GEOCHEMISTRY OF THE CRETACEOUS-PALEOGENE BOUNDARY CLAY FROM THE STARKVILLE-SOUTH SITE (THE RATON BASIN, USA): VANADIUM

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Over 80 marine sites worldwide with unusually high concentrations of Ir have been found in the sediments at the Cretaceous-Paleogene boundary. Alvarez *et al.*[1] (1980) explained the high Ir concentration in terms of the impact of an asteroid depositing a worldwide layer of Ir. Most of these Ir anomalies were discovered in marine sedimentary rocks, but in the Raton Basin the Cretaceous-Paleogene boundary occurs in a rock sequence deposited in fresh water swamps and flood plains. In addition to Ir the boundary clays in the Raton Basin are also enriched in other trace metals, such as vanadium (V). We report here a preliminary study of V in the boundary clay from the Starkville-South Site (SVS).

At SVS a thin shaly bed, between the base of the coal and kaolinitic-clay layer contains the highest concentrations of Ir (56 ppm) and V (110-180 ppm). Mineralogical analysis shows that the SVS boundary clay contains major authigenic mineral kaolinite and minor detrial mineral anatase. The distribution of V in the various fractions boundary clay indicates that V is mainly (>90 %) associated with the kaolinite.

Many of our previous studies have shown that VO^{2+} ions are excellent geochemical indicators of paleoenvironmental conditions of sedimentation. This fact led us to search for VO^{2+} ions in the boundary clay at SVS which may contribute to a general understanding of the origin and nature of this clay and its kaolinite component. For this purpose, we employed electron spin resonance (ESR).

The investigation of the untreated boundary clay yielded a partly multiline ESR spectrum similar to the spectrum of Mn^{2+} in the $CaCO_3$. After removal of the carbonate fraction, by treating with acetate buffer, the Mn^{2+} lines diminished. The ESR spectrum of the carbonate-free fraction was identical to the spectrum of VO^{2+} ions associated with natural kaolinites. These ions disappeared completely during the boiling HCl treatment. It is suggested that the VO^{2+} ions are located either on the surface or in the kaolinite structure.

1. Alvarez W.L., Alvarez W., Asaro F., Michel H.V. (1980). Extraterrestrial cause for the Cretaceous/Tertiary extinction. Science, 208 1095-1108.

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