

Isotopic Microanalysis of Calcite in the Permian Kupferschiefer System (Saale Subbasin, Eastern Germany)

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The Kupferschiefer districts in Central Europe contain some of the world's highest-grade sediment-hosted Cu deposits. Stratiform to stratabound Cu, Zn, and Pb sulfides are hosted in calcareous, organic matter-rich shales and mudstones of the marine Kupferschiefer (T1), the underlying continental Rotliegend sandstone (S1), and the overlying Zechstein Limestone (Ca1). Detail petrography (cathodoluminescence, CL; scanning electron microscopy, SEM) and carbon and oxygen isotope microanalysis (secondary ion mass spectrometry, SIMS) have been combined to show the paragenetic relationships and origin of the calcite cement in samples ($n = 47$) from three drill holes (Wallendorf, Sangerhausen, Allstedt) in the Saale subbasin (Eastern Germany). Petrographic data show extensive in situ alteration of detrital clasts in the S1 unit. Primary porosity occluding early diagenetic calcite cement and subordinate dolomite and detrital clasts have been partially replaced by Cu- and Zn-Pb sulfides (bornite, sphalerite, galena) in the three units. Overlapping $\delta^{13}\text{C}$ (VPDB) and $\delta^{18}\text{O}$ (VSMOW) values in calcite cement in samples from the S1 and T1 in the Sangerhausen and Wallendorf drill cores show the calcite cement was derived from fluids of similar isotopic composition. The low $\delta^{13}\text{C}$ values of calcite cement in samples from the S1 (-15‰ to 1.3‰) and T1 (-15‰ to 0.7‰) in the two drill cores indicate sources of carbon and alkalinity from seawater-derived fluids and diagenetic pore fluids influenced by the oxidation of organic matter. The wide range in $\delta^{18}\text{O}$ values in calcite cement in the S1 ($\sim 18\text{‰}$ to 31‰) and T1 ($\sim 22\text{‰}$ to 31‰) often varies at micro-scales, suggesting pore fluid chemistry was influenced by early diagenetic alteration of volcanic rock fragments, perhaps with minor contributions from the influx of meteoric waters and evaporated seawater.