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Red bed and basement sourced fluids recorded in hydrothermal Mn–Fe–As veins, Sailauf (Germany): A LA-ICPMS fluid inclusion study

Tobias Fusswinkel [a,*], Thomas Wagner [a], Thomas Wenzel [b], Markus Wälle [c], Joachim Lorenz [d]

[a] Department of Geosciences and Geography, Division of Geology, University of Helsinki, Gustaf Hällströmin katu 2a, FI-00014 Helsinki, Finland
[b] Department of Geosciences, Eberhard Karls University Tübingen, Wilhelmstrasse 56, D-72074 Tübingen, Germany
[c] Institute of Geochemistry and Petrology, ETH Zurich, Clausiusstrasse 25, CH-8092 Zürich, Switzerland
[d] Graslitzer Strasse 5, D-63791 Karlstein am Main, Germany

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ABSTRACT

The hydrothermal Mn–Fe–As vein mineralization at Sailauf (Germany) hosts a complex sequence of oxide and carbonate minerals that record a protracted fluid history. The mineralization is related to a major unconformity that separates Permian (Zechstein) sedimentary rocks from underlying Variscan crystalline basement. The hydrothermal veins contain two principal mineralization stages, which are Mn oxides associated with calcite and hematite associated with Mn-calcite. The fluid evolution of the hydrothermal system has been reconstructed from fluid inclusion petrography, microthermometry, and LA-ICPMS microanalysis, coupled with stable isotope geochemistry of carbonate and oxide minerals. The fluid inclusions are high salinity sodic–calcic brines and the bulk fluid properties show no major differences between the Mn oxide and the hematite stage. LA-ICPMS analysis of major and trace elements demonstrates that the mineralization formed from chemically distinct fluid pulses characterized by variations in their K, Li, B, Pb and Zn concentrations. The fluid that precipitated the Mn oxide stage has anomalous Pb/Zn and Li/B ratios, which closely resemble fluids found in fracture fillings in red beds of the Permian Rotliegend basin. By contrast, the fluids associated with the hematite stage have Pb/Zn and Li/B ratios typical of crustal fluids that were derived from interaction with crystalline basement. Both fluids possess characteristic element ratios including Cl/Br, but variable absolute concentrations of most metals. This suggests that both fluids were modified by mixing with a common metal-depleted brine that had a similar Cl/Br ratio, most likely a formation water from the overlying Zechstein sedimentary rocks. The Sailauf mineralization provides insight into the protracted post-Variscan fluid evolution at the basement–cover interface. The compositionally anomalous fluid that precipitated the Mn oxides is comparable to brines derived from interaction with red beds and likely represents the ore fluid of Kupferschiefer-type sediment-hosted Cu deposits. Conversely, the fluid that deposited the hematite mineralization resembles fluids that typically form basement- and sediment-hosted Pb–Zn deposits.

1. Introduction

Aqueous fluids drive formation of hydrothermal ore deposits in a wide range of crustal settings, including large sedimentary basins (Sangster, 1990; Hitzman et al., 2005; Leach et al., 2005), crystallizing shallow hydrous intrusions (Hedenquist and Lowenstern, 1994), and collisional orogens (Groves et al., 1998). Despite considerable research, our understanding of the controls on the major and trace elements composition of crustal fluids remains incomplete because only recently microanalytical techniques became available that make it possible to obtain multi-element data for fluid inclusions (Günther et al., 1998; Heinrich et al., 2003). Understanding the dynamics of hydrothermal systems requires insight into the time–space evolution of ore fluids which might reflect transient processes such as changes in fluid sources, fluid mixing and phase separation. Major progress in understanding the feedback between variations in fluid composition and mineral precipitation in hydrothermal systems comes from in-situ microanalysis of fluid inclusions using LA-ICPMS coupled with well-constrained reconstruction of mineral paragenesis and textural evolution (Audétat et al., 1998; Wilkinson et al., 2009; Fusswinkel et al., 2013a).

The importance of fluid mixing processes across basement–cover unconformities for formation of sediment-hosted hydrothermal ore deposits has been recognized in many geological settings worldwide (Raffensperger and Garven, 1995; Garven et al., 1999). Prominent examples include post-Variscan fluorite–barite–Pb–Zn vein deposits throughout central and western Europe (Behr and Gerler, 1987; Behr et al., 1987; Lüders and Möller, 1992; Staude et al., 2009; Fusswinkel et al., 2013a), carbonate-hosted Pb–Zn deposits of the Mississippi-Valley Type (Muchez et al., 2005; Stoffell et al., 2008), shale-hosted Cu deposits of the Permian Kupferschiefer and in the Central African Copper belt (Rentzsch, 1974; Jowett, 1986; Sweeney et al., 1991), and

* Corresponding author.
E-mail address: tobias.fusswinkel@helsinki.fi (T. Fusswinkel).

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the world-class U deposits of the Athabasca basin in Canada (Kotzer and Kyser, 1995; Derome et al., 2005; Richard et al., 2011, 2012). Recent fluid inclusion and stable isotope studies of these ore deposit types have increasingly emphasized the importance of basement rocks as major source of ore metals (Goldhaber et al., 1995; Boiron et al., 2010; Wilkinson, 2010; Fusswinkel et al., 2013a), although in the case of Kupferschiefer-type Cu deposits the potential role of continental red beds as key metal supply is controversially debated (see Blundell et al., 2003 for an overview).

The structurally controlled hydrothermal vein-type Mn–Fe–As mineralization at Sailauf (Spessart, central Germany) is located at the unconformity between Variscan crystalline basement and overlying Permian sedimentary rocks. The mineralization records a complex sequence of hydrothermal carbonate minerals associated with Fe and Mn oxide minerals and subordinate arsenate phases (Fusswinkel et al., 2013b). Most importantly, the vein system hosts two texturally distinct mineralization stages with Mn oxides and calcite evolving into hematite and Mn-rich calcite (Fusswinkel et al., 2013b). This shift in mineral assemblages records substantial changes in pH and oxidation state of the fluid system involved, which can be related to dynamic fluid mixing processes between oxidized basement-derived fluids and reducing fluids originating in the sedimentary cover rocks (Fusswinkel et al., 2013b). Fluid inclusions from the Sailauf mineralization have therefore great potential to provide detailed insight into the chemistry of fluid mixing processes at basement–cover interfaces.

This study reports the results of a detailed fluid inclusion study of the Sailauf Mn–Fe–As mineralization, combining fluid inclusion petrography, microthermometry and LA-ICPMS microanalysis of individual fluid inclusions. The fluid inclusion data are combined with stable isotope data (carbon, oxygen, hydrogen) of carbonates, Fe and Mn oxides and sheet silicates. The fluid inclusion dataset comprises the concentrations of major cations, trace ore metals and sulfur, and the Cl/Br ratios, and is used to reconstruct the fluid evolution of the hydrothermal system. We observe significant chemical differences in terms of base metal and other cation ratios between fluids of the early Mn mineralization stage and those of the later Fe oxide stage, which are used to trace the fluid sources.

2. Geological setting

The Sailauf Mn–Fe–As mineralization is located at the unconformity between the Variscan basement of the Spessart Crystalline Complex (SCC) and the Paleozoic to Mesozoic cover comprising sedimentary rocks of Lower Permian to Triassic age (Fig. 1). The SCC is part of the Mid-German Crystalline Rise (MGCR), the internal zone of the European Variscan orogen (Kroner et al., 2008). It comprises a sequence of NE–SW trending metasedimentary, metagranitic and metabasic lithologies (Okrusch and Weber, 1996). The MGCR represents a former active plate margin along which the Rheic ocean basin was closed by SE directed subduction between the Silurian and Carboniferous (Kroner et al., 2008). In the SCC, this is evidenced by intercalations of metapelitic to metapsammitic paragneiss units with two orthogneiss complexes, whose granodioritic to granitic protoliths were emplaced in an active continental margin setting during the uppermost Silurian to lowermost Devonian (Okrusch and Richter, 1986; Dombrowski et al., 1995).

During the Variscan orogeny, the crystalline rock units attained metamorphic grades of medium pressure amphibolite facies conditions (Okrusch and Weber, 1996). Uplift and cooling of the SCC occurred between 325 and 315 Ma (Dombrowski et al., 1994). Extension and basin formation during the Lower Permian was associated with widespread bimodal volcanic activity in central Europe (McCann et al., 2008). Thick volcaniclastic sequences were deposited in northern Germany (Neumann et al., 2004) and inside Permo-Carboniferous basins (McCann et al., 2008), while more localized subvolcanic bodies intruded crystalline basement rocks in southern Germany, among them the Hartkoppe rhyolite (Okrusch et al., 2011) which hosts the Sailauf Mn–Fe mineralization.

The SCC is unconformably overlain by Permian sedimentary rocks. Most parts of the Spessart area were geographic highs during the Lower Permian (Okrusch et al., 2011), and the Lower Permian red beds of the Rotliegend are therefore restricted to the NW part. During the Upper Permian, sedimentary rocks of the marginal facies of the Zechstein basin were deposited, which comprise the basal manganiferous breccia and conglomerate, the Kupferschiefer black shale (only occurring in the NE part) and bituminous dolomites of the Werra cycle. An intermittent regression of the Zechstein Sea led to deposition of clay- and marlstones of the Aller and Leine cycle. These include the uppermost stratigraphic unit, a well-defined claystone (Käding, 2005). Continental mudstones, sandstones and conglomerates of the Lower Triassic Bunter Sandstone and limestones of the Lower Middle Triassic Muschelkalk conformably overly the Permian rocks (Okrusch et al., 2011). Middle Triassic to Upper Jurassic sedimentary rocks originally covering the area were completely eroded during regional uplift (Okrusch et al., 2011).

Both the crystalline basement and the sedimentary cover rocks are crosscut by two major systems of post-Variscan faults. The predominant system strikes NW–SE and hosts most of the hydrothermal veins, while a subordinate system striking NE–SW is only weakly mineralized. Large-scale post-Variscan extensional tectonics activated both fault systems and caused significant fluid flow, as evidenced by the frequent occurrence of barite-quartz and base metal vein mineralization (Ziegler, 1987; Wagner and Lorenz, 2002; Okrusch et al., 2007; Wagner et al., 2010).

3. The Sailauf Fe–Mn–As mineralization

The hydrothermal vein-type Mn–Fe–As mineralization comprises a set of 5 NW–SE trending, steeply dipping, discontinuously mineralized fault systems that crosscut the Lower Permian Hartkoppe rhyolite dome (Fusswinkel et al., 2013b). The porphyritic subvolcanic rock is exposed over an area of approximately 400 by 200 m and is emplaced within a small slab of biotite schist that is intercalated with orthogneisses of the Rotgneiss complex (Dombrowski et al., 1995). The top of the rhyolite marks the unconformity to the Permian Zechstein sediments and is directly overlain by bituminous dolomites of the Upper Permian Zechstein. The hydrothermal veins range in thickness between 1 and 25 cm and are mineralized by a complex sequence of different hydrothermal carbonates that are associated with Mn and Fe oxides. Reflecting the present level of erosion, it is not possible to confirm if the veins originally extended into the cover rock sequence.

The paragenesis and mineral chemistry of the Sailauf Mn–Fe–As mineralization was described by Fusswinkel et al. (2013b), and a summary diagram showing the most important minerals is given in Fig. 3. Four stages of mineralization can be distinguished, which are (1) the pre-ore stage, (2) ore stage 1 (Mn oxide stage), (3) ore stage 2 (hematite stage) and (4) the late alteration stage. The pre-ore stage contains calcian rhodochrosite, fluorite and subordinate amounts of celadonite, illite, and anhydrite. The Mn oxide stage hosts abundant Mn-oxides (braunite, hausmannite, manganite and bixbyite) along with calcite and subordinate fluorite. The hematite stage is dominated by specularitic hematite associated with Mn-calcite, whereas Mn oxides are completely absent. Rarely, a second calcite generation enriched in Fe and subordinate Mg (Fe-calcite) along with small amounts of quartz occurs in the hematite stage, postdating the Mn-calcite. The hematite stage mineralization appears both as discrete veins and as replacement of calcite from the Mn oxide stage. In the latter case, the occurrence of hematite is strictly confined to the alteration zones (Fusswinkel et al., 2013b). The final alteration stage comprises several generations of carbonates associated with arsenate minerals that locally replace and overgrow the primary mineralization.

The paragenetic sequence that is characterized by the distinct mineral assemblages of the Mn oxide stage and the hematite stage