Bi-Te-S biomineralization in Precambrian Volyn biota (Ukraine)

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The Volyn biota represent an ancient subsurface lithautotrophic microecosystem with a minimum age of ca. 1.5 Ga (Franz et al. 2023). The fossils are exceptionally well preserved in 3D due to their occurrence in cavities of pegmatites of the 1.8 to 1.7 Ga old Korosten Pluton in NW Ukraine, which experienced no diagenesis, metamorphism or deformation, which is very often the case in sediments. The fossilization occurred during influx of hot, HF-bearing fluids from the granitic source into the large miarolitic cavities, producing a µm-wide rim of Al-silicate minerals (Franz et al., 2022). Some of the fossils were interpreted as biofilms (extracellular protein substance), others show similarities to filamentous fungi-like organisms, supported by the presence of chitosan, others are interpreted as methanogenic organisms.

In some of these filamentous and bulbous fossils we identified mineral inclusions with a size of approximately 50 to 100 nm. These nano-inclusions occur in the central part of the fossils, excluding their origin as post-mortem inclusions. Their composition is variable in the samples, but all are characterized by Bi-Te-S. In one sample they are randomly oriented in a distance of several micrometer. The composition is close to the minerals ingodite Bi(S,Te) or joseite $Bi_4(S,Te)_3$.

In another sample, they occur in a central channel of the organisms, characteristic for some of the filamentous fossils. These nanoparticles are up to approximately 200 nm large, concentrated in aggregates, and their composition is dominantly Bi-Cu-S with Te and Pb as additional components. Electron diffraction patterns of these mosaic crystals indicate an orthorhombic phase with a = 7.70 Å, b = 10.4 Å, c = 6.75 Å, consistent with the phase Cu_3BiS_3. Crystals away from the channel show the same composition Bi-Te-Pb-Cu.

In a bulbous fossil object, the nano-sized biominerals are arranged in groups of several crystals. Their composition is dominantly Bi-Te-S. These crystals are connected by a filament of amorphous material, a few nanometers wide, and similar filamentous extensions from the nanocrystals were observed (Fig. 1).

In modern fungi, Liang et al. (2019) observed the formation of Te- (and Se-) nanoparticles during growth experiments with different fungal species, and microbial reduction of Te (and Se) species shows the immobilization of these elements in intracelular and extracelular nanoparticles (Liang et al., 2020), supporting the interpretation of the fossils as fungi-like organisms.

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Liang X, Perez MAM-J, Zhang S, Song W, Armstrong JG, Bullock LA, Feldman J, Parnell J, Csetenyi L, Gadd GM (2019): Fungal formation of selenium and tellurium nanoparticles. - Appl Microbiol Biotech 103, 7241

Liang X, Perez MAM-J, Zhang S, Song W, Armstrong JG, Bullock LA, Feldman J, Parnell J, Csetenyi L, Gadd GM (2020): Fungal transformation of selenium and tellurium located in a volcanogenic sulfide deposit. Env Microbiol 22, 2346

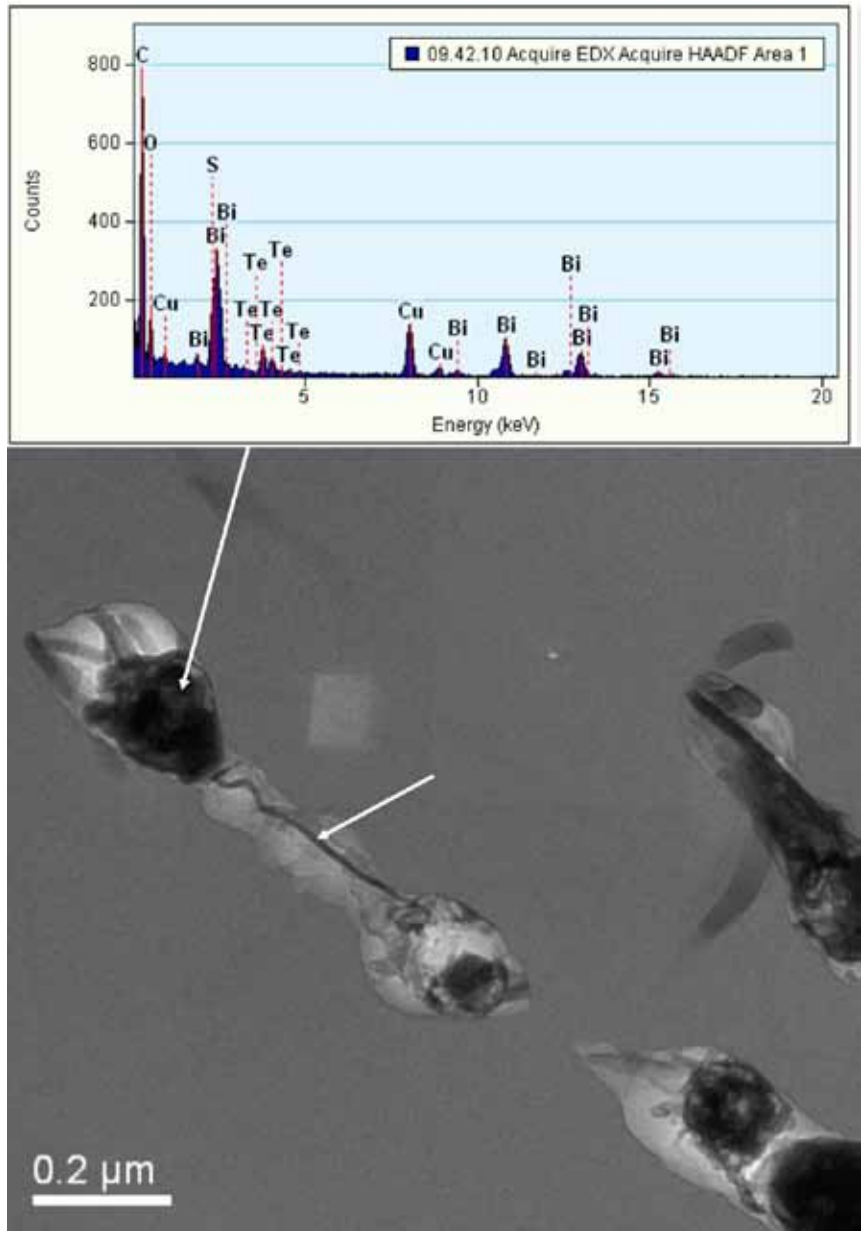

Fig. 1: TEM image and EDS analysis of biominerals in the Volyn biota. Arrows point to the location of the analysis and the thin connection of the nanoparticles.