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Fluid mixing and metal sources in unconformity related ore deposits: A LA-ICPMS fluid inclusion study

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Unconformity related hydrothermal vein deposits occur in various geological environments and typically show very diverse metal associations. Prominent examples are Kupferschiefer-type Cu deposits, U deposits of the Athabasca basin, five-element Co-Ni-Bi-Ag-As veins, and basement hosted Pb-Zn-Ag-fluorite-barite veins. Fluid mixing processes are often invoked to explain efficient ore precipitation, and many studies have used isotopic evidence or bulk chemical analysis of fluid inclusions to support this hypothesis. The well-studied Schwarzwald ore district in SW Germany hosts hundreds of vein type Pb-Zn-Ag-fluorite-barite ore deposits. The majority of these veins formed in an extensional setting during the Mesozoic by mixing of basement derived brines with saline formation waters, whereas a group of younger veins are structurally related to the opening of the Rhine graben rift during the Paleogene and mixing of basement fluids with meteoric water. We present a combined microthermometric and LA-ICPMS study of well constrained fluid inclusion assemblages in quartz from both vein generations, which provide a detailed geochemical characterization of the fluids involved. The Mesozoic fluids show an unexpected variability in Cl/Br mass ratios and metal concentrations, which is even visible at the scale of individual growth zones. Conversely, the bulk fluid salinity (about 25 wt.% NaCl+$CaCl_2$) and the Na/Ca ratios are almost constant for different fluid inclusion generations. The variation of the Zn and Pb concentrations was found to be correlated with the Cl/Br ratio, with low Cl/Br mass ratios (about 50) typical of basement derived fluids having high metal contents (>500 ppm), and higher Cl/Br (>288) mass ratios of fluids with low metal contents (<500 ppm). The Paleogene fluids are more variable in their salinity (7-15 wt.% NaCl+$CaCl_2$), and the lower salinities correlate with increasing Cl/Br ratios, eventually approaching the composition of seawater. The fluid composition data provide compelling evidence for fluid mixing processes that are visible on a small scale. In the case of the Mesozoic vein deposits the data allow to identify the principal metal sources in the crystalline basement.