Vertical Zoning in Hydrothermal U-Ag-Bi-Co-Ni-As Systems: A Case Study from the Annaberg-Buchholz District, Erzgebirge (Germany)

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Abstract

The Annaberg-Buchholz district is a classic occurrence of hydrothermal five-element (U-Ag-Bi-Co-Ni-As) veins in the Erzgebirge (Germany) with an historic production of ~8,700 metric tons (t) Co ore, 496 t U ore, and 26.9 t Ag. Multiple mineralization stages are recognized in polyphase veins hosted by Proterozoic paragneiss. Fluorite-barite-Pb-Zn mineralization occurs across the entire vertical profile of the district, whereas U and five-element veins are restricted to the upper 400 m below surface, coinciding with a graphite-rich gneiss lithology.

Here, we present field and petrographic observations, electron probe microanalysis and fluid inclusion data, as well as thermodynamic calculations to characterize five-element and fluorite-barite-Pb-Zn associations, and to constrain the origin of the vertical zoning in the Annaberg-Buchholz district. Microthermometric analyses of fluid inclusions related to the fluorite-barite-Pb-Zn stage yield homogenization temperatures between 78° and 140°C and salinities between 21.9 and 27.7 equiv wt % (NaCl-CaCl2). A correlation of fluid inclusion Na/(Na + Ca) ratios with salinity suggests fluid mixing as a likely precipitation mechanism and relates ore formation tentatively to regional tectonics of the Mesozoic opening of the Atlantic.

Thermodynamic calculations indicate that U is more sensitive to reduction than As, predicting that arsenide minerals are precipitated more distally relative to uraninite upon reduction along the fluid-flow path. This implies that the observed vertical zoning is not a primary feature but is the result of hydrothermal remobilization. The observations made in the Annaberg-Buchholz district have general importance to the understanding of U-rich five-element mineralization and may be relevant for exploration targeting in unconformity-related U deposits.

Introduction

The Annaberg-Buchholz district is located in the central part of the Variscan Erzgebirge/Krušné Hory metallogenic province and is among the most important native metal-arsenide deposits in the world (Ondruš et al., 2003a, b, c; Schleman-Alberoda (Hiller and Schuppah, 2008), and Schneeberg (Lipp and Flach, 2003) one of the classic localities for five-element (Ag-Bi-Co-Ni-As) and associated U vein-type mineralization. Five-element veins refer to a globally occurring mineralogically distinct style of mineralization characterized by native elements, which are enclosed by a succession of Co-Ni-Fe arsenides with carbonates most commonly occurring as major gangue minerals (Kissin, 1992; Markl et al., 2016; Burisch et al., 2017). According to their distinct mineralogical features, five-element veins are referred to as native metal-arsenide veins in this contribution. Uranium is often spatially associated with native metal-arsenide mineralization (Zálesí and Jáchymov deposits/Czech Republic, Ondruš et al., 2003a, b, c; Dolníček et al., 2009; Wittichen district/Germany, Staude et al., 2012; Great Bear Lake district/Canada, Changkakoti et al., 1986) but may also be entirely absent (Suessgaard and Edenwald districts/Germany, Wagner and Lorenz, 2002; Burisch et al., 2017; Kongsberg district/Norway, Kotková et al., 2018). In the Erzgebirge, most of the native metal-arsenide deposits are associated with abundant U, which contributed significantly to the U reserves of the former German Democratic Republic (GDR; Wismut GmbH, 1999). Prior to this period, native metal-arsenide mineralization in the Erzgebirge was exploited for centuries for Ag, Co, and Ni. A recent increase in lithium-ion-battery production and the associated demand for Co and Ni led to a renewed interest in alternative resources of these commodities, including native metal-arsenide veins (Faure et al., 2018). Although native metal-arsenide veins are a potential high-grade source for Co and Ni, the exploitation of this deposit type is challenging due to the usually narrow thickness (<1 m) and discontinuous nature of high-grade mineralization, as well as the environmental issues related to associated U and As. Consequently, only a few operations are currently mining native metal-arsenide deposits for Co, Ni, and Ag, all of them located in Morocco (e.g., Bou Azzer and Inmier deposits; Essarraj et al., 2005, 2016).

A genetic model for native metal-arsenide veins has been recently proposed by Markl et al. (2016) and Burisch et al. (2017). This model includes the mixing of highly saline base-mine brines with reducing hydrocarbon-bearing sedimentary fluids related to continental rift settings (Kissin, 1992; Burisch et al., 2017). Hydrocarbons in fluid inclusions have also been reported from native metal-arsenide veins elsewhere, i.e., Cobalt-Gowganda/Canada and Bou Azzer/Morocco districts (Kerrich et al., 1996; Essarraj et al., 2005). Hydrocarbons seem to be in many cases involved in the formation of native metal-arsenide mineralization and seem to be important for ore formation, particularly where the occurrence of the...
veins cannot be related to a lithologic control (Kissin, 1992; Burisch et al., 2017; Scharrer et al., 2019). However, other processes such as reaction with carbon-rich lithologies or lithologies rich in ferrous Fe could also potentially cause the reduction of As$^{III}$ to As$^{II}$, eventually resulting in arsenide precipitation (Robinson and Ohmoto, 1973; Kerrich et al., 1986; Ondrus et al., 2003b; Markl et al., 2016; Burisch et al., 2017; Kreissl et al., 2018). An overview of available mineralogical and geochemical data from various localities worldwide was published by Kissin (1992) and recently updated by Scharrer et al. (2019). For the Erzgebirge, detailed studies of the geology and the petrography of the districts of Schlema-Alberoda (Schuppan et al., 1994; Hiller and Schuppan, 2008) and Schneeberg (Lipp and Flach, 2003) are available. Yet, none of the available literature contains modern geochemical data such as Co-Ni-Fe arsenide compositions and fluid inclusion analyses.

The Annaberg-Buchholz district comprises abundant native metal-arsenide veins, which are accompanied by multiple stages of U as well as Ag sulfides and fluorite-barite-Pb-Zn mineralization occurring in the same vein structures (Müller, 1894; Wismut GmbH, 1999; Kuschka, 2002). The different mineral associations predominate at different depths resulting in a distinct vertical mineralogical zoning (Wismut GmbH, 1999).

A significant difference to many other native metal-arsenide deposits (in the Erzgebirge and elsewhere; Kissin, 1992; Markl et al., 2016; Scharrer et al., 2019, and references therein) is the apparent lithologic control for native metal-arsenide and U mineralization; their occurrence in the Annaberg-Buchholz district is restricted to an ~200- to 400-m-thick graphite-rich zone within the metasedimentary host-rock succession, which are only present in the upper 400 m below the present-day land surface (Wismut GmbH, 1999).

Between 1701 and 1850, ~8,700 metric tons (t) Co ore (at >3.24 wt %, calculated from Co-Ni ore associated with U mineralization extracted in the 20th Century, which results in a reduction of 3.24 wt % Co, 7.53 wt % Ni, and 0.69 wt % Cu from veins 303, 303a, and 115 (Uranus I mine; Fig. 1) as a by-product of U mining. Remaining proven reserves were reported as ~196 t of ore at 3.4 wt % Co, 7.5 wt % Ni, and 0.7 wt % Cu (Wismut GmbH, 1999) based on Minkin, 1958). Despite the economic potential and the long history of mining, available studies of the native metal-arsenide stage in the Annaberg-Buchholz district are descriptive and do not include mineral and fluid geochemistry (Müller, 1894; Wismut GmbH, 1999, based on Minkin, 1958), and hence the genesis and the underlying processes that cause the reported vertical zonation of the native metal-arsenide and U mineralization at Annaberg-Buchholz remain poorly constrained.

Here we present new petrographic, fluid inclusion, and mineral chemical data of native metal-arsenide mineralization from the Annaberg-Buchholz district. These results are compared and critically evaluated in terms of recently proposed genetic models (Markl et al., 2016; Burisch et al., 2017). Furthermore, we carried out thermodynamic calculations (activity-activity diagrams) in order to better understand the underlying processes (U and As redox sensitivity) that cause the observed vertical zoning of Co-Ni-As, U, and Ag, and discuss these results in the general context of U-Ag-Bi-Co-Ni-As-bearing hydrothermal mineral systems.

Geologic Setting and Mineralization Styles

Regional geology

The Erzgebirge/Krušné Hory metallogenic province spans across East Germany and the northwest Czech Republic (Fig. 1A) with the Annaberg-Buchholz district located in the central part of the German Erzgebirge. Veins in the Annaberg-Buchholz district are hosted by Cenozoic sedimentary and igneous rocks (Tichomirova et al., 2012) of the Saxo-Thuringian zone of the Variscan orogenic belt (Rötzler and Plessen, 2010). These rocks were deformed and metamorphosed during the Paleozoic collision of Gondwana and Laurussia (Kroner and Romer, 2013), with the peak metamorphism at 340 Ma (Pb-Pb evaporation on metamorphic zircons by Kröner and Willner, 1998). The metamorphic basement units were subsequently exhumed and intruded by voluminous granitoids and associated dikes (ryholite and lamprophyre dikes; Fig. 1A; Seckendorff et al., 2004; Förster and Romer, 2010), as well as (sub-)volcanics of late Variscan age (330–295 Ma; Förster et al., 2007; Tichomirova and Leonhardt, 2010; Hoffmann et al., 2013).

The post-Variscan geologic evolution of the Erzgebirge is poorly constrained due to the lack of preservation of the former sedimentary record. It has, however, been inferred that subsidence and coenmit basin formation associated with Perminian and Jurassic rifting led to deposition of a thick sedimentary cover, overlying the Variscan basement units (Pälichen and Walter, 2008). This sedimentary cover was already mostly eroded by the end of the Cretaceous. Apatite fission-track thermochronology suggests that the maximum thickness of the sedimentary cover reached 2 to 3 km during the Mesozoic (Wolff et al., 2015b). During the Cretaceous, the Elbe graben rift system, forming the northeastern limit of the Erzgebirge/Krušné Hory metallogenic province, was reactivated; this is expressed by marine transgressions and sedimentation. The southern limit of the metallogenic province is defined by the Cenozoic Eger graben rift system, with rifting accompanied by sedimentation, but also phonolitic and basaltic magmatism (Ulych et al., 2011). These rifting events resulted in uplift and erosion of the Erzgebirge/Krušné Hory block, eventually resulting in exhumation of the metamorphic units and the ore deposits hosted within them (Pälichen and Walter, 2008).

Geology of the Annaberg-Buchholz district

The Annaberg-Buchholz district represents an area of 40 km² located within the NE-SW-striking Annaberg-Marienberg an-
ticline, which is bound by the fault systems of Schlettau in the southeast and Wiesenbad in the northeast (Hoth et al., 1980). The Annaberg-Marienberg anticline comprises a suite of various para- and orthogneisses as well as mica schists and phyllites that are locally referred to as the Annaberg-Wegefarth Group (Fig. 1B; Tichomirowa et al., 2012). The dominant host lithology of the hydrothermal veins in the Annaberg-Buchholz district is a paragneiss locally called “gray gneiss” (“Augengneise”/”Obere Graugneise” with a protolith age of ~575 Ma, Pb-Pb evaporation and U-Pb SHRIMP on zircon;
Tichomirowa et al., 2012), which mainly consists of quartz, plagioclase, orthoclase, biotite, muscovite, and accessory minerals such as garnet, chloride, tourmaline, amphibole, epidote, apatite, pyrite, and graphite. Embedded in the paragneiss, smaller lenses of amphibolite, orthogneiss (mostly in the west and northwest part of the district, locally referred to as “Rotgneise”), mica schist, phyllite, and graphicgneiss occur (Fig 1B). The graphitic gneiss occurs mainly in the central part of the Annaberg-Buchholz district, with a thickness up to 10 m, and hosts up to 20-cm-thick graphite-rich horizons dipping into the southeast or north (locally referred to as “Schwebende,” Wismut GmbH, 1999 based on Minkin, 1958). Graphite-rich horizons are crosscut by mineralized NE-striking veins, indicating that they are older than ~276 Ma. In the nine workings of the central part of the district, these graphite-rich horizons were intersected from near-surface down to 400 m below present-day land surface (b.g.s.), the interval where native metal-arsenide and U mineralization mostly occur (e.g., in the Markus Röhlind mine; Wismut GmbH, 1999, based on Schönherr, 1958).

Postmetamorphic igneous rocks in the district include an undated, small finger-like Li-F-rich monzogranite stock that intruded into the metamorphosed host rocks (20-30 m thick and 75° to the N dip; Wismut GmbH, 1999), as well as Cenozoic basalts (Pöhlberg; Ulrych et al., 2011) to the east of the district. Lamprophyres oriented north-northeast and up to 5 m thick occur locally in the district (Wismut GmbH, 1999). The majority of the faults in the district follow two main orientations: NE-SW-trending structures with a 45° to 80° NW dip that are related to Variscan tectonics (Müller, 1894; Kuschka, 2002) and NW-SE-trending veins dipping 45° to 70°, which are related to Mesozoic tectonics (Romer et al., 2010); both fault systems host polyphase hydrothermal mineralization (Kuschka, 2002).

Hydrothermal mineralization in the Annaberg-Buchholz district

The overall paragenetic sequence of hydrothermal vein mineralization in the Annaberg-Buchholz district is briefly described in Müller (1894) and Kuschka (2002). Hydrothermal mineralization in the district comprises several stages, which can generally be divided into two main hydrothermal mineralization phases: The first hydrothermal phase comprises cassiterite-wolframite-quartz, Zn-Pb-Cu-Ag-quartz-(carbonate), quartz-calcite-uraninite, and fluorite-quartz mineralization stages (Müller, 1894; Wismut GmbH, 1999; Kuschka, 2002). These mineral assemblages have been related to magmatic-hydrothermal activity linked to the late- and postcollisional stages of the Variscan orogeny (Zhang et al., 2017; Burisch et al., 2018, 2019; Ostendorf et al., 2019). This late Paleozoic (350−250 Ma) mineralization phase is restricted to NE-SW- and E-W-trending faults in the Annaberg-Buchholz district.

The second phase of hydrothermal mineralization includes dolomite-uraninite-fluorite, fluorite-barite-Pb-Zn, native metal-arsenide, U, and quartz-Fe-Mn mineralization stages, which are related to post-Variscan tectonic events (opening of the North Atlantic Ocean, Eger graben rifting; Hautmann and Lippolt, 2000; Wolff et al., 2015a, b; Ostendorf et al., 2019). Mesozoic and Cenozoic mineralization may occur on reactivated Variscan NE-SW- and younger NW-SE-trending faults (Kuschka, 2002; Romer et al., 2010, and references therein). The relative timing of the different mineralization stages is generally based on crosscutting relationships in underground exposures, hand specimens, and thin sections. The available geochronological data for the Annaberg-Buchholz district are limited to crosscutting relationships and minimum mineralization ages of ~100 to 75 Ma for the fluorite-barite-Pb-Zn stage (Wolff et al., 2015a). Therefore, geochronological data of similar mineralization stages of other districts in the Erzgebirge metallogenic province are used here to, at least, tentatively constrain their absolute timing (Table 1).

Late Paleozoic mineralization phase: Minor cassiterite-wolframite-quartz mineralization forms the first stage of this phase (Table 1); it is limited to the west of the Annaberg-Buchholz district (Alte Thiele and Schlettau areas; Müller, 1894; Wismut GmbH, 1999); it was extensively mined for Sn during medieval times (Wismut GmbH, 1999). In the district, this assemblage comprises three different substages consisting of diverse assemblages of wolframite, cassiterite, tourmaline, and sulfides in fluorite-fluorite gangue (Table 1; Müller, 1894; Kuschka, 2002).

The cassiterite-wolframite-quartz stage is followed by a Zn-Pb-Cu-Ag-quartz-(carbonate) stage occurring in east-northeast veins dipping 45° to 65° to the north or south (up to 1 m thick; Müller, 1894). Based on mineralogical and textural similarities, this stage has been regarded as an equivalent to the homologous assemblage (Table 1) of the Freiberg district (also located in the Erzgebirge; Müller, 1901; Burisch et al., 2018; Bauer et al., 2019), where it has been dated to 276 ± 16 Ma (Rb-Sr isotope analysis of sphalerite and pyrite; Ostendorf et al., 2019). The Zn-Pb-Cu-Ag-quartz-(carbonate) stage of the Annaberg-Buchholz district, due to its minor quantity, was never economic and was only mined if accompanied by other mineralization stages (Wismut GmbH, 1999). It is characterized by abundant arsenopyrite, pyrite, sphalerite, chalcopyrite, tetrahedrite, galena, cassiterite, stannite, and minor Ag sulfides and sulfosalts accompanied by massive, mostly anhedral quartz, while carbonate (mainly dolomite) is rare (Müller, 1894; Kuschka, 2002; Bauer et al., 2019).

The quartz-calcite-uraninite stage (Schuppan et al., 1994; Hillier and Schuppan, 2008) constitutes the oldest U mineralization in the district, based on crosscutting relationships, and it appears younger than the Zn-Pb-Cu-Ag-quartz-(carbonate) stage. This stage is referred to as U1 in this contribution and was dated to 250−267 Ma by U-Pb isotope analysis of uraninite in the nearby district of Schlema-Alberoda (Schuppan et al., 1994, based on Tugarinov et al., 1967 and Velikhin et al., 1983; Förster and Haack, 1995; Golubev et al., 2000). It may form up to decimeters-thick northeast-southwest veins but is significantly less prominent in the Annaberg-Buchholz district compared to, e.g., the neighboring Schlema-Alberoda district (Schuppan et al., 1994; Hillier and Schuppan, 2008). Symmetrically zoned vein infills consist of abundant chalcedony and colorless-white to brown palisade quartz. Quartz contains sphalerite aggregates of goethite, which are also commonly present along vein selvages and often accompanied by pale green-violet to dark (especially in contact with uraninite) fluorite. Fluorite is followed by prismatic and partly sphenolithic coaffeine and abundant colloform, reniform or botryoidal
In the Annaberg-Buchholz district, it has previously been recognized that the hydrothermal mineralization stage constitutes the second uraniferous mineralization stage and is referred to as U2 in this contribution. This stage has U-Pb uraninite ages between 190 ± 4 and 140 Ma in the Schlema-Alberoda district (Schuppan et al., 1994, based on Tugarinov et al., 1967 and Velichkin et al., 1983; Förster and Haack, 1995; golubev et al., 2000). Dolomite-uraninite-fluorite stage (U2) mineralization has been mainly identified in the Himmlisch Heer Stehender, Merkur Stehender, Sina Facher, and Uranus Facher veins (Wismut GmbH, 1999; Baumann et al., 2000). The mineralogy of U2 consists of abundant dolomite, which pseudomorphically replaces calcite of the U1 stage (e.g., Schlema-Alberoda district; Schuppan et al., 1994; Hiller and Schuppan, 2005). Mechanically brecciated and/or corroded uraninite I of U1 is often recognized and is partially or completely overgrown by the dolomite of U2. Dolomite is intergrown with coeval uraninite II, both being accompanied by Pb-, Ag-, and Cu-selenides, chalcopryte, galena, fahlore, and dark fluorite ("antozonite" variety). Based on replacive relationships between uraninite I (U1) and uraninite II (U2), the latter has traditionally been interpreted as remobilized U1 uraninite (Schuppan et al., 1994; Hiller and Schuppan, 2008).

An abundant fluorite-barite-Pb-Zn stage is paragenetically younger than the U2 assemblage and has been mined for Ag, Pb, Zn, and fluorite in the Annaberg-Buchholz district from medieval times until 1957. Fluorite from the Annaberg-Buchholz district has an average composition (U-Th-Sm)/He age of 80.6 ± 9.2 Ma (Wolff et al., 2015a). Similar fluorite-barite-Pb-Zn mineralization in the Freiberg district has recently been dated to 121.3 ± 2.0 and 101 ± 18 Ma (Ostendorf et al., 2019). Fluid inclusion and sulfur isotope systematics indicate fluid mixing between two highly saline brines in conjunction with extensional tectonics associated with the opening of the northern Atlantic Ocean (Bauer et al., 2019; Haschke et al., 2021). In the Annaberg-Buchholz district, this stage has been documented as particularly abundant in the Glück Flacher and Grindonnerstag Spatlagh veins (Müller, 1894; Hösel et al., 1997; Baumann et al., 2000). The fluorite-barite-Pb-Zn stage is characterized by red to brown hematite, chalcocody, white to red barite associated with colorless, brown, purple, blue to green fluorite, and quartz (Müller, 1984). The U-Ag-Bi-Co-Ni-As stage includes the spatially associated native metal-arsenide and U (referred to as U3 in this contribution) mineralization presented in this contribution. In the Annaberg-Buchholz district, it has previously been considered to be younger than the fluorite-barite-Pb-Zn stage (Müller, 1894; Kuschka, 2002). However, petrographic observations in this study suggest that the native metal-arsenide stage coincides with the fluorite-barite-Pb-Zn stage (more details below). Geochronological data directly related to the native metal-arsenide and U3 stages in the Annaberg-Buchholz district are not available. However, uraninite associated with a similar native metal-arsenide assemblage from the neighboring district of Schlema-Alberoda has yielded variable groups of U-Pb ages ranging from 120 ± 6 to ~7 Ma (Schuppan et al., 1994, based on Tugarinov et al., 1967 and Velichkin et al., 1983; Förster and Haack, 1995). The U3 and native metal-arsenide assemblages are reported from more than 160 veins of the Annaberg-Buchholz district. The veins are between 0.1 and 1 m thick (Müller, 1894; Wismut GmbH, 1999) and are often associated with other mineral assemblages such as the U1, U2, and fluorite-barite-Pb-Zn stages. The native metal-arsenide stage consists of two native metal and arsenide substages (native Bi, Ag, and As, skutterudite, rammelsbergite, nickeline, safflorite, loellingite) followed by an Ag-Bi-(As)-S substage composed by base metal sulfosalts and sulfides, and uraninite and coinnite associated with U3. The substages composing the native metal-arsenide stage are described in more detail in the “Results” sections. Prominent gangue minerals are dolomite, ankerite, fluorite, siderite, and barite. The U3 stage consists mainly of uraninite, which was most likely formed by remobilization of uraninite from the U1 and U2 stages (Schuppan et al., 1994; Hiller and Schuppan, 2008; Romer and Cuney, 2018). In the Annaberg-Buchholz district, only uraninite from U3 associated with native metal-arsenide mineralization was considered as an economic resource on its own during the German Democratic Republic period (Wismut GmbH, 1999), whereas U1 and U2 mineralization only contributed subordinately to the U resource.

The youngest mineralization stage consists of a quartz-Fe-Mn assemblage, which comprises mainly hollandite group and lithiophorite-asbolane minerals. It was dated 20 to 1 Ma by Ar-Ar geochronology (Hautmann and Lippolt, 2000), which coincides with the Cenozoic Eger graben rifting (Pflächen and Walter, 2008).

Vertical mineralogical zonation: Documentation of the distribution of the hydrothermal mineralization stages is based on field observations (Markus Röhling mine) complemented by descriptions of Müller (1894) and unpublished technical reports by the SAG/SDAG Wismut (Wismut GmbH, 1999). These reports included geologic observations from ~20 down to ~450 m b.g.s. of the historic underground workings (Wismut GmbH, 1999). Minor cassiterite-wolframite-quartz, Zn-Pb-Cu-Ag-quartz-(carbonate), and U1 veins (northeast-southeast) occur across the entire vertical profile in the district and are crosscut by younger NW-SE-trending veins that host U2, fluorspar-barite-Pb-Zn, native metal-arsenide, and U3 stage mineralization. At the district scale, the occurrence of Co-Ni arsenides and associated uraninite (U3) ore shoots are restricted to vein intersections in the upper ~350 m b.g.s. of the vertical profile, where the graphite-rich gneiss is hosting the veins. Below about 300 to 350 m b.g.s., the host lithology changes to a (graphite-free) gneiss, which is associated with a transition to a mainly fluorite-barite-Pb-Zn-dominated vein mineralogy that is present throughout the entire vertical profile. Vertical zoning in the older NE-SW-trending vein
system is poorly documented, since neither Zn-Pb-Cu-Ag-quartz-(carbonate) nor U1 have been considered as economic in the Annaberg-Buchholz district. The two older U stages are, however, well documented from the nearby Schlema-Alberoda district, where an increase in vein thickness of U1 and a decrease of U2 with depth is documented (Schuppan et al., 1994; Wismut GmbH, 1999; Hiller and Schuppan, 2008; Romer and Cuney, 2018). The same principal vertical mineralogical zoning within the older northeast-southwest veins is assumed to occur as well in the Annaberg-Buchholz district.

At the vein scale, a vertical mineralogical zoning is observed within the younger veins (mainly NW-SW-trending): U3 association occurs preferentially at 0 to 150 m b.g.s. whereas Co-Ni arsenides occur down to 350 m b.g.s. (Figs. 2, 3A-B; Wismut GmbH, 1999, based on Schönherr, 1958). Moreover, a Ag-Bi-(As)-S substage occurs preferentially in the upper part of the vertical profile, whereas its abundance decreases significantly below 200 m b.g.s. (Wismut GmbH, 1999, based on Minkin, 1958). The described vertical mineral zonation of the Annaberg-Buchholz district is also reported from the nearby district of Niederschlag (~10 km from Annaberg-Buchholz; Kuschka et al., 2002).

Methods

Sample selection

Twenty-six hand specimens were selected from the geoscientific collections of the Technische Universität Bergakademie Freiberg, in Germany (Fig. 3). Due to health safety regulations, only samples with minor radioactivity were used for thin section preparation, resulting in a particular dominance of samples from the native metal-arsenide mineralization stage. The samples are from the historic mine sites of Altväter/König David, Bäuerin, Himmlisch Heer, Markus Röhling, Neu Bäuerin, St. Andreas, and Uranus I (see Fig. 1B for reference). The depth is known (n = 13) or has been estimated from descriptions of the locations (n = 9) for 22 samples, which cover...
a vertical profile from approximately 50 to 352 ± 40 m b.g.s. A dozen additional samples were collected from the König David underground mine in the accessible part of the historic Markus Röhlöing under the electron beam, a beam diameter of 10 µm was used. A beam of 1- to 6-µm-diam at an acceleration voltage of 20 kV with a current of 30 nA was used for ore mineral analysis, except for silver-bearing minerals (acanthite, native Ag, pearceite, and proustite). Due to their instability under the electron beam, a beam diameter of 10 µm was used. Native As could not be analyzed because of its quick oxidation under the electron beam, a beam diameter of 10 µm was used. Native As could not be analyzed because of its quick oxidation

### Petrography

Mineral identification and texture were observed on 28 polished thin sections under transmitted and reflected light, using a Carl Zeiss® Axio Imager M1m light microscope. Photomicrographs were taken with a Zeiss Axio Cam MRc5 camera. Textural observations and mineral identification were supported by scanning electron microscopy analysis (SEM) and backscattered electron (BSE) images, carried out on an FEI Quanta 650F SEM equipped with two Bruker Quantax X-Flash 5030 energy-dispersive X-ray spectrometers (EDS) at the Technische Universität Bergakademie Freiberg. A beam current of 15 nA was used with a 25-kV acceleration voltage for ore minerals. Furthermore, the same SEM-EDS system was also used at 15-kV acceleration voltage to analyze carbonates qualitatively, to produce BSE images of compositional zoning in carbonates and to select samples suitable for electron probe microanalysis.

#### Electron probe microanalysis

Arsenide, sulfoarslate, and sulfide quantitative chemical compositions were determined using a JEOL JXA 5830F electron probe microanalysis (EPMA) at the Helmholtz Institute Freiberg for Resource Technology. This EPMA is equipped with five wavelength-dispersive spectrometers and a field emission electron gun. A beam of 1- to 6-µm-diam at an acceleration voltage of 20 kV with a current of 30 nA was used for ore mineral analysis, except for silver-bearing minerals (acanthite, native Ag, pearceite, and proustite). Due to their instability under the electron beam, a beam diameter of 10 µm was used. Native As could not be analyzed because of its quick oxidation under the electron beam, a beam diameter of 10 µm was used. Native As could not be analyzed because of its quick oxidation under the electron beam, a beam diameter of 10 µm was used. Native As could not be analyzed because of its quick oxidation under the electron beam, a beam diameter of 10 µm was used.

| Homogenization temperature (°C) | Salinity (equiv wt % NaCl) | Age (Ma) | References |
|---------------------------------|---------------------------|----------|------------|
| Late–Paleozoic (350-250 Ma phase) | n.d. | 325.6 ± 3.5 to 323.2 ± 2.8 (U-Pb on cassiterite, Ehrenfriedersdorf district) | Zhang et al. (2017) and references therein |
| 255-341 (Freiberg district) | 0.5-6 | 276 ± 16 (Rb-Sr isotopes on sphalerite and pyrite, Freiberg district) | Bauer et al. (2019); Ostendorf et al. (2019) |
| 80-175 (Schlema-Alberoda district) | n.d. | 250-267 (U-Pb isotopes on uraninite, Schlema-Alberoda district) | Tugarinov et al. (1970); Schuppan et al. (1994) [based on Tugarinov et al. (1967), Velickin et al. (1983)]; Förster and Haak (1995); Golubev et al. (2000); Hiller and Schuppan (2008) |
| 347 ± 19; 295 ± 17; 172 ± 33 and 140-180 (Marienberg and Niederschlag districts) | 0.5-12 and 7-20 | n.d. | Seifert and Baumann (1994); Haschke et al. (2021) |

| Mesozoic to Cenozoic (250-15 Ma phase) | | | |
|---------------------------------------|--------------------------|--------------------------|--------------------------|
| 115-145 | n.d. | 190 ± 4-140 (U-Pb isotopes on uraninite, Schlema-Alberoda and Breitenbrunn districts) | Tugarinov et al. (1970); Schuppan et al. (1994) [based on Tugarinov et al. (1967), Velickin et al. (1983)]; Förster and Haak (1995); Golubev et al. (2000); Hiller and Schuppan (2008) |
| 80-120 (Niederschlag district) | 18-27 (Niederschlag district) | 98.9 ± 10.7 to 75.3 ± 8.8 [(U-Th-Sm)/He thermochronology on fluorite, Annaberg-Buchholz district], 121 ± 4.2 and 101 ± 18 (respectively Rb-Sr dating of sphalerite and fahlore, and Sm-Nd isotopes on fluorite, Freiberg district) | Wolf et al. (2015a); Ostendorf et al. (2019); Haschke et al. (2021) |
| 92-156 (Schlema-Alberoda district) | n.d. | n.d. | Tugarinov et al. (1970); Kuschka (2002); Hiller and Schuppan (2008) |
| 30-40 (Schlema-Alberoda district) | n.d. | 120 ± 6, 110-90, 30 and 16-7 (U-Pb isotopes on uraninite, Schlema-Alberoda district) | Tugarinov et al. (1970); Kuschka (2002); Hiller and Schuppan (2008) |
| n.d. | n.d. | 20-1 (40Ar/39Ar on K-Mn oxides, Schwarzenberg and Geyer areas) | Schuppan et al. (1994) [based on Tugarinov et al. (1967), Velickin et al. (1983)]; Förster and Haak (1995); Golubev et al. (2000); Hiller and Schuppan (2008) |

Table 1. (Cont.)
TeL, βBiM, and βAuM. Major elements showing concentrations exceeding 5 wt % were corrected for machine drift assuming linear drift between two successive analysis of reference materials measured as unknowns. Concentrations below the quantification limit automatically calculated by the JEOL software were indicated as below limit of quantification (b.l.q.). Mineral chemistry and measurement conditions are provided in Appendix Tables A2, A3, A4.

Microthermometry

Eleven samples were selected for investigation of fluid inclusion in fluorite, dolomite-ankerite, calcite, quartz, and proustite. A total of 24 doubly polished thick sections (200–250 µm) were investigated for fluid inclusion by petrography and microthermometry. Twenty samples including native metal-arsenide association were carefully checked for suitable fluid inclusions. Only very few contained visible fluid inclusions (hosted by dolomite-ankerite, calcite, quartz, and proustite) of which most of them could unfortunately not be measured due to metastability or insufficient size (<5 µm). Only one sample with Co-Ni arsenides and dolomite-ankerite contained detectable fluid inclusions. Although postore fluorite contains some fluid inclusions, all analyses were discarded due to metastability, which is evident from different temperatures of phase transitions during repeated heating/freezing runs. Fluid inclusion assemblages were classified as isolated (i), cluster (c), primary (p), pseudosecondary (ps), and secondary (s), according to Roedder (1984) and Goldstein (2001). Fluid inclusions suitable for microthermometry analysis were detected in dolomite-ankerite and fluorite (all of primary nature). An Olympus BX53 microscope equipped with a Linkam THMSG600 heating-cooling stage and coupled to a QImaging Retiga 2000R CCD HD camera was used for the microthermometric measurements at the Technische Universität Bergakademie Freiberg. The vapor/liquid ratio of each fluid inclusion was determined with the Linksys built-in image processing software. A synthetic H2O-CO2 standard with CO2 melting at -56.5°C and a pure H2O standard with Tm(ice) at 0.0°C and Th at 374°C were used to calibrate the heating-freezing stage daily before each measurement campaign. For each fluid inclusion, freezing temperature (Tf), eutectic temperature (Te), final hydrohalite melting temperature (Tm(HH)), final ice melting temperature (Tm(ice)) and total homogenization temperature (Th) were measured three times. In all analyzed fluid inclusions, the deviation between these three runs was smaller than 3°C for Tf, 0.1°C for Tm(ice)/Tm(HH) and 1°C for Th. The average temperature of the three measurement runs is reported (App. Table A5). Temperatures were corrected for daily machine drift as long as standard measurements turned out with less than 0.3°C. Total salinities [equiv wt % (NaCl-CaCl2)] were calculated using Tm(ice) and Tm(HH) according to Steele-MacInnis et al. (2011) in the ternary NaCl-CaCl2-H2O system. Fluid inclusions showing postentrapment modifications (necking for example) were excluded. Assuming that these veins formed under hydrostatic pressures, no pressure correction was applied since trapping temperatures do not significantly deviate from homogenization temperatures for high-salinity fluid inclusions.

Attempts to detect hydrocarbons with Raman spectroscopy in carbonates failed due to the small size of the fluid inclusions (mainly ≤5 µm), as well as the strong signal of the carbonate host mineral with the fluid inclusion-derived Raman signal.

Thermodynamic modeling

Activity-activity diagrams were calculated using the Act2 module of Geochemist’s Workbench (GWB, Version 11.0.7). The focus was on the behavior of U and As upon reduction. Uraninite was chosen as a representative of U and nickeline (NiAs, the paragenetically oldest arsenide) as a representative of the arsenide minerals. Log activities of aqueous species of UO22+ for U, H2AsO3- for As, and Ni2+ for Ni were calculated using the Geochemist’s Workbench’s spreadsheet (GSS) at 150°C (at saturated vapor pressure) with a pH of 7 and a salinity of 25 equiv wt % (NaCl-CaCl2) (temperature constraints were based on microthermometric data from this study) as this seems to be characteristic for native metal-arsenide systems (Markl et al., 2016; Scharer et al., 2019). Species activities were converted concentrations using the extended
Debye–Hückel equation. The dataset used was Thermodem_MAJ2016_final6d (Blanc et al., 2012; Blanc, 2017). The activity-activity diagrams were calculated with U and As activities corresponding to concentrations of 100, 500, and 1,000 mg/kg with a constant Ni concentration of 50 mg/kg, based on the estimates by Scharrer et al. (2019).

Results

Ore petrography

The ore petrographic description focuses on the native metal-arsenide stage with native metal, arsenide, and Ag-Bi-(As)-S substages that are the predominant assemblages in the investigated samples (Table 1; Figs. 3D-F, 4A-D). However, investigated samples do also comprise minor amounts of other hydrothermal stages that are briefly described.

Fig. 3. Photographs of underground exposures (A-B) and hand specimens (C-F). A. Graphite-rich horizon (GH) in the graphitic gneiss, Uranus I mine (level 120 m b.g.s., photograph by M. Schaling), Annaberg-Buchholz. B. Exposure of König David vein, level 128 m b.g.s. in the Markus Röhling mine, with disseminated Co-Ni arsenides and erythrite (Ert) associated with purple to dark fluorite (Fl) and quartz (Qz). C. Sample S21-Schw-2 of graphite-rich horizon (GH) from the Uranus I mine in Annaberg-Buchholz (120 m b.g.s.). Graphite-rich horizon (distinctively darker) superimposed by erythrite (Ert), purple fluorite (Fl), pyrite (Py), and barite (Brt). D. Nickeline (Nk), rammelsbergite (Rmb), and loellingite (Loel) of the Bi-Ni-Co-Fe-As assemblage superimposing older fluorite (Fl) of the fluorite-barite-Pb-Zn assemblage (sample 62885). E. Dendrites of native silver (Ag) enclosed by rammelsbergite (Rmb), native arsenic (As), loellingite (Loel), dolomite-ankerite (Dol-Ank), and proustite (Prou) of the As-Ag-Fe assemblage (sample 8066). F. Co-Ni arsenides superimposed by uraninite (Urn) and erythrite (Ert) in sample 62955. Yellow fluorite (Fl) occurs with the Co-Ni arsenides. Abbreviation: m b.g.s. = meters below ground surface.

The oldest mineral in the hydrothermal vein infill is fluorite (Fig. 4A-B). Fluorite is rarely associated with barite and belongs to the fluorite-barite-Pb-Zn stage (Fig. 5). The native metal and arsenide substages consist of native Ag or native Bi overgrown by arsenides, namely rammelsbergite, skutterudite, nickeline, safflorite, and loellingite (Fig. 5B). Uraninite and coffinite are younger than safflorite and loellingite. Arsenides are encapsulated by dolomite-ankerite and/or quartz.

Detailed petrographic descriptions of the native metal and arsenide substages: The native metal and arsenide substages are represented by a variety of mineral assemblages, which can be grouped into Bi-Ni-Co-Fe-As, Ag-Ni-Co-Fe-As,
As-Ag-Fe assemblages (Figs. 6, 7). Most samples comprise the younger Ag-Bi-(As)-S substage. Within the native metal and arsenide substages, primary Ag has never been observed together with native Bi. The three varieties of native metal-arsenide associations appear to be cogenetic and are thought to reflect spatial rather than temporal substages (Fig. 5). However, the complete dissolution/replacement by younger minerals of primary native Ag and Bi in some samples renders it impossible to identify what native metal was originally precipitated during the native metal substage.

**Bi-Ni-Co-Fe-As:** This assemblage consists of small grains (only a few μm in size), dendritic, fern-like aggregates of native Bi of variable size (10–300 μm; Figs. 5, 6A-B), which are overgrown by colloform or irregularly shaped nickeline (few μm to 1,000 μm thick), rammelsbergite (up to 400 μm thick), and euhedral skutterudite that may form crystals and layers up to several millimeters thick (Fig. 6A-F). When no nickeline is formed, rammelsbergite and skutterudite-nickelskutterudite directly overgrow native Bi (Fig. 6A). Safflorite-clinosafflorite and loellingite typically form the youngest arsenides, forming layers or crusts of a few- to 500-μm thickness on older arsenides (Fig. 6B, F). Safflorite and loellingite often form intergrowths, hence successions of safflorite followed by younger loellingite are also observed. The native metal-arsenide sequence is commonly enclosed by dolomite-ankerite or, less frequently, by quartz. Within a few millimeters to the native metal-arsenide aggregates, euhedral, often star-shaped crystals of safflorite or loellingite occur within the gangue (Fig. 6C-D). Platy hydrothermal graphite as inclusion in quartz is recognized close to the arsenide aggregates (Fig. 4C; Burisch et al., 2017). Micrometer-sized grains of uraninite and coffinite overgrow safflorite and loellingite (Fig. 6D-E). Native Bi can be partially or entirely replaced by bismuthinite (Fig. 6A). Gersdorffite is occasionally observed, usually replacing skutterudite (Fig. 7A).

**Ag-Ni-Co-Fe-As:** This assemblage shows many similarities to the Bi-dominated assemblage described above. Therefore, the following description will focus on the differences. The paragenetic sequence starts with native Ag, which usually forms dendritic mesh textures or small isolated aggregates. As is the case with native Bi, native Ag is encapsulated by a succession of arsenides that commonly commences with nickeline (up to mm in size) and rammelsbergite (up to 2 mm) followed by skutterudite (100 μm–1 mm). The abundance of rammelsbergite is conspicuously higher in Ag- rather than Bi-dominated samples. Locally, native As occurs as small, irregularly shaped aggregates which are younger than the early arsenides. Native As is overgrown by later loellingite and safflorite. Safflorite (up to 500 μm thick) and loellingite (few μm up to 100 μm thick) form rims and euhedral crystals around previously described arsenides. Carbonates overlap paragenetically with loellingite and overgrow the arsenide-rich succession (Fig. 7B).

**As-Ag-Fe:** In the As-Ag-Fe assemblage, native Ag occurs as very small grains (few μm in size) or aggregates (up to 250 μm) with corroded grain boundaries, which are overgrown by a layer of colloform rammelsbergite (50 μm–2 mm; Fig. 7B-C). Sometimes, native Ag is overgrown by euhedral skutterudite and nickelskutterudite (100 μm–2 mm). Native As overgrows rammelsbergite and forms up to 600-μm large ir-
regular or cauliflower-shaped aggregates. Euhedral safflorite and loellingite form up to 30-µm thin layers, overgrowing native As. Arsenides and native As form aggregates up to 2 mm in size, which are typically encapsulated by carbonate gangue (mostly ankerite, less dolomite; Fig. 7B).

**Ag-Bi-(As)-S substage:** The Ag-Bi-(As)-S substage consists, in sharp contrast to the native metal and arsenide substages, of a diverse suite of sulfides and sulfosalts, which mainly include proustite, acanthite, bismuthinite, tetrahedrite, gersdorffite, pyrite, and sphalerite. Silver-bearing sulfosalts/sulfides are present in all investigated samples, but their abundance varies strongly. Sulfides of the Ag-Bi-(As)-S substage extensively replace native metals of the native metal substage (Figs. 6F, 7B-D).

Proustite is the most abundant sulfosalts- and Ag-bearing mineral. Proustite forms anhedral and euhedral crystals between 10 and 500 µm in size, which are usually related to samples that contain native Ag and As, while anhedral aggregates of bismuthinite are commonly observed in samples containing native Bi. Proustite, and to a lesser extent bismuthinite, are accompanied by abundant acanthite and freibergite (tetrahedrite; Fig. 7D), which usually form anhedral masses. Acanthite and tetrahedrite (freibergite) may be observed in Bi-, Ag-, and As-dominated samples, but acanthite is particularly more abundant in Ag-dominated samples. Minor quantities of argentopyrite, pyrargyrite-miargyrite, lenaite, pyrrhotite,
Fig. 6. Photomicrographs of representative ore textures related to the native metal, arsenide, and Ag-Bi-(As)-S substages (Bi-Ni-Co-Fe-Ax assemblage). A. Reflected light in air (RLair) image of skeletal native bismuth (Bi) overgrown by rammelsbergite (Rmb) and skutterudite (Sk) encapsulated by fluorite (Fl). Bismuth is partially dissolved and replaced by bismuthinite (Bis). B. RLair image of partially dissolved native bismuth (Bi) inclusions hosted by nickelskutterudite (Nsk) sometimes intergrown with skutterudite (Sk), which is overgrown by rammelsbergite (Rmb), nickeline (Nk), safflorite-clinosafflorite (Sfl-Csfl), and dolomiteankerite (Dol-Ank). Proustite (Prou) can be observed as late-stage cavity infill. C. RLair image of euhedral skutterudite (Sk), showing oscillatory zoning encapsulated by quartz (Qz), which hosts euhedral safflorite-loellingite (Sfl/Loel) crystals (often star-like triplets). Safflorite-loellingite is also present in void spaces within skutterudite. Proustite (Prou) is present on fractures within the skutterudite. D. Backscattered electron (BSE) image of euhedral skutterudite (Sk) overgrown by loellingite (Loel) and uraninite (Urn) and enclosed by dolomite-ankerite (Dol-Ank). Uraninite is superimposing loellingite. E. BSE image of minute inclusions of native bismuth (Bi) in nickeline (Nk) rimmed by rammelsbergite (Rmb) and safflorite-loellingite (Sfl/Loel). Small grains of coffinite (Coff) can be observed on top of safflorite-loellingite and encapsuled by quartz (Qz). F. RLair image of rammelsbergite (Rmb) and safflorite-loellingite (Sfl/Loel). Skeletal native bismuth (Bi) is replaced by euhedral safflorite-loellingite (Sfl/Loel) and proustite (Prou), indicating that native bismuth was remobilized prior to the precipitation of safflorite-loellingite and proustite.
Fig. 7. Photomicrographs of representative ore textures related to the native metal, arsenide, and Ag-Bi-(As)-S substages (A, F: Bi-Ni-Co-Fe-As assemblage; B, C: As-Ag-Fe assemblage; D, E: no native metal observed): A. Reflected light in air (RLair) image of euhedral skutterudite (Sk); some zones of the skutterudite are selectively replaced by gersdorffite (Ger) and quartz (Qz). B. BSE image of partially dissolved native silver (Ag), which is overgrown by rammelsbergite (Rmb), native arsenic (As), and loellingite (Loel), forming rims around native As and occurring in dolomite-ankerite (Dol-Ank) with minor occurrence of pyrrhotite (Po). Silver is partly replaced by acanthite (Ac). C. BSE image of dendritic native silver (Ag) hosted by rammelsbergite (Rmb). Silver is partly replaced by acanthite (Ac). D. RLair image of a succession of rammelsbergite (Rmb) and safflorite-loellingite (Sfl/Loel), followed by pyrite (Py), freibergite (Fg), proustite (Prou), and calcite (Cal). Pyrite and proustite replace native silver. E. BSE image of rammelsbergite (Rmb), nickelskutterudite (Nsk), loellingite (Loel), lenaite (Len), proustite (Prou), pyrite (Py), and chalcopyrite (Ccp). The cauliflower-like texture of rammelsbergite is typical for assemblages that contained native arsenic. The calcite (Cal) in the core of the arsenide most likely replaced native arsenic. F. RLair image of euhedral gersdorffite (Ger) crystals, which comprise inclusions of pyrite (Py) that are spatially associated with skutterudite (Sk) in quartz (Qz).
matildite, polybasite, pentlandite, chalcopyrite, and galena have been noted (Fig. 7E).

**Mineral chemistry**

The composition of native metals (Ag, Bi), nickeline, skutterudite-nickelskutterudite, rammelsbergite, safflorite-clinosafflorite, and loellingite related to the native element and arsenide substages as well as proustite, gersdorffite, acanthite, argentopyrite, and lenaite associated with the Ag-Bi-(As)-S substage was analyzed with EPMA. Major compositional variations of arsenides are given as mole fractions $X_A$, $X_{Ni}$, $X_{Co}$, and $X_{Fe}$. The complete compositional data set is provided in the Appendix Tables A3 and A4. Minimum, mean, and maximum compositions for each mineral are compiled in Tables 2 to 4. Systematic variations in mineral composition between mineral assemblages (Bi-, Ag-, or As-dominated) were not recognized.

Native metals: Native Bi ($n = 4$) contain only traces of As ($\leq 0.15$ wt %), Ni ($\leq 0.23$ wt %), and Co ($\leq 0.05$ wt %; Table 2). Native Ag suitable for EPMA is rare since most of the Ag is replaced and remnant Ag aggregates are usually porous and very fine grained. Only three grains of native Ag (all partially dissolved) were analyzed; these show minor concentrations of As ($\leq 3.59$ wt %), Ni ($\leq 1.09$ wt %), and Hg (0.21–0.31 wt %).

Monoarsenide: Nickeline ($n = 8$) has an $X_A$ [molar As/(As + S + Sb)] of ~1.0 and an $X_{Ni}$ [molar Ni/(Ni + Co + Fe)] of 0.97 to 1.0 with minor amounts of Co (0.18–1.38 wt %), Bi (≤0.65 wt %), and a negligible content of S ($\leq 0.19$ wt %) (Table 3; Fig. 8A).

Diarsenides: Rammelsbergite ($n = 17$) has an $X_A$ of 0.98 to 1.0 due to substitution of As by S, a high $X_{Co}$ of 0.85 to 0.96, an $X_{Ni}$ of 0.03 to 0.13, and a low $X_{Fe}$ [molar Fe/(Fe + Co + Ni)] of 0.0 to 0.06. Rammelsbergite may incorporate up to 1.12 wt % Cu (Table 3; Fig. 8A). Sulfur concentrations are in the range of 0.12 to 1.16 wt %, Minor amounts of Bi ($\leq 0.77$ wt %) may be due to the presence of fine-grained native Bi inclusions in rammelsbergite.

Safflorite ($n = 7$) has an $X_A$ of 0.98 to 1.0 due to substitution of As by S, an $X_{Co}$ of 0.49 to 0.77, an $X_{Fe}$ of 0.21 to 0.49, and an $X_{Ni}$ of 0.0 to 0.07. Clinossafflorite ($n = 12$) has an $X_A$ of 0.98 to 1.0 due to substitution of As by S, an $X_{Co}$ of 0.51 to 0.71, an $X_{Fe}$ of 0.07 to 0.20, and an $X_{Ni}$ of 0.10 to 0.42 (Table 3; Fig. 8A).
Safflorite and clinooarsenolite may both incorporate Cu (0.49–2.56 wt %) and S (0.27–1.51 wt %). They also contain minor Ag (up to 0.07 wt %) and Bi (up to 0.32 wt %), most likely due to mixed analyses of native metals and arsenides. Loellingite (n = 12) has an X As of 0.96 to 1.0 due to substitution of As by S, an X Fe of 0.92 to 1.0, an X Co of 0.09 to 0.42, and an X Ni of 0.0 to 0.03. Loellingite shows 0.13 to 3.06 wt % of S, 0.15 to 2.75 wt % of Cu, and ≤0.17 wt % of Bi. All diarsenides (rammelsbergite, safflorite-clinoarsenolite, and loellingite) show a negative correlation between S and As corresponding to substitution of As by S (Fig. 8B).

**Triaresenides:** Skutterudite (n = 121) shows significant compositional variations of Co and Ni content. Cobalt-dominated skutterudite (n = 15) has an X As of 0.98 to 1.0, due to minor substituion of As by S, an X Fe of 0.33 to 0.72, an X Ni of 0.09 to 0.42, and an X Co of 0.15 to 0.35. Nickelskutterudite (n = 106) has an X As of 0.97 to 1.0, an X Fe of 0.10 to 0.42, an X Ni of 0.38 to 0.86, and an X Co of 0.01 to 0.26. Up to 3 wt % Bi has been detected in both skutterudite and nickelskutterudite, most likely reflecting mixed analyses. Nickelskutterudite has remarkably lower Fe concentrations compared to skutterudite. Other elements detected are Cu (≤3.58 wt %), S (≤2.44 wt %), and Ag (≤0.19 wt %). A negative correlation between S and As is observed (Fig. 8B).

**Sulfides and sulfosalts:** Gersdorffite (n = 4) has an average composition of 44.7 wt % As, 31.5 wt % Ni, and 19.5 wt % S. Moreover, it contains 1.27 to 5.29 wt % Fe, ≤0.27 wt % Co, and ≤0.74 wt % Bi (Table 4, App. Table A3). Proustite (n = 22) has an average composition of 65.1 wt % Ag, 19.7 wt % S, and 14.2 wt % As (Fig. 8C; App. Table A3). Minor amounts of Fe (≤1.67 wt %), Ni (≤0.19 wt %), Co (≤0.11 wt %), Cu (≤0.13 wt %), and Zn (≤0.22 wt %) were detected, which seem to scatter randomly. Argentopyrite (n = 9) has an average composition of 34.7 wt % Fe, 33.5 wt % Ag, and 31.0 wt % S with Cu (≤1.02 wt %) and minor amounts of As (≤0.52 wt %), Ni (≤0.44 wt %), and Co (≤0.15 wt %). Acanthite (n = 3) has an average composition of 85.5 wt % Ag, 13.0 wt % S with minor amounts of As (≤0.22 wt %), Ni (≤0.19 wt %), Fe (0.09–0.16 wt %), and Co (≤0.07 wt %). Lenaite (n = 9) is only observed in two samples and has an average composition of 46.7 wt % Ag, 28.9 wt % S, and 24.2 wt % Fe. Most of the analyzed grains contain Cu (≤0.85 wt %), Ni (≤0.68 wt %), As (≤0.17 wt %), and Co (≤0.06 wt %). Hg was not detected in any of the analyzed sulfides or sulfosalts.

**Fluid inclusions**

The milky appearance of gangue minerals related to the native metal-arsenide stage at Annaberg-Buchholz, the small size (often <5 µm in dolomite-ankerite) and the frequent metastable behavior of fluid inclusions limited the number suitable for microthermometric investigations significantly. A total of 21 fluid inclusion assemblages (around 136 fluid inclusions; only primary fluid inclusions) were analyzed in fluorite I (fluorite-barite-Pb-Zn stage) and dolomite-ankerite (native metal-arsenide stage from the As-Ag-Fe assemblage described above; App. Table A1; Fig. 9). A summary of the fluid inclusion data is presented in Table 5. Measurements of all fluid inclusions are provided in Appendix Table A5.

Sixteen primary fluid inclusion assemblages (116 fluid inclusions) were measured in fluorite I. Individual fluid inclusions vary between 10 and 50 µm in size (Fig. 9A-B) and are two-phase fluid inclusions with vapor/liquid ratios between 0.04 and 0.15. The eutectic temperature (T e) is around –52°C; homogenization temperatures (T h) range between 78° and 140°C (Fig. 10A). Ice melting temperature (T m(ice)) and hydrotalite melting temperature (T m(HH)) occurred between –29.9° and –20.1°C and between –25.4° and –6.0°C, respectively, resulting in an average salinity of 25.4 equiv wt % [NaCl-CaCl2] (Table 5, Figs. 9B, 10B). The Na/(Na + Ca) ratios vary between 0.55 and 0.82.

Five primary fluid inclusion assemblages (20 fluid inclusions) were measured in the core of the dolomite-ankerite crystals, which seems to be coeval with safflorite and loellingite (arsenide substage; Fig. 7B). Analyzed fluid inclusions are 5 to 12 µm in size. They are invariably two-phase liquid-vapor fluid inclusion assemblages having vapor/liquid ratios between 0.03 and 0.08 (Fig. 9C-D). Eutectic temperatures could not precisely be determined but are around –60° to –50°C. The carbonate-hosted inclusions show T e between 102° and 132°C (Fig. 10A). The few T m(ice) values that could be obtained range between –41.8° and –27.2°C, but their consistency could not be verified as only single inclusion of a fluid inclusion assemblage could be measured (Table 5). However, nucleation of hydrotalite could not be observed or deter-

### Table 4. Chemical Composition of Sulfosalts and Sulfides from the Ag-Bi-(As)-S Substage (in wt %, analyzed by EPMA)

| Mineral  | Gersdorffite | Proustite | Acanthite | Argentopyrite | Lenaite |
|----------|--------------|-----------|-----------|--------------|--------|
|          | Wt %         |           | Wt %      | Wt %         | Wt %   |
| As       | 41.4         | 44.7      | 12.3      | b.l.q.       | 0.97   |
| Ni       | 29.1         | 31.5      | 0.11      | 0.11         | 0.11   |
| Co       | 9.00        | 0.17      | 0.11      | 0.08         | 0.11   |
| Fe       | 1.27         | 3.59      | 1.41      | 0.14         | 1.67   |
| S        | 18.6         | 19.5      | 19.2      | 19.7         | 20.6   |
| Ag       | 83.7         | 85.5      | 64.1      | 65.1         | 65.9   |
| Hg       | 8.97         | 8.97      | 8.97      | 8.97         | 8.97   |
| Bi       | 0.12         | 0.74      | 0.22      | 0.22         | 0.22   |
| Cu       | 0.86         | 1.13      | 0.96      | 0.96         | 1.13   |
| Zn       | 0.11         | 0.11      | 0.11      | 0.11         | 0.11   |
| Sb       | 0.12         | 0.12      | 0.12      | 0.12         | 0.12   |
| Total    | 99.2         | 100.0     | 100.6     | 98.2         | 102.0  |

Notes: n = the number of analyses; b.l.q. = values below the level of quantification; EPMA = electron probe microanalysis.
mined due to the metastable behavior of hydrohalite in the fluid inclusions investigated; thus, reliable salinities could not be calculated.

Thermodynamic modeling

Solubility fields of uraninite and nickeline in the pH-log $f_{O_2}$ space for different U and As activities are summarized in Figure 11. Both minerals preferentially precipitate at relatively low $f_{O_2}$ and neutral pH. Even for low U concentrations (100 mg/kg U), uraninite saturation is reached at higher $f_{O_2}$ compared to that of nickeline. Consequently, even for small U/As ratios, uraninite is predicted to precipitate prior to nickeline upon reduction.

Discussion

Petrographic observations, mineral chemistry, and fluid inclusion data provide constraints for the conditions of ore formation and the time-space evolution of the Annaberg-Buchholz mineral system. Supported by thermodynamic computations, this knowledge is then used to suggest exploration vectors in U-bearing native metal-arsenide vein systems.

The native metal-arsenide (Ag-Bi-Co-Ni-As) stage

The dendritic textures of native metals and the distinctive paragenesis, including arsenides, sulfosalts, and sulfides at the Annaberg-Buchholz district, are characteristic of native metal-arsenide veins worldwide (see compilation of Scharrer et al., 2019, and references therein). The systematic trend from mono- to di- and eventually triarsenide mineral assemblages is reported from many other examples of native metal-arsenide veins, e.g., other localities in the Erzgebirge/Germany (Kuschka, 2002, Kuschka et al., 2002; Ondruš et al., 2003b; Hiller and Schuppan, 2008), the Odenwald/Germany (Burisch et al., 2017), the Harz/Germany (Cabral et al., 2017), the Schwarzwald/Germany (Staude et al., 2012), and the Anti-Atlas/Morocco (Essarraj et al., 2005; Ahmed et al., 2009; Gervilla et al., 2012). The arsenide sequence also shows a distinct chemical evolution from Ni-rich at the contact to the native elements toward Co- and Fe-rich at the rims of the arsenide aggregates (Figs. 5B, 6B-D). This zoning is similarly reported for most native metal-arsenide occurrences and has been interpreted as a result of decreasing $f_{O_2}$ during the native metal and arsenide substages (Scharrer et al., 2019).

Uraninite and coffinite, spatially associated with the native metal-arsenide stage, are mostly younger than the native metal and arsenide substages in the Annaberg-Buchholz district. At other occurrences with U in association with native metal-arsenide veins, U-bearing minerals are usually not coeval with, but pre- and/or postdate the native element and arsenide assemblages (Kissin, 1992; Staude et al., 2012). The dissolution and/or replacement of native elements (mostly Ag and As) observed in the Annaberg-Buchholz district is another common feature of native metal-arsenide veins (Scharrer et al., 2019, and references therein). Even the presence of a distinct Ag-Bi-(As)-S substage following on the typical native metal-arsenide assemblage is documented at other native metal-arsenide vein occurrences, it is usually thought to reflect a younger, more oxidizing hydrothermal overprint causing reimmobilization and proximal reprecipitation of elements of the native metal and arsenide substages (Burisch et al.,

Fig. 8. A. Iron-Co-Ni ternary diagram, showing the composition of mono-(black), di- (light gray), and triarsenides (dark gray) compositions as mole fractions. B. Sulfur and As compositions (mol %) of diarsenides (light gray) and triarsenides (dark gray). C. Ternary Ag-As-S diagram (mol %), including native silver (native Ag), acanthite, proustite, lenaite, and argentopyrite composition.
Noteworthy, the arsenides are not affected by this late-stage hydrothermal overprint, an observation that has tentatively been attributed to the kinetically hindered oxidation of arsenides.

Temperature and salinity of the metal-bearing hydrothermal fluid

Homogenization temperatures of fluid inclusions related to the fluorite-barite-Pb-Zn and native metal-arsenide stages constrain the temperature of ore formation to 78° to 140°C. Fluid inclusions hosted by fluorite predating the native metal-arsenide stage have salinities between 21.9 and 27.7 equiv wt % (NaCl-CaCl₂). The observed temperature and salinity range is consistent with fluid inclusion data from the arsenide substage and associated fluorite-barite-Pb-Zn stage at other localities in the Erzgebirge (e.g., Jáchymov, Ondruš et al., 2003b; Schneeberg, Lipp and Flach, 2003; Schlema-Alberoda, Hiller and Schuppan, 2008; Niederschlag, Kuschka et al., 2002; Haschke et al., 2021), and native metal-arsenide vein occurrences in Europe and elsewhere (e.g., Schwarzwald/Germany, Staude et al., 2007, 2012; Odenwald/Germany, Burisch et al., 2017; Bou Anzer/Morocco, En-Naciri et al., 1997; Essaraj et al., 2005; Cobalt-Gowganda and Great Bear Lake/Canada, Changkakoti et al., 1986; Kerrich et al., 1986; Marshall et al., 1993). It is important to note that salinities of >20 wt % appear to be a prerequisite for the formation of native metal-arsenide assemblages, whereas temperatures of ore formation may vary from 100° to 450°C (Kissin, 1992; Scharrer et al., 2019).

Mixing and reduction of the ore fluid

Evidence provided by this study identifies fluid mixing as well as localized reduction as relevant ore-forming processes in the Annaberg-Buchholz district. Recent studies have shown reduction to be the most critical physicochemical process to induce precipitation of native element arsenide assemblages from metal-bearing hydrothermal fluids (Markl et al., 2016; Burisch et al., 2017; Scharrer et al., 2019). In the case of the Annaberg-Buchholz district, the direct spatial relationship between graphite-rich horizons and U as well as native metal-arsenide mineralization (Fig. 2) strongly supports that the local presence of a reductant is a critical parameter for ore formation. Reduction of the metal-bearing hydrothermal fluid may have been due to (1) fluid-rock interaction with graphite, (2) fluid-fluid reaction of the metal-bearing fluid with fluids that equilibrated with the graphite-rich horizons prior to mixing, and/or (3) fluid-gas interaction involving hydrocarbons associated with the graphite-rich horizons. Unfortunately, robust evidence to identify the exact mode of reduction is lacking as attempts to detect hydrocarbons with Raman spectroscopy in carbonates were unsuccessful.

The mixing of two aqueous fluids, on the other hand, is identified as the most relevant ore-forming process for the fluorite-barite-Pb-Zn stage (fluorite I). The scatter in salinity
Table 5. Summary of Fluid Inclusion Data Analyzed in Fluorite I (fluorite-barite-Pb-Zn stage), Dolomite-Ankerite (native metal-arsenide stage, arsenide substage)

| Sample | Section | Host mineral | FIA number | Number of FI | Liquid fraction average (°C) | T<sub>f</sub> average (°C) | T<sub>mel</sub> range (°C) | T<sub>mic</sub> range (°C) | T<sub>sub</sub> range (°C) | Salinity range [equiv wt % (NaCl–CaCl₂)] | Na/(Na + Ca) ratio range (molar) |
|--------|---------|--------------|------------|--------------|-------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------------------|----------------------------------|
| Fluorite–Barite–Pb–Zn stage | 62877 C | Fluorite | 12 | 8 | 0.92 | ~–52 | 25.2 to 20.1 | -24.4 to -12.1 | 104 to 117 | 21.9 to 26.2 | 0.76 to 0.82 |
|       | 62877 D | Fluorite | 8 | 12 | 0.92 | ~–52 | 22.1 to 20.6 | -24.9 to -24.3 | 107 to 124 | 22.1 to 22.9 | 0.75 to 0.79 |
|       | 62877 D | Fluorite | 9 | 9 | 0.90 | ~–52 | 25.0 to 21.4 | -24.2 to -21.8 | 104 to 115 | 24.6 to 25.1 | 0.75 to 0.78 |
|       | 62877 D | Fluorite | 10 | 6 | 0.90 | ~–52 | 22.2 to 21.1 | -24.7 to -24.4 | 96 to 109 | 22.4 to 23.1 | 0.76 to 0.78 |
|       | 62877 D | Fluorite | 9 | 5 | n.d. | ~–52 | 26.4 to 25.2 | -13.9 to -10.4 | 96 to 108 | 26.0 to 26.6 | 0.70 to 0.76 |
| 62893 F | Fluorite | 1 | 5 | n.d. | ~–52 | 25.9 to 25.5 | -18.9 to -14.3 | 101 to 120 | 25.7 to 26.2 | 0.71 to 0.74 |
| 62893 F | Fluorite | 2 | 8 | n.d. | ~–52 | 25.7 to 25.6 | -14.4 to -13.6 | 99 to 113 | 26.0 to 26.2 | 0.73 |
| 45819 | Dolomite–ankerite | 1 | 9 | n.d. | ~–52 | 25.3 to 24.8 | -25.4 to -24.4 | 95 to 122 | 24.5 to 24.9 | 0.71 to 0.75 |
| 45819 D | Dolomite–ankerite | 2 | 5 | n.d. | ~–52 | 24.3 to 22.6 | -25.0 to -24.6 | 109 to 120 | 23.3 to 24.2 | 0.74 to 0.77 |
| 45945 E | Fluorite | 1 | 3 | n.d. | ~–52 | 26.2 to 25.9 | -13.7 to -11.2 | 111 to 117 | 26.2 to 26.6 | 0.71 to 0.72 |
| 45945 E | Fluorite | 2 | 9 | n.d. | ~–52 | 26.0 to 25.2 | -13.2 to -11.4 | 113 to 119 | 26.2 to 26.4 | 0.72 to 0.76 |
| 45945 E | Fluorite | 3 | 9 | n.d. | ~–52 | 26.1 to 25.6 | -15.0 to -10.6 | 106 to 130 | 25.9 to 26.6 | 0.71 to 0.73 |
| 45822 B | Fluorite | 1 | 6 | n.d. | ~–52 | 27.7 to 26.9 | -11.9 to -6.0 | 100 to 130 | 26.7 to 27.3 | 0.65 to 0.67 |
| 45822 B | Fluorite | 2 | 6 | n.d. | ~–52 | 29.9 to 26.9 | -13.3 to -6.8 | 104 to 140 | 28.6 to 27.7 | 0.55 to 0.67 |
| 45822 G | Fluorite | 1 | 6 | n.d. | ~–52 | 26.9 to 25.3 | -11.4 to -9.0 | 84 to 117 | 26.3 to 26.9 | 0.68 to 0.76 |
| 45822 G | Fluorite | 2 | 7 | n.d. | ~–52 | 26.8 to 25.8 | -13.3 to -9.0 | 75 to 109 | 26.3 to 26.9 | 0.68 to 0.73 |

Native metal–arsenide stage (arsenide substage)

| Sample | Section | Host mineral | FIA number | Number of FI | Liquid fraction average (°C) | T<sub>f</sub> average (°C) | T<sub>mel</sub> range (°C) | T<sub>mic</sub> range (°C) | T<sub>sub</sub> range (°C) | Salinity range [equiv wt % (NaCl–CaCl₂)] | Na/(Na + Ca) ratio range (molar) |
|--------|---------|--------------|------------|--------------|-------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------------------|----------------------------------|
| 8066 B | Dolomite–ankerite | 1 | 4 | n.d. | n.d. | n.d. | n.d. | 116 to 125 | n.d. | n.d. |
| 8066 B | Dolomite–ankerite | 2 | 5 | n.d. | ~–52 | 27.2 | n.d. | 108 to 132 | n.d. | n.d. |
| 8066 J | Dolomite–ankerite | 1 | 3 | n.d. | n.d. | n.d. | n.d. | 104 to 132 | n.d. | n.d. |
| 8066 K | Dolomite–ankerite | 1 | 3 | 0.94 | n.d. | n.d. | n.d. | 100 to 105 | n.d. | n.d. |
| 8066 C | Dolomite–ankerite | 1 | 5 | 0.93 | ~–52 | 41.8 and -38.6 | n.d. | 117 to 120 | n.d. | n.d. |

Notes: The lack of information and the temperatures, which could not be measured for some fluid inclusions, are indicated with n.d. (no data)
[21.9–27.7 equiv wt % (NaCl-CaCl₂)] and the variation of Na/ (Na + Ca) ratios (0.55–0.82) of fluid inclusions provide ample evidence for this suggestion and is consistent with genetic models for comparable fluorite-barite-Pb-Zn mineralization across Europe (Boiron et al., 2010; Fusswinkel et al., 2013; Walter et al., 2016; Haschke et al., 2021).

The presence of multiple fluorite stages, both older and younger than the native metal-arsenide stage in the Annaberg-Buchholz district, indicates that episodic fluid mixing persisted for a relatively longtime span. It remains unclear, though, why only in a relatively short paragenetic window, the conditions were favorable to precipitate U-bearing native metal-arsenide mineralization. Another observation that highlights the transient and singular nature of the “native metal-arsenide window” is the lack of multiple generations of native metals and arsenides, an observation that has also been documented in most other native metal-arsenide vein occurrences (Kissin, 1992; Burisch et al., 2017; Scharrer et al., 2019).

The time-space evolution of the Annaberg-Buchholz district

The vertical zoning observed in the Annaberg-Buchholz district is related to polyphase first- and second-order processes that are mainly caused by contrasts in redox sensitivities of U and As causing selective polyphase hydrothermal remobilization. The paragenetically oldest U mineralization in the district, the quartz-calcite-uraninite stage (U1), reflects the primary introduction of uranium into the Annaberg-Buchholz vein system. The textural observations from nearby deposits (e.g., Schlema-Alberoda) suggest that dissolution and precipitation of U1 uraninite results in the endowment of U in the U2 dolomite-uraninite-fluorite stage (Schuppan et al., 1994; Hiller and Schuppan, 2008; Romer and Cuney, 2018). This remobilization caused redistribution of U toward shallower depths within the veins, where the graphite-rich gneiss is present (Hösel et al., 1997; Kuschka et al., 2002). Fluorite-barite-Pb-Zn mineralization is apparently not controlled by the host-rock composition and thus, the fluorite-barite-Pb-Zn stage is not concentrated at specific depths but occurs throughout the entire vertical profile. The occurrence of the native metal-arsenide assemblage from 20 to 350 m b.g.s. can also directly be linked to the reduction of the ore-fluid by the interaction with the graphite-rich gneiss, preferentially at the intersection with the mineralized late Paleozoic NE-SW-oriented veins.

Although the uraninite of U3 is spatially associated with the native metal-arsenide stage, petrographic observations and thermodynamic considerations indicate that these two stages are genetically unrelated. If Ni, Co, As, and U would have been transported in the same ore fluid, the U3 uraninite should have been, due to the higher redox sensitivity of U, precipitated earlier and deeper than Co-Ni arsenides at a vein scale (Fig. 2). Yet, the opposite can be observed in some of the veins. Thus, the U3 mineralization must be regarded as a separate hydrothermal event that is not, as previously assumed by Kuschka et al. (2002), related to the native metal-arsenide stage. More likely, the native metal-arsenide stage reflects a shallower analogue of the U2 stage, which would be consistent with thermodynamic considerations predicting that uraninite was initially precipitated earlier/deeper than the arsenides in the vein system. This is furthermore supported by the similar mineralogy of the associated gangue minerals of...
both the native metal-arsenide and the U2 stages (Schuppan et al., 1994). Yet, unequivocal textural and/or geochronologic evidence for a genetic link between U2 stage and the native metal-arsenide stage is still lacking.

The U3 stage rather seems to coincide with the formation of Ag sulfides and sulfosalts of the Ag-Bi-(As)-S substage related to late hydrothermal remobilization of previous mineralization stages. Remobilization of native elements and uraninite of U1 and U2 requires fluids that are more oxidizing than the fluids related to the native metal and arsenide substages (Figs. 6F, 7B-D; Burisch et al., 2017). As these fluids were subsequently reduced when they encountered reactive rock or methane in the upper parts of the graphitic gneiss, Ag sulfides, sulfosalts, and uraninite (U3) eventually precipitated close to the present-day surface. The wide range in U-Pb ages from 120 ± 6 to 7 Ma of U3 uraninite (Schlema-Alberoda district, Schuppan et al., 1994, based on Tugarinov et al., 1967 and Veličhkin et al., 1983; Förster and Haack, 1995) indicates that the process of remobilization continuously or discontinuously prevailed over a long period of time. Remarkably, arsenides are not affected by the late-stage overprint and thus remain as relics at their original vertical position. This is further confirmed by thermodynamic computations (Fig. 11) that predict that Co-Ni arsenides precipitate later and shallower as compared to uraninite when the ore fluid encounters a reactive barrier, i.e., a suitable source of reducing constituents such as CH₄. This would imply that the position of the Co-Ni arsenides marks the (initial) top of the mineralization, which in turn suggests that major U mineralization should have initially been located below this arsenide cap. The present-day architecture in some of the veins of the Annaberg-Buchholz district is thus a result of a long-lasting polyphase hydrothermal history (at least 250 Ma), which includes multiple events of ore formation and subsequent (selective) remobilization.

Conclusions

The native metal-arsenide (five-element) veins in the Annaberg-Buchholz district show many typical characteristics, including mineral assemblages, textures, and fluid inclusion systematics that have been reported of native metal-arsenide veins, elsewhere. Formation of native metal-arsenide veins at the Annaberg-Buchholz district is tentatively related to hydrothermal activity in conjunction with the continental rifting associated with Mesozoic extensional tectonics, as has previously been proposed for other unconformity related vein deposits in Europe. Local precipitation of the native metal-arsenide assemblage can be attributed to structural factors and host-rock-controlled reduction of the hydrothermal fluid. Uranium was introduced into the system at an early stage (quartz-calcite-uraninite stage, U1), with subsequent stages of hydrothermal mineralization only remobilizing and reconcentrating the U tenor. In response to repeated remobilization, U was transferred to shallower depths and reconcentrated in the immediate vicinity of the graphite-rich gneiss units, which comprise the only suitable reactive barrier in the system. Whereas native metals of the native metal-arsenide stage are also extensively dissolved by late-stage hydrothermal overprinting, arsenides are the ore minerals most resistant to remobilization. The vertical zonation observed in some of the veins of the Annaberg-Buchholz district is thus a result of a long-lasting polyphase hydrothermal history (at least 250 Ma), which includes multiple events of ore formation and subsequent (selective) remobilization.

Acknowledgments

The authors would like to thank two anonymous reviewers, whose constructive comments improved a former version of this manuscript significantly, and Lawrence Meinert for the editorial handling. We are grateful to Christin Kehrer for access to the geoscientific collections of the Technische Univer-
sität Bergakademie Freiberg and for help during the selection of samples. We thank Marc Schwan and the team of the Markus Röhlung mine in Frohnau (Annaberg-Buchholz) for giving us access to the underground vein exposures, providing valuable information and support during sampling. Roland Würkert, Andreas Bartzsch, and Michael Stoll are thanked for the sample preparation at the Helmholtz Institute Freiberg for Resource Technology. We also thank Sabine Gilbricht (Technische Universität Bergakademie Freiberg) for support with the SEM. Michael Schaling is thanked for providing photographs of underground exposures. This project was partly funded by the European Social Fund and the Federal State of Saxony (Project 100339454 received by M. Burisch).

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