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TRACE ELEMENT AND ISOTOPE GEOCHEMISTRY OF CRETACEOUS/TERTIARY BOUNDARY SEDIMENTS: IDENTIFICATION OF EXTRA-TERRESTRIAL AND VOLCANIC COMPONENTS; S.V. Margolis and E. F. Doehne, Department of Geology, University of California, Davis, Davis, California, 95616

We have performed trace element and stable isotope analyses on a series of sediment samples crossing the Cretaceous/Tertiary boundary from critical sections at Zumaya and Sopelano, Spain. Our aim is to possibly distinguish extraterrestrial vs. volcanic or authigenic concentration of platinum group and other elements in K/T boundary transitional sediments.

These sediments also have been shown to contain evidence for step-wise extinction of several groups of marine invertebrates, associated with negative oxygen and carbon isotope excursions occurring during the last million years of the Cretaceous (1,2). These isotope excursions have been interpreted to indicate major changes in ocean thermal regime, circulation, and ecosystems that may be related to multiple "events" during latest Cretaceous time (3).

Our results to date on the petrographic and geochemical analyses of the Late Cretaceous and Early Paleocene sediments indicate that diagenesis has obviously affected the trace element geochemistry and stable isotope compositions at Zumaya. The degree of diagenetic alteration is correlated with lithology. The best preserved samples are soft marls with high clay contents and limestones that have undergone early, permeability-reducing marine cementation. More porous sandstones and bedding plane veins show the greatest alteration and depleted stable isotope values (3,4).

Mineralogical and geochemical analysis of Cretaceous/Tertiary boundary sediments at Zumaya suggest that a substantial fraction of "anomalous" trace elements in the boundary marl are present in specific mineral phases. Trace element data show that the boundary marl is enriched in Ir, Ni, Cr, As, Pb, Cu, Zn, Ba, and Sr. Siderophile and chalcophile trace elements are concentrated in the following minerals: platinum in native platinum grains; Ni and Cr in spinels and spherules; As and Ni in pyrite/arsenopyrite; and Pb, Cu, Zn, Sn, and Sb in sulfides. Pt, Cr, Ni and As concentrations and spherules have been found only at the boundary. No other noble metals, such as Ir were detected in specific mineral phases (4).

The platinum and nickel grains perhaps represent the first direct evidence of siderophile-rich minerals at the boundary. The presence of spinels and Ni-rich particles as inclusions in aluminosilicate spherules from Zumaya suggests an original, non-diagenetic origin for the spherules. The chemistry and morphology of the Pt grains, spinels, spherules and Ni-rich grains most closely matches chondritic fireball or ablation debris (5). This suggests that a substantial portion of any proposed K/T bolide(s) may have burned up in the Earth's atmosphere (4). A volcanic origin for the boundary particles is not compatible with the chemistry of the Zumaya particles. Chalcophile elements appear to have an authigenic origin and may be derived from seawater or an early diagenetic enrichment (4,5).

Similar spherules from Southern Spain (Caravaca), show a strong marine authigenic overprint. The Zumaya spherules, however, are mineralogically more diverse, contain spinel and Ni-rich inclusions and appear to be less altered than spherules from Italy, Southern Spain and New Zealand. The higher background sedimentation rate at Zumaya may have quickly buried the "fallout" layer protecting the spherules from early marine diagenesis (5).

This research represents a new approach in trying to directly identify the sedimentary mineral components that are responsible for the trace element concentrations associated with the K/T boundary. These techniques are currently being used on several other well preserved marine and terrestrial K/T sections and may provide valuable information that could resolve the controversy surrounding the possibility of multiple K/T boundary events, the volcanic vs. impact origin for anomalous geochemical concentrations as well as the relationship to biotic extinctions.

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