

relative chronology of colonization and glaciation provides additional evidence; the presence of trace fossils on glacially influenced landforms indicates that the endolithic community was present before the last glaciation of the area (4).

Formation of trace fossils of microbial colonization may not be limited to the case reported here. Similar processes may have occurred in the past and are preserved in the geological record.

Trace fossils of endolithic microbial colonization in a cold desert environment inspire speculations about possible scenarios for exobiology (13). Evidence for the presence of water during the early history of Mars raises the possibility of the appearance of primitive life forms there (14). If such forms were present, during loss of atmosphere, water, and concomitant cooling of Mars, these organisms may have withdrawn into

porous rocks—the last habitable niche in a deteriorating environment. Under these conditions, trace fossils may have been formed. Because much of the surface structures of Mars is thought to have remained intact over geological time (15), the preservation of such near-surface fossils is a distinct possibility. The search for such structures is a legitimate goal for the future exploration of Mars (13).

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## Shocked Quartz in the Cretaceous-Tertiary Boundary Clays: Evidence for a Global Distribution

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Shocked quartz grains displaying planar features were isolated from Cretaceous-Tertiary boundary clays at five sites in Europe, a core from the north-central Pacific Ocean, and a site in New Zealand. At all of these sites, the planar features in the shocked quartz can be indexed to rational crystallographic planes of the quartz lattice. The grains display streaking indicative of shock in x-ray diffraction photographs and also show reduced refractive indices. These characteristic features of shocked quartz at several sites worldwide confirm that an impact event at the Cretaceous-Tertiary boundary distributed ejecta products in an earth-girdling dust cloud, as postulated by the Alvarez impact hypothesis.

THE FIRST MINERALOGIC EVIDENCE supporting the existence of an impact by an extraterrestrial body at the Cretaceous-Tertiary (K-T) boundary 66 million years ago (1) was the discovery of shock-metamorphosed quartz grains in a claystone at this boundary near Brownie Butte in the Hell Creek area of east-central Montana (2). This discovery was crucial to the confirmation of the Alvarez scenario (3) that a large meteorite or asteroid had struck the earth at the end of the Cretaceous period, throwing up a dust cloud that circled the globe for a substantial period of time and causing major extinctions of flora and fauna through blockage of sunlight and changes in temperature and climate.

Previously, the principal evidence for this scenario was the presence of anomalously high amounts of iridium and other siderophile elements measured in several boundary clay sites around the world. The number of

sites with measured iridium anomalies has now increased to more than 75 (4), but the Montana location had been the only site at

which shocked quartz had been unequivocally confirmed. Recently, Izett and Pillmore (5) and Badjukov *et al.* (6) reported the occurrence of shocked quartz and feldspar at the K-T boundary in the Raton Basin in the United States, and in the Soviet Union.

We now report the confirmed presence of shocked quartz at several K-T boundary sites around the world that also contain iridium anomalies. These data answer the objections of some investigators that shocked quartz at the Montana site may have resulted from erosion of localized shocked material from older impacts in the area (7). These data also suggest that shocked quartz and other shocked minerals are to be expected in every K-T boundary clay layer that contains a substantial iridium anomaly anywhere in the world.

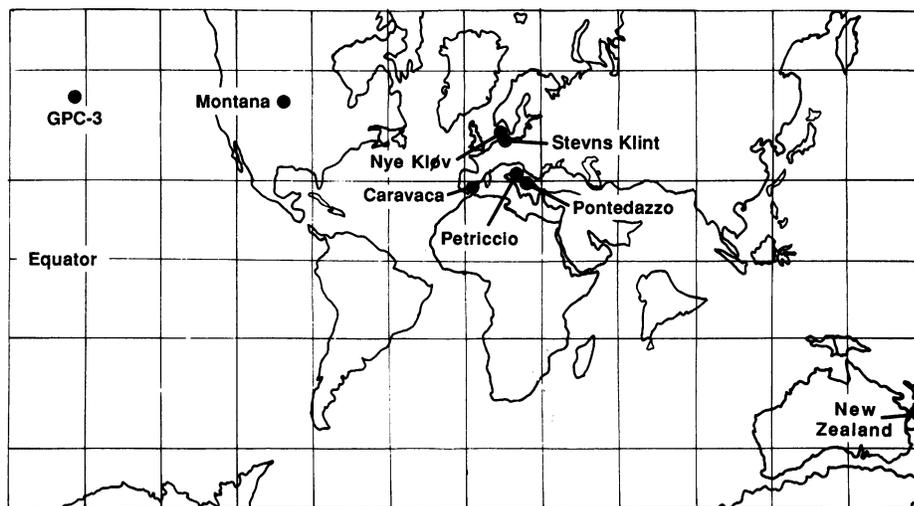


Fig. 1. Map (Mercator projection) of the world 60 million years ago showing K-T boundary sites where we have confirmed the presence of shocked quartz. The original discovery site in Montana is also shown. [Adapted from Smith and Briden (25)]

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The sites that we studied (Fig. 1) are located at Stevns Klint and Nye Kløv in Denmark (8), Petriccio and Pontedazzo in Italy (9, 10), Caravaca in Spain (11), Giant Piston Core No. 3 (GPC-3) from the north-central Pacific Ocean basin (12), and Woodside Creek in New Zealand (13). At all of these sites the K-T boundary is found in marine rocks, whereas the Brownie Butte site (2) is located in continental (nonmarine) rocks. Where possible, only the basal few millimeters of the boundary clay at these sections were processed, inasmuch as experience with marine sections has shown that this is the stratigraphic level where the shocked quartz is most abundant. Grains of shocked quartz from only one of the two sites at the Danish and Italian localities (Stevns Klint and Pontedazzo, respectively) were completely characterized, although shocked quartz was visibly identified at the other two sections (Nye Kløv and Petriccio) as well. Photomicrographs of shocked quartz displaying multiple sets of planar features from six of these sites are shown in Fig. 2.

The tests used to confirm the presence of shocked quartz at these new sites are the same as those applied by Bohor *et al.* (2) to the quartz recovered from the Brownie Butte site. Multiple intersecting sets of parallel planar features that index to rational crystallographic directions in the quartz crystal lattice were measured on the Wilcox spindle stage with respect to the grain's  $c$ -axis. Histograms were constructed from grains at each site, relating the frequency distribution of sets of planar features to the angles that their normals (poles perpendicular to the planes) make with the  $c$ -axis.

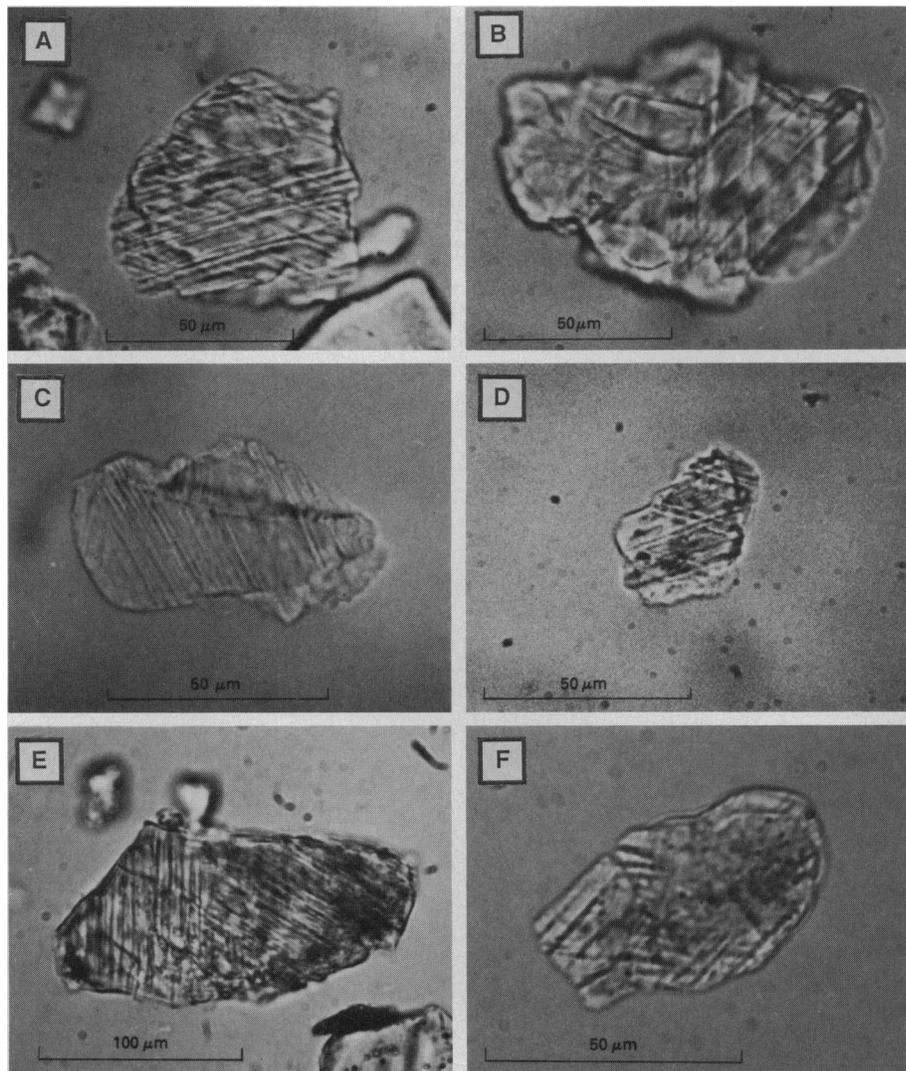
The histograms of the optical data from our sites are shown in Fig. 3. Differences in the histograms between sites can be attributed to random variation between the fairly small number of grains (and sets) examined. The crystallographic orientation designated by  $\omega$  {1013} (the rhombohedral plane) is the dominant direction at all the sites examined, as it was at Brownie Butte and as has been reported from most known meteorite impact sites (2). The orientation designated by  $\pi$  {1012} is usually the next most common direction. Other crystallographic directions are less frequently represented. These less frequent orientations at higher angles of the planar normals to the  $c$ -axis were assigned on the basis of Miller indices; only those having low (single digit) Miller indices were used (14). The planar pole angles to the  $c$ -axis can be measured to no better than  $\pm 1^\circ$ , so the data for these angles were grouped and plotted in  $2^\circ$  intervals on the histograms. Generally, fewer than 10% of the sets from each site did not correspond to rational

crystallographic orientations.

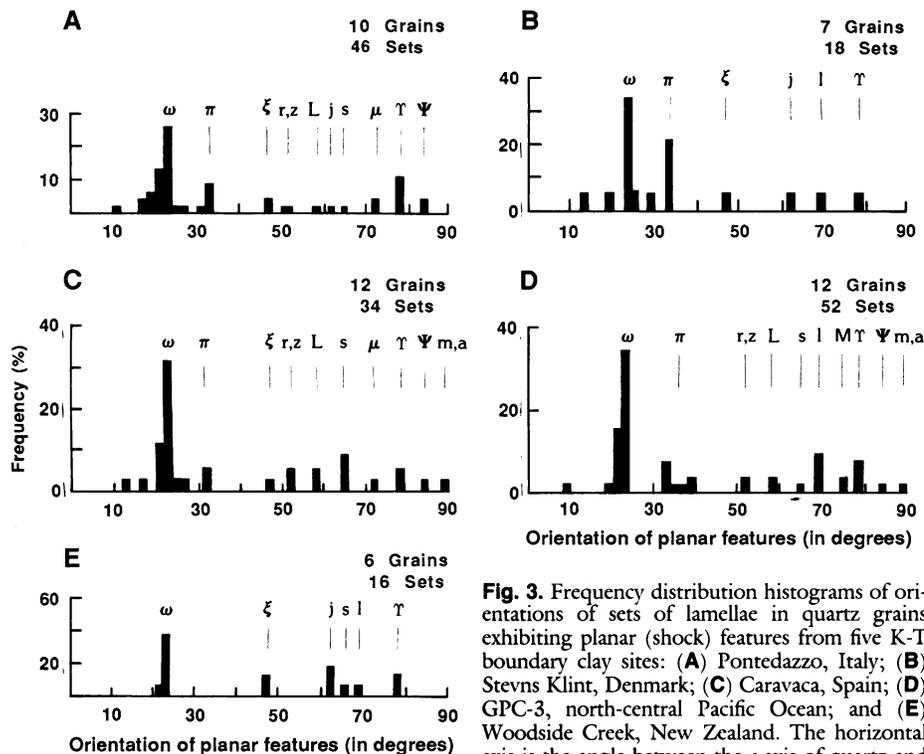
The histogram of the optical data for the Woodside Creek sample was constructed from many fewer data than the histograms from the other sites because of the difficulty of finding shocked quartz grains among the flood of detrital quartz grains in the Woodside Creek sample. Some of these detrital grains with strong undulose extinction exhibit features similar to planar features, except that they are not strictly planar but are slightly curved and indistinct. When plotted on a stereographic net, these sets of features in general do not index to rational crystallographic indices of quartz. Their histogram displays a featureless curve of distributions, with a slight maximum at around  $15^\circ$ , resembling the angular distribution ascribed to Böhm lamellae, which result from tectonic deformation (2). These grains are not included in the Woodside Creek histogram of Fig. 3; the only data plotted are from six grains with strong, parallel sets that we are

confident are planar features or planar fractures. In contrast, almost no detrital quartz was observed at the GPC-3 site because of its location in the North Pacific gyre, where the rate of detrital influx is extremely low (12). Even though the sample size from GPC-3 was small, we had no problem in identifying an abundance of planar features on the quartz grains recovered.

Recently, Carter *et al.* (15) published data on quartz grains in thin sections from approximately 75,000-year-old silicic ignimbrites associated with the Toba eruptive center in Sumatra. These data, purporting to show dynamic deformation microstructures in quartz similar to those found at the K-T boundary, consist of single sets of parallel features found in only a minute portion of the quartz grains present (only 24 grains in 9 of the 17 sections studied, or  $\ll 1\%$  of the total grains). In contrast, Bohor *et al.* (2) found multiple sets of shock lamellae in more than 25% of the quartz grains separat-



**Fig. 2.** Photomicrographs of shocked quartz grains exhibiting planar features (shock lamellae) from (A) Pontedazzo, Italy; (B) Petriccio, Italy; (C) Stevns Klint, Denmark; (D) Caravaca, Spain; (E) GPC-3, north-central Pacific Ocean; and (F) Woodside Creek, New Zealand.



**Fig. 3.** Frequency distribution histograms of orientations of sets of lamellae in quartz grains exhibiting planar (shock) features from five K-T boundary clay sites: (A) Pontedazzo, Italy; (B) Stevns Klint, Denmark; (C) Caravaca, Spain; (D) GPC-3, north-central Pacific Ocean; and (E) Woodside Creek, New Zealand. The horizontal axis is the angle between the  $\epsilon$ -axis of quartz and poles (normals) to planar features. Greek and Roman letters designate specific crystallographic planes in quartz.

ed from the K-T boundary clay at Brownie Butte, Montana. In the present study, as much as 40% of the quartz grains separated from GPC-3 in the North Pacific gyre, where detrital input is low, displayed multiple sets of shock lamellae; a common average for all K-T boundary clays studied is about 25%. Izett and Pillmore (5) found shock lamellae in about 30% of the grains separated from K-T boundary clays from the Raton Basin in Colorado and New Mexico. Thus, the rarity of quartz grains from the Toba eruption that show deformation microstructures argues against any comparison with the K-T boundary clays on a quantitative basis.

Qualitatively, the data of Carter *et al.* (15) show only single sets of planar features per quartz grain, whereas those from K-T boundary clays described here and in other studies (2, 5, 6) invariably include a majority of grains with multiple intersecting sets, as do those from shock-metamorphosed rocks associated with known impacts (16). Bunch (17) stated that the occurrence of two or more sets of planar features in quartz grains appears to be unique to impact sites (among natural occurrences). Therefore, although the histogram of Carter *et al.* (15) showing orientations of sets of planar features in quartz from Toba eruptive rocks appears similar to those of Bohor *et al.* (2) and to those described in this report from K-T boundary clays, the data used to construct them were not comparable. Carter *et al.* (15)

attributed the lack of multiple sets of planar features in their samples to post-eruptive healing (annealing) at high temperatures. However, this scenario does not explain why only one set per grain (of variable orientations) survived in all cases, or why this annealing would not be equally effective in the case of shocked rocks associated with impact craters (which experienced even higher temperatures). These and other criteria, such as lack of data for silicic eruptives indicating siderophile elements in cosmic proportions (as is found in K-T boundary clays) and other mineralogical concerns, as expressed by Izett and Bohor (18), lead us to conclude that quartz microstructures from volcanic rocks, such as the Toba ignimbrites, cannot account for the global occurrence of shocked quartz at the K-T boundary.

Another characteristic used to define shock-metamorphosed quartz is a lowering of the refractive index below that of normal quartz (mean refractive index is 1.5485). The refractive index of each quartz grain displaying planar features was measured by both the Becke line and central focal masking techniques to within  $\pm 0.001$  (19). The results for five sites are given in Table 1. All of the quartz grains measured showed a lower mean refractive index than that of normal quartz, but none of these grains had a refractive index equal to the lowest mean refractive index measured on the Brownie Butte sample, possibly because of the smaller number of quartz grains analyzed per site

**Table 1.** Refractive indices of shocked quartz grains displaying planar features.

Number of grains	$n_o$	$n_e$	$(n_o + n_e)/2$ (mean)
<i>Stevns Klint</i>			
1	1.542	1.551	1.5465
1	1.541	1.550	1.5455
1	1.540	1.550	1.545
1	1.540	1.548	1.544
1	1.539	1.548	1.5435
1	1.538	1.548	1.543
<i>Pontedazzo</i>			
1	1.542	1.551	1.5465
1	1.542	1.550	1.546
2	1.541	1.550	1.5455
2	1.540	1.550	1.545
4	1.540	1.549	1.5445
<i>Caravaca</i>			
1	1.543	1.552	1.5475
1	1.543	1.551	1.547
2	1.542	1.551	1.5465
1	1.541	1.551	1.546
1	1.541	1.550	1.5455
1	1.541	1.549	1.545
2	1.540	1.550	1.545
1	1.540	1.548	1.544
1	1.539	1.548	1.5435
<i>GPC-3</i>			
1	1.544	1.552	1.548
2	1.543	1.552	1.5475
4	1.542	1.551	1.5465
1	1.542	1.550	1.546
2	1.541	1.550	1.5455
1	1.541	1.549	1.545
1	1.540	1.550	1.545
<i>Woodside Creek</i>			
1	1.543	1.553	1.548
3	1.543	1.552	1.5475
1	1.542	1.551	1.5465
1	1.541	1.551	1.546
<i>Ideal quartz</i>			
	1.544	1.553	1.5485

for these five new sites. No consistent change in birefringence is apparent in the data of Table 1.

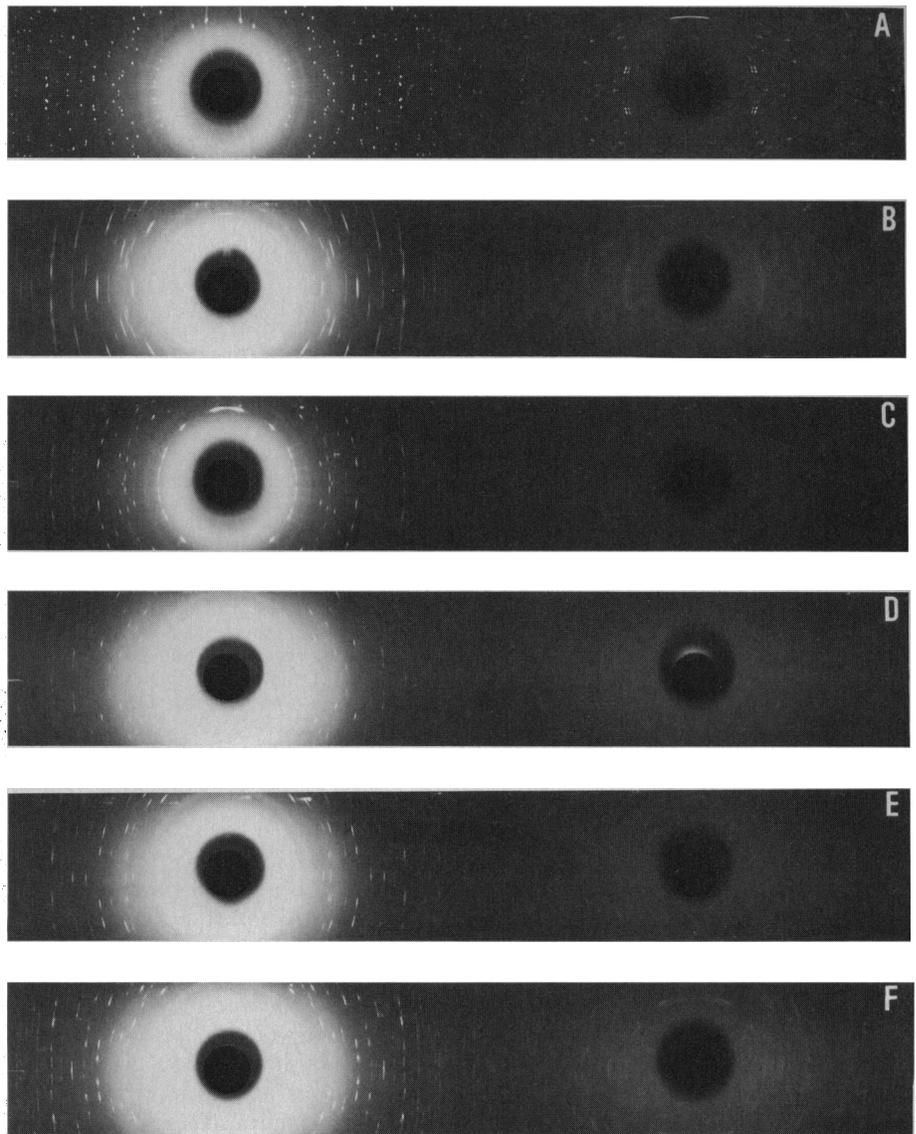
A third test for characterizing shock metamorphism is the streaking of diffraction points on Debye-Scherrer x-ray patterns of single quartz crystals. Under these conditions, normal unshocked quartz displays a pattern of discrete, sharp spot reflections concentrically arranged, but shock metamorphism causes these reflections to elongate around the cone of diffraction. Figure 4 shows Debye-Scherrer x-ray diffraction films of a typical quartz grain displaying planar features from each of the five sites, compared with a film of normal (unshocked) quartz. All grains with planar features that we examined showed streaking and blurring (elongation) of the diffraction spots to varying degrees, in addition to loss of diffraction intensity in the back reflection regions. Streaking (elongation) of diffraction spots is sometimes referred to as "asterism" (20), but this term should probably be restricted

to x-ray techniques (such as precession and Laue) in which the crystal is held motionless with respect to the recording film (21).

Precession camera photographs of shocked quartz from Woodside Creek and Brownie Butte show considerable streaking (asterism) of the diffraction maxima. The diffraction spots seen in normal quartz when the precession technique is used are perfectly circular. Thus, films from both the Debye-Scherrer and precession diffraction techniques show major disruptions to the lattice periodicity of quartz grains displaying planar features (shocked quartz). Quartz grains with pronounced undulose extinction from tectonically metamorphosed rocks also give x-ray diffraction patterns that display asterism. However, the quartz grains with planar features from the K-T boundary clay sites that we selected for x-ray studies had little or no undulose extinction, but still displayed asterism.

None of the data on shocked quartz from these marine sites appear to be significantly different from those originally reported by Bohor *et al.* (2) from the Brownie Butte site in continental rocks. The conclusion of those investigators that a minimum shock pressure of 90 kbar was required to produce these effects remains valid, with an upper limit of about 300 kbar indicated by the absence of diaplectic (thetomorphic) glass. This pressure range is far above what would be expected in a volcanic regime.

In summary, this study confirms the presence of shocked quartz at several widely separated K-T boundary sites around the world. It shows that the association of shock-metamorphic effects in quartz grains with strong iridium anomalies in K-T boundary clays is not unique to the original discovery site in Montana (2) but is to be expected at this event horizon wherever it may be found worldwide. The Alvarez hypothesis of an earth-girdling dust cloud of ejecta from the impact of a large extraterrestrial body is strongly supported by these data. The ejection mechanics and transport mechanism for dispersal of these rather large-sized particles of shocked and comminuted target rock around the world have yet to be determined, but recent work on shocked quartz grains from these same sites has shown a particle-size gradation that may be inversely related to distance from the impact site (22). The terminal Cretaceous impact event was powerful enough to disperse ejecta products of significant size and distinctive composition (siliceous) worldwide. This should place a lower limit on the size of the impacting body and, therefore, the size of the resulting crater. The ubiquitous presence in the K-T boundary layer of shocked quartz, feldspar, and composite sili-



**Fig. 4.** Debye-Scherrer x-ray diffraction photographs of rotated single quartz grains, showing spot diffraction maxima from (A) unshocked low-temperature vein quartz from Arkansas and streaked diffraction maxima from shocked quartz grains with planar features from (B) Brownie Butte, Montana; (C) Pontedazzo, Italy; (D) Stevns Klint, Denmark; (E) Caravaca, Spain; and (F) GPC-3, north-central Pacific Ocean.  $\text{CuK}\alpha$  radiation, 57.3-mm camera.

ceous grains argues against the oceanic impacts suggested by some workers (10, 23). We support the hypothesis of a large asteroid impacting into a continental crustal terrain.

*Note added in proof:* Alexopoulos *et al.* (24) recently used detailed microscopic observations to compare quartz grain deformational features from a known impact structure with those from a K-T boundary clay and three other geologic environments, including the Toba tuff studied by Carter *et al.* (15). Alexopoulos *et al.* (24) concluded that the appearance and orientation of planar features in quartz grains from a known impact structure and those from the K-T boundary clay are essentially identical and that although other lamellar deformational features in quartz can result from other

geologic processes (such as volcanism), they only superficially resemble those from K-T boundary clays and known impact structures.

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## Polychlorinated Biphenyl Dechlorination in Aquatic Sediments

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The polychlorinated biphenyl (PCB) residues in the aquatic sediments from six PCB spill sites showed changes in PCB isomer and homolog (congener) distribution that indicated the occurrence of reductive dechlorination. The PCB dechlorinations exhibited several distinct congener selection patterns that indicated mediation by several different localized populations of anaerobic microorganisms. The higher (more heavily chlorinated) PCB congeners that were preferentially attacked by the observed dechlorination processes included all those that are either pharmacologically active or persistent in higher animals. All the lower (less heavily chlorinated) PCB congeners formed by the dechlorinations were species that are known to be oxidatively biodegradable by the bacteria of aerobic environments.

**D**ESPITE GREAT PUBLIC AND REGULATORY concern over the accumulation of polychlorinated biphenyls (PCBs) in the environment, little is known about their actual fate in specific environmental niches (1). Recently, however, we found that agents capable of attacking PCBs may leave residues that exhibit characteristic signatures in their capillary gas chromatographic (GC) patterns. These characteristic patterns occur because all the PCBs that were used commercially were complex mixtures of isomers and homologs (congeners) that were produced in fixed relative proportions by the chlorination process used and because each physical, chemical, or biological alteration process exhibits its own set of relative activities toward the individual PCB congeners. Thus many strains of aerobic bacteria that oxidize PCBs were found to exhibit, at least under laboratory conditions, PCB congener depletion patterns that were clearly distinguishable from each other (2) and from the more familiar patterns shown by animals that have mixed function oxidase systems based on cytochrome P-450 (3–5).

To see whether such characteristic transformation signatures were present in environmental samples, we have reviewed several hundred chromatograms of the PCB residues in soils, sediments, and water. In the soil and water samples the alterations in the GC patterns, if any, could be readily related to known types of transformation processes such as simple evaporation from dry soils or aerobic microbial degradation in rivers or groundwater. Alterations of a different type, however, were seen in aquatic sediments from several PCB spill sites.

PCB mapping and transport studies have indicated that the upper Hudson River contained 134 metric tons of PCB in 1977, with much of it concentrated at depths of 15 to 30 cm in areas of low hydrodynamic shear as "hot spots" that have PCB concentrations greater than 50 ppm (6). Our sediment analyses and existing plant records indicate that this PCB was originally almost entirely Aroclor 1242 that was released from capacitor manufacturing operations at Hudson Falls and Fort Edward, New York, between 1952 and 1971. For PCB transformation studies we collected and sectioned sediment cores from four "hot spots" distributed around river reach 8 (the stillwater that is

located immediately below Fort Edward village and that extends from 4 to 12 km below the major PCB release point) as well as 15 "surface grab" sediment samples distributed around the same section of the river (7). Analyses were performed as previously described (8) with a DB-1 polydimethylsiloxane-coated capillary GC column that was capable of resolving environmental PCB mixtures into 118 distinct peaks.

The chromatograms showed congener distributions that generally tended toward one of four major limiting patterns, which have been designated A, B, B', and C (8) and are illustrated in Fig. 1. Pattern A looked similar to that of Aroclor 1242 except for some modest quantitative differences. Patterns B, B', and C all showed markedly lower levels of most tri-, tetra-, and pentachlorobiphenyls and increased levels of mono- and dichlorobiphenyls. They were most easily distinguished from each other by the presence of three, two, or one strong dichlorobiphenyl peaks, respectively (Fig. 1). Two minor variants (not illustrated) were pattern D, which showed enhancement of two trichlorobiphenyls (8), and pattern E, which exhibited several distinctive alterations among the penta-, hexa-, and heptachlorobiphenyls.

To determine how representative these patterns might be, we reviewed the numerically reduced data for 2000 upper Hudson River samples analyzed during the 1977 New York State survey (6) and about 100 of the original packed-column chromatograms (9). All of the PCB-containing sediment specimens that were collected between Fort Edward and Troy, New York (a river distance of 69 km), exhibited patterns that resembled A, B-B', or C. (The resolution of the older chromatograms was not sufficient to distinguish B from B' or to detect the variant patterns D or E.) Pattern A was typically associated with lightly contaminated but extensive surface deposits, which have been estimated to contain a total of 57 metric tons of PCBs (6), whereas patterns

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