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## Fossil Charcoal in Cretaceous-Tertiary Boundary Strata: Evidence for Catastrophic Firestorm and Megawave

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*Preprint*: Kruge, M.A., Stankiewicz, B. A., Crelling, J. C., Montanari, A. and Bensley, D. F., 1994, Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic firestorm and megawave. *Geochimica et Cosmochimica Acta* **58**:1393-1397. [https://doi.org/10.1016/0016-7037\(94\)90394-8](https://doi.org/10.1016/0016-7037(94)90394-8)  
<https://www.sciencedirect.com/science/article/abs/pii/0016703794903948>

Kruge, M.A., Stankiewicz, B. A., Crelling, J. C., Montanari, A. and Bensley, D. F., 1996, Reply to the comment by T. P. Jones on "Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic firestorm and megawave". *Geochimica et Cosmochimica Acta* **60**:721-722. [https://doi.org/10.1016/0016-7037\(95\)00438-6](https://doi.org/10.1016/0016-7037(95)00438-6)  
<https://www.sciencedirect.com/science/article/abs/pii/0016703795004386>

### **Fossil Charcoal in Cretaceous-Tertiary Boundary Strata: Evidence for Catastrophic Firestorm and Megawave**

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**Abstract** — Organic matter separated from calcareous sandstone from the upper portion of a deep-water tsunami deposit at Arroyo el Mimbral, Taumalipas (Mexico), which marks the biostratigraphically-defined Cretaceous-Tertiary boundary, consists primarily of fossil charcoal, including semifusinite and pyrofusinite. Analytical pyrolysis-gas chromatography/mass spectrometry revealed the highly aromatic and polyaromatic character of the organic matter assemblage, typical of the products of partial combustion. The organic matter probably originated as terrestrial vegetation that was caught in a firestorm and subsequently transported far offshore in the backwash of a megawave. These data are consistent with the hypothesis of combustion of large masses of vegetation triggered by a giant extraterrestrial impact in the Gulf-Caribbean region (probably forming the Chicxulub crater in Yucatán) at the very end of the Cretaceous Period.

## **INTRODUCTION**

The recognition of megawave deposits at the Cretaceous-Tertiary (K-T) boundary in the Gulf of Mexico and adjacent on-shore areas (Smit and Romein, 1985; Bourgeois et al., 1988; Hildebrand and Boynton, 1990; Alvarez et al., 1992; Smit et al., 1992) has intensified the debate over the nature of the boundary event. The postulated bolide impact at Chicxulub in the northern Yucatán (Penfield and Camargo, 1981; Pope et al., 1991; Hildebrand et al., 1991, Sharpton et al., 1993) may have triggered an extraordinary tsunami capable of producing these deposits in the Gulf region (Smit et al., 1992; Hildebrand et al., 1991). The outcrop at Arroyo el

Mimbral in northeastern Mexico contains an unusual, 3 m thick coarse clastic unit at the biostratigraphically-defined K-T boundary, which interrupts a sequence of pelagic marls and marly limestones of upper Maastrichtian and Paleocene age, and exhibits sedimentological features implying a genetic relationship to the nearby impact (Smit et al., 1992). Alternative interpretations have recently been formulated (Keller et al., 1993; Stinnesbeck et al., 1993) suggesting that the Mimbral sequence is the product of shallow water deposition occurring over a long time period, but at this point the bulk of the evidence seems to favor the impact hypothesis. Radiometric dating ( $^{40}\text{Ar}/^{39}\text{Ar}$ ) indicates that impact glass droplets from this outcrop are coeval with melt rock from the Chicxulub site, and impact glass from the K-T boundary section at Beloc, Haiti (Swisher et al., 1992; Sharpton et al., 1992). A bolide impact would have produced extreme heating in nearby areas from IR radiation produced by a) passage of the bolide through the atmosphere, b) rise of the impact fireball and c) reentry of ejecta droplets (Melosh et al., 1990). These combined phenomena could have triggered a firestorm, charring standing terrestrial vegetation. Evidence for such fires at a continental or global scale has been inferred from the presence of soot and polycyclic aromatic hydrocarbons consistent with a combustion source in several K-T boundary sites around the world (Wolbach et al., 1985; 1988; 1990a; 1990b; Venkatesan and Dahl, 1989). It is estimated from carbon isotopic data that  $\approx 25\%$  of terrestrial biomass was consumed by fire at the end of the Cretaceous (Ivany and Salawitch, 1993). Wood and other plant debris, some described as carbonized, were reported to be present in the upper, laminated portion of the clastic deposit (Smit et al., 1992). In the present study, we have sought to characterize the organic material in the Mimbral deposit, assess its degree of thermal alteration, and determine its probable origin, using the standard techniques of the coal petrologist and organic geochemist.

## METHODS

A 500 g sample of the mid-upper portion of the Mimbral "clastic sub-unit II", a coarse-grained, laminated calcarenite (Smit et al., 1992), yielded 1 g of organic matter concentrate, after standard demineralization procedures (treatment with HCl and HF, then centrifugation in an aqueous solution of CsCl with a density of 1.6 g/ml). The sample was collected  $\approx 1.5$  m above the top of the "spherule bed" (at lateral meter 24, as marked on the outcrop by Smit), and contains no spherules itself. The Ir-enriched layer characteristic of K-T boundary sites around the world occurs above the position of this sample, at the top of the overlying "clastic sub-unit III" (Smit et al., 1992).

An aliquot of the concentrate was embedded in an epoxy pellet, polished and examined microscopically using reflected white and blue light. In white light, observations were made of the morphological details of the organic particles as a first step in their classification. Their reflectance properties were also measured, using the rotational polarization method (Houseknecht et al., 1993). In general, reflectance values for sedimentary organic particles range from near 0 to about 7% of the incident light intensity and are higher for material that has experienced more extensive thermal

alteration. Reflectances can also be used as supplemental criteria for classification. Under blue light, the pellet was examined for fluorescing organic particles, another technique important in classification of sedimentary organic matter.

We subjected a second aliquot of the concentrate (pre-extracted with CH<sub>2</sub>Cl<sub>2</sub>) to analytical pyrolysis-gas chromatography/mass spectrometry (py-GC/MS). Py-GC/MS provides a relatively rapid semi-quantitative chemical characterization of solid sedimentary organic matter on the molecular level. Pyrolysis was at 610° C for 20 sec., using a CDS 120 Pyroprobe coupled to an HP 5890A GC and an HP 5970B Mass Selective Detector. The GC was equipped with a 25 m OV-1 column (0.2 mm i.d., 0.33 µm film thickness), initially held at 0° C for 5 min., then raised to 300° at 5°/min., then held for 15 min. The mass spectrometer was in full scan mode with an ionizing voltage of 70 eV. A second sample, collected about 1 m below the first and reported to contain "abundant, reddish-brown fossilized plant debris" (Smit et al., 1992), yielded only traces of organic matter, the original material having been mineralized. This sample was not analyzed further.

## RESULTS AND DISCUSSION

Petrographic analysis indicates that 70% (by volume) of the organic material isolated from the Mimbral sample is semifusinite (partially charred plant tissue). An additional 20% consists of pyrofusinite (charred plant tissue). The remaining 10% is represented by vitrinite (diagenetically altered plant cell-wall material). Semifusinite and fusinite are members of the inertinite (fossil charcoal) group of macerals, which are ubiquitous, though usually minor, constituents in both peats and coals. They are most often ascribed to natural alteration of plant tissues at high temperature prior to deposition. Remarkably, inertinite macerals comprise 90% of the organic matter in the Mimbral sample. Excellent botanical detail, including xylem cell texture, vessel members and side wall pits, is preserved in the fragments of fusinite and semifusinite (Fig. 1).

The Mimbral macerals exhibit great variability in their reflectances (Fig. 2). The mean random reflectance in oil of 1.3% measured for the Mimbral vitrinite, while low when compared to the inertinites, is considered quite high for vitrinite (Tissot and Welte, 1984). Relatively slow geothermal heating *after* burial is generally interpreted to be the cause of increases in the reflectance of vitrinite, whereas the elevated reflectance values of inertinites are largely inherited from the flash heating experienced *prior* to burial. The observed mean vitrinite reflectance of 1.3% would in fact indicate a level of thermal alteration much higher than that which would be expected from the relatively shallow maximum burial depth reported for the sample (<1 km, W. Alvarez, pers. comm.). The interpretation of the vitrinite reflectance values is further complicated by the extensive weathering (natural oxidation at the outcrop) observed in these samples, which tends to shift reflectances to lower values. In view of the shallow burial and weathering, the vitrinite reflectance values can only be interpreted as anomalously high. It may be that the elevated vitrinite reflectance is

due to the unusual and severe nature of the impact's thermal pulse and its immediate aftermath.

Semifusinite typically exhibits the widest reflectance range of all macerals due to the various degrees of charring experienced by the preserved plant tissues. Semifusinite measured from the Mimbral deposit shows a mean reflectance of 2.6% and the typical broad reflectance distribution commonly associated with this maceral group (Fig. 2). Pyrofusinite, in contrast to semifusinite, typically shows a higher but more limited reflectance range consistent with its origin from totally charred plant material. The Mimbral samples of pyrofusinite have a mean reflectance 4.9%, which is almost double that of the semifusinite.

The striking absence of the volatile liptinite macerals (alginite, sporinite, etc.) is consistent with the flash heating from an impact event. However, along with the relatively high vitrinite reflectance, it is also consistent with an advanced stage of coalification. The high vitrinite reflectance and destruction of liptinite macerals could be produced by burial in a sedimentary basin with a high geothermal gradient. It is noted that the Mimbral area has experienced basaltic volcanism during the Late Tertiary (Muir, 1936). However, there is no evidence of contact metamorphism or igneous intrusion at the Mimbral outcrop. Furthermore, the predominance of fusinites in the sample suggests that the organic matter is largely the product of the passage of a fire through standing terrestrial vegetation. This unusual maceral assemblage could not have been produced by contact or burial metamorphism.

Py-GC/MS analysis of the organic concentrate reveals a predominance of mono-, di- and triaromatic hydrocarbons, including benzene, toluene, naphthalene, biphenyl and phenanthrene (Fig. 3). Several compounds containing oxygen or sulfur are also important, namely phenol, dibenzofuran and dibenzothiophene. Phenol in particular, while characteristic of vitrinite from low rank coals, would not be expected in a normal coal of high rank (Senftle et al., 1986). The oxygenated compounds may thus be the hallmark of weathering or partial combustion. Larger polyaromatic hydrocarbons are also detected, such as fluoranthene, pyrene, chrysene, benzo[*a*]anthracene and several pentaaromatic compounds. Straight chain hydrocarbons are present only as trace components. Alkylated polyaromatics are only of minor importance in this sample, as is characteristic of combustion products (Venkatesan and Dahl, 1989). The thoroughly aromatic character of the sample confirms the high level of thermal alteration apparent from the organic petrologic data. Such a distribution of compounds in the pyrolyzate is compatible with the sample originating as burned terrestrial vegetation and supports the conclusions drawn from the petrology.

While conflagrations are not unusual natural events, it must be asked how an organic assemblage consisting almost entirely of charred plant remains came to be entrained with coarse clastic sediments and deposited in a deep-water ( $\approx 600$  m) marine environment (Smit et al., 1992). Fusinite at the K-T boundary has been previously observed in a coal bed in Colorado (Tschudy et al., 1984), presumably formed *in situ* by fire within a peat bog. Sedimentological evidence suggests that the Mimbral sequence was formed by a megawave (Smit et al., 1992). The backwash of

a seismically-induced (i.e., "normal") tsunami or even a strong turbidity current could conceivably have transported some charred wood, but would also have entrained unburned vegetation, producing an organic assemblage dominated by vitrinite, unlike the Mimbral. For the same reason, the gradual, shallow-water deposition scenario for the Mimbral sequence (Keller et al., 1993; Stinnesbeck et al., 1993) also appears unlikely. A major coastal volcanic eruption might have provoked a coincidental fire and tsunami, which could have produced an inertinite-rich assemblage like the Mimbral. However, this is unlikely in the present case, as there are no coeval pyroclastics or other evidence of volcanism, except for a very thin ash layer below the K-T boundary clastic unit (Smit et al., 1992). The available evidence is compatible with a bolide impact at the K-T boundary, the first effect of which would have been a thermal pulse, inducing a firestorm which charred proximal terrestrial vegetation. Impact on the Yucatán platform would have then produced a megawave, which quenched the firestorm in coastal areas. The backwash would have transported the charred material along with coarse clastic sediments to a deep-water site of deposition. The sequence would then have been capped by finer sediment that settled gradually, including air-fall deposits. Additional geologic evidence, such as the presence of impact glass, shocked minerals and an anomalous iridium abundance (Smit et al., 1992), supports this scenario and argues against the mere coincidence of a standard, seismically-induced tsunami subsequent to a normal coastal forest fire.

Figure 1 — Photomicrographs in reflected light. A) Cross section of xylem cell structure in semifusinite featuring a large lumen of a vessel member. B) Cross section of xylem cell structure. The upper particle (semifusinite) shows two cell vessel lumens. The lower particle (pyrofusinite) shows side wall pits in the cell walls. C) Longitudinal section of xylem cell structure in pyrofusinite featuring large vessel members. D) Vitrinite particle. The darkening and fracturing at the edges of the particle are indications of weathering.

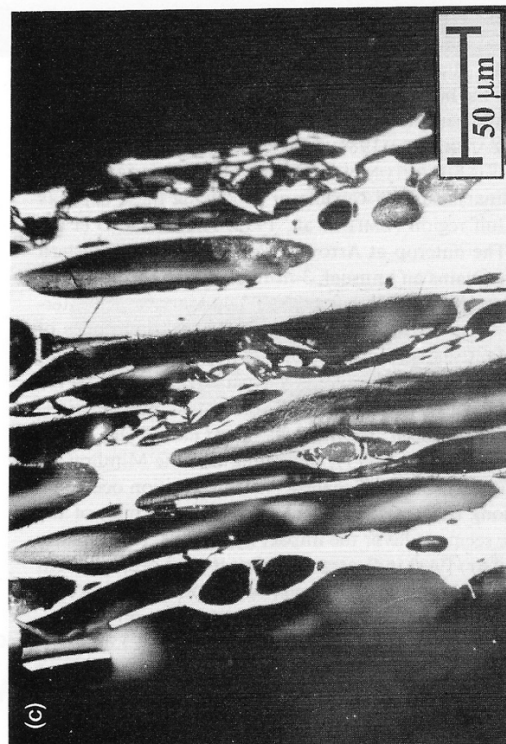
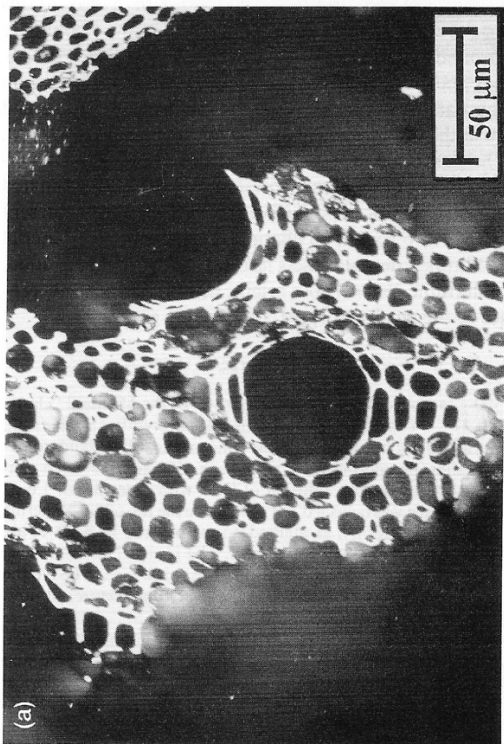
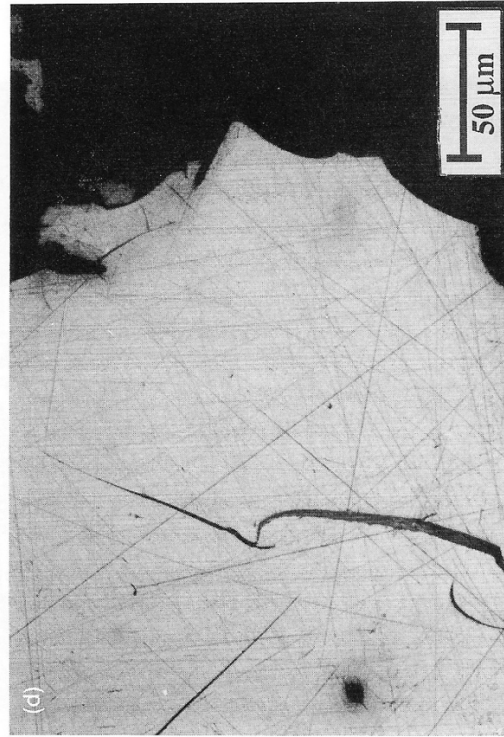
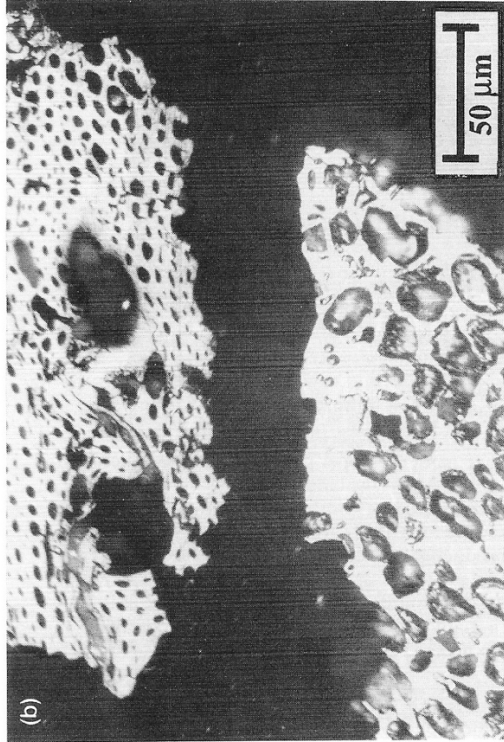


Figure 2 — Reflectance histograms of vitrinite, semifusinite and pyrofusinite in the Mimbral sample. Fifty points were measured for each maceral type, but results are weighted proportionally to the percentage of each group present in the sample (vit.: 10%, semifus.: 70% and pyrofus.: 20% by volume).

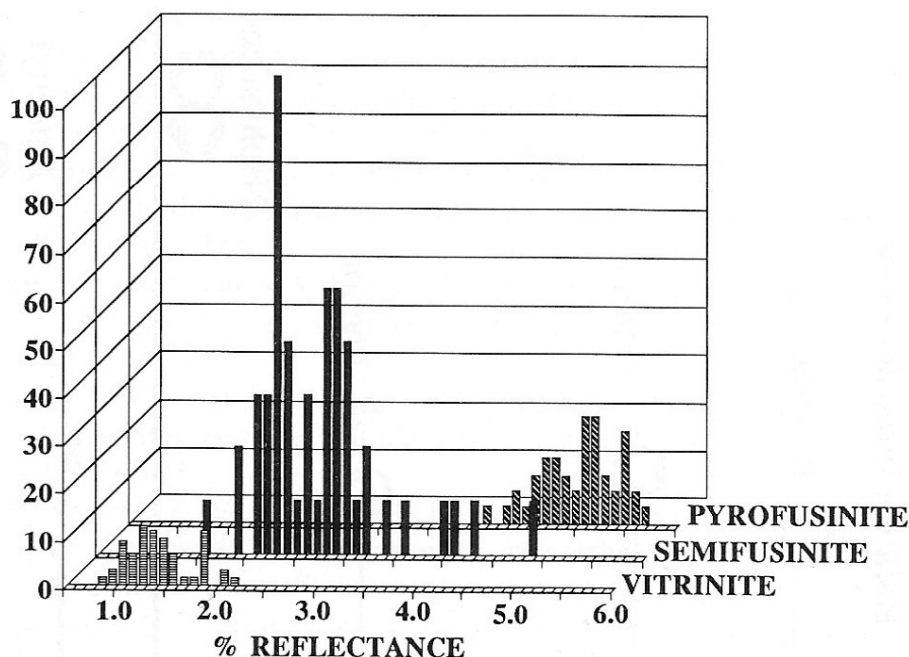
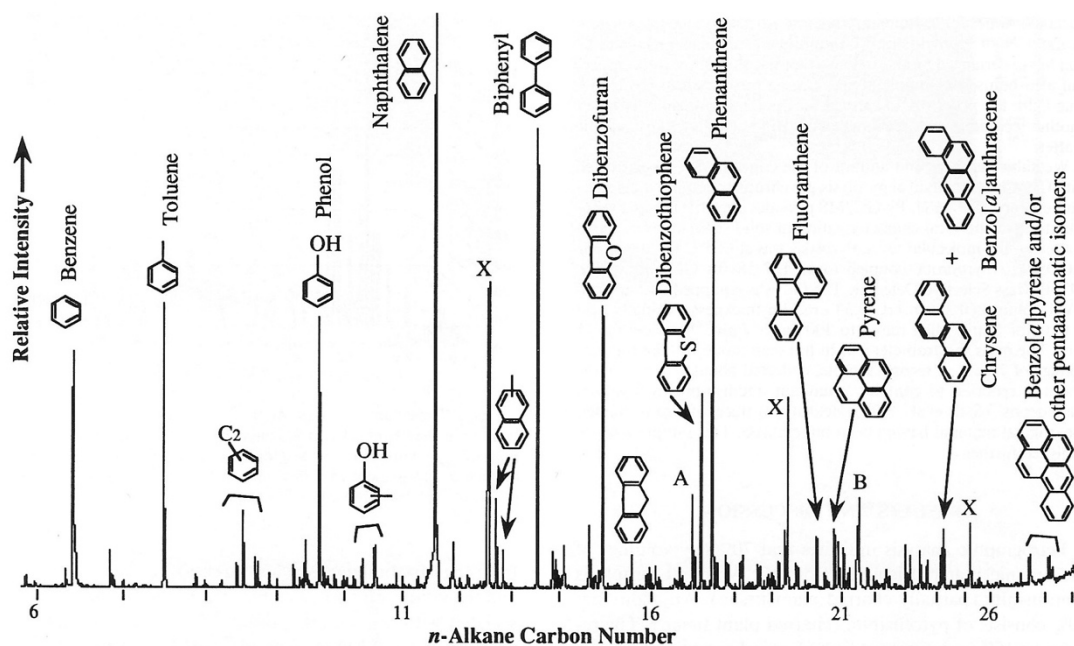


Figure 3 — Py-GC/MS total ion current trace of the organic concentrate from the Mimbral sample. Molecular structures and names are used to identify the principal peaks, determined by mass spectral and retention time data and by comparison with other samples and the literature. Peaks "A" and "B" are tentatively identified as fluoren-9-one and acridinone, based on matches with library spectra in the N.B.S. Mass Spectral Database. Peaks "X" are obvious contaminants (phthalates and silanes). Numerals mark expected elution times of straight-chain saturated hydrocarbons of the corresponding carbon number, determined from other samples run under the same conditions, for which both aliphatics and aromatics are detected.





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#### Acknowledgments

This research was partially supported by a National Science Foundation grant (A. Montanari). Field work was supported by Piero and Alberto Angela of RAI television. We would like to thank Walter Alvarez for helpful discussion and critical review of the manuscript. We would also like to thank C. Koeberl, W. Wolbach and R. Schmitt for their thoughtful reviews.

**Reply to the Comment by T. P. Jones on "Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic firestorm and megawave"**

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Jones (1994) finds the presence of woody charcoal within the thick, coarse-grained unit immediately underlying the Cretaceous-Tertiary (K-T) boundary Ir layer at Mimbral (Krug et al., 1994) reason to question the interpretation that the bed is the result of an impact-generated megawave. We have no dispute with many of his general statements on the occurrence of fossil charcoal and wood in the sedimentary record. In fact, some of his comments reiterate the arguments and concerns that we presented in our paper. However, one must also take into account the geological and sedimentological context of the organic matter under discussion.

In the usual sedimentary situation, low density ( $0.4 \text{ g/cm}^3$ ), dry wood charcoal would either be incorporated in shallow-water, nearshore sediments, or would float for weeks far out to sea, and after being waterlogged, would settle on the deep seafloor along with fine-grained, pelagic or hemipelagic sediments. Jones thus considers the interpretation by Keller et al. (1993) of a shallow-water, nearshore environment for the KT coarse bed in the Mimbral section to be consistent with the presence of charcoal. According to Keller and coworkers, the K-T elastic unit took several millennia to form. In this view, the presence of wood remains and charcoal in such an environment would be an ordinary geological occurrence. However, the arguments by Keller et al. (1993) proposing a normal shallow water, nearshore depositional environment for the K-T clastic unit, have been strongly rejected by Smit et al. (1994a,b).

The undisturbed marly limestones underlying and overlying the K-T clastic unit contain benthic foraminifers indicating a paleodepth greater than 600 m, and represent a tranquil, pelagic depositional environment. Planktonic foraminifers indicate that very little time is unrepresented in the deep water sequence, making uplift to shallow depths and subsequent sinking improbable.

The clastic unit is an unusual feature for three main reasons: (1) it occurs exactly at the K-T boundary in numerous outcrops distributed over an enormous area stretching from Alabama through Texas, northeastern Mexico, all the way to Chiapas (Smit et al., 1992, 1994c; Montanari et al., 1994), in Haiti (Izett, 1991), and in several deep-sea cores throughout the Gulf of Mexico-Caribbean Sea (Alvarez et al., 1992); (2) it exhibits a complexity of sedimentary features which are common to many different high energy deposits like tempestites, turbidites, debris flows, dunes, channel fillings, etc., and paleocurrent indicators showing reversals of paleocurrent directions (Smit et al., 1994c); and (3) it lies immediately on top of proximal impact ejecta such as tektites and shock-metamorphosed minerals, and immediately below fine-grained sediments containing impact fallout material (i.e., the iridium anomaly; Smit et al., 1992). Thus, the K-T clastic unit is an exceptional sedimentological event well explained as a tsunamite triggered by a giant impact at Chicxulub, on the Yucatan peninsula, as originally proposed by Smit et al. (1992).

In conclusion, Jones wonders ". . . what mechanism would provide the energy to redeposit [the charcoal remains] in 600 m water .... " We think that a  $10^8$  Mton impact explosion centered on Yucatan would do the job. Such an extraordinary event would have caused magnitude 12 earthquakes, a fire ball hundreds of kilometers in diameter, and displacement of seawater to form megawaves hundreds of meters high. We agree with Jones that a full understanding of the sedimentology of proximal giant-impact deposits is, and will remain, a subject of lively debate for years to come. However, any further research on this complex subject will have to take into account new evidence and discoveries from increasingly interdisciplinary investigations on these unusual sedimentary deposits. The results of our specific work on the K-T boundary tsunamite at Mimbral reaffirm the exceptional character of impact sedimentology based on the unusual presence of fossil wood and charcoal in an unusual open sea, deep water clastic deposit.

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