Mysterious silver microparticles of the Cretaceous-Paleogene boundary Fish Clay (Stevns Klint, Denmark)

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Alvarez et al. (1980) explained the presence of anomalous iridium (Ir) in prominent marine Cretaceous-Paleogene (KPB) clays, including those at Højerup (Stevns Klint), by proposing a late Cretaceous asteroid impact. This suggestion was followed by reports of the Ir anomaly in many other marine/continental boundary clays worldwide. These clays mark one of the most significant impact events in the Phanerozoic, which was probably largely responsible for one of the greatest extinctions in Earth history.

Detailed lithology of the Fish Clay constituent of the Rødvig Formation near the village of Højerup was described by Surlyk et al. (2006). The basal layer is red and 2-4 mm thick. The basal layer is overlain by a black-to-brown marl, which is commonly 2-5 cm thick. Ir is enriched in the bottom of the marl (Schmitz, 1988).

The red layer contains well-preserved impact-related goethite-rich microspherules, altered nano-size glasses and goethite grains (altered meteorite fragments) (Graup et al., 1992; Bauluz et al., 2000), and a very few shocked quartz grains (Schmitz, 1992). This layer also contains geochemical markers, including some siderophile elements, compatible with the KPB impact event (Premović, 2009). It appears that deposition of the red layer occurred over several decades, and at most a century (Premović, 2009). Most researchers consider that the red layer is directly related to the KPB impact and represents the original ejecta fallout based on its stratigraphic position.

We report here a new find of the occurrence of micrometer-sized silver (Ag) particles in the red layer that appear to have been embedded into the biogenic calcite matrix. These microparticles were hand-picked under a binocular stereomicroscope and we recovered about 100 microparticles for analysis. Energy dispersive X-ray analysis (EDS) analysis (Fig. 1A) indicates that these microparticles are composed of pure silver (>99 % of the total weight).

The number of Ag microparticles (AgMPs) in the specimen studied exceeds the number of impact-related goethite spherules by a factor 20-50. A rough estimate of the Ag content of this specimen, based on weight of all these microparticles, is on the order of a tenth of one percent. However, no AgMPs have been found below or above the red layer.

Stereomicroscopy shows that the AgMPs are shiny black or light brown. SEM images show that their shapes are irregular and predominantly rounded with rugged surfaces that often contain a few pits and voids (Fig. 1B). Aggregates of irregular microparticles are also observed (Fig. 1C). Numerous AgMPs are spherical (Fig. 1D), and some of them exhibits dendritic textures (Fig. 1E). They may have already been in their present shape when dendritic crystalization began.

The AgMPs of irregular shape have an approximate length of about 30-270 microns, an approximate width between about 20-200 microns and an approximate thickness between about 5-50 microns. The diameter of spherical microparticles ranges from approximately 20-100 microns.

These AgMPs are unknown among modern or ancient sedimentary rocks of marine or continental origins, including more than 140 KPB beds worldwide. Moreover, AgMPs of these sizes and shapes have not been reported in any other natural or artificial system until now.

Although the presence of the AgMPs in great number may be largely fortuitous, their occurrence is scientifically important because of their intimate association with the impact-derived markers in the red layer, implying that they may have an impact-related origin. Whatever their form or size, these microparticles all bear indication that they were formed from a molten state by rapid cooling. The spherical shape and dendritic surface texture of some spherical AgMPs supports this view. During the KPB impact event, molten AgMPs originating from the extraterrestrial impactor or target rocks were probably dispersed globally by the impact plume. Preliminary consideration, however, makes the extraterrestrial source less tenable.

The AgMPs could have been deposited in the Fish Clay direct airborne dispersal followed by settling through the seawater column. Alternatively, they could have been transported from nearby soils by surface water runoff.

References and notes

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Figure Captions

Fig. 1. AgMP from the red layer of the Fish Clay: (A) EDS spectrum; and SEM micrographs of samples: (B) rounded; (C) aggregate; (D) common spherical; and, (E) spherical with dendritic surface texture.

Fig. 1A

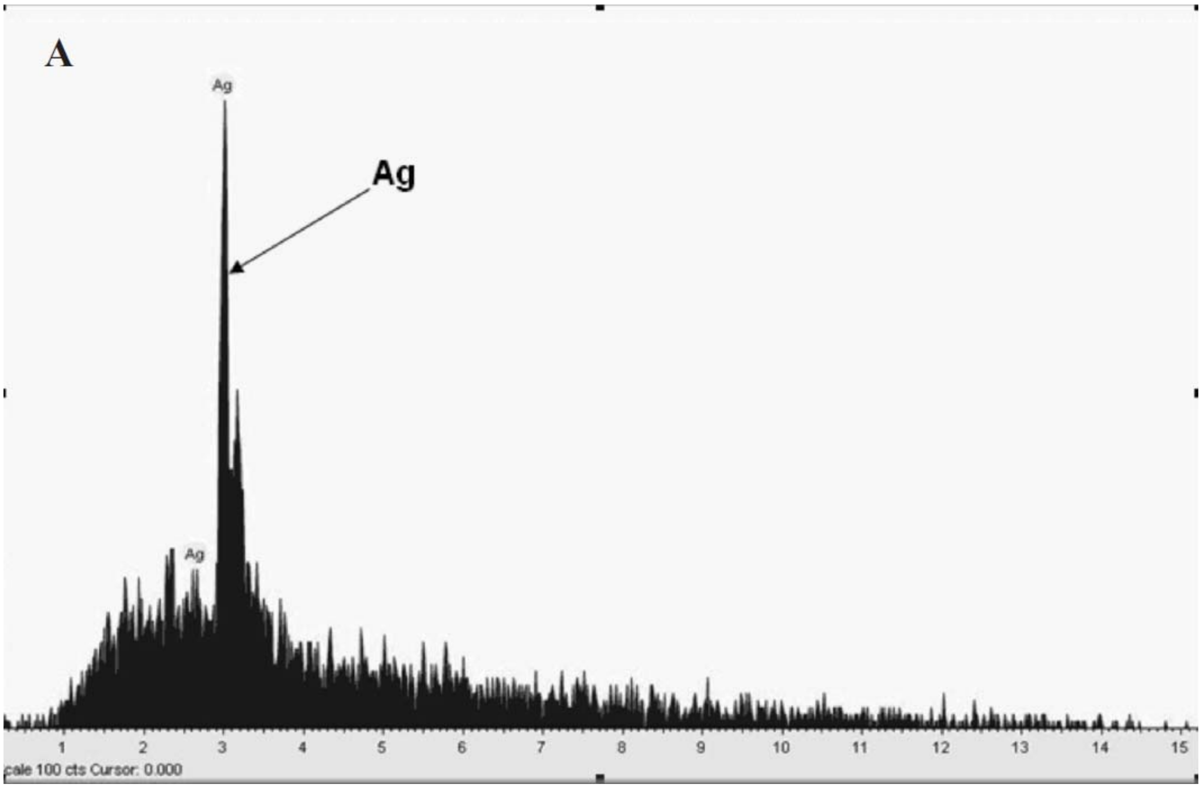

Fig. 1B

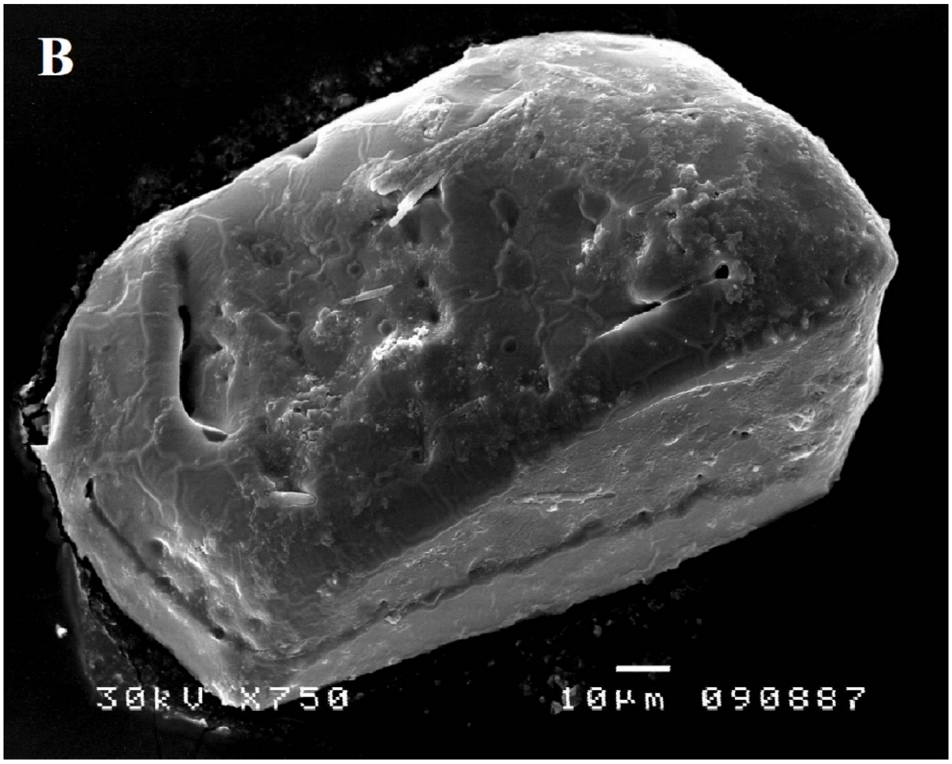

Fig. 1C

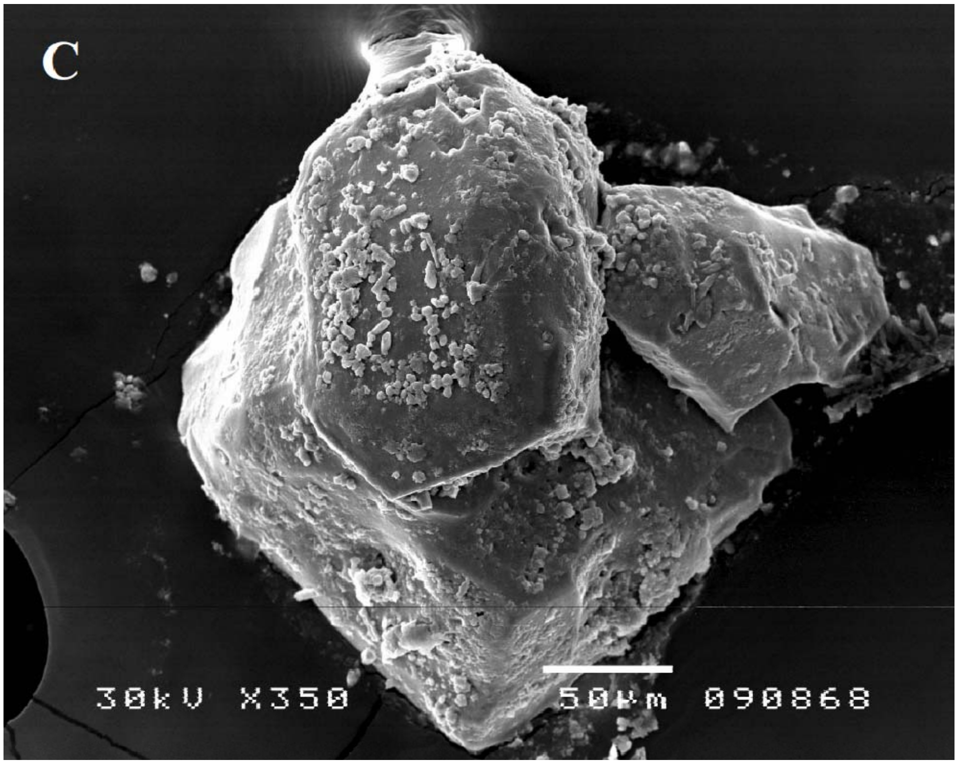

Fig. 1D

Fig. 1E