

## Can NSO compounds help to better understand the role of organic matter in ore-forming processes in the Kupferschiefer?

The Late Permian Kupferschiefer Formation, a fine-grained, organic-rich marine sediment in north-central Europe, is one of the world's most significant sediment-hosted stratabound copper (SSC) deposits. Economically important accumulations of base metals (Cu, Zn, Pb), rare earth and other metals also occur in the underlying Lower Permian sandstones and in the overlying Ca1 carbonate, summarized as the so-called "Kupferschiefer system". Despite a long history of exploration and research, the mechanisms and precise timing of the formation as well as the source of mineralizing fluids remain debated. Growing evidence supports a multi-phase epigenetic mineralization model involving basinal brines and hydrothermal fluids. The precipitation of metal sulfides was likely driven by the interaction of sulfate-poor but chloride-rich and oxic aqueous fluids with an anoxic pore fluid in micro-environments in the shale (Mohammedyasin et al., 2025). These reactions are expected to have established redox gradients leading to zonation, with copper sulfides enriched near an oxidized zone characterized by hematite staining, the so-called "Rote Fäule", and subsequent zones dominated by lead and zinc sulfides precipitating under progressively more reducing conditions and distance to the Rote Fäule (Hitzman et al., 2010).

Organic matter (OM) is considered to have played a significant role in the Kupferschiefer metallogenesis. Previous studies have reported a strong alteration of OM in mineralized zones close to the Rote Fäule, as particularly indicated by bulk geochemical parameters and non-polar biomarkers (Bechtel and Gratzner, 2001; Püttmann et al., 1991). However, more subtle changes in OM alteration in terms of molecular composition might remain undetected. Recent work from Poetz et al. (2022) has introduced nitrogen-, sulfur-, and oxygen-bearing (NSO) organic compounds as potential sensitive tracers of OM alteration and fluid-rock interaction. However, a systematic investigation of their alteration in mineralized versus unmineralized zones of Kupferschiefer that allows to conclude on their role during mineralization (active player versus by-product) was not conducted yet.

This study aims to fill this gap by examining samples from five boreholes representing different zones of mineralization and redox conditions in the Kupferschiefer. The sample set consists exclusively of TOC-rich Kupferschiefer T1 and includes two boreholes from the Mansfeld district (Cu-rich zone near the Rote Fäule and Pb/Zn zone), and one borehole from a nearly barren Zn-bearing zone from the north of Saxony Anhalt, along with two additional samples from the oxidized Rote Fäule (southern Saxony Anhalt). To assess OM alteration and its role in fluid-rock interactions, conventional geochemical analyses (e.g., Rock-Eval pyrolysis, GC-MS) were combined with high-resolution molecular data obtained by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and compared with previously published data from Poetz et al. (2020) about two Spremberg boreholes located in Cu-dominated and Pb/Zn-dominated mineral zones. While bulk geochemical parameters and biomarker data are available for the entire sample set, FT-ICR-MS data are currently limited to the boreholes from the Mansfeld district.

The main focus of the NSO compound analysis is to trace any secondary alteration of the OM caused by, e.g., contact with mineralizing fluids like oxidation, which has been proposed as a key driver in the Kupferschiefer alteration (Püttmann et al., 1989), and to examine sulfur species in order to assess whether organically bound sulfur may have contributed the formation of metal sulfides. Initial ESI-FT-MS data show depth-related changes in the NSO composition in the Kupferschiefer. Among the acidic NSO compounds, a slight increase in the O/C ratio of the bitumen fraction with depth is observed, while the bulk oxygen index (OI) of the kerosene decreases. This suggests a stronger oxidation of the bitumen in the deeper parts of the Kupferschiefer formations in these boreholes. Nevertheless, the lack of correlation between O/C data and both the mineral distribution in the Kupferschiefer and redox conditions (distance to the Rote Fäule) in the individual boreholes suggests that the depth-related oxygen variations are not directly linked to mineralization but rather reflect a by-product of fluid interactions.

In the Cu-rich zone of the Mansfeld borehole, located right above the Rote Fäule, acidic NSO compounds show a consistent trend with depth of decreasing carbon numbers, molecular weights and hydrogen index (HI) alongside increasing double bond equivalents (DBE), suggesting enhanced demethylation and aromatization of the OM. This transformation is supported by rising phenanthrene/methylphenanthrene (Phen/MePhen) ratios and elevated PAH concentrations with decreasing distance from the Rote Fäule. Similar trends can be observed between boreholes, which are affected to varying degrees by the Rote Fäule.

Acidic sulfur-bearing NSO compounds in mineralized samples from Mansfeld are broadly similar to those described by Poetz et al. (2020) in Spremberg. First results on the sulfur components in the Mansfeld district show minor increases in S/C ratios and sulfur-bearing species with depth are noted, which might also indicate redox processes at the Kupferschiefer base.

To better understand NSO compound alteration associated with mineralization in the Kupferschiefer, further comparisons with FT-ICR-MS data from the barren Zn zone and Rote Fäule samples are ongoing.

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