What happened after the meteoroid impact at the end of the Cretaceous Period? - Paleoenvironmental reconstruction based on synchrotron XRF images

Biodiversity has not been constant throughout Earth's history. Declines in biodiversity within a short period of geologic time, roughly 10^5 years or less, can be observed in fossil records and are known as mass extinctions. Although varying degrees of mass extinctions have occurred, "Big Five" mass extinctions were the five most severe events. One of these severe mass extinctions occurred at the Cretaceous-Paleogene (K–Pg) boundary (66 million years ago). The K–Pg mass extinction is considered to have been triggered by the impact of a 10-km-diameter meteoroid. In the sedimentary record, this boundary is characterized by a thin clay layer, called K–Pg boundary clay, which contains materials derived from the impact, such as fragments of the meteoroid and impacted target rocks and condensates from impact-induced vapor. The K–Pg boundary clay contains anomalously high concentrations of siderophile elements that favorably concentrate in the metallic phase and are therefore depleted in the Earth's crust and mantle. The elemental ratios of these siderophile elements in the K–Pg boundary clay are very similar to those of carbonaceous chondrites [1,2], indicating that a meteoroid impact triggered the K–Pg mass extinction.

The K–Pg boundary clay contains high concentrations of chalcophile elements, which preferentially concentrate in sulfides, as well as siderophile elements. As the ratios of chalcophile to siderophile elements, such as Zn/Ir, As/Ir, and Sb/Ir, are one to two orders of magnitude larger than those of chondrites [3], the chalcophile elements in the K–Pg boundary clay were likely derived from surface processes rather than the meteoroid. Such processes might be related to environmental perturbations that directly induced the K–Pg mass extinction. As mentioned above, the extinction was triggered by the meteoroid impact, but was directly caused by environmental perturbations that occurred following the K–Pg meteoroid impact. Sunlight shielding, global wildfires, global warming, acid rain, ultraviolet exposure, and ozone toxicity have been proposed as environmental perturbations [4]; however, it is unclear which of these perturbations actually occurred and most severely affected biota at the end of the Cretaceous Period. This is because the necessary time-resolved information (annual to millennial scale) is absent from the sedimentary record. To determine which processes occurred immediately after the K–Pg meteoroid impact, the chemical compositions of major and trace elements in the K–Pg boundary clay from Stevns Klint, Denmark, were analyzed [5].

The concentrations of major and trace elements, including chalcophile and siderophile elements, of the K–Pg boundary clay varied among the samples analyzed herein, even between the samples collected from neighboring outcrops. The concentrations of some chalcophile elements such as Cu, Ag, and Pb were correlated with those of iridium, all of which in the K–Pg boundary clay were derived from the meteoroid (Figs. 1(a–c)). Therefore, these chalcophile elements might have been enriched during the period after iridium was supplied by the meteoroid impact and before iridium was removed from oceans. Synchrotron X-ray fluorescence (SXRF) microscopic images obtained using SPring-8 **BL37XU** showed that Cu and Ag were present as trace elements in pyrite (FeS_2) grains and as discrete 1–10 μm phases enriched in Cu or Ag [5] (Fig. 2). The pyrite grains also contained

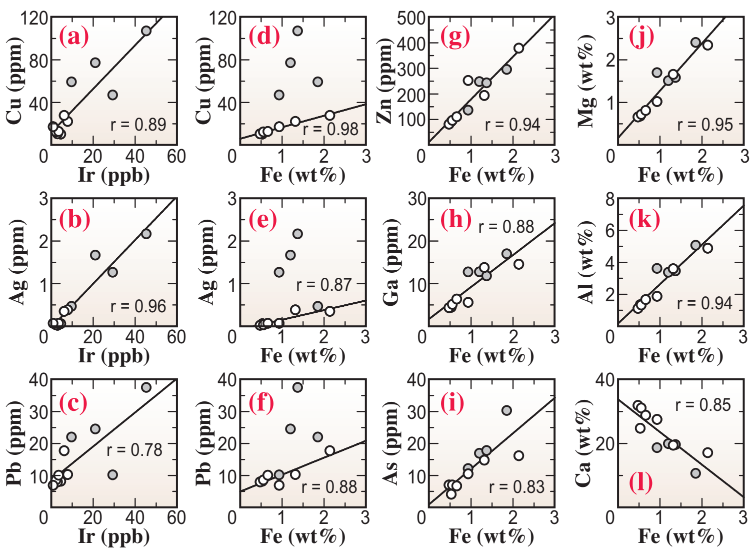

Fig. 1. Concentrations of trace and major elements of **(a)** Cu, **(b)** Ag, and **(c)** Pb compared with Ir, and of **(d)** Cu, **(e)** Ag, **(f)** Pb **(g)** Zn, **(h)** Ga, **(i)** As, **(j)** Mg, **(k)** Al, and **(l)** Ca compared with Fe. Solid lines in **(d)–(l)** are regression lines based on the data shown by open circles for samples in which Cu concentrations correlated with Fe concentrations. [5]

chalcophile elements (Zn, Ga, As, and Pb) other than Cu and Ag, whereas the discrete grains consisted mainly of Cu or Ag. The concentrations of some chalcophile elements (Zn, Ga, and As) were positively correlated with those of Fe, whereas correlations for the concentrations of Cu, Ag, and Pb with those of Fe were observed only in some of the data (closed circles in Figs. 1(d–i)). This implies that the concentrations of Ag, Cu, and possibly Pb can be explained by the mixing of two components for chalcophile elements: one component related to pyrite and containing other chalcophile elements in addition to Ag, Cu, and Pb, and a component especially enriched in Cu, Ag, and Pb. The SXRF images (Figs. 2(a,b)) also support two-component mixing for Ag and Cu. The two proposed components might accompany iridium; therefore, both components may have been supplied to the oceans immediately after the meteoroid impact.

Although iron is present in the form of pyrite (FeS_2) in the Stevns Klint K–Pg boundary clay, Fe might have been supplied to the oceans as high-temperature condensates of iron oxide, as indicated by the correlations between Mg and Al concentrations and those of Fe (Figs. 1(j,k)). This is because Mg and Al oxides were supplied to the oceans as condensates from the impact-induced vapor (Figs. 3(a,b)). Iron oxide on the seafloor can be reduced to Fe^{2+}, which could react with hydrogen sulfide produced by sulfate-reducing bacteria and be converted into pyrite containing chalcophile elements.

The component unrelated to pyrite was enriched especially in Ag, Cu, and Pb, which is typically present in acid-soluble sulfides, such as chalcocite, sphalerite, and galena. Thus, these elements might have been supplied to the oceans via leaching caused by highly acidic rain that occurred immediately following the K–Pg meteoroid impact (see references in [4]). In summary, the presence of two components related to chalcophile enrichments in the K–Pg boundary clay may reflect environmental perturbations such as impact heating and highly acidic rain immediately following the meteoroid impact (Fig. 3).

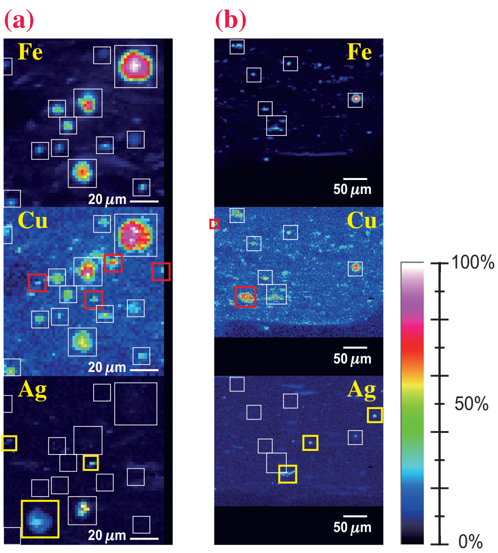

Fig. 2. Synchrotron-XRF images of Fe, Cu, and Ag in two regions **(a)** and **(b)** of a thin section from the Setvns Klint K–Pg boundary clay. The intensities were normalized using the maximum intensities in the field of view. White squares indicate the locations of typical pyrite grains. Red and yellow squares indicate the locations of Cu- and Ag-enriched grains, respectively. [5]

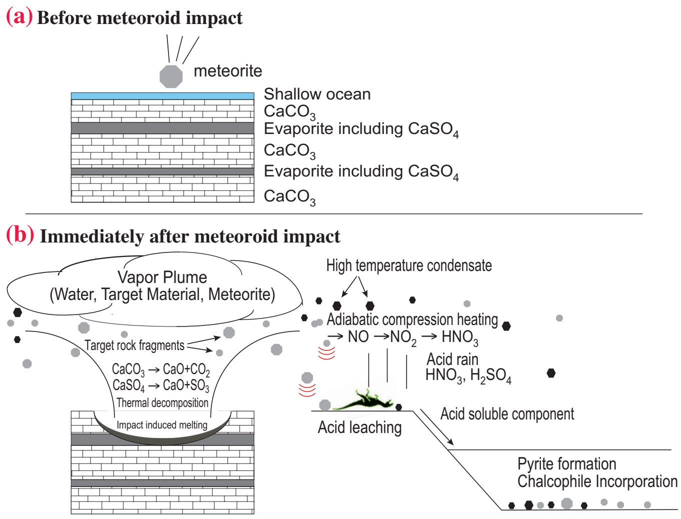

Fig. 3. Schematic drawing depicting the K–Pg meteoroid impact: **(a)** prior to the impact and **(b)** immediately after the impact. A vapor plume incorporating vaporized target rock and meteoroid materials might have been produced by the impact, from which high-temperature condensates (including Mg, Al, and Fe oxides) might have been produced. At the seafloor, Fe oxide may have been converted to pyrite containing chalcophile elements. The adiabatic compression of air by falling target rock fragments may have produced nitrogen oxide, which could have produced nitric acid rain. The thermal decomposition of $CaSO_4$ in the target rock may have released SO_3, which could have produced sulfuric acid rain.

Teruyuki Maruoka

Faculty of Life and Environmental Sciences,
University of Tsukuba

Email: maruoka.teruyuki.fu@u.tsukuba.ac.jp

References

[1] L.W. Alvarez *et al*.: Science **208**(1980) 1095.
[2] R. Ganapathy: Science **209** (1980) 921.
[3] I. Gilmour and E. Anders: Geochim. Cosmochim Acta **53** (1989) 503.
[4] T. Maruoka: Astrobiology (ed. A. Yamagishi *et al*.) (2019) 303.
[5] *T. Maruoka, Y. Nishio, T. Kogiso, K. Suzuki, T. Osawa, Y. Hatsukawa and Y. Terada: GSA Bulletin **132** (2020) 2055.*