Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.34573

Inversion of Fe–Zn Sulfidation Fronts Driven by Rhizosphere Redox Heterogeneity in a Carbonate-Buffered Mine Wetland

BEATA SMIEJA-KRÓL[1], MIROSŁAWA PAWLYTA[2], FRANCO MAGURNO[1], PAULINA BINIECKA[1], MARIOLA KĄDZIOŁKA-GAWEŁ[1] AND ZOFIA SEGET-PIOTROWSKA[1]

[1]University of Silesia in Katowice
[2]Silesian University of Technology

Sediments deposited in a small river valley by turbid discharges from a Zn–Pb mine are currently evolving into a densely vegetated wetland (Biała River wetland, S Poland). The 1–2 m thick deposit (52 ha) consists of fine-grained carbonate material containing ~3% primary sulfides and stores ~3,927 Mg Zn and 1,887 Mg Pb [1]. We investigated redox-driven mineral transformation and redistribution of Fe, Zn, Pb, and As along two 0.5 m sediment profiles intersecting a 15–20 cm thick organic-rich rhizosphere.

SEM–EDS and TEM analyses reveal pronounced vertical secondary mineral zonation. The organic surface layer is dominated by XRD-amorphous Fe(oxyhydr)oxides forming porous aggregates around plant roots and containing up to 18 wt% Pb and 6.8 wt% As. Within the same interval, aggregates of submicrometre-scale ZnS globules occur in association with root remains. TEM confirms a cubic (sphalerite-type) structure, and SEM–EDS/TEM–EDS indicate As enrichment up to 2.3 wt%.

At the transition to the underlying mineral sediment, mackinawite (TEM-confirmed) appears, consistent with Fe(oxyhydr)oxide sulfidation. Framboidal pyrite and greigite (SEM, Mössbauer spectroscopy) occur only below ~20 cm depth, mostly within thin organic intercalations.

Molecular analyses show significantly higher abundance of sulfate-reducing bacteria (SRB) in the organic surface layer, dominated by Desulfobaccales and Thermodesulfobacteriota. Despite active sulfate reduction near the surface, Fe remains largely stabilized as Fe(III) (oxyhydr)oxides, likely sustained by root-mediated oxygen transport. This restricts Fe^{2+} availability and diverts biogenic sulfide toward preferential ZnS precipitation within reducing microsites.

The resulting sequence—Fe(III) (oxyhydr)oxides and ZnS in the rhizosphere overlying Fe sulfides at depth—represents a spatial inversion of the expected Fe–Zn sulfidation stratification along the redox gradient. These results demonstrate that vegetation-driven microscale redox compartmentalization reorganizes contaminant mineralization fronts and reshapes trace-metal partitioning across sediment profiles.

[1] Wójcik, W. et al. (2004). Ołów i cynk w środowisku oraz rola mokradeł w ich usuwaniu. Wydawnictwa AGH, Kraków.