

## Enrichment of chalcophile elements in Cretaceous–Paleogene boundary clays

\*Teruyuki Maruoka<sup>1</sup>, Yoshiro Nishio<sup>2</sup>

1. Faculty of Life and Environmental Sciences, University of Tsukuba, 2. Research and Education Faculty, Kochi University

Cretaceous–Paleogene (K–Pg) boundary clays are enriched in chalcophile elements along with siderophile elements [1]. As elemental ratios of siderophile elements in the K–Pg boundary clays are very similar to chondritic values, the enrichment of siderophile elements in the K–Pg boundary clays results from the incorporation of meteorite condensates. On the other hand, it cannot be assumed that the chalcophile elements in the K–Pg boundary clays were supplied by meteorite condensates, because the ratios of chalcophile and siderophile elements in the K–Pg boundary clays, such as Zn/Ir, As/Ir, and Sb/Ir, are one to two orders of magnitude higher than those in chondrites. In this study, to elucidate the processes that could have contributed to the enrichment of chalcophile elements in the K–Pg boundary clays, we analyzed the chemical compositions of major and trace elements in the K–Pg boundary clays from Stevns Klint in Denmark.

The concentrations of major and trace elements in the K–Pg boundary clays varied among the collected samples even from neighboring outcrops. Cross plots of the concentrations of these elements suggested the mixing of three materials with different chemical compositions. The first component was enriched in all chalcophile elements and iron. The second component was depleted in chalcophile elements and enriched in calcium. The third component was enriched particularly in copper, silver, and lead. The first and third components included iridium that was obviously supplied at the K–Pg meteorite impact. Therefore, these two components were produced by phenomena related to the K–Pg meteorite impact. We propose that chalcophile elements were supplied to the K–Pg boundary clays by a combination of impact heating of the target rocks and intense acid rain following the impact.

Iron oxide/hydroxide grains with sizes of one to several tens of nanometers have been previously observed in the K–Pg boundary clays [2]. These likely condensed from the vapor plume that formed by impact heating at the K–Pg meteorite impact. These iron oxides/hydroxides could absorb chalcophile and siderophile elements from seawater. Such materials would have been converted to pyrites incorporating chalcophile elements under the reductive conditions on the seafloor. In addition, the correlations between the concentrations of chalcophile elements and soot have been observed in the K–Pg boundary clays [3]. This soot could have been produced by the impact heating of hydrocarbons in the target rocks. Bacterial sulfate reduction and subsequent pyrite production occur in reducing environments where hydrocarbon deposition occurs, thus resulting in the simultaneous accumulation of pyrite and hydrocarbons. Therefore, chalcophile elements accompanied by soot may have been released by impact heating of pyrite in the target rocks. Both chalcophile elements and iron, which were enriched in the first component, could have been provided by the impact heating of the target rocks.

Copper, silver, and lead, which were concentrated in the third component, are generally concentrated in acid soluble sulfides such as sphalerite and galena. Therefore, the third component was possibly supplied by intense acid rain after the K–Pg impact.

In summary, chalcophile elements in the K–Pg boundary clays comprises two components, one that is enriched in all chalcophile elements and another that is enriched particularly in copper, silver, and lead. These components were likely supplied by phenomena associated with the meteorite impact at the K–Pg boundary, such as the impact heating of the target rocks and intense acid rain.

References [1] Schmitz (1985) *Geochim. Cosmochim. Acta* 49, 2361–2370 [2] Belza et al. (2017)

Geochim. Cosmochim. Acta 202, 231-263 [3] Gilmour and Anders (1989) Geochim. Cosmochim. Acta 53, 503-511

Keywords: meteorite impact, impact heating, acid rain