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Terminal Cretaceous Environmental Events

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Summary. The geologic record of terminal Cretaceous environmental events indicates that iridium and other associated elements were not deposited instantaneously but during a time interval spanning some 10,000 to 100,000 years. The available geologic evidence favors a mantle rather than meteoritic origin for these elements. These results are in accord with the scenario of a series of intense eruptive volcanic events occurring during a relatively short geologic time interval and not with the scenario of a single large asteroid impact event.

Although there is general agreement that the end of Cretaceous time is marked by one of the most significant faunal and floral transitions in the Phanerozoic record, there is less agreement about the causes.

In one scenario, suggested by Alvarez *et al.* (*1*) and other investigators (*2*), the impact of a large asteroid, an instantaneous event, is proposed. This scenario had its origin in the discovery of anomalously large concentrations of iridium associated with the Cretaceous-Tertiary (K/T) transition. The proposed impact origin of the iridium raises a basic question about whether a single, instantaneous event of the magnitude presumed could have led to the global geochemical, faunal, and floral changes observed. In this regard Kent (*3*) referred to the Toba eruption of 75,000 years ago, the largest documented Quaternary volcanic eruption (*4*). The Toba caldera is 100 by 35 km, and Kent (*3*) estimated that the atmospheric effects of the Toba eruption were about 400 times those of the 1883 Krakatoa eruption. Alvarez *et al.* (*1*) estimated the possible asteroid impact to produce effects 1000 times those of Krakatoa. There are no known massive extinctions or other extraordinary effects on life associated with the Toba eruption.

Another scenario (*5–14*) invokes a series of intense volcanic events during a geologically short time interval to explain the K/T environmental changes. The investigations of Kennett and his coworkers (*15*) on the record of Cenozoic volcanism indicate that worldwide volcanism is indeed episodic, with short periods of intense activity separated by longer intervals of relative quiescence.

The causes of biostratigraphic changes are important not only in understanding the physical development of the earth but also biological evolution. Because there should be information in the terminal Cretaceous and beginning Paleocene that will allow us to choose between the two scenarios, or others for that matter, the record of significant events in the vicinity of the discontinuity has been examined.

The Nature of the Record

An instantaneous event is difficult to discern in the geologic record. The record is often disturbed, even beneath the deep sea (*16*), and even when well preserved, it has often been subjected to bioturbation (that is, vertical mixing of sediment particles through feeding processes by benthic burrowing animals). When examining biological, chemical, or other changes on scales of the order of a few centimeters in exposed geologic sections or from Deep Sea Drilling Project (DSDP) cores, these bioturbation processes must be carefully considered. Their effect is to smear out a given chemical or biological signature through the depths in which the animals burrow. Bioturbation acts as a low pass filter for any signal and limits the depth, or time, interval discrimination that can be made. The important parameter is the effective mixing depth (d) appropriate to a particular geologic section or core.

There is good information on the bioturbation mixing conditions for the world oceans at present and in the recent geologic past. Berger and Killingley (*17*) determined mixing depths from radiocarbon observations in 29 box cores from the western and eastern equatorial Pacific. They found an average mixing depth of 11 ± 3 centimeters. Officer and Lynch (*18*) determined mixing depths from tektite, ash, and pumice distributions in 16 piston cores from the Atlantic, Pacific, and Indian oceans. Their result is 11 ± 5 cm. For a compacted or lithified K/T section the mixed layer thickness will be reduced by around one-half or slightly more. If bioturbation conditions were similar at K/T time to those at present, we would expect the bioturbation smearing effect through depth intervals of about 5 to 6 cm.

For any geologic section or core, the effects of bioturbation may also be estimated from the thickness interval over which sudden changes appear to have occurred. For example, for an original instantaneous or step function flux input, the leading edge will remain sharp and the trailing edge will decrease approximately exponentially with a decay constant of $1/d$ as one proceeds upward in the section (*18*). Of particular relevance to the geologic sections to be discussed

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below are the following observations on mixing intervals: at DSDP site 524, the $\delta^{13}C$ values from the Cretaceous nannofossils decrease from a value of 2.8 per mil at 108.0 cm in the K/T core to −0.6 per mil at 104.5 cm and then increase to 2.1 per mil at 99.0 cm (*19*). At Gubbio, Italy, burrows in the limestones suggest that bioturbation extended to a depth of 5 cm in the compacted sediment (*20*). Both of these indicators suggest bioturbation depths of around 5 cm for K/T geologic sections.

Temporal Aspects of Terminal K/T Events

There have been several observations of K/T iridium as well as other associated elements at various locations throughout the world (*21*). Pertinent results are shown in Figs. 1 through 3. The temporal patterns are not the same. They can be separated into two groups, one in which the iridium is distributed over an extended depth interval in the section (Figs. 1 and 3) and the other in which the iridium appears as a sharp spike over a bioturbation depth interval (Fig. 2).

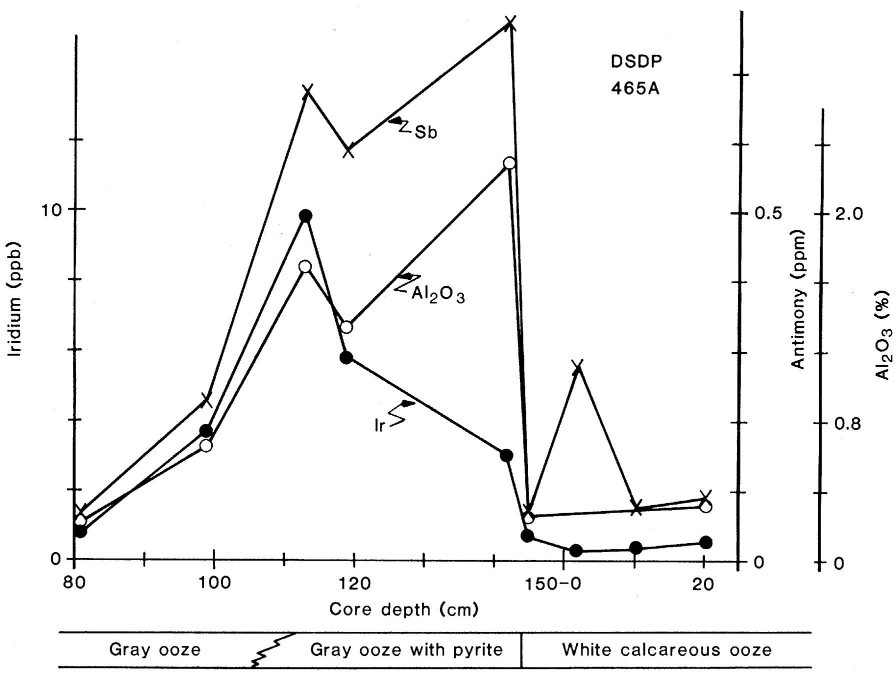

Fig. 1. Concentrations of iridium, antimony, and aluminum oxide plotted as functions of core depth from DSDP site 465 K/T section (*23*).

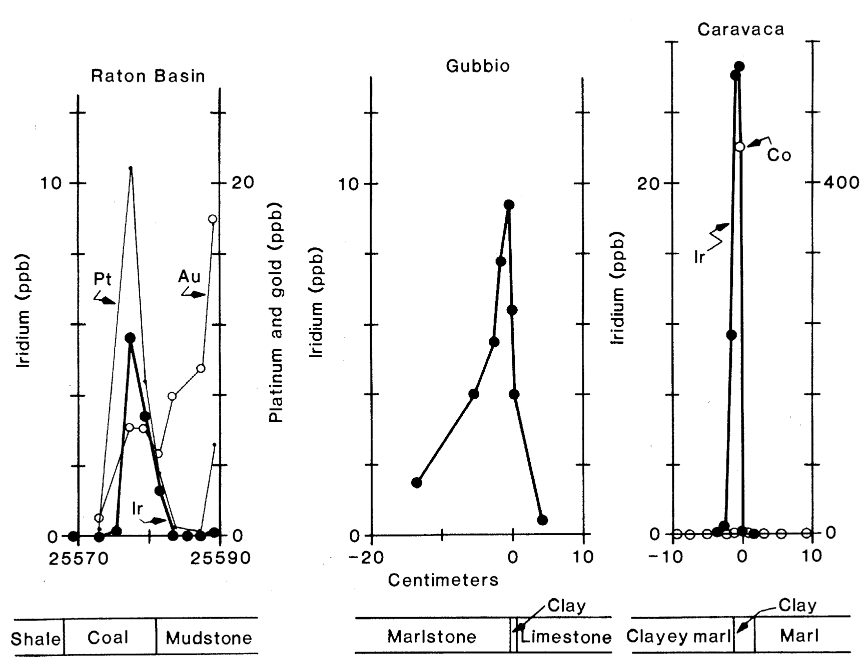

Fig. 2. Plot of iridium concentrations as a function of depth in K/T sections from the Raton Basin, New Mexico; Gubbio, Italy; and Caravaca, Spain (*1*, *25*, *26*).

Texas. A relatively small iridium anomaly was measured at the K/T Brazos River section in Texas (*22*). The lithology is a silty shale, characteristic of a shelf environment. The iridium anomaly has a peak of 2.0 parts per billion (ppb). It extends upward in the section at a level of 0.7 to 0.8 ppb through an interval of 45 cm, and the upper limit is unbounded by the observations. The depth interval is considerably greater than that expected for bioturbation effects. It might be argued that diagenetic effects have led to an upward mobilization of the iridium in the section. However, as discussed below, other constituent elements as well as the clay fraction have the same depth pattern as the iridium. There is no indication that a separate migration of iridium has been important. From the Paleocene faunal sequences it is estimated that the sedimentation rate was around 1.2 cm per 1000 years, which gives a time interval of more than 38,000 years for the incidence of the iridium flux at the Brazos River section.

DSDP site 465A. A distributed iridium anomaly was observed at DSDP site 465A in the northwestern Pacific (*23*). It correlates with the clay fraction as well as with antimony and other constituent elements (Fig. 1). The anomalies extend through an interval of 30 cm, excluding the uppermost portion of the section, and this can be interpreted as an exponential decrease resulting from bioturbation effects. The lithology is a calcareous ooze, and the sedimentation rates have been estimated to be 1.8 cm per 1000 years in the upper Maastrichtian and 0.4 cm per 1000 years in the lower Paleocene (*24*), which gives a time interval of 17,000 to 75,000 years for the incidence of the iridium flux. But there is an indication of some drilling disturbance for the K/T section at this site, which may invalidate the time interval estimate.

DSDP site 524. A distributed iridium anomaly was also observed at DSDP site 524 in the eastern South Atlantic (*19*). It also correlates with the clay fraction and extends over 43 cm with observed anomaly values of 1.1, 3.4, and 2.5 ppb. The sedimentation rates at K/T time were high, around 2.8 cm per 1000 years, reflecting inputs of volcanic origin from the nearby Walvis Ridge (*19*), which gives a time interval of 15,000 years for the incidence of the iridium flux.

Raton Basin, Gubbio, and Caravaca. Sharp iridium anomalies have been observed in the Raton Basin, New Mexico (*25*), at Gubbio, Italy (*1*), and at Caravaca, Spain (*26*). None of the distributions can be distinguished from an instantaneous flux input within the anticipated bioturbation smearing (Fig. 2). The geologic section at each location, however, has distinct lithologic boundaries within the depth range of the iridium anomalies. The lithology for the Raton Basin is a coal seam within a shale sequence and that at Gubbio and at Caravaca is a thin clay layer in a limestone or marl sequence. Cobalt shows a single isolated spike at Caravaca (Fig. 2), and the distributions of chromium, nickel, antimony, arsenic, and selenium are reported to be similar to that of cobalt (*26*). An iridium anomaly of 6 ppb has been observed at a nearby section at Biarritz, France (*27*), but the depth distribution of the iridium anomaly has not yet been determined.

Although iridium for the Raton Basin section does show a distinct anomaly coincident with the coal seam, the patterns for the associated trace elements, gold and platinum, show different distributions. Gold shows a gradual increase as a function of depth, with a peak value at the deepest measurement location. Platinum does show a peak coincident with iridium but also shows an increase at the deepest data point. No estimates are given for the geologic time represented by the mudstone-coal-shale sequence.

Arthur and Fischer (*20*) described the lithology of the section at Gubbio as consisting of bedding couplets of massive limestones, varying in thickness from 10 to 85 cm, which alternate with thin clay interbeds, that vary in thickness from a few millimeters to several centimeters. This alternating sequence extends for a considerable geologic time interval both above and below the K/T transition from the Turonian to the Eocene. Arthur and Fischer (*20*) estimate that each couplet has a duration of between 20,000 and 100,000 years and that a given clay interbed represents about half of that. Kent (*28*) reached a similar conclusion for the temporal duration of the K/T clay.

Stevns Klint. Rocchia *et al*. (*29*) made detailed measurements of iridium at Stevns Klint, Denmark. The iridium values correlate with the clay fraction and extend above background level for a considerable depth interval in the section both above and below the K/T fish clay (Fig. 3). Rocchia and his co-workers interpret the results to indicate that the influx of iridium-enriched material started during the Maastrichtian, 40 cm below the K/T stratigraphic boundary, and lasted for a part of the Danian, giving an estimated time interval of between 7,000 and 150,000 years.

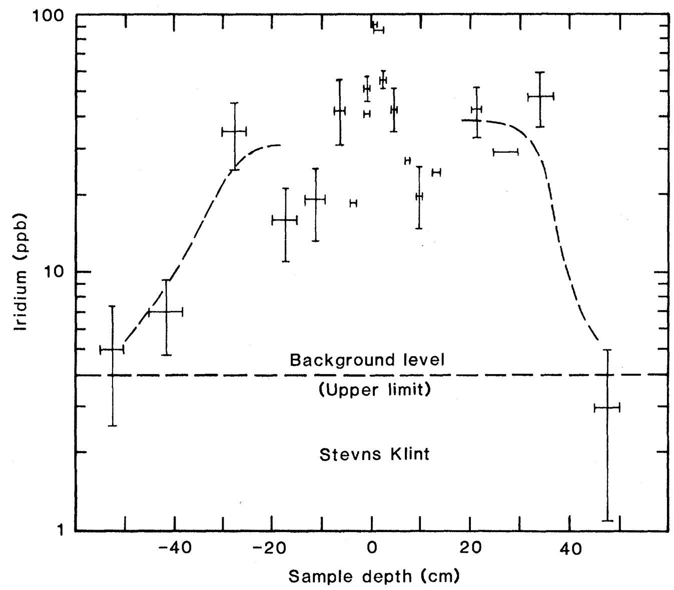

Fig. 3. Iridium concentration expressed on a carbonate-free basis and plotted as a function of section depth for the Stevns Klint, Denmark, K/T section (*29*). The fish clay extends from 0 to 10 cm.

In summary, the available measurements from the DSDP sections as well as those from Texas and Stevns Klint indicate that there was a flux of iridium during a time interval of between 10,000 and 100,000 years. The measurements from the Raton Basin, Gubbio, and Caravaca, on the other hand, show a distinct spike within anticipated bioturbation smearing. These latter three sections have distinct lithologic discontinuities, in one case represented by a coal seam and in the other two by a clay layer, which preclude precise geologic time discrimination. It will be of interest to see whether data from more recent DSDP sections, which have a continuous calcareous ooze sequence across the K/T boundary, also show an extended iridium distribution.

Signature Aspects of Terminal K/T Events

Iridium and other associated elements were not deposited instantaneously at all sites at K/T time; at some sites, there was an excess influx of these constituents during a relatively short geologic time interval on the order of 10,000 to 100,000 years. This excess influx is difficult to explain by a single asteroid event. It is possible, nevertheless, to hypothesize various other extraterrestrial source mechanisms that might produce an iridium flux over a geologically measurable time interval. Thus, it is important to ascertain whether iridium and other geochemical signatures associated with the K/T transition were of terrestrial or extraterrestrial origin. This is not easy to do because many of the signatures can be satisfied by either a mantle or meteoritic source. However, some signatures do show characteristics suggesting a mantle origin rather than meteoritic origin, particularly the arsenic and antimony concentrations and the clay mineralogy.

Iridium. The excess iridium concentrations found at Gubbio and Stevns Klint were initially interpreted to be of meteoritic origin (*1*). Little was known about mechanisms for moving iridium from the mantle to the earth's surface before the discoveries of Zoller *et al*. (*30*). They found that airborne particles collected from a recent eruption of a hot-spot volcano, Kilauea, were enriched in iridium by a factor of 10,000 to 20,000 times the concentrations found in a normal Hawaii basalt. This implies iridium concentrations in the airborne particles of around 600 ppb, which is comparable to concentrations associated with meteorites.

Other geochemical signatures. Turekian (*31*) suggested that a method for determining whether the observed iridium was of mantle or meteoritic origin, as contrasted with a crustal origin, was to examine the ratio of ^{187}Os to ^{186}Os of the companion element osmium. For a mantle or meteoritic origin the ratio should be about 1 and for a crustal origin about 10. Luck and Turekian (*32*) found $^{187}Os/^{186}Os$ in two samples at Stevns Klint to be 1.660 ± 0.027 and 1.654 ± 0.004; in a sample from the Raton Basin the value was 1.29 ± 0.04. They concluded that the osmium could be either of mantle or meteoritic origin. They also note that the value for the Raton Basin is significantly lower than those at Stevns Klint and that if there were no crustal-derived contamination, it would indicate two separate events. They caution, however, that

Table 1. Comparison of observed concentrations of arsenic, antimony, and iridium and the ratios As/IR and Sb/Ir from various K/T sections and for Cl chondrites and the atmospheric particulates collected at Kilauea. The values for the Kilauea particles were calculated from the given enrichment factors relative to a standard Hawaiian basalt (*30, 53*).

Location	As (ppb)	Sb (ppb)	Ir (ppb)	As/Ir	Sb/Ir	Reference
Caravaca	760,000	17,000	57	13,000	300	(*49*)
Gubbio	18,500	2,460	9	2,100	270	(*50*)
Stevns Klint	83,000	9,400	47	1,800	200	(*49*)
DSDP 465A	6,400	670	10	640	67	(*23*)
GPC 3	58,000	4,900	10	5,800	490	(*51*)
Chondrites	1,800	138	514	3.5	0.27	(*52*)
Kilauea	6,000,000	48,000	630	9,500	80	(*30*)

crustal contamination cannot be ruled out.

De Paolo *et al.* (*33*) determined two other isotopic ratios, $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$, at Caravaca, DSDP site 465A, and Giant Piston Core 3. They found that the ratios vary in a manner similar to those for the iridium concentration, and concluded that most of the clay was derived from a terrestrial source and that the observed anomalies could be explained either in terms of a mantle or meteoritic origin.

Varekamp and Thomas (*34*) examined the potassium-rich feldspar (sanidine) spherules as well as other large particles from Caravaca, Giant Piston Core 3, and Gubbio. They concluded that no common characteristic for a supposedly extraterrestrial material can be found in the sediments from these localities. De Paolo *et al.* (*33*) concluded that the sanidine spherules are predominantly authigenic and may have formed after the time of deposition. Montanari *et al.* (*35*) also examined sanidine spherules from various K/T sites. They interpret them as diagenetically altered microcrystalline spherules of basaltic composition produced by the impact of a large asteroid. Of particular importance to these investigations are the observations by Vannucci *et al.* (*36*) that large spherules as well as iron-rich particles are found in various clay-layer levels both above and below the K/T boundary as well as in the K/T clay at Gubbio. From the composition of the spherules, they conclude that they are of volcanic origin.

Lamellar quartz features. Bohor *et al.* (*37*) examined the quartz component of a thin claystone layer in Montana. The layer is nonmarine in origin, has an iridium anomaly of 1 ppb, and corresponds with a palynological K/T transition. The nonclay fraction amounted to about 0.01 percent of the total sample; 90 percent of this fraction was quartz. Scanning electron microscope examination showed that about 25 percent of the quartz grains had prominent lamellar features. The authors conclude that the quartz features are high pressure or shock metamorphic in origin and represent silicic material injected into the stratosphere by the impact of a meteor. The grains are of fairly large size (50 to 100 μm). If distributed through the atmosphere, they could not have been carried great distances. If carried on ballistic trajectories, it is reasonable to ask why annealing on reentry would not have destroyed the lamellar features. It should be noted that several buried impact craters of Mesozoic age were found in the vicinity of the Montana samples during exploration for oil (*38*).

The presence of lamellar quartz features does not in and of itself demonstrate a meteor impact origin. High pressure or shock metamorphic features are characteristic of materials associated with meteor craters, but they are also associated with underground nuclear explosions (*39*). Lamellar features in quartz grains are also a characteristic of both normal tectonic metamorphism and shock metamorphism, although the normal tectonic features are quite different from the shock features (*40*). Of particular interest is the recent discovery of coesite in eclogite sequences (*41, 42*) as well as its occurrence in certain nodules in kimberlite pipes (*43*). Coesite is a high-pressure polymorph of quartz that is formed at pressures of about 30 kilobars or greater. Smith (*42*) suggested that the occurrence of coesite in the eclogite sequences implied tectonic overpressures of relatively large magnitude and short duration associated with the deformation process.

The pertinent question is whether all these naturally occurring features are necessarily of external origin, that is, meteor impacts, or whether some are of internal origin, that is, intense volcanic or tectonic overpressure events of deep-seated origin (*44*). This question applies to the cryptovolcanic structures discussed by Bucher and others (*45*) as well as to such large-scale features as the massive ultrabasic intrusion at Sudbury, Ontario, and the massive granitic intrusion at Vredefort, South Africa. At Sudbury, shock metamorphic features are a distinct characteristic of the quartz grains in the formation overlying the intrusion. The two possible origins for these features that have been suggested are either a large meteor impact, which somehow triggered the intrusion, or a large overpressure event associated with the intrusion of the magma (*46*). Investigations indicate that the shock metamorphic features of the Vredefort structure are of internal origin. Lilly (*47*) has shown that there were two shock events ($\sim$100 kbar) and that these two events were separated in time. Schreyer (*48*) has shown that the dynamic, or shock, metamorphic events postdate the onset of the static, or high-temperature, metamorphic process. Although, as cited by Bohor *et al.* (*37*), the occurrence of closely spaced, intersecting laminae does indicate a shock metamorphic origin, the source of the overpressure is less certain. Investigations at other sites should establish whether lamellar features of high-pressure origin are a distinct feature of K/T geologic sections and may add to our information about their origin.

Arsenic and antimony. Several of the diagnostic elements that one might use to distinguish between a mantle and a meteoritic source have comparable normalized ratios. Consideration of individual source differences, either among mantle samples or meteoritic samples, and the chemical pathways from source to final lithification in a sedimentary sequence preclude too close a comparison of such normalized ratios; agreement within roughly an order of magnitude is not unexpected. However, there are two elements that are found in association with iridium in K/T samples whose abundances are far in excess of what would be expected for a meteoritic source. These elements are arsenic and antimony.

Observed arsenic, antimony, and iridium concentrations and the ratios As/Ir and Sb/Ir for various K/T sections are shown in Table 1 (*23, 49–51*). Also shown are the corresponding values and ratios for C1 chondrites (*52*) and for the airborne particles from Kilauea analyzed by Zoller *et al.* (*30*) with reference to a standard Hawaiian basalt (*53*). Both the As/Ir and Sb/Ir are three orders of magnitude too large for a source chondritic in composition. The comparison with the corresponding ratios for the Kilauea airborne particulates is reasonable.

Clay. As noted above, the observed iridium anomalies show a direct correlation with the clay fraction in each of the K/T sections. It might be expected that if a portion of the increased clay fraction were related to extraterrestrial events that it would have a different mineralogy than clays elsewhere in the sedimentary section. This is not the case. Rampino and Reynolds (*54*) examined K/T boundary layer clays as well as clays both above and below the boundary at Stevns Klint, Gubbio, Caravaca, and El Kef, Tunisia. They found that the boundary clay is neither mineralogically exotic nor distinct from the clays above and below the boundary. The clay mineralogy, smectite and smectite-illite, suggest to them that the clays in and near the boundary layers were formed by alteration of glassy volcanic ash or represent local detrital sources. Wezel *et al.* (*14*) and Bonté *et al.* (*27*) were also unable to find any exotic components at the Gubbio and Biarritz sections. While obtaining similar results to Rampino and Reynolds, Kastner *et al.* (*55*) concluded, on the basis of the presence of spherules and iridium, that the clay was formed by meteoritic impacts rather than by volcanism.

Most of the investigations to date for iridium and associated elements have concentrated on measurements at the K/T transition. It seemed relevant to look elsewhere in the Upper Cretaceous and Paleocene for these elements. There are several clay layers in the geologic section at Gubbio. Wezel *et al.* (*14*) and Vannucci *et al.* (*36*) observed iridium anomalies of 1 to 6 ppb in various clay layers within a few meters both above and below the K/T boundary as well as in the boundary layer clay, and Sighinolfi (*56*) observed palladium anomalies of 3 to 23 ppb in various clays through the same depth range. Additional clay layer samples have been collected across a section range of 219 m extending down from the boundary layer clay, which covers a geologic time interval from Maastrichtian to Turonian. Trace element analyses (*57*) and chondritic values for the same elements (*53*) are shown in Table 2. The results show the iridium concentration in the K/T clay to be distinct from the other clays, but there are no obvious differences in gold, platinum, and palladium concentrations among the clays.

Table 2. Analyses of iridium, gold, platinum, and palladium concentrations in clay-layer samples throughout the Upper Cretaceous of the Scaglia Rossa formation at Gubbio, Italy. Depths are in meters below the K/T boundary layer clay.

Sample	Depth (m)	$CaCo_3$ (%)	Ir (ppb)	Au (ppb)	Pt (ppb)	Pd (ppb)
347.60 G	0	25.2	2.8	3.0	31.5	11
345.80 G	1.80	39.1	0.2	1.3	23.6	15
258.00 G	89.60	49.8		3.8	13.4	8
223.30 G	124.30	65.8		0.8	34.4	3
202.30 G	145.30	12.5	0.2	1.2	5.2	23
134.45 G	213.15	32.5	0.2	0.2	28.6	4
128.70 G	218.90	75.5		5.3	15.0	2
Chondrite			514	152	900	460

In summary, the concentrations of arsenic and antimony and the clay mineralogy suggest a mantle source rather than a meteoritic one. The iridium anomalies and the high-pressure lamellar quartz found in Montana can be related to either a mantle or meteoritic source. The high concentrations of gold, platinum, and palladium in the Maastrichtian to Turonian clays at Gubbio cannot be explained by a single asteroid impact at K/T time.

Direct Evidence of Terminal K/T Events

Whatever the origin of the major K/T environmental events that led to the observed faunal and floral changes, it would be encouraging to find some direct legacy of the event itself. For the asteroid impact hypothesis, this would be the crater itself or some evidence of it. For the intense, eruptive volcanism hypothesis, this would be some direct evidence of massive vertical movements of mantle material to the earth's surface at K/T time.

There is as yet no evidence of a large diameter crater at K/T time (*1, 58*). There is direct evidence that there were massive vertical movements of mantle material to the earth's surface at K/T time and that this emplacement occurred during a relatively short geologic time interval. These are the Deccan traps. They are one of the largest continental flood basalts known throughout the Phanerozoic, covering an area of more than 500,000 km^2 with an estimated volume of between 500,000 and 1,000,000 km^3 (*59*). Volcanism in the Deccan trap region continued with varying degrees of activity from 100 to 30 million years ago (*60*). The major episode of volcanism, however, occurred during the Late Cretaceous and early Paleocene and has been dated by potassium-argon from 60 to 65 million years ago or possibly older (*59, 61*). The marine beds underlying these traps are Late Cretaceous and the intertrappean beds contain fossil plants and fishes thought to be Paleocene in age (*61*). These traps show a small reversed and normal paleomagnetic sequence at their base, a reversed interval for the emplacements of most of the traps, and a small normal interval at their top (*62*). If the middle reversed interval corresponds to 27R, 28R, or 29R, which seems reasonable, then the emplacement of most of the traps occurred during a time interval of 430,000 to 880,000 years (*63*).

The Deccan traps indicate extensive vertical movements of mantle material at the K/T transition and, in conjunction with other locales, may have been the source location for the observed iridium anomalies, as also suggested by Zoller *et al.* (*30*). We are not aware of any iridium measurements for the Deccan traps, but Crocket and Skippen (*64*) have investigated palladium in these and other continental flood basalts and in ocean island basalts. The three Deccan trap samples showed palladium concentrations of 1, 27, and 29 ppb, the latter two being the highest concentrations found in the 20 basalt samples measured. There is no assurance that iridium concentrations are comparable; but if they are, then the volume of associated explosive volcanism required to provide an amount of iridium equivalent to that of a 10-km bolide (500 ppb) would be only 13,000 km^3.

We note that the Siberian traps, which cover an area and have a volume comparable to those of the Deccan traps (*65*), are Permian to Triassic in age. At that time, the next major faunal extinction event preceding the K/T event occurred.

Faunal and Floral Transitions at K/T Time

Officer and Drake (*66*) have previously presented arguments that the K/T transition effects related to the faunal and floral changes did not occur instantaneously but took place during a period of 100,000 years or possibly longer. Similar proposals have been advanced by others

(*67*), and these proposals have engendered a variety of responses (*68*). For instance, Alvarez *et al.* examined the invertebrate fossil record at K/T time and conclude that there was a sharp truncation in species that was synchronous with a presumed instantaneous, asteroid impact; they do not, however, mention extinctions occurring within a geologic time interval on the order of 100,000 years, and this is critical to any scenario. Surlyk and Johansen report that the Cretaceous brachiopod extinctions in Denmark were abrupt, but from their figure 1, it appears that the extinctions occurred throughout an interval of 100 cm in the section, or approximately 100,000 years. Smit and van der Kaars reexamined the Montana K/T section originally investigated by others (*69*). Pillmore *et al.* continued the examinations in the Raton Basin where there is a sharp iridium anomaly that is coincident with the extinction of five palynofloral species. Despite the various criticisms, Officer and Drake stand by their original arguments (*66*).

Conclusions

We conclude that iridium and other associated elements were not deposited instantaneously at the K/T transition, but rather that there was an intense and variable influx of these constituents during a relatively short geologic time interval on the order of 10,000 to 100,000 years. Further, we suggest that the available evidence favors a mantle origin rather than a meteoritic origin for these constituents.

The scenario that the major environmental event at K/T time was an intense period of volcanic events appears reasonable. On the basis of the results discussed herein and the investigations by Kennett *et al.* (*15*), Vogt (*13*), and Zoller *et al.* (*30*), we suggest that this volcanism is related to an immense increase in mantle plume (that is, hot spot) activity for a relatively short geologic time interval and that the mantle plume activity probably occurred simultaneously at several localities throughout the world including the Deccan Plateau. There may be a correlation between breakup and drifting of continents and the occurrence of major faunal extinction events.

Various investigators have discussed some of the possible implications of such a scenario. These include the effects of increased carbon dioxide emissions on global atmospheric temperature conditions, the effects of increased volatile emanations on depletion of the ozone layer with consequent increased ultraviolet radiation, and the variety of effects that these atmospheric chemical and temperature changes would have on ocean circulations and carbon-sulfur-oxygen relations. A reasonable next step is quantitative paleoclimatic and paleoceanographic modeling of the cumulative effects of increased volcanism during a period on the order of 10,000 to 100,000 years would provide insight into changes in the world's atmosphere and hydrosphere and help in explaining the variety, timing, time intervals, and hiatuses for the geochemical, faunal, and floral changes that are observed (*66, 67, 70*). Modeling of this type has been suggested as a significant component in the proposed International Geosphere Biosphere Program (*71*).

References and Notes

1. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208**, 1095 (1980).
2. K. J. Hsu, *Nature (London)* **285**, 201 (1980); R. Ganapathy, *Science* **209**, 921 (1980).
3. D. V. Kent, *Science* **211**, 648 (1981).
4. J. Westerveld, *Geol. Soc. Am. Bull.* **63**, 561 (1952).
5. D. I. Axelrod, *Geol. Soc. Am. Spec. Pap. 185* (1981).
6. J. Campsie, G. L. Johnson, J. E. Jones, J. E. Rich, *Eos* **65**, 796 (1984).
7. J. M. Doreen, *Micropaleontology* **20**, 178 (1974).
8. A. A. Ekdale and R. G. Bromley, *J. Sediment. Petrol.* **54**, 681 (1984).
9. M. L. Keith, *Eos* **61**, 400 (1980); M. L. Keith, *Geochim. Cosmochim. Acta* **46**, 2621 (1982).
10. D. M. McLean, *Eos* **63**, 562 (1982); D. M. McLean, *Cretaceous Res.*, in press.
11. N.-A. Mörner, *J. Geol.* **90**, 564 (1982).
12. L. M. Van Valen, *Paleobiology* **10**, 121 (1984).
13. P. R. Vogt, *Nature (London)* **240**, 338 (1972).
14. F. C. Wezel, S. Vannucci, R. Vannucci, *C.R. Acad. Sci.* **293**, 837 (1981).
15. J. P. Kennett and R. C. Thunell, *Science* **187**, 497 (1975); *ibid.* **196**, 1231 (1977); J. P. Kennett, A. R. McBirney, R. C. Thunell, in *Island Arcs, Deep Sea Trenches and Back Arc Basins*, M. Talwani and W. C. Pitman, Eds. (American Geophysical Union, Washington, D.C., 1977), p. 348; J. P. Kennett *et al.*, *Am. J. Sci.* **279**, 52 (1979).
16. C. D. Hollister and I. N. McCave, *Nature (London)* **309**, 220 (1984).
17. W. H. Berger and J. S. Killingley, *Mar. Geol.* **45**, 93 (1982).
18. C. B. Officer and D. R. Lynch, *ibid.* **52**, 59 (1983).
19. K. J. Hsü *et al.*, *Science* **216**, 249 (1982).
20. M. A. Arthur and A. G. Fischer, *Geol. Soc. Am. Bull.* **88**, 367 (1977).
21. W. Alvarez, L. W. Alvarez, F. Asaro, H. V. Michel, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 305.
22. R. Ganapathy, S. Gartner, M.-J. Jiang, *Earth Planet. Sci. Lett.* **54**, 393 (1981).
23. H. V. Michel, F. Asaro, W. Alvarez, L. W. Alvarez, *Init. Rep. Deep Sea Drill. Proj.* **62**, 847 (1981).
24. Shipboard Scientific Party, *ibid.*, p. 199.
25. C. J. Orth, J. S. Gilmore, J. D. Knight, C. L. Pillmore, R. H. Tschudy, J. E. Fassett, *Science* **214**, 1341 (1981); C. J. Orth *et al.*, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 423.
26. J. Smit, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 329.
27. Ph. Bonté *et al.*, *Geophys. Res. Lett.* **11**, 473 (1984).
28. D. V. Kent, *Geology* **5**, 769 (1977).
29. R. Rocchia, M. Renard, D. Boclet, Ph. Bonté, *Geol. Soc. Fr. Bull.*, in press; R. Rocchia, D. Boclet, Ph. Bonté, C. Jehanno, M. Renard, in preparation.
30. W. H. Zoller, J. R. Parrington, J. M. P. Kotra, *Science* **222**, 1118 (1983).
31. K. K. Turekian, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 243.
32. J. M. Luck and K. K. Turekian, *Science* **222**, 613 (1983).
33. D. J. De Paolo, F. T. Kyte, B. D. Marshall, J. R. O'Neill, J. Smit, *Earth Planet. Sci. Lett.* **64**, 356 (1983).
34. J. C. Varekamp and E. Thomas, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 461.
35. A. Montanari *et al.*, *Geology* **11**, 668 (1983).
36. R. Vannucci, S. Vannucci, A. Muzzucotelli, S. Meloni, M. Oddone, *Rend. Soc. Ital. Mineral. Petrol.* **38**, 413 (1981).
37. B. F. Bohor, E. E. Foord, P. J. Modreski, D. M. Triplehorn, *Science* **224**, 867 (1984).
38. E. S. Parson, *Bull. Am. Assoc. Petrol. Geol.* **58**, 910 (1974); H. B. Sawatsky, *ibid.* **59**, 694 (1975); E. S. Parson, W. Henderson, L. J. Conti, *ibid.*, p. 2197; H. B. Sawatsky, *ibid.* **60**, 1409 (1960).
39. B. M. French and N. M. Short, Eds., *Shock Metamorphism of Natural Materials* (Mono Books, Baltimore, 1968).
40. W. H. Scott, E. Hansen, R. J. Twiss, *Am. J. Sci.* **263**, 729 (1965); N. L. Carter and M. Friedman, *ibid.*, p. 747.
41. C. Chopin, *Terra Cognita* **3**, 183 (1983); *ibid.* **4**, 35 (1984).
42. D. C. Smith, *Nature (London)* **310**, 641 (1984).
43. J. R. Smyth and C. J. Hatton, *Earth Planet. Sci. Lett.* **34**, 384 (1977).
44. B. M. French, in (*39*), p. 1.
45. W. H. Bucher, *Am. J. Sci.* **261**, 597 (1963); R. S. Dietz, *ibid.*, p. 650; F. G. Snyder and P. E. Gerdemann, *ibid.* **263**, 465 (1965).
46. B. M. French, in (*39*), p. 383.
47. P. A. Lilly, *J. Geophys. Res.* **86**, 10689 (1981).
48. W. Schreyer, *J. Petrol.* **24**, 26 (1983).
49. F. T. Kyte, J. Smit, J. T. Wasson, *Earth Planet. Sci. Lett.*, in press.
50. J. Smit and W. G. H. Z. ten Kate, *Cretaceous Res.* **3**, 307 (1982).
51. F. T. Kyte and J. T. Wasson, *Geochim. Cosmochim. Acta*, in press.
52. B. Mason, Ed., *Handbook of Elemental Abundances in Meteorites* (Gordon & Breach, New York, 1971); V. Krähenbühl, J. Morgan, R. Ganapathy, E. Anders, *Geochim. Cosmochim. Acta* **37**, 1353 (1973).
53. E. S. Gladney and W. E. Goode, *Geostandards Newsl.* **5**, 31 (1981); J. S. Gilmore, J. D. Knight, C. J. Orth, C. L. Pillmore, R. H. Tschudy, *Nature (London)* **307**, 224 (1984).
54. M. R. Rampino and R. C. Reynolds, *Science* **219**, 495 (1983).
55. M. Kastner, F. Asaro, H. V. Michel, W. Alvarez, L. W. Alvarez, *ibid.* **226**, 137 (1984).
56. G. P. Sighinolfi, *Period. Mineral. Roma* **50**, 91 (1981).
57. J. H. Crocket, C. B. Officer, G. D. Johnson, F. C. Wezel, unpublished data.
58. R. A. F. Grieve, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 25.
59. I. Kaneoka and H. Haramura, *Earth Planet. Sci. Lett.* **18**, 229 (1973).
60. P. O. Alexander, in *Deccan Volcanism*, K. V. Subbarao and R. N. Sukheswala, Eds. (Memoir 3, Geological Society of India, Bangalore, 1981), p. 244.
61. P. Wellman and M. W. McElhinny, *Nature (London)* **227**, 595 (1970).
62. H. Wensink and C. T. Klootwijk, *Tectonophysics* **11**, 175 (1971); C. T. Klootwijk in *Geodynamics of Pakistan*, A. Farah and K. A. De Jong, Eds. (Geological Survey of Pakistan, Quetta, 1979), p. 41; H. Wensink *et al.*, in *Fourth International Gondwana Symposium*, B. Laskar and C. S. Rajarao, Eds. (Hindustani Publishing, Delhi, 1979), p. 832.
63. G. Ness, S. Levi, R. Couch, *Rev. Geophys. Space Phys.* **18**, 733 (1980).
64. J. H. Crocket and G. B. Skippen, *Geochim. Cosmochim. Acta* **30**, 129 (1966).
65. V. A. Naumov and A. M. Mukhina, *Int. Geol. Rev.* **19**, 951 (1977); G. F. Makarenko, *ibid.*, p. 1089; V. S. Bochkarev and M. Ya. Rudkevich, *Geotectonics* **9**, 181 (1975).
66. C. B. Officer and C. L. Drake, *Science* **219**, 1383 (1983).
67. T. Birkelund and R. G. Bromley, in *Cretaceous-Tertiary Boundary Events*, T. Birkelund and R. G. Bromley, Eds. (Univ. of Copenhagen Press, Copenhagen, 1979), vol. 1, p. 5; J. D. Archibald and W. A. Clemens, *Am. Sci.* **70**, 377 (1982); L. J. Hickey, R. M. West, M. R. Dawson, D. K. Choi, *Science* **221**, 1153 (1983).
68. W. Alvarez, E. G. Kauffman, F. Surlyk, L. W. Alvarez, F. Asaro, H. V. Michel, *Science* **223**, 1135 (1984); F. Surlyk and M. B. Johansen, *ibid.*, p. 1174; J. Smit and S. van der Kaars, *ibid.*, p. 1177; C. L. Pillmore, R. H. Tschudy, C. J. Orth, J. S. Gilmore, J. D. Knight, *ibid.*, p. 1180; W. Alvarez, L. W. Alvarez, F. Asaro, H. Michel, *ibid.*, p. 1183.
69. L. Van Valen and R. E. Sloan, *Evol. Theory* **2**, 37 (1977); W. A. Clemens and J. D. Archibald,

Mem. Soc. Geol. Fr. **139**, 67 (1980); J. D. Archibald, *Nature (London)* **291**, 650 (1981); L. J. Hickey, *ibid.* **292**, 529 (1981).
70. N. D. Newell, *Geol. Soc. Am. Spec. Pap. 180* (1982), p. 257; H. Tappan, *ibid.*, p. 265; K. Perch-Nielsen, J. McKenzie, Q. He, *ibid.*, p. 353; T. Birkelund and E. Hakansson, *ibid.*, p. 373; H. R. Thierstein, *ibid.*, p. 385; W. A. Clemmens, *ibid.*, p. 407; T. J. M. Schopf, *ibid.*, p. 415.
71. J. A. Eddy, W. S. Broecker, C. L. Drake, R. J. Cicerone, R. B. McElroy, *Eos* **65**, 177 (1984).
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Single-Carbon Chemistry of Acetogenic and Methanogenic Bacteria

J. G. Zeikus, R. Kerby, J. A. Krzycki

There has been considerable chemical research on the technological application of single-carbon (C_1) transformations. Synthesis gas (syngas), a mixture of hydrogen and carbon monoxide has long been used as a feedstock for production of industrial chemicals. Although syngas has been derived from methane it is rived from syngas by copper-zinc chromite–containing catalysts) and CO to acetic acid depends on homogeneous rhodium-containing catalysts (Monsanto process), although cobalt was used initially and efforts to produce suitable nickel-containing catalysts are under way.

Summary. Methanogenic and acetogenic bacteria metabolize carbon monoxide, methanol, formate, hydrogen and carbon dioxide gases and, in the case of certain methanogens, acetate, by single-carbon (C_1) biochemical mechanisms. Many of these reactions occur while the C_1 compounds are linked to pteridine derivatives and tetrapyrrole coenzymes, including corrinoids, which are used to generate, reduce, or carbonylate methyl groups. Several metalloenzymes, including a nickel-containing carbon monoxide dehydrogenase, are used in both catabolic and anabolic oxidoreductase reactions. We propose biochemical models for coupling carbon and electron flow to energy conservation during growth on C_1 compounds based on the carbon flow pathways inherent to acetogenic and methanogenic metabolism. Biological catalysts are therefore available which are comparable to those currently in use in the Monsanto process. The potentials and limitations of developing biotechnology based on these organisms or their enzymes and coenzymes are discussed.

increasingly manufactured from coal and may be derived from nonfossilized forms of biomass. The role of syngas and C_1 chemistry in the production of polymeric chemicals and fuels may increase as the supply of petroleum-derived chemicals becomes limiting (*1*).

The conversion of single-carbon compounds to higher molecular weight products depends on metal-containing catalysts (*2*). The conversion of syngas to methane and higher hydrocarbons (Fischer-Tropsch reaction) and of methane to ethanol occur in the presence of iron-, cobalt-, or nickel-containing catalysts. The conversion of methanol (itself de-

There are similarities between many of these C_1 transformation reactions and metabolic reactions occurring in at least two groups of anaerobic bacteria (acetogens and methanogens) that consume various single-carbon substrates and acetate as energy sources. The acetogens produce acetic, butyric, or mixtures of both acids, while the methanogens produce methane. These bacteria are notable for (i) their complements of unusual enzymes and coenzymes in which nickel, cobalt, iron, tungsten, molybdenum, selenium, and zinc are present either singly or in various combinations; and (ii) their unusual energy-yielding mechanisms, which do not necessarily rely on the breakdown of carbon substrates. Thus, the usual connection between catabolism and degradation of carbon-carbon bonds is not found in the catabolic processes of acetogens and methanogens when they are grown on C_1 substrates.

Early studies on acetogens and methanogens have followed a fairly parallel course because they are found in similar environments and because they utilize some of the same substrates (*3*). Thus, research on cultures enriched for growth of methanogens (*3*) recorded methane and "vinegar acid" formation from H_2 and CO_2. Soon representative species were isolated including the acetogen *Clostridium aceticum*, which consumes saccharides and H_2 plus CO_2, and the methanol- and acetate-catabolizing methanogen, *Methanosarcina barkeri*.

We review the C_1 chemistry of anaerobes that can consume C_1 compounds as their sole electron donors and acceptors including both acetogens and methanogens; however, we exclude those species in which sulfate is used as an electron acceptor (*4*) and the acetogens that degrade purines and amino acids (*5*).

Microbial Acetogenic Transformations

Table 1 (top) shows the physiological properties of widely studied acetogenic bacteria. Many other species have also been described, including *Clostridium thermoautotrophicum* which can grow on methanol at temperatures higher than 60°C (*6*). Analysis of RNA sequences from diverse acetogens has not revealed a unifying correlation between this catabolic process and phylogeny (*7*). As in

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