Terrestrial Carbon and Nitrogen Isotopic Ratios from Cretaceous-Tertiary Boundary Nanodiamonds

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One hypothesis for the origin of the nanometer-size diamonds found at the Cretaceous-Tertiary (K-T) boundary is that they are relict interstellar diamond grains carried by a postulated asteroid. The $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios of the diamonds from two sites in North America, however, show that the diamonds are two component mixtures differing in carbon and nitrogen isotopic composition and nitrogen abundance. Samples from a site from Italy show no evidence for either diamond component. All the isotopic signatures obtained from the K-T boundary are material well distinguished from known meteoritic diamonds, particularly the fine-grain interstellar diamonds that are abundant in primitive chondrites. The K-T diamonds were most likely produced during the impact of the asteroid with Earth or in a plasma resulting from the associated fireball.

Since the original discovery by Alvarez and colleagues (*1*) of excess Ir at the K-T boundary, various unsuccessful attempts have been made to identify meteoritic signatures in boundary clays, including those of noble gases (*2*), trace elements (*3*), and Os isotopes (*4*). Recently Carlisle and Braman discovered nanometer-size diamonds in samples from the K-T boundary at Knudsens' farm, Canada (*5*). Because diamonds, sometimes called C_8, are ubiquitous in primitive chondrites (*6–8*), it was suggested (*5*) that the K-T diamonds may have come from the impacting asteroid or comet. If the diamonds could be shown to be of meteoritic origin, not only would the impact theory be confirmed but the identity of the impactor could be narrowed to a small number of candidate meteorite types.

Nanometer-size diamonds were first identified in acid-resistant residues from carbonaceous and enstatite chondrites by Lewis and co-workers in 1987 (*6*) and have since been isolated from all chondrite groups in amounts up to 940 ppm (*7, 8*). They were recognized as presolar grains (*6–9*) on the basis of the presence of the highly anomalous noble gas component xenon-HL and of extremely negative N isotope compositions (*10*) of approximately −343 ± 16 per mil. However, the diamonds themselves have typical solar system–like C isotopic compositions of −32 to −38 per mil. If the K-T diamonds are meteoritic in origin, the above elemental and isotopic properties could be used to identify them.

To characterize the nanometer-size diamonds at the K-T boundary, we undertook a systematic study of acid-resistant residues from three boundary sites in North America and Europe using six independent criteria: diamond size distribution, C isotopic composition, N isotopic composition, N abundance, C release profiles obtained in stepped heating experiments, and N release profiles.

Samples of the fireball layer (*11*) and the rocks lying 6 to 8 cm below the boundary from Brownie Butte, Montana, the fireball layer from Berwind Canyon, New Mexico, and total boundary clay from Pettricio, Italy, were used. Bulk samples (70 g for Berwind Canyon, 8 g for Brownie Butte, and 20 g for Pettricio) were cycled in 9 M HF–1 M HCl and 1 M HCl at 20°C followed by treatment with 0.4 N $Cr_2O_7^{2-}$ in H_2SO_4 and fuming $HClO_4$, our standard procedure for isolating the interstellar grains of diamond and SiC from meteorites (*7, 12*). Because the residues were to be analyzed for N, the ammonia suspension technique (*5, 6*) for the colloidal separation of diamond from coarser minerals was not used. Aliquots of the residues were subjected to transmission electron microscopy (TEM) examination to confirm the presence or absence of diamond and to determine its crystal habit. The method used for C and N isotope analysis of the residues (on aliquots of 40 to 500 μg) consisted of high-resolution stepped combustion (*13–15*) (temperature increments of 25°C) coupled with static mass spectrometry (*16*). When applied to meteorites, these two procedures have produced release profiles showing that C and N associated with diamond can be satisfactorily resolved from other C- and N-containing phases (*17*).

Transmission electron microscopy (Fig. 1) showed that the acid residues from the Brownie Butte and Berwind Canyon fireball layers contained both inorganic and carbonaceous components. The principal inorganic minerals recognized were high in Ti, Zr, and W, presumably from the presence of rutile and zircon. Electron diffraction patterns for the carbonaceous component in the two samples showed predominant d-spacings (interatomic distances) at 2.06, 1.26, and 1.08 Å, characteristic of cubic diamond. If the hexagonal form, normally considered to be the impact-produced polytype, does occur, it is greatly subordinate. The diamonds occur as clumps; individual crystals are ~6 nm in size and vary in morphology from irregular to near-cubic crystals. Examination of the sample from 6 to 8 cm below the boundary at Brownie Butte and the boundary clay sample from Petriccio showed no signs of any diamonds or other ordered forms of C. The grain size of the diamonds examined here is similar to that reported by Carlisle and Braman (*5*) for the samples from Knudsens' farm but is larger than the typical 2 to 3 nm of meteoritic diamonds.

Analysis by stepped combustion showed that the fireball layer from Brownie Butte contained a little more than 3% C by weight, equivalent to 3.6 ppm C in the whole rock. Of this C, 25% combusted below 400°C and probably was mostly organic blank that resulted from processing the sample before analysis (Fig. 2A). The peak yield of CO_2 occurred in the 425° to 450°C step, but some C combusted at temperatures as high as 700°C. The $\delta^{13}C$ values measured for the temperature interval 400° to 600°C showed a U-shaped pattern characteristic of the combustion of more than one component. There were no high $\delta^{13}C$ values characteristic of meteorite SiC in the highest temperature steps. The background sample, from 6 to 8 cm below the boundary at Brownie Butte, yielded a factor of 15 less C, 221 ppm in the residue, equivalent to 0.5 ppm in the whole rock, 77% of which combusted below 500°C and had an isotopic composition of −25.5 to −24.6 per mil.

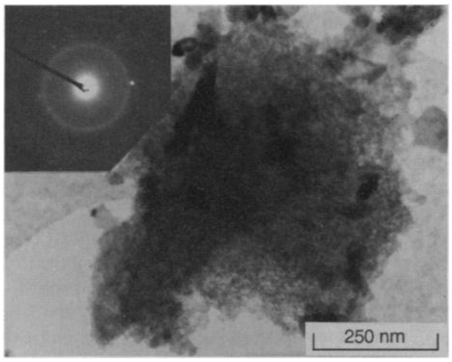

Fig. 1. Bright-field transmission electron photomicrograph with corresponding selected-area diffraction pattern (inset) of a cluster of microdiamonds in an acid residue. Image taken from the K-T boundary at Berwind Canyon, New Mexico.

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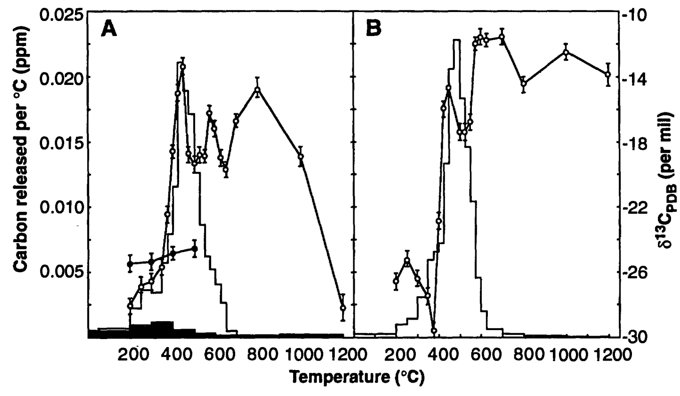

Fig. 2. (**A**) Stepped combustion profile of C from the Brownie Butte fireball layer (open symbols) and a background sample 6 to 8 cm below the boundary (filled symbols). The histograms give yield information and the line graph corresponds to the isotopic composition. (**B**) Stepped combustion profile for Berwind Canyon fireball layer; PDB, Pee Dee belemnite standard.

Some minor quantities of C were combusted at temperatures up to 1200°C.

The fireball layer sample from Berwind Canyon (Fig. 2B) gave results similar to those for Brownie Butte. In this case the residue was 3.5% C by weight (3.2 ppm in the whole sample); 17% was combusted below 400°C and had a δ^{13}C that drops to −27.5 per mil, which suggests organic contamination. The peak yield of CO_2 occurred at a slightly higher temperature than for the Brownie Butte sample in the 475° to 500°C step. Although some C combusted at temperatures up to 800°C, ^{13}C-enriched values were not great at these or higher temperatures. The isotope profiles are also similar to those of Brownie Butte. The shift in the peak combustion temperatures from the Brownie Butte (425° to 450°C) to Berwind Canyon samples (475° to 500°C) indicates that the isotopically lighter component is more abundant in the latter.

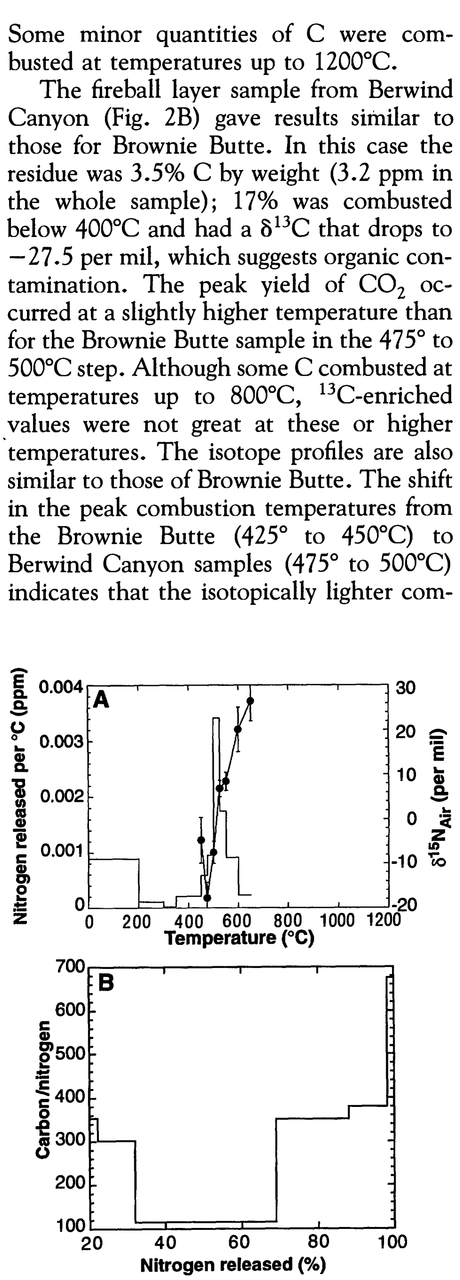

Fig. 3. (**A**) Stepped release profile for N from the Brownie Butte fireball layer. (**B**) Ratio of C to N for simultaneously released C and N from the Brownie Butte fireball layer.

The Petriccio sample, which shows no evidence of diamonds in the TEM, gave different results. Of the C, 81% (39 ppm of the whole rock) had combusted by 450°C, 33% had combusted in a single step between 400° and 425°C, and δ^{13}C values varied over a narrow range from −26.4 to −22.5 per mil.

Given that diamond is the only carbonaceous phase so far identified in the TEM and that the process of preparing the residues mitigates the survival of less robust forms of C, it is assumed that both the components seen in the Brownie Butte and Berwind Canyon fireball layers are diamondiferous. The C oxidation profiles extend over a wider temperature range compared to those for diamond isolated from primitive meteorites (*18*) and, furthermore, reach higher temperatures. Because the combustion properties of diamond depend on grain size, it would seem that the K-T diamonds both are larger and span a greater size range than those for diamonds of any of the meteorites. This interpretation is consistent with the overall TEM observations. Carlisle reported (*19*) a δ^{13}C measurement for the diamonds at Knudsens' Farm of −48 per mil and argued that this ratio is compatible with the presence of C_δ, although the veracity of the arguments has been questioned (*20*). However, −48 per mil is outside the range for C_δ (−32 to −38 per mil). Other forms of diamond found in meteorites include those in the enstatite chondrite Abee (δ^{13}C = −1.8 per mil) (*21*), ureilites (δ^{13}C $\sim$ −6 to −2 per mil) (*22, 23*), and IAB iron meteorites (δ^{13}C = −5.7 per mil) (*24*). All of these δ^{13}C values are different from the results observed here, and thus such meteorites are not likely sources of the K-T diamonds. Interestingly, the δ^{13}C data for the K-T samples is far from constant; this suggests that two components are present that remain unresolved by stepped combustion. The more easily burned portion has a δ^{13}C greater than −13.4 per mil, whereas the more stable of the two has a δ^{13}C of less than −19.4 per mil.

Nitrogen isotope analysis by stepped combustion of the sample of the Brownie Butte fireball layer showed that little N was released below 400°C (Fig. 3A), with a peak yield of N between 500° and 525°C. The minimum δ^{15}N observed was −17 per mil between 450° and 475°C. However, for the two steps in which most of the N was released, the δ^{15}N rose to +6.9 and +8.5 per mil. A bulk δ^{15}N value of +5.5 per mil was determined by addition of the individual steps. The total N released corresponded to 82 ppm of the residue, equivalent to 9 ppb of N in the whole rock. During the N experiment, C abundance data can be acquired simultaneously. When we consider only the temperature regime where noncontaminant C is believed to be released (>400°C), the C/N ratio for the middle 40% of the N released is 114, a factor of 3 lower than that for the N released at higher temperatures (Fig. 3B). This observation suggests the presence of two N components, one superimposed on the other.

From the data available, neither of these components appears to be the primitive meteorite form of diamond, C_δ. Such diamond is characterized by a δ^{13}C of −32 to −38 per mil, 3,000 to 15,000 ppm N, a C/N ratio of 333 to 66, a δ^{15}N of −345 ± 16 per mil, and a sharp combustion temperature of 400° to 500°C with a peak at 495° ± 10°C (*7*). The components seen here have N concentrations similar to those of C_δ, but their δ^{15}N values do not remotely approach the diagnostic value, although the samples could be impure. If C_δ diamond is present in the fireball layer at either of the two K-T sites investigated, it must be a third component in the mixture and therefore minor. Because the diamond-SiC ratio for a CM2 meteorite, for example, is $\sim$50 (*18*), some indication of elevated δ^{13}C at 1000°C and above might have been expected if the K-T boundary diamond was from such a source; no δ^{13}C in excess of −13 per mil was encountered.

Because the isotopic systematics of the K-T diamonds do not match known meteorite data, they might have formed as a result of the impact. There are several conceivable mechanisms. One would be production by shock alteration of C from the target rock or asteroid. Another would be a mechanism akin to chemical vapor deposition, producing diamonds in a plasma associated with the fireball. Meteoritic diamonds might have still acted as a seed crystal for the process. The C isotopic compositions of the samples studied do not match that of any major crustal reservoir of C such as carbonate or organic C, although such a composition could be obtained by mixing. The C isotopes are also distinct from other forms of reduced carbon (for example, soot) that have been observed at the K-T boundary (*25*). The $\delta^{13}C$ values are unusual but not impossible for kimberlite or lamproite diamonds (*24*), but the C/N ratio of 114 is much greater than that seen for any deep-Earth or laboratory-synthesized diamonds (*26*). Indeed, the variations in $\delta^{13}C$, N abundance, and $\delta^{15}N$ indicate the presence of more than one C source and mechanism. Perhaps coincidentally, the $\delta^{13}C$ of the diamonds is close to the typical isotopic composition of macromolecular or amorphous C from carbonaceous chondrites (*27*). Although most larger shocked diamonds are hexagonal in structure, diamonds produced by the explosive detonation of TNT were also found to be cubic and to have morphologies, grain size, and high N contents (*28*) similar to those of the K-T diamonds.

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10. Light-element isotopic compositions are expressed as δ values where, for example:

$$\delta^{15}N = \left[\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{standard}} - 1\right] \times 1000$$

standards are for N, air, and C, a belemnite fossil, from the Pee Dee formation.
11. Two clay layers can be identified at some K-T boundary sites. The upper layer, termed the fireball layer, is typically 2 to 4 mm thick, occurs globally, and contains anomalously high amounts of siderophile and chalcophile trace elements, shocked minerals, and spherules with spinels. It is thought to be formed by vaporization of the projectile and target. On and near North America, a clay layer up to 50 cm thick and with similar impact-related constituents underlies the fireball layer. Termed the ejecta layer, it may represent geographically restricted facies of less energetic ejecta; A. R. Hildebrand and W. V. Boynton, *Science* **248**, 843 (1990); W. Alvarez *et al.*, *Geology* **20**, 697 (1992); C. C. Swisher III *et al.*, *ibid.* **257**, 954 (1992).
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A High-Resolution Record of Holocene Climate Change in Speleothem Calcite from Cold Water Cave, Northeast Iowa

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High-precision uranium-thorium mass spectrometric chronology and ^{18}O-^{13}C isotopic analysis of speleothem calcite from Cold Water Cave in northeast Iowa have been used to chart mid-Holocene climate change. Significant shifts in $\delta^{18}O$ and $\delta^{13}C$ isotopic values coincide with well-documented Holocene vegetation changes. Temperature estimates based on $^{18}O/^{16}O$ ratios suggest that the climate warmed rapidly by about 3°C at 5900 years before present and then cooled by 4°C at 3600 years before present. Initiation of a gradual increase in $\delta^{13}C$ at 5900 years before present suggests that turnover of the forest soil biomass was slow and that equilibrium with prairie vegetation was not attained by 3600 years before present.

Midcontinental climatic records with decade resolution have been difficult to obtain beyond the last two millennia. A geologic record that received much attention in the 1970s is that preserved in the carbon and oxygen isotopic composition of speleothem (cave) calcite (*1*). Although this method has been used successfully to interpret climatic changes, the large sample sizes required for analysis precluded the routine use of speleothems for high-resolution paleoclimatic studies. Improvements in mass spectrometric techniques in the last decade now allow uranium series age-dating of subgram-sized carbonate samples with extremely small analytical errors (*2–4*). Because many continental regions contain karsted limestone terrains, the possibility of using speleothems for paleoclimatic reconstruction deserves renewed attention. In this study we analyze calcite from a stalagmite to demonstrate the feasibility of extracting a high-resolution climatic record from speleothem calcite.

Thirty $\delta^{18}O$ and $\delta^{13}C$ analyses (*5*) were obtained from stalagmite 1s from Cold Water Cave, northeastern Iowa (43° 28′ N, 91° 58′ W) (Fig. 1). Conditions in Cold Water Cave are ideal for isotopic equilibrium deposition of calcite (*6*). Stalagmite 1s was cored from the bottom up to within a centimeter of the top surface with a 2.5-cm-diameter coring apparatus (*7*). The core was split and thin sections of core material were inspected by standard polarizing light microscopy to evaluate the possibility that the calcite had recrystallized. We extracted materials for stable isotopic, alpha, and mass spectrometric U-Th analysis (*8*) from the split and polished core using a carbide dental burr on a microscope-mounted drill

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