Biogenic sphalerite and galena formation in peatlands polluted by atmospheric deposition

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Peatlands are redox-sensitive sediments where most metal-containing dust particles dissolve shortly after deposition on the surface. Studies on polluted peatlands showed that the metals are often re-sequestered in secondary reduced phases [1, 2].

Here, we combine scanning (SEM), transmission electron microscopy (TEM), and bulk elemental analyses to characterize the distribution, morphology, and structure of Zn and Pb sulfides formed in two peatlands located close to Pb-Zn smelter. Additionally, Mössbauer spectroscopy is used to investigate Fe speciation.

Biogenic sulfide mineralization was found in metal-enriched (up to 2,300 mg Zn/kg, 1,100 mg Pb/kg) ~30cm layer, located 10cm below the peat surface. ZnS is most abundant and occurs in the form of spheroids (<1-6μm), plant cell infillings, or pseudomorphs after Ca oxalate. Pb sulfides occur as small inclusions (<1μm) between ZnS or as flat irregular or square patches on plant root macrofossils.

TEM reveals that the ZnS is composed of low- and high-density bands which has a polycrystalline sphalerite structure. Randomly oriented, 10-20nm crystalline domains prevail in low-density regions. Large (~300nm), radially arranged crystals form the high-density bands. They are rich in planar defects and commonly nano-twinned. PbS is in the form of defect-free large (>200nm) galena crystals.

No Fe sulfides were found, nor Fe is present in Zn and Pb sulfides. The Mössbauer spectroscopy indicates that the iron occurs entirely in the ferric state in the peat. Probably, the organic matter preserves the oxidation state of the air-deposited Fe allowing to precipitate the less common metal sulfides in the peat. The study gives insights into the formation of low-temperature biogenic metal sulfide deposits.

[1] Sonke et al. (2002) *Sci Total Environ* **292**, 101-119. [2] Smieja-Król et al. (2010) *Sci Total Environ* **408**, 5924-5931.

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