

Cu- or Ag-enriched grains in the K-Pg boundary clays: New evidence for acid rain immediately after the meteorite impact

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Cretaceous-Paleogene (K-Pg) boundary clays are enriched in both chalcophile elements as well as siderophile elements [1]. As the elemental ratios of siderophile elements in these clays are very similar to chondritic values, the enrichment of siderophile elements results from the incorporation of meteorite condensates. As the ratios of chalcophile and siderophile elements (such as Zn/Ir, As/Ir, and Sb/Ir) are one to two orders of magnitude higher than those in chondrites, chalcophile elements in these clays include components not related to meteorite condensate [2]. The chemical compositions of such components should thus reflect the processes that might have enhanced the concentrations of chalcophile elements in seawater. Moreover, as these clays may consist of materials from various origins, it is important to distinguish materials related to meteorite impact from those deposited before and after this event in order to clarify environmental perturbations induced by the meteorite impact. In this study, we used synchrotron X-ray fluorescence (SXRF) microscopy to distinguish materials from various origins in the K-Pg boundary clays from Stevns Klint, Denmark.

The concentrations of major and trace elements in the Stevns Klint K-Pg boundary clays varied, even in samples collected from neighboring outcrops. Cross plots of elemental concentrations suggested the mixing of three components (a, b, c) with different chemical compositions. Component a was enriched in chalcophile elements and iron; this may be related to pyrite. Component b was depleted in chalcophile elements and enriched in calcium; this may be related to calcite, judging from its Ca concentration (~40 wt%). Component c was particularly enriched in Cu, Ag, and Pb. Components a and c included iridium (obviously supplied by the K-Pg meteorite impact), suggesting that these components were related to immediately subsequent events after the meteorite impact. Cu and Ag levels in these components were adequate to allow SXRF-microscopy to obtain their micro-distributions.

This SXRF analysis indicated two phases incorporating Cu: pyrite with Cu as a trace element and discrete Cu-enriched grains. These potentially correspond to the two chalcophile-containing components (a and c, respectively). The Cu-enriched grains did not contain measurable Ag, although Ag was present in discrete Ag-enriched grains. Although both Cu- and Ag-enriched grains existed as discrete grains, there was a positive correlation between the Cu and Ag concentrations in the K-Pg boundary clays, suggesting that a common process was involved in supplying these elements to sediments. Both Ag and Cu can be transported by organic matter from seawater to the seafloor. Cu is scavenged by complexation with organic matter in seawater, whereas strong organic Ag complexes have not been observed in seawater. Ag scavenging probably occurs as a result of Ag₂S precipitation within oxygen-depleted microenvironments inside organic particulates [3]. The ability of organic matter to accumulate both Cu and Ag in the oceans by different mechanisms may have led to discrete grains of Ag and Cu in the K-Pg boundary clays with a strong correlation between their concentrations. Cu, Ag, and Pb concentrated in component c generally exist in acid soluble sulfides such as sphalerite and galena. Therefore, the chalcophile elements in component c may have been supplied to seawater by intense acid rain after the K-Pg impact.

References [1] e.g., Kyte et al., 1980, *Nature* 288, 651-656; Schmitz, 1985, *Geochim. Cosmochim. Acta* 49, 2361-2370; Schmitz, 1988, *Geology*, 16, 1068-1072; Schmitz, 1992, *Geochim. Cosmochim. Acta* 56, 1695-1703. [2] Gilmour and Anders, 1989, *Geochim. Cosmochim. Acta*, 53, 503-511. [3] McKay and Pedersen, 2008, *Global Biogeochemical Cycles* 22, GB4010.

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