the siderophiles Co and Cr reach 53 and 85 ppm, respectively, in sample YC-120 (Fig. 2). The rare earths change very little except in the mudstone near the coal-mudstone contact (sample YC-121), where their concentration is about doubled.

A heavy isotope that is sometimes considered as an indicator of a supernova burst, one of the possibilities advanced as a cause of the great extinction, is ^{244}Pu. Alvarez *et al.* (*1*) analyzed several of their Gubbio K-T boundary samples for this nuclide and set an atom ratio abundance limit $^{244}\text{Pu/Ir} < 5 \times 10^{-5}$; a ratio of $\cong 5 \times 10^{-4}$ would be expected from a supernova source. They noted, however, that these two elements could have been fractionated with respect to one another by marine chemical processes. We analyzed for ^{244}Pu in samples taken from the Ir peak (YC-119), the base region (YC-121), and a presumed "blank" coal layer at a depth of 266 m (Fig. 1), using ^{236}Pu tracer and mass spectrometric isotopic analysis (*9*). In none of the three samples was a ^{244}Pu signal observed above the dark-current background, setting an atom ratio abundance limit $^{244}Pu/Ir \leqq 1 \times 10^{-7}$. Thus, this line of evidence appears to discount a supernova event as the source of this Ir anomaly.

In summary, we have found a strong Ir abundance anomaly that coincides stratigraphically with the disappearance of several Cretaceous pollen species, which marks the K-T boundary throughout the western interior of North America. We believe that this is the first observation of the anomaly in conjunction with the palynological K-T boundary and in freshwater sediments. The $^{244}Pu/Ir$ atom ratio at the anomaly zone is $\leqq 1 \times 10^{-7}$, about two orders of magnitude lower than would be expected from a supernova event.

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8. J. S. Gilmore, in *Collected Radiochemical Procedures*, compiled by J. Kleinberg and H. L. Smith (Report LA-1721, Los Alamos National Laboratory, Los Alamos, N.M., ed. 4, 1979), p. 66.
9. Preparation of the samples for ^{244}Pu mass spectrometric analysis was performed by L. Liepins. The mass spectrometric analysis was performed by R. E. Perrin.
10. We express our gratitude to the Kaiser Steel Corporation for their cooperation in arranging the sampling operation in York Canyon, and particularly to Roger Carlson and Stephen Kotlar for their expertise and assistance in the drilling and coring. We express our admiration for the professional skill and efficiency of the Finley Drilling Company team, who provided us with essentially complete core recovery under harsh winter conditions. We are indebted to the Los Alamos National Laboratory Reactor Group for performing the neutron irradiations and for deriving chemical abundance data for about two dozen trace elements with their automated system, and to Sharon Van Loenen of the U.S. Geological Survey for preparing the samples for palynological analysis. Three of us (J.S.G., J.D.K., and C.J.O.) thank the U.S. Department of Energy for support.

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Tetramesityldisilene, a Stable Compound Containing a Silicon-Silicon Double Bond

Abstract. *Irradiation of 2,2-bis(2,4,6-trimethylphenyl)hexamethyltrisilane in hydrocarbon solution produces tetramesityldisilene, which can be isolated as a yellow-orange solid stable to room temperature and above in the absence of air. Like the olefins of carbon chemistry, tetramesityldisilene undergoes addition reactions across the silicon-silicon double bond.*

The diversity of organic chemistry arises in part because carbon readily forms multiple covalent bonds with other elements. The electronic structure of silicon is analogous to that of carbon, but the diversity of silicon chemistry has been limited by the lack of doubly bonded compounds, despite numerous attempts to synthesize them over the past six decades (*1*). Even compounds with a Si=C bond are rare, the first isolable one having been reported only this year (*2*). Evidence has been published for the transient existence of molecules with a Si=Si bond, analogous to the alkenes of organic chemistry, but such disilene species have been postulated only as reaction intermediates (*3, 4*). They have also attracted the attention of theoreticians (*5*).

We report the isolation and characterization of tetramesityldisilene, a bright orange-yellow crystalline solid. In this compound, the Si=Si bond is sterically stabilized by the presence of two 2,4,6-trimethylphenyl (mesityl) groups bonded to each silicon. Tetramesityldisilene was synthesized by the photolysis of 2,2-bis(mesityl)hexamethyltrisilane in hydrocarbon solution (*6*) (Fig. 1). The best

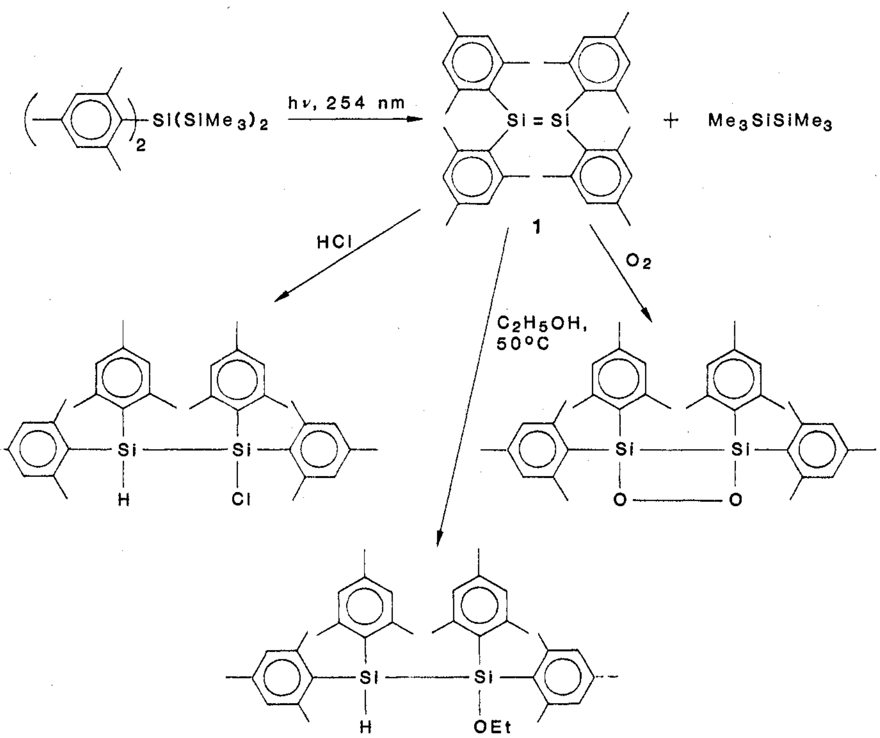

Fig. 1. Proposed scheme for the synthesis of tetramesityldisilene (**1**) and for the reaction of **1** with HCl, ethanol, and O_2; Me, methyl; Et, ethyl.

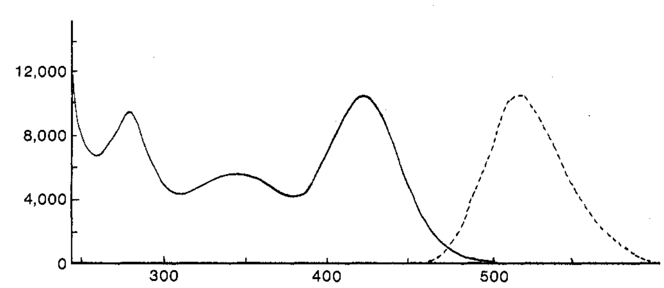

Fig. 2. Absorption (solid line) and fluorescence (dashed line) spectra of purified tetramesityldisilene (3-methylpentane, 77 K); ϵ is the molar extinction coefficient (M^{-1} cm^{-1}). The absorption spectrum in hexane solution is identical.