

## **Chemical Evolution of Continental Basement Brines—the Relation of Evaporites with Metal-Bearing Hydrothermal Fluids in the Tethyan Belt**

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Highly saline, deep-seated basement brines are a common phenomenon worldwide. Here, we present the chemical evolution of a continental basement fluid from the Carboniferous to the Paleogene from the Schwarzwald in southwest Germany, which is part of the Tethyan belt. The chemical evolution of the fluid composition over 320 m.y. is deduced from fluid inclusions in hydrothermal veins of various ages, preserving the fluid signature at the time of formation. A combination of detailed microthermometry with crush leach analyses made it possible to characterize different fluid types, which can be, due to their known ages, directly related to specific periods of time: During the Carboniferous, late magmatic quartz-tourmaline veins with rare W and Sn ores precipitated from a low-salinity (<4.5 wt % NaCl + CaCl<sub>2</sub>), high-temperature (up to 390°C) H<sub>2</sub>O-NaCl-(CO<sub>2</sub>-CH<sub>4</sub>) fluid with Cl/Br ~100. In the Permian, cooling H<sub>2</sub>O-NaCl-(KCl-CaCl<sub>2</sub>) metamorphic fluids (T ≤ 250°C, 2–4.5 wt % NaCl + CaCl<sub>2</sub>, Cl/Br = 70–100) led to the precipitation of quartz veins with rare Au and Sb ores. Barren quartz-hematite veins formed at the Triassic/Jurassic boundary and contain alternating growth zones which show (a) the Permian fluid type and (b) a high-salinity fluid (T = 100°–320°C, >20 wt % NaCl + CaCl<sub>2</sub>, Cl/Br = 70–110) cannot be recognized prior to the Triassic/Jurassic boundary. Large amounts of Pb-Zn-Ag, Fe-Mn, and U-Bi-Co-Ni occur for the first time in Jurassic-Cretaceous fluorite-barite-quartz-(carbonate) veins. Fluid inclusions of these veins record fluid mixing, involving an older bittern brine (Cl/Br ~ 80) and a younger halite dissolution brine (Cl/Br >1,000), both showing similar salinities. The mixed fluid is an H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> brine (75°–140°C, 23–26 wt % NaCl + CaCl<sub>2</sub>, Cl/Br = 80–570). In post-Cretaceous times, fluid inclusion chemistry is variable and can be described as H<sub>2</sub>O-NaCl-CaCl<sub>2</sub>-(SO<sub>4</sub>-HCO<sub>3</sub>) fluid (70°–190°C, 5–25 wt % NaCl-CaCl<sub>2</sub>, Cl/Br = 10–140). Post-Cretaceous quartz-barite veins show significant but variable Pb ± Zn ± Cu ± Bi ± As mineralizations. The first occurrence of a high-salinity brine in the basement is recorded in veins formed just a few m.y. after the deposition of halite in the Muschelkalk ocean (epicontinental Tethys) at shallow depth. This temporal relation indicates an external (evaporitic) source of the basement brine's salinity and halogen budget. The same observation can be made elsewhere in central Europe. Fluid inclusions from hydrothermal veins of the Spessart and the Harz mining districts, which are also Variscan basement windows, show the same relation between highly saline fluid compositions with low Cl/Br and surficial halite deposition. In these cases, the timing of halite precipitation was earlier in the Zechstein (Permian). Hence, the deep-seated, low Cl/Br, highly saline brine, which is recognized as a metal source for ore formation of unconformity-related hydrothermal veins in the central European Tethyan belt, is most likely derived of bittern brines related to surficial halite deposition. Fluid inclusion chemistry indicates that these bittern brines were later modified by fluid-rock interaction (metal uptake) and mixed with a halite dissolution brine or with younger meteoric fluids, which caused ore precipitation.