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Multi-reservoir fluid mixing processes in rift-related hydrothermal veins, Schwarzwald, SW-Germany

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ABSTRACT

Fluid mixing is an important process in the formation of many hydrothermal vein-type deposits. Here, we present evidence from hydrothermal fluorite-barite-quartz veins with Pb-Zn-Cu-(Ag)-sulfides and associated mineralization, indicating that mineral precipitation was initiated by mixing of fluids derived from multiple sources, including mixing between more than two end-member fluid compositions. Based on our observations, we relate the diversity of the hydrothermal veins of the Schwarzwald mining district in terms of mineral assemblage and fluid inclusion chemistry to the disturbed and transient geological environment during ongoing rifting. Literature data on the regional geology, current groundwater reservoirs, formation processes and hydraulic features are augmented by new fluid inclusion analyses from post-Cretaceous, hydrothermal vein minerals including microthermometry, crush leach, Microraman and LA-ICP-MS analyses of individual fluid inclusions.

Petrography and microthermometry of fluid inclusions show complex sequences of alternating fluid signatures within different growth zones of one crystal. High (20–26 wt% NaCl + $CaCl_2$), moderate (5–20 wt% NaCl + $CaCl_2$) and low salinity (< 5 wt% NaCl + $CaCl_2$), sulfate- and/or CO_2-bearing primary fluids were trapped during crystal growth. Such variations are commonly observed in minerals from different localities. Bulk crush leach analyses show significant variations in major element composition of the trapped fluids, within the overall Na-Ca-Cl-SO_4-HCO_3-system. These variations are caused by mixing of fluids from different aquifers and in various proportions. Ancient fluids show chemical similarities to modern groundwater aquifers that are available for direct sampling, such as granitic basement, Lower Triassic sandstones or Middle Triassic limestones and evaporites. Analyses of individual fluid inclusions by LA-ICP-MS support this interpretation and document the multi-component fluid mixing processes at individual localities recorded on the scale of single crystal growth zones. The latter data are used in a diffusion model to obtain the duration of mineral growth (before the fluid is homogenized), which implies very short-lived fluid events on the order of seconds to hours.

By defining end member fluids and their proportions, we show that nearly all fluid mixtures are saturated with respect to barite. By contrast, fluorite-saturated fluids can only be modelled by mixing of a basement brine with fluids from Triassic sandstones. All fluid mixtures are strongly undersaturated with respect to galena, chalcopyrite and sphalerite, the most commonly observed ore minerals in the hydrothermal veins. As the calculated fluid mixtures are typically relatively oxidized and contain high sulfate/sulfide ratios, precipitation of sulfides was probably related to short-lived reduction events caused by an influx of hydrocarbons, by reactions with graphitic wall rocks in fractures by sulfidation related to fluid-rock reaction with the surrounding host rocks or an external influx of hydrocarbon-bearing fluids. The multi-aquifer fluid mixing processes involving aquifers of different chemical and physical constitution were triggered by brittle deformation related to rifting of the Rhine graben. This appears to be essential for the formation of a large number of mineralogically diverse hydrothermal ore deposits.

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1. Introduction

The chemical and hydraulic properties of fluids causing the formation of unconformity-related hydrothermal vein-type (specifically base-metal) ore deposits are key factors in the genesis of these systems. Most studies related to this are based on a combination of microthermometry (Wilkinson, 2010), stable and radiogenic isotopes (Bau et al., 2003; Kessen et al., 1981; Shouakar-Stash et al., 2007; Staude et al., 2011; Wilkinson et al., 2005), trace element studies of fluids and gangue (Fusswinkel et al., 2013; Pfaff et al., 2011) or paleo-hydrological modelling (Garven et al., 1999). Examples include the Athabasca basin in Canada (Richard et al., 2016), Alaskan Brooke Range (Leach et al., 2004), the South East Basin in France (Aquilina et al., 2011), the Irish Midlands (Banks et al., 2002), the Massif Central in France, the Maestrat basin and the Catalan Coastal Ranges in Spain and Upper Silesia in Poland (Boiron et al., 2010), the St. Lawrence rift in Canada (Carignan et al., 1997) and the Otavi Mountainland in Namibia (Deane, 1995). Previous studies found that fluid mixing typically takes place between hot, deep-seated fluids from the crystalline basement, and cooler, sediment-derived fluids from the overburden sequence (e.g. Hoeve and Sibbald, 1978; Duane and De Wit, 1988; Tornos et al., 1991; Carignan et al., 1997; McCaig et al., 2000; Wilkinson, 2010, Fusswinkel et al., 2013, 2014, Bons et al., 2014, Walter et al., 2015, 2016, 2017a, 2017b; Richard et al., 2016). Metals are dominantly transported by basement brines or deep-seated basinal fluids (Fusswinkel et al., 2013; Boiron et al., 2010) and most previous studies thus have focused on this deeper sourced, metal-rich fluid. However, the model of a two-component mixing system can only be applied to geological environments where the two reservoirs are spatially separated, which is often an over-simplified assumption, unable to explain the diversity of fluid compositions and mineral assemblages in hydrothermal veins related to rift systems or large scale lineaments (e.g. Yukon Territory, Rio Grande Rift, Illinois, Nova Scotia, Newfoundland, Sardinia; Van Alstine, 1976) and these examples indicate that more than two fluid types were involved during vein formation. It is typical of such districts that veins of different gangue and ore mineral assemblages are observed within a relatively small area (e.g. Bjørlykke et al., 1990; Van Alstine, 1976). The same holds true for the Schwarzwald mining district (SW Germany) bordered by the post-Cretaceous Rhine graben rift, where mineralogically diverse hydrothermal veins occur along and in the vicinity (up to 50 km) of the graben boundary fault (e.g. Metz et al., 1957; Bliedtner and Martin, 1986; Baatartsogt et al., 2007; Staude et al., 2009). These veins occur in various types of sedimentary and basement host rocks brought into contact with each other during rifting. Consequently, juxtaposition of various lithologies during rifting would provide opportunities for mixing of fluids from various sources, and resultant diversity of hydrothermal veins. This work focuses on the following aspects:

- An integrated study on ore-forming fluids using microthermometry, crush-leach analysis, and LA-ICP-MS analyses on various types of post-Cretaceous mineralization across the entire mining district;
- Geochemical characterization of possible fluid sources and their connection to modern formation fluids;
- The links between the various fluid sources/aquifers and the different types of mineralization;
- The details of mixing on the scale of a mining district, a single locality and a single crystal

The samples for this study were selected based on a large dataset of hundreds of samples from the Schwarzwald mining district. These data include microthermometry, major, minor and trace element compositions of gangue, ore and supergene minerals, age-dating, stable isotope data, paleo-hydrological modelling and studies on modern thermal and mineral waters (e.g., Bons et al., 2014; Fusswinkel et al., 2013; Walter et al., 2015, 2016, 2017a, 2017b and references therein). The well constrained geology of the Schwarzwald region (Geyer and Gwinner, 2011 and references therein) and numerous studies on modern water chemistry and hydraulic properties of the different aquifers (Stober and Bucher, 2015a, 2015b; Bucher and Stober, 2010, Ludwig et al., 2011 and references therein) make this region ideal for the present study. It is important to note that the Upper Rhine graben rift is still tectonically active and > 20 thermal and mineral wells occur along the boundary faults and in their vicinity (Göb et al., 2013), clearly indicating ongoing hydrothermal activity up to the present day.

The sedimentary rocks present on top of the partially eroded basement and along the graben shoulders are the same as during the onset of rifting in the Paleogene. Hence, it seems reasonable to assume that modern groundwater compositions retain at least some similarity to those which formed the hydrothermal veins since the onset of rifting during the Paleogene (Walter et al., 2016, 2017a, 2017b and references therein). This approach – linking vein fluid compositions to compositions of groundwater in modern aquifers – thus enables interpretation of vein- and ore-forming processes.

1.1. Regional geology

The Schwarzwald consists of exhumed Variscan basement gneisses and granites covered by Permian to Upper Jurassic sedimentary units (Fig. 1). The paragneisses and migmatite units locally contains orthogneisses, granulites and amphibolites, all of which being intruded by post-collisional S-type granites between 335 and 315 Ma (Altherr et al., 2000; Hann et al., 2003; Kalt et al., 2000; Todt, 1976). During the Rotliegend (Permian), local basins were filled by redbed arkoses and conglomerates (Geyer and Gwinner, 2011; Jenkner, 1986; Nitsch and Zedler, 2009). In the early Triassic, quartz sandstones units (Buntsandstein: up to 400 m thick in the northern and < 50 m thick in the southern Schwarzwald) were deposited, while middle Triassic limestones (Muschelkalk) and evaporites (halite or gypsum in some facies) reached a thickness of 160–220 m. The Late Triassic (Keuper) is dominated by clastic sediments and evaporitic units (mainly gypsum), with a thickness decreasing from about 300 m in the north to < 100 m in the south (Geyer and Gwinner, 2011). About 1000 m of clastic sediments and carbonates were deposited on the shallow continental Tethys shelf during Jurassic times, including organic-rich shales during the lower Jurassic (Lias ε). No sediments were deposited during the Cretaceous.

During the Paleogene, the breakup of rifting of the Upper Rhine graben resulted in the deposition of about 400 m of clastic sediments and evaporites (gypsum, anhydrite, dolomite, Na-K-Mg halides) in the rift valley (Geyer and Gwinner, 2011; Rupf and Nitsch, 2008). The rifting was accompanied by the uplift of the rift shoulders, associated with erosional exhumation of the crystalline basement. Uplift and erosion was stronger in the southern relative to the middle and northern Schwarzwald. While the basement-cover unconformity is preserved to the present day in the middle and northern Schwarzwald, the southern Schwarzwald is eroded to a depth of about 1.5–2 km below the former unconformity (Rupf and Nitsch, 2008; Walter et al., 2017a, 2017b).

1.2. Hydrothermal veins in SW Germany

Hydrothermal veins in the Schwarzwald formed in basement rocks and their Permian and Triassic sedimentary cover since about 300 Ma (Loges et al., 2012; Pfaff et al., 2009; Staude et al., 2009).

Based on structural, mineralogical and microthermometric arguments five formation stages for the hydrothermal veins are distinguished (Table 1; Walter et al., 2015, 2016, 2017a, 2017b): (i) Carboniferous, (ii) Permian, (ii) Triassic-Jurassic; (iv) Jurassic-Cretaceous and (v) post-Cretaceous veins. This study focuses on the latter group (v) only. These veins formed during Paleogene rifting along Upper Rhine graben-parallel NE-SW to NNE-SSW-striking fault systems. They consist of barite and quartz, various carbonates or barite-quartz-