

## **Aragonite-calcite precipitation in vertical fractures of the “Erzberg” siderite deposit (Austria): Hydrogeochemical and neotectonic implications**

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The ore deposit “Erzberg” represents the worldwide largest  $\text{FeCO}_3$  occurrence and is amongst Austria’s most prominent geological places due to its historic, economic and scientific value. The iron-ore (siderite/ankerite) bearing Devonian carbonates of the open pit mine locally host sequential aragonite-calcite precipitates infilling vertical fractures. These typically laminated carbonates are referred to as erzbergite in mineral collections. To study their formation conditions we recovered samples on-site, i.e. from the rare veins being cm to dm in horizontal and tenths of meters in vertical extension. Additionally, samples from our university collection and private collectors were investigated. Some of the fractures filled with aragonite/calcite further exhibit cataclastic sediments, damage zones and slickenside striations. Modern water samples were collected from fractures currently accessible to conduct hydrochemical analyses and modeling. Selected precipitates were analyzed applying microscopic techniques, XRD, electron microprobe elemental mapping, stable and clumped isotopes, and  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  radiometric dating.

Erzbergite veins show either uni- or bidirectional growth, i.e. on one or both fracture/fault planes toward complete infilling depending on vadose water flow. The laminated precipitates are dominated by aragonite relative to pristine as well as partially diagenetic (Mg)-calcite. Intercalated and recurrent brownish Fe-rich layers consisting of goethite, quartz, muscovite are probably of detrital origin. Stable C and O isotopes of the precipitates reveal pronounced spatiotemporal variations in which low  $\delta^{18}\text{O}$  values (-10.4 to -5.1 ‰ VPDB) reflect a meteoric origin and low temperatures of the erzbergite depositing solutions. Carbonate clumped isotope measurements verify formation temperatures  $\leq 25$  °C. High  $\delta^{13}\text{C}$  values (-0.7 to +6.8 ‰ VPDB) of the precipitates indicate an origin from dissolution of local ankerite and limestone, without a significant proportion from soil  $\text{CO}_2$ . Prominently high  $\delta^{13}\text{C}$  in DIC ( $\leq +3.8$  ‰) were also measured in modern fracture waters next to elevated sulfate (up to 226 mg/l) and high total dissolved solid contents (up to 1273 mg/l). These results suggest intense water-rock interaction based on sulfide oxidation and sulfuric acid evolution providing an efficient mechanism for host rock dissolution, mobilization and typically rapid aragonite-calcite mineralization. Sulfide accessories are widespread at Erzberg and the brownish Fe-rich layers within erzbergite could be explained by corrosion of Fe-sulfides and/or Fe-carbonates. The aragonite-calcite lamination is interpreted as an event lamination (not annual), i.e. variable aqueous  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios and  $\text{CaCO}_3$  supersaturation states triggering the polymorphism.

U-Th analyses yielded surprisingly young ages for erzbergite dated so far, i.e. late Pleistocene and mostly younger than the last glacial maximum. A 4 cm thick sample composed of aragonite exclusively and filling a tenths of meters extending fracture formed  $10.4 \pm 0.2$  (sample base, initiation) to  $1.03 \pm 0.04$  kyr BP (top, fracture filled). Another 25 cm laminated aragonite-calcite precipitate covers  $14.2 \pm 0.2$  to  $5.0 \pm 0.2$  kyr. Thus, the precipitates support geologically young and rather short time intervals of infilling and we consider it unlikely that the fractures are much older. An intimate connection with neotectonic activity entailing new vadose water flow routes and fresh reaction surfaces in fractures would be in accordance with our hydrogeochemical and field observations.