Combustion of fossil organic matter at the Cretaceous-Paleogene (K-P) boundary

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ABSTRACT

Recognition of elevated concentrations of aciniform soot in Cretaceous-Paleogene (K-P) boundary sediments worldwide led to the hypothesis that global-scale forest wildfires could have been generated by the K-P boundary bolide impact and might have contributed directly to the extinction event. The wildfires are estimated to have injected 10^{13} t of CO_2 into the atmosphere, resulting in an interval of greenhouse warming. Yet minimal amounts of charred plant remains and abundant noncharred material occur in various K-P boundary locations across North America. This refutes the inference that wildfires occurred on a global scale, and requires an alternative explanation for the aciniform soot. Here we describe significant concentrations of carbon cenospheres in K-P boundary sediments from New Zealand, Denmark, and Canada. Carbon cenospheres are thought to derive solely from incomplete combustion of pulverized coal or fuel-oil droplets, which suggests that the impact may have combusted organic-rich target crust. The Chicxulub impact crater is located adjacent to the Cantarell oil reservoir, one of the most productive oil fields on Earth. This indicates that abundance of organic carbon in the Chicxulub target crust was likely to have been above global mean values. But even if we discount Chicxulub's organic-rich locality, the global mean crustal abundance for fossil organic matter is more than adequate to account for observed concentrations of both carbon cenospheres and aciniform soot, therefore making the global wildfire hypothesis unnecessary.

Keywords: Cretaceous-Paleogene, Cretaceous-Tertiary boundary, extinction, fire, impacts, soot, aciniform, ash, K-T, anthropogenic pollutants, kerogen.

INTRODUCTION

Evidence for an impact event at the Cretaceous-Paleogene (K-P) boundary was first provided by recognition of a global iridium anomaly (Alvarez et al., 1980), and reinforced by discovery of the Chicxulub crater in the Gulf of Mexico (Hildebrand et al., 1991). In addition to iridium, K-P boundary sediments worldwide contain a thin, spinel-bearing "fireball layer" (Kyte and Bostwick, 1995). The impact fireball, a mixture of melted and vaporized target crust and impactor, rose from the Chicxulub crater, expanded and cooled above the atmosphere, then collapsed and flowed hydrodynamically around the Earth, depositing the globally distributed fireball layer (Pope, 2002). The spinel was originally present as inclusions within less resilient mineral microspherules, which are sometimes lost during postdepositional diagenesis or in laboratory preparation (Montanari et al., 1983; Kyte and Bostwick, 1995). The microspherules originated as impact fireball condensates (Ebel and Grossman, 2005), and have structural similarities with modern, industrially derived fly ash (Cisowski, 1988; Bohor and Triplehorn, 1987). Associated layers of black carbon (aciniform soot) (Fig. 1A) (Wolbach et al., 1990), mineral microspherules (see above), and pyrolitic polycyclic aromatic hydrocarbons (Venkatesan and Dahl, 1989) provide compelling evidence that the K-P boundary mass extinction was associated with a combustion event. The combustion event may have contributed an interval of intense global warming from released greenhouse gases (Wolbach et al., 1990).

The provenance of organic material that provided the carbon component of the ashes remains undetermined. Some authors have suggested that aciniform soot found at the K-P boundary was produced by forest wildfires (Wolbach et al., 1990; Durda and Kring, 2004), whereas others have postulated a fossil carbon source (Cisowski, 1988; Belcher et al., 2003, 2005). Because aciniform soot can be produced both by burning vegetation or fossil carbon (hydrocarbons), it cannot be used to determine fuel source. Therefore, this study will assess the morphology, composition, and abundance of carbon cenospheres (Fig. 1D) from K-P boundary sediments. Carbon cenospheres can only be formed by heating of fossil hydrocarbons, and have been previously reported in a K-P section at Lattengebirge, Germany (Graup and Spettel, 1989).

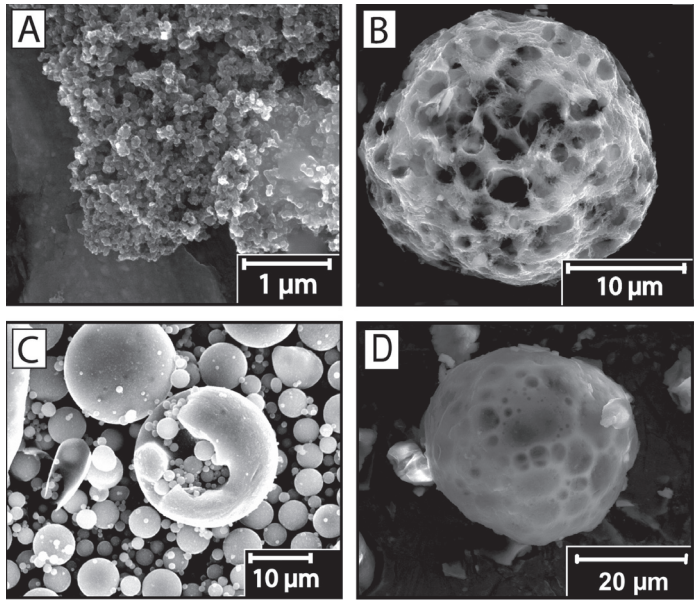

Figure 1. Scanning electron microscope photos. A: Aciniform soot from acetylene combustion. Note "grape bunch" morphology. B: Industrial contaminant carbon cenospheres from Monte Pietralata (Italy). Note porous morphology that distinguishes industrial contaminants from Cretaceous-Paleogene (K-P) boundary carbon cenospheres. C: Inorganic ash spherule (IAS) fly ash from coal-fired boiler (image courtesy Gretchen Hoffman, New Mexico Bureau of Geology). D: K-P boundary carbon cenospheres from Rock Creek East (Canada). Note bubble surface texture that distinguishes K-P boundary carbon cenospheres from industrial contaminants.

MATERIALS AND METHODS

Carbonaceous particles were examined at eight marine K-P boundary locations from New Zealand, Italy, Denmark, and Spain. Five nonmarine K-P locations were examined from the USA and Canada. All sites contain an iridium enrichment, shocked quartz, or microspherules (for details, see Table DR5 in the GSA Data Repository[1]). In New Zealand

[1]GSA Data Repository item 2008089, sampling details, stratigraphy, methodologies, Tables DR1–DR6, and Figures DR1–DR8, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

and Italy, samples spanning the boundary were collected to quantify background concentrations of carbonaceous particles. Control samples were collected in New Zealand and Italy from soil adjacent to the outcrop in order to eliminate the possibility of contamination from industrial particles. Boundary sediments from Denmark, Spain, and North America were provided without control samples by other researchers (for detailed stratigraphy of sample locations, see the Data Repository).

After collection, samples were weighed, stored, and processed in prewashed centrifuge tubes to prevent contamination. Samples were subjected to chemical digestion following the established method of Rose (1994), with the addition of three rinse and centrifugation cycles to the final step of the procedure to increase detection limits. After digestion, residues were examined by scanning electron microscope (SEM) and their trace element contents were analyzed by energy dispersive spectroscopy (EDS). Identification of carbon cenospheres was based on morphology (Griffin and Goldberg, 1981), EDS analysis of individual carbon cenospheres that showed a strong carbon signal, and by light microscopy (Figs. DR1–DR7; see footnote 1). Carbon cenosphere concentrations were quantified using a systematic grid search for counting under SEM (Data Repository).

RESULTS AND DISCUSSION

Aciniform Soot and Carbon Cenospheres at the K-P Boundary

K-P boundary samples from New Zealand, Italy, Denmark, and Spain all contain aciniform soot, in agreement with previous work (Wolbach et al., 1990). K-P boundary sediments from the fireball layer at Woodside Creek (New Zealand) show between 10^3 and 10^4 carbon cenospheres per gram (CC g^{-1}) of dried sediment, with a mean carbon cenosphere diameter of 6.1 µm (Figs. 2A and 2B; Table 1). Carbon cenospheres were examined from above, and from an angle of 55°, which revealed their spheroidal morphology (Fig. DR8). Carbon cenospheres were not detected in sediments from above (Paleogene) or below (Cretaceous) the boundary at Woodside Creek. Trace abundances (0–11 CC g^{-1}) of large mean diameter (47 µm) contaminant carbon cenospheres found in Woodside Creek control samples distinguish the K-P boundary population as an original component of the boundary sediments. Industrial coal use in the South Island of New Zealand is a likely source of the contaminant carbon cenospheres.

Samples from layers 3 and 4 (fireball layer) and layers 4+ at Stevns Klint (Denmark) show between 10^2 and 10^3 CC g^{-1}, with a mean diameter of 5.9 µm (Figs. 2C and 2D; Table 1). The impermeable nature of the raw boundary sediment (hard claystone) at Stevns Klint makes contamination from industrially derived carbon cenospheres unlikely at the concentrations we observe. Samples from ejecta and lower satiny (fireball) layers at Rock Creek East (Canada) show between 10^2 and 10^3 CC g^{-1}, with a mean carbon cenosphere diameter of 26 µm (Figs. 2E and 2F; Table 1). The large diameter of Rock Creek East carbon cenospheres allowed their examination by light microscope, revealing a light brown color (Fig. DR6) and strong fluorescence under ultraviolet light. Light coloration distinguishes these carbon cenospheres from modern carbon cenospheres, which are always black, and suggests derivation from immature (light colored) marine kerogen (Peters et al., 1977), or light-colored hydrocarbon.

All K-P boundary carbon cenospheres have bubble surface texture (Figs. 2A–2F) and show a dominant carbon signal when examined by SEM-EDS (Figs. DR2, DR4, and DR7). Bubble texture distinguishes K-P boundary carbon cenospheres from pollen and spores, and from industrially derived carbon cenospheres (also known as speroidal carbonaceous particulate [SCP]; Fig. 1B), which have a porous surface (Griffin and Goldberg, 1981; Rose, 1996). Bubble texture is consistent with light coloration of the Rock Creek East carbon cenospheres, both features suggesting that the cenospheres boiled but did not ignite; during heating, carbon cenospheres bubble at lower temperatures (300–800 °C), then form pores, and blacken at higher temperatures (>800 °C) as the bubbles burn away (Lightman and Street, 1983).

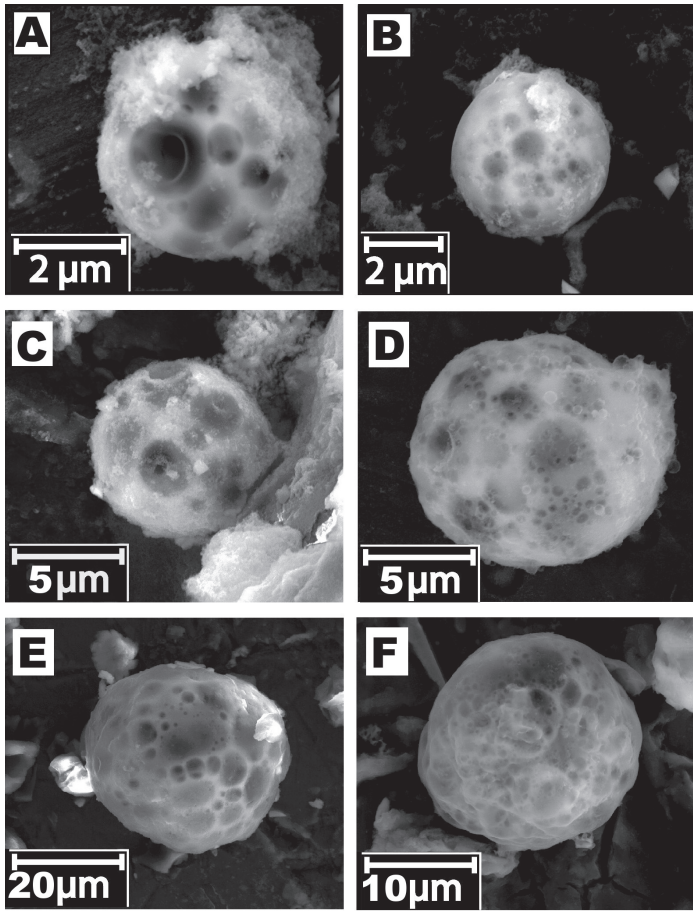

Figure 2. Scanning electron microscope photos of carbon cenospheres. A, B: Woodside Creek, New Zealand. C, D: Stevns Klint, Denmark. E, F: Rock Creek East, Canada. Note bubble surface texture of carbon cenospheres.

TABLE 1. CRETACEOUS-PALEOGENE BOUNDARY CARBON CENOSPHERES

Location	Sample	Mean concentration (carbon cenospheres g^{-1})*	Mean diameter (µm)†
Woodside Creek, New Zealand	Fireball layer	4994	6.1
Stevns Klint, Denmark	Layers 3 and 4 (fireball layer)	646	5.1
	Layers 4+	150	8.5
	Total	398	5.9
Rock Creek East, Canada	Ejecta layer	83	25.2
	Lower satiny (fireball layer)	875	26.6
	Total	479	26.0

*From GSA Data Repository Table DR4 (see footnote 1).
†From GSA Data Repository Tables DR1–DR3.

Low abundances of porous carbon cenospheres were detected at Monte Pietralata (Italy) (10^1–10^2 CC g^{-1}). The presence of porous carbon cenospheres at much higher abundance (10^3–10^4 CC g^{-1}) in nearby topsoil clearly indicates that this outcrop is contaminated with modern material. Elsewhere, the problem of outcrop contamination is well documented, as at Gubbio, Italy (Montanari, 1986). Raw data are presented in Tables DR1–DR4. The presence of carbon cenospheres at Woodside Creek, Stevns Klint, and Rock Creek East is consistent with carbon cenospheres previously reported in a K-P boundary section at Lattengebirge, Germany (Graup and Spettel, 1989). Mean diameter and abundance

(CC cm^{-2}) at Lattengebirge were not reported, but carbon cenospheres are shown cemented within a thin section cut parallel to bedding plane, from one of several sandstone turbidite layers interbedded in the K-P boundary limestone sequence. The cement is an authigenic matrix of calcite and calcareous tests, which demonstrate that the carbon cenospheres were deposited in an ancient marine environment, therefore eliminating the possibility of modern contamination.

Carbon cenospheres were not detected at Caravaca (Spain), or at four of the five North American K-P locations (Table DR4). This can be explained by site-specific processes, or by detection limits of the method. Chemically, site-specific redox conditions may produce varying rates of black carbon oxidation over geological time scales. Postdepositional oxidation of black carbon is known to occur in sediments (Herring, 1985), and was reported for central Pacific K-P boundary locations (Wolbach et al., 2003). Physically, the supply of black carbon to sediments likely varied from region to region during the K-P boundary event. Detection limits for carbon cenospheres are imposed by varying amounts of fine material surviving the chemical digestion, which can coat the sample after centrifugation, obscuring carbon cenospheres beneath.

Evidence for Dispersal and Heating of Crustal Material at the K-P Boundary

Spinel originating from mineral microspherules is a common component of K-P boundary sediments worldwide (Kyte and Bostwick, 1995). The host microspherules likely originated as condensates from the Chicxulub impact plume, which comprised an oxidizing high-temperature mixture of bolide and target crust (Ebel and Grossman, 2005). These high temperatures would have been capable of melting and igniting fossil carbon in the target rocks.

K-P boundary mineral microspherules are close analogs of anthropogenic inorganic ash spherules (IAS; Fig. 1C) in terms of their morphology (Cisowski, 1988; Bohor and Triplehorn, 1987), mineralogy (including spinel), and magnetic behavior (Cisowski, 1988). Magnetite spinel (Fe_3O_4) inclusions in anthropogenic IAS derive from pyrite (Fe_2S) present in fossil fuel, which is oxidized during combustion. Combustion of dispersed fossil fuel (pulverized coal or sprayed oil) in industrial furnaces produces IAS, carbon cenospheres, and aciniform soot simultaneously (Rose, 1996; Medalia et al., 1983), which makes these particles ubiquitous in the modern atmosphere and postindustrial sedimentary record (Griffin and Goldberg, 1983; Rose, 1996). The known derivation of carbon cenospheres and IAS from rapid heating of sprayed and/or pulverized fossil fuels and their environmental ubiquity have led to their use in numerous sedimentary studies as a datum defining the onset of industrialization (Griffin and Goldberg, 1981; Rose, 1996). The presence of IAS (mineral microspherules) in K-P sediments worldwide provides strong evidence for a natural process resulting in the simultaneous dispersal and heating of large volumes of crustal material. If fossil carbon was present in the target crust, then this process could also produce carbon cenospheres. The discovery of carbon cenospheres in K-P sediments worldwide provides support for this prediction; simultaneous dispersal and heating of fossil carbon occurred during the boundary event.

Origin of the K-P Boundary Aciniform Soot Anomaly

Global wildfires would be expected to result in geographically widespread enrichments of charcoal. Yet Belcher et al. (2003, 2005) found charcoal concentrations to be below Late Cretaceous background levels in an examination of K-P boundary sediments from eight nonmarine North American sites. Belcher et al. argued that low abundance of charcoal and high abundance of noncharred material in both the ejecta and fireball layers are inconsistent with forest wildfires on a global scale, and suggested that the K-P boundary aciniform soot anomaly more likely resulted from combustion of fossil organic matter. An additional weakness of the global forest wildfire hypothesis arises from the marine location of the Chicxulub impact, which requires theoretical secondary ignition mechanisms. These mechanisms include thermal energy released by impact ejecta reentering the atmosphere (Durda and Kring, 2004), or lightning strikes produced by atmospheric charge separation during settling of ejecta (Wolbach et al., 1990). Conversely, the impact and vaporization of organic-rich crust at Chicxulub provides a direct explanation for the K-P boundary aciniform soot anomaly.

The formation of the supergiant Cantarell oil field in the Gulf of Mexico is a direct consequence of the K-P impact (Grajales-Nishimura et al., 2000). At impact, the K-P boundary bolide shattered the submerged carbonate platform that forms the western Yucatan Peninsula, resulting in the Cantarell breccia. More than 80% of recovered Cantarell oil derives from Late Jurassic source rock (Guzman-Vega and Mello, 1999). This figure indicates that Jurassic age hydrocarbons were abundant at the time of impact, but not their proximity to the Chicxulub target crust. Hydrocarbon inclusions within diagenetic dolomite record the timing of oil migration at Cantarell, showing that the breccia was permeated by hydrocarbons prior to the precipitation of other minerals in the paragenetic sequence (Martinez-Ibarra et al., 2003). While not providing an absolute date, this does support a relatively early arrival of hydrocarbons into the newly formed breccia reservoir, which increases the probability that abundant hydrocarbons were present in the Chicxulub target region at the time of impact. The $\delta^{13}C$ values of the Cantarell whole oil range between −25‰ and −27‰ (Guzman-Vega and Mello, 1999), bracketing the globally averaged K-P boundary black carbon (−25.8‰ ± 0.6‰). Carbon cenospheres, IAS, and aciniform soot are all produced simultaneously in modern furnaces from finely dispersed organic-rich crust. Similarly, organic and mineral matter excavated from the target crust by the K-P impact may have been heated and dispersed sufficiently to produce a worldwide layering of these three particle types.

Carbon Cenospheres at Woodside Creek, Stevns Klint, and Rock Creek East

Formation of carbon cenospheres requires a dispersion of organic matter into tiny droplets or particles prior to heating (Lightman and Street, 1983). This excludes passive combustion of exposed fossil organic matter and forest wildfires as processes by which carbon cenospheres may be generated. The spheroidal shape and bubble surface of K-P boundary carbon cenospheres require an organic source material able to exist in the liquid state, and boil. This further eliminates forest wildfire as a potential source. The absence of a natural carbon cenosphere background in preindustrial lake sediments (Griffin and Goldberg, 1981; Rose, 1996) provides empirical support for these arguments. At Woodside Creek, the absence of carbon cenospheres in sediments from above or below the boundary confirms the association of these particulates with the boundary event.

This raises the question of whether the likely volume of organic sediments combusted by the Chicxulub impact would have been sufficient to generate the observed carbon cenospheres anomaly. The Woodside Creek boundary clay examined in this study has a density of 4.5 g cm^{-3}, a thickness of 0.6 cm, and mean carbon cenospheres content of 4994 CC g^{-1}, giving a carbon cenospheres abundance of 1.3×10^4 CC cm^{-2}. Assuming that Woodside Creek is representative in terms of carbon cenosphere abundance and mean diameter (6.1 μm), then a bulk carbon cenosphere density of 0.28 g cm^{-3} (Baltrus et al., 2001) provides a global K-P boundary carbon cenosphere inventory of 2.3×10^{12} g. Assuming that 0.003% of the original organic matter was converted by impact to this form of carbon, as occurs in pulverized coal-fired industrial facilities (Rose et al., 1996), accounting for a global layer of carbon cenospheres requires 7.6×10^{16} g of dispersed organic material. Applying the same calculation to carbon cenosphere populations at Stevns Klint and Rock Creek East provides estimates of 9.2×10^{16} g and 9.4×10^{17} g, respectively (Table DR6): these mass estimates increase with proximity to Chicxulub (~12,000, 9000,

and 3000 km, respectively), which is expected if Chicxulub is the source of the carbon cenospheres. However, additional estimates from geographically dispersed locations would be required to confirm Chicxulub as the source. The Chicxulub impact crater is ~200 km in diameter (Sharpton et al., 1992) and mean crustal abundance of fossil organic matter is 2550 g cm^{-2} (Hunt, 1979), so the impact could have excavated ~10^{18} g of organic matter, more than required for observed carbon cenosphere concentrations and aciniform soot abundances (Wolbach et al., 1985).

The location of the Chicxulub crater adjacent to the supergiant Cantarell oil field makes it unnecessary to invoke global-scale forest wildfires to explain K-P boundary aciniform soot enrichment. But even if we discount Chicxulub's locality, the global mean crustal abundance for fossil organic matter is more than adequate to account for observed concentrations of both carbon cenospheres and aciniform soot. Global-scale forest wildfires rely on theoretical ignition mechanisms, and are not supported by charcoal records across North America. A simpler explanation, and one supported by the observation of carbon cenospheres in this study, is that anomalous occurrences of carbon cenospheres and aciniform soot in K-P boundary sediments worldwide result from an impact into the organic-rich crust at Chicxulub.

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