Geochemical characterization of the K-T boundary at Beloc/Haiti

D. Stüben
U. Kramar

Institute of Petrography and Geochemistry, University of Karlsruhe, D-76128 Karlsruhe, Germany

W. Stinnesbeck

Institute of Geology, University of Karlsruhe, D-76128 Karlsruhe, Germany

Major environmental changes at the K-T boundary caused by the impact of an asteroid or some other extraterrestrial body or by extensive volcanic activity play the leading roles in the discussion of the worldwide environmental stress in the ocean (a Review is given in Glasby and Kunzendorf 1996) resulting in a marked impact on ocean chemistry, ocean productivity and sea level drop.

Geochemical characterization of the sediment layers of the K-T boundary can help to reconstruct the story of this time period. $\delta^{13}C$ values of plantonic skeletons reflect a drastic decrease in the primary productivity (Hsu and McKenzie 1985) with no corresponding change in value for benthic skeletons. This was interpreted as being due to an almost complete reduction in oceanic plankton production and the elimimation of the surface to bottom carbon isotope gradient of the oceans by mixing within a few decades. Oxygen isotope data indicate a cooling of 2–3°C, up to 6 °C (Sarkar *et al.*, 1992) followed by a rapid warming (10°C). Late Cretaceous is characterized by a regression (over 100 m during 0.5 my) followed by an equally rapid rebound after the event (Haq *et al.*, 1987).

Concerning the worldwide Ir anomaly at this boundary, it can be calculated that this Ir-rich layer accumulated at an average rate of 5.977 my Ir/cm^2 ky over a period of 18.000 years which is somewhat less than the residence time of Ir in seawater (Glasby and Kunzendorf 1996).

Work has been done on the complex pattern of trace elements, pyrite is the major carrier for Ni, Co, As, Sb, and Zn. This idea is supported by the similarity in the contents of Au, Pt, Ni and Co with those of black shales (e.g. Schmitz 1985). Ir is most probably absorbed on fine particles during the volcanic event (Hansen *et al.*, 1988).

Glasby and Kunzendorf (1996) showed that the elements reach peaks in the Fish clay grading upwards in the sequence Fe-Co-Zn-As-Sb, Ir-Cr, Au, *REE* and U. Thompson *et al.* (1993) showed that although the sediment was deposited under anoxic conditions the peaks do suggest the influence of diagenetic processes on the element distribution.

Analytic

We have investigated in detail the Beloc3 profile. A total of 42 samples was taken from a section below and above the 'Red Layer', which commonly is used to mark the K/T-boundary. The sampling interval ranges from 150 cm below up to 70 cm above this layer.

Trace element contents (Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Ba, Ce and Pb, as well as Ca, Mn, Ti and Fe in bulk sediments were analysed by energy dispersive X-ray fluorescence (EDXRF). $\delta^{13}C$ and $\delta^{18}O$ isotope ratios were determined from the carbonate CO_2.

In 19 of these samples, the platinum group elements Rh, Pd, Ir and Pt were determined by ICP/MS (after preconcentration by nickel sulphide fire assay).

Results and discussion

Ca showed CaO values between 7.5% and 57% i.e. from sediments, nearly free of Calcite at the Red Layer to practically pure carbonates. The Red Layer at 150 cm, a spherule rich horizon 50 cm below, rich in material of volcanic origin (ash, pumice) and a horizon with large sperules 110 cm below the Red Layer are enriched in Ni, Cu, Zn, As, Mo, Cd, Ba and Pb but also in elements which can be regarded as markers for clastic sedimentation or volcanogenic origin such as Ti, Zr and Nb (Fig. 1). These three horizons show more negative $\delta^{13}C$ and $\delta^{18}O$ values than the neighboured sediments and are accompanied by distinct PGE anomalies. The Beloc 3 profile exhibits not one anomaly but three ones, which can not be explained with a single event at the KT-boundary. The anomalies show Peak concentrations (from top to bottom) of 0.56, 1.0 and 0.2 μg/kg iridium, 6.9, 0.4, 3.9 μg/kg platinum and 8.9, 2 and 2.2 μg/kg palladium. The Red Layer is anomalous in all of the PGE's with Pd/Ir ratios up to 40 and Pt/Ir

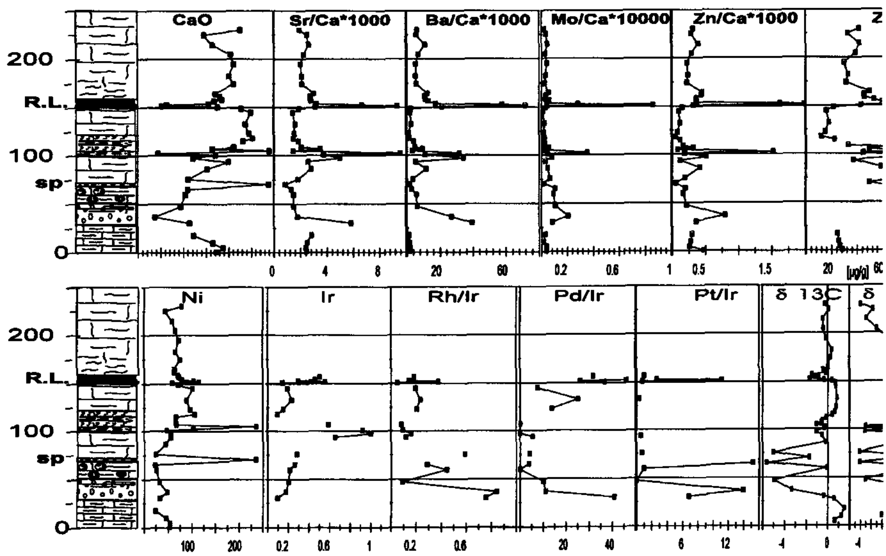

FIG. 1. Depth profiles of trace elements (normalized to Ca), PGE - elements and $\delta^{13}C$ and $\delta^{18}O$ isotope ratios at BELOC3. (R.L. = Red Layer; sp = spherule horizon).

ratios up to 12. The layer rich in volcanic material shows the highest Ir concentrations but low Pd/Ir and Pt/Ir ratios and the spherules layer and below shows constantly Ir values but several peaks in Rh, Pd and/ or Pt. This section shows also sharp deflections to more negative $\delta^{13}C$ and $\delta^{18}O$ values.

The Sr/ Ca ratios of the calcite rich samples may indicate sealevel variations, whereas this effect is superimposed by dilution or Sr from volcanogenic or clastic origin in the low calcium section. In the section 50 cm below R.L., where volcanic material is present, Pt/Ir and Pd/Ir ratios show Ir enrichment compared to C1 ratios (Mc Donough and Sun, 1995). Compared to C1 ratios, platinum and Pd are enriched in the Red layer itself and in the spherules layer.

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