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Methane and the origin of five-element veins: Mineralogy, age, fluid inclusion chemistry and ore forming processes in the Odenwald, SW Germany

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ABSTRACT

Five-element veins (Ag, Bi, Co, Ni, As) have been valuable mineral deposits since medieval times. The characteristic occurrence of large aggregates of native metals (up to several dm) surrounded by a succession of arsenides makes this vein-type attractive for mining industry, natural history museums and private mineral collectors. Nevertheless, the exact formation process of these specific vein types has not been fully understood. This is the first case study applying a new model, which includes methane as a reducing agent to two typical examples of such mineralisations from the Odenwald, SW Germany. We analysed all mineralogical varieties (Ag-, As- and Bi-dominated) of the five-element veins in the Odenwald (SW Germany) in terms of ore textures, mineral chemistry, fluid inclusion compositions (microthermometry and Raman spectroscopy), stable isotopes (C, O and S) and in-situ U-Pb age dating of calcite and prehnite.

A variety of Ag-, Bi- and As-dominated native metal-arsenide-calcite veins, sulphide-calcite veins and arsenide-free Ag-Hg-barite veins occurs in the Odenwald and has been examined in this study. All arsenide veins have in common that up to dm-sized, often dendritic native metals are overgrown by a succession of arsenides, followed by carbonate and finally sulphides. The succession of arsenides shows a distinct spatial and temporal chemical trend in their composition. This trend evolves from Ni- to Co and finally Fe-dominated compositions from the core to the rim. In contrast, spatially closely related Ag-Hg-barite veins consist of almost mono-mineralic amalgam inter-grown with barite.

In-situ U-Pb age dating of low-U calcite and prehnite was applied to constrain the age of hydrothermal mineralisation. The results imply that the five-element veins formed at 170–180 Ma from Na-Ca-Cl fluids at 290 °C, salinities of ~27 wt.% and Ca/(Ca + Na) of 0.30 to 0.35 in the presence of methane. The age data clearly relate the relevant fluid migration to extension and crustal thinning caused by the opening of the North Atlantic. Ternary mixing of a deep-seated metal-rich basement brine (fluid A), a sulphide-bearing (H_2S and HS^-) basinal/sedimentary brine (fluid B) and methane-dominated fluid/gas (fluid C) induce ore formation. Mixing of such chemically contrasting fluids results in a strong chemical disequilibrium of the mixed fluid, which potentially leads to rapid precipitation of native metals and arsenides with these specific ore textures. In contrast, sulphide-bearing calcite veins formed under similar P-T-conditions due to mixing of fluid A and B, while fluid C was absent. Additionally, U-Pb analyses of post-ore calcite yields ages of ~60 Ma, which indicates that a second calcite formation event is associated with the onset of the Upper Rhine Graben rifting.

Veins with amalgam and barite form as a consequence of post-ore oxidation of Ag_2S at ~135 °C. Conspicuously, this secondary silver II has Hg contents of up to ~30 wt.%, in contrast to Hg contents below 1 wt.% of primary silver I and Ag_2S. The formation of amalgam was most likely related to decrease of the S^{2-}/SO_4^{2-} ratio due to cooling of the late hydrothermal fluid resulting in the destabilisation of Hg-bisulphide complexes in this fluid.

1. Introduction

Hydrothermal vein deposits with native Ag, As or Bi overgrown by a succession of Ni-, Co- and Fe-arsenides and typically entirely encapsulated by carbonate gangue minerals are called five-element veins, based on the elements Ag, As, Co, Ni and Bi (Kissin, 1992). Although this nomenclature does not correctly describe all subtypes of this mineralisation type, since some elements do not occur at some localities and/or elements like Sb and U may additionally occur in others, it is used for simplification.

Five-element deposits are typically of relatively low tonnage, but very high grade, and therefore have been of great economic importance

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as Ag, Co and U ores since medieval times. The most widely known and the best investigated deposits are probably Schneeberg/Germany (Lipp and Flach, 2003), Jachymov/Czech Republic (Ondrus et al., 2003a; Ondrus et al., 2003b; Ondrus et al., 2003c), Kongsberg-Modum/Norway (Bugge, 1931), Cobalt-Gowganda/Canada (Andrews et al., 1986), Thunder Bay/Canada (Franklin et al., 1986), Batopilas/Mexico (Wilkerson et al., 1988), Imiter/Morocco (Cheilletz et al., 2002) and Bou Azzer/Morocco (Ahmed et al., 2009).

Hydrothermal five-element veins can be sediment-, unconformity- and/or basement-hosted and the host rock composition is very variable and includes igneous, metamorphic and sedimentary rocks. Reported formation temperatures range from ~150 to 450 °C, and hence, the mode of host rock alteration is also variable (Kissin, 1992; Staude et al., 2012). Although the mineral assemblages and the ore textures are very similar implying that all of these deposits have similarities in their general genetic process, formation temperature, fluid salinity, host rock and alteration type strongly vary for each locality (Kissin, 1992; Staude et al., 2012). Kissin (1988) suggested that the formation of five-element veins is caused by the circulation of connate brines in environments of continental rifting. Marshall et al. (1993) proposed that silver deposition is caused by a decrease of chlorine activity due to mixing of silver-rich highly saline fluid with (paleo-) meteoric fluids. An alternative model, recently proposed by Markl et al. (2016) links the formation of five element veins to the influx of methane and/or hydrocarbon-bearing fluids into pre-existing hydrothermal systems. Oxidation of CH_4 to CO_2 subsequently results in very reducing conditions of the mixed ore fluid, which facilitates the precipitation of the native metals and arsenides. The progressive oxidation of methane leads to precipitation of calcite at the end of the ore succession as a consequence of the dissolution of CO_2 and concomitant increase in HCO_3^- activity (Markl et al., 2016).

The majority of the existing work on five-element veins is relatively old and therefore does often not contain modern analytical data of e.g. fluid inclusions using Raman spectroscopy (see compilations in Bastin, 1939; Kissin, 1992; Staude et al., 2012; and Markl et al., 2016). Some exceptions are Marshall et al. (1993), Ahmed et al. (2009), Ondrus et al. (2003b), Staude et al. (2012) and Essarraj et al. (2005). Only two contributions report methane-bearing fluid inclusions in five-element veins from the Cobalt-Gowganda deposit (Kerrich et al., 1986) and the Bou Azzer deposit (Essarraj et al., 2005). In contrast to previous work, the importance of fluid reduction upon methane oxidation is emphasized in this contribution.

The five-element veins at Nieder-Beerbach and Mackenheim in the Odenwald of SW Germany were first briefly described by Ramdohr (1923 and 1975), and later in more detail by Fettel (1978 and 1982), but have never been investigated in detail, using modern analytical techniques. Fluid chemistry, formation conditions and timing of ore precipitation were, hence, insufficiently understood. The investigated localities are sub-economic, but their relatively small dimensions and the excellent outcrop situation enabled comprehensive sampling of all kinds of mineralogical variations with locality, time and depth of exposure. This opened up a unique opportunity to investigate the complex connections of a “big picture” on a spatially small scale.

Investigation of ore textures, mineral chemistry, fluid inclusions (including microthermometry and Raman spectroscopy), stable isotope (C, O and S) analysis of gangue and sulphide minerals and radiometric U-Pb age dating (in-situ) of arsenides and gangue minerals (calcite and prehnite) were used to constrain the conditions and processes during formation of the Odenwald veins and to compare them to the new general genetic model of Markl et al. (2016).

2. Geological setting

2.1. Regional geology

The crystalline complex of the Odenwald is a deeply eroded basement window of a former subduction-related volcanic arc, situated at the northern margin of the Saxothuringikum also known as the mid-German Crystalline High (Stein, 2001). The subduction was related to the convergent plate tectonics of the Variscan orogeny, 380 to 300 Ma ago (Oncken et al., 1999). The Odenwald crystalline window is bordered to the west by the Cenozoic Upper Rhine Graben, to the north by the Saar-Selke Trough and to the south and east by the Permo-Triassic sedimentary cover (Nickel, 1975). The crystalline Odenwald consists of two units: the larger, western Bergsträsser Odenwald and the eastern Böllstein Anticline, which are separated by the sinistral strike-slip Otzberg fault (Fig. 1).

The Böllstein Anticline consists of amphibolite facies orthogneisses (410 ± 10 Ma, S-type protolith), paragneisses and schists (375 ± 5 Ma)(Stein, 2001), while the Bergsträsser Odenwald consists dominantly of calc-alkaline (I-type) magmatic rocks (90 vol.%), which can be subdivided into 4 individual diapiric intrusions (from north to south: Frankenstein complex, Weschnitz pluton, Tromm and Heidelberg granite) and the strongly deformed NNE-SSW trending Flasergranitoid zone, a complex mixture of dominantly meta-granitoid rocks, which are interrupted by four metamorphic units (“Schieferzüge”). In general, the composition of the magmatic rocks (excluding the complex Flasergranitoid zone) of the Bergsträsser Odenwald shows a trend towards more felsic rocks from north (gabbros and diorites) to south (mostly granites) (Stein, 2001).

The investigated Ag-dominated hydrothermal veins at Nieder-Beerbach are hosted by igneous rocks of the Frankenstein pluton in the north (Fig. 1B), which is the oldest intrusive complex of the Bergsträsser Odenwald (365 Ma) and consists of medium- to coarse-grained pyroxene-hornblende and olivine gabbros. Diorites occur at the northern and southern margins of the complex, while granodioritic and granitic dykes exclusively occur in the north (Stein, 2001).

Four metamorphic units form narrow zones, which interrupt the magmatic intrusions, of which the most important ones are the Eberstadt-Rossdorf, the Auerbach-Grossbieberau, the Heppenheim and the Weinheim-Waldmichelbach Schieferzug (Fig. 1A and C). The last one hosts the investigated Bi-dominated five-element veins of the southern Odenwald (Mackenheim, Fig. 1C). These units consist of a variety of amphibolite facies (sometimes retrograded to greenschist facies) rocks, where meta-greywackes and amphibolites are predominant, specifically fine-grained biotite-plagioclase gneisses, muscovite gneisses and schists, biotite-muscovite gneisses and hornblende gneisses and quartzites (Stein, 2001).

Prior to erosion, the crystalline basement was covered by organic-rich upper Carboniferous and Permo-Triassic silicio-clastic and chemical sediments with estimated thicknesses of at least 600 m (Nickel, 1975). Carbonate-dominated sediments of the Jurassic and Cretaceous were present (Faupl, 2000), but their precise local thicknesses are poorly documented. Formation and migration of methane in Upper Cretaceous organic-rich sediments due to the thermal decomposition of organic matter during basin subsidence is documented in fluid inclusions of fracture minerals in the Northern German Basin (Lüders et al., 2005).

2.2. Ore geology

Numerous five-element veins occur in the northern, middle and southern Odenwald (Table 1), always accompanied by sulphide-bearing and to lesser extent by U-bearing veins. Although the difference in stratigraphic depth of formation between the northern and the southern hydrothermal veins is very small (100 m), the mineral assemblages show distinctly different compositions. Silver-dominated gabbro-hosted veins occur only in the north, while in the middle and southern Odenwald five-element veins are Bi-dominated and hosted by marble and gneiss, respectively.

The northern-most Ag-Ni-Co-Fe-As-calcite veins are accompanied by arsenide-free Pb-Zn-Cu-calcite and Ni-U-Cu-calcite ±