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Evolution of a hydrothermal fluid-rock interaction system as recorded by Sr isotopes: A case study from the Schwarzwald, SW Germany

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a) Deceased. This paper is dedicated to the memory of Prof. Borwin Grauert

Abstract

Metasomatic and Sr-isotopic changes, associated with formation of zoned alteration halos along hydrothermal veins, are documented for a gneiss from the Artenberg quarry near Steinach (Kinzigtal, Schwarzwald, SW Germany). Veins are postorogenic, SW-NE-oriented, and cut straight through metaquartzdioritic Variscan gneiss, where flow of low-temperature fluids (~100-200°C) caused adularia-quartz-sericite-type alteration. Fluid-rock interaction occurred nearly 50 Ma after Variscan metamorphism, as constrained by a Rb-Sr multimineral isochron for unaltered gneiss of 327.1 ± 3.1 Ma, and by two independent ages of 279.2 ± 3.1 Ma and 274 ± 13 Ma, based on Rb-Sr systematics of late-stage quartz from the veins. In a profile from unaltered gneiss towards a vein, alteration-induced mineralogical changes correlate with metasomatic net addition of K, Rb, and Cl to the alteration zone, combined with net loss of Na, Ca, and Sr. Strontium isotopes give a more detailed insight into the fluid-rock interaction process. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in a profile across the alteration zone are incompatible with simple Sr leaching but reflect partial replacement of the rocks' Sr by fluid-derived Sr, the isotopic composition of which varied with time. Early fluids, with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to unaltered gneiss, evolved into fluids with somewhat lower ratios, and finally reached a second maximum in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This Sr-isotopic fluid evolution is equally revealed by the mineral sequence of the vein mineralization. It appears that the compositional evolution of the fluids correlates with the sequence of mineral breakdown reactions in the gneissic host rock, and that the Sr-isotopic evolution of the fluids can be fully explained as the result of internal, progressive reaction of fluid with the local rocks. Results also show that the spatial distributions of Sr isotopes in metasomatic alteration zones may reflect the complex evolution of fluid-rock interaction systems, and ultimately constrain the factors controlling both fluid compositions and alteration patterns.

Introduction

Hydrothermal systems play a key role in the interaction between the geo- and hydrosphere. They facilitate fluid flow and fluid-rock interaction at elevated temperatures in the upper crust, and give rise to a variety of petrologically and economically important effects. Among these are the formation of hydrothermal ore deposits, metasomatic enrichment or depletion of elements in the crust by reactive fluid flow, mineralization and weakening of fault zones, or maintenance of potentially exploitable geothermal anomalies, to name a few. A large number of attempts have been made to trace fluid sources, to get insight into the processes driving fluid flow, and to decipher the factors controlling the formation, evolution and chemical fluid-rock interaction history of hydrothermal systems. Commonly applied tools include chemical and petrological characterization of altered rock and vein precipitates, fluid inclusion analysis, analysis of fluids in active systems, analysis of stable isotopes, and K-Ar-based geochronology. In contrast, the number of studies employing Sr isotopes and the Rb-Sr decay system to investigate the evolution of hydrothermal systems is fairly limited. This is surprising given that Sr isotopes offer the potential to trace fluid compositions, element redistribution, and to obtain absolute age constraints.

The Schwarzwald, SW Germany, is an area well-known for its abundance of hydrothermal veins. The veins are developed within gneisses and granitoids of the Variscan high-grade crystalline basement, and partly also affect Mesozoic sedimentary cover sequences. In an area of roughly 100 x 40 km, more than 400 individual vein occurrences have been described, a number of which have been intermittently mined since at least medieval times (Metz et al. 1957; Bliedtner and Martin 1986). Many of these veins were studied in detail and by various means, so that some knowledge on tectonic regimes during fluid activity, on fluid properties, mineralization styles, and wallrock alteration already exists (e.g., Baatarsoigt et al. 2007 and references therein). Earlier Sr isotope investigations on hydrothermal vein minerals of the Schwarzwald (Hofmann and Baumann 1984; von Gehlen et al. 1984; Baumann and Hofmann 1988) as well as Pb isotope studies (Lippolt et al. 1983a) have shown that considerable variations in isotopic compositions occur, both within and between different veins. Notably, Baumann and Hofmann (1988) found systematic variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in a profile across a multistage, m-wide vein of the Clara mine, Central Schwarzwald. These results highlight the isotopic variability of the transient fluids in hydrothermal Schwarzwald veins, and indicate that a vein system cannot be characterized by a single, characteristic isotopic signature. The results have been claimed to indicate either a local origin of vein precipitates, or advection of different fluids from different local 'source rocks'. However, the reasons for this isotopic variability and, in particular, the isotopic evolution of individual hydrothermal systems remained unclear. Strontium- and Pb-isotopic variability may, in some Schwarzwald vein systems, be due to repeated reactivation at different times. In particular for the Clara mine veins such repeated reactivation from Permian to Jurassic times has been described (Bonhomme et al. 1983; Lippolt et al. 1986; Mertz 1987). Here we present Sr isotopic data for a hydrothermal vein system exposed in the Artenberg quarry, Kinzigtal, central Schwarzwald (Fig. 1). Field observations suggest that this system was formed in a single-stage hydrothermal event. We investigate the Sr isotopic composition of minerals of the vein mineralization sequence, and also study the distribution of Sr isotopes across the related metasomatic alteration halo. Isotopic data are combined with data on modal rock compositions, and with geochemical data on metasomatic effects. We show that Sr

isotopes may not only serve as a tracer for fluid composition and fluid origin, but that the spatial variation of Sr isotopic compositions across metasomatized zones and related veins may delineate the evolution of hydrothermal fluid-rock interaction systems through time.

Another key information required to understand the formation and evolution of hydrothermal systems is precise age data for the mineralizations. In particular in areas with polystage hydrothermal activity, time constraints are essential to construct temporal and genetic links between mineralization stages and potential regional-scale geologic controls on fluid movements. Hydrothermal mineralizations only occasionally include phases which can be routinely employed for isotopic dating by standard techniques (like white mica using K-Ar and Rb-Sr; e.g., Blisniuk et al. 2001; or adularia using $^{40}\text{Ar}/^{39}\text{Ar}$; e.g., Mauk and Hall 2004). In absence of phases suitable for direct isotopic dating, techniques like K-Ar analysis of illite-rich clay from vein wallrocks (Halliday and Mitchell 1983; Clauer and Chaudhuri 1995) or evaluation of binary Rb-Sr isotopic paleomixing lines (Haack and Lauterjung 1993; Schneider et al. 2003) have been applied with mixed success. Additional options for isotopic dating of low temperature hydrothermal mineralizations would thus be desirable. Quartz, which is among the most abundant phases in hydrothermal mineralizations, has recently attracted interest for its U-Pb systematics, particularly in cryptocrystalline varieties, as a potential geochronometer (Amelin and Back 2006; Neymark and Amelin 2008). Rb-Sr systematics of quartz and of fluid inclusions in quartz appears to be a promising but underevaluated approach (Shepherd and Darbyshire 1981; Pettke and Diamond 1995). Here we show that Rb-Sr dating of epithermal mineralizations by means of the Rb-Sr system of quartz and its inclusions is feasible.

Geological Setting

Samples for this study were collected from a hydrothermal vein crosscutting the Central Schwarzwald Gneiss Complex (CSGC). This complex, forming part of the Moldanubian Zone of the Paleozoic Variscan orogen of Europe (Fig. 1), is dominated by high-grade gneisses and migmatites, of both metaigneous and metasedimentary origin. Within the complex, several units can be distinguished, characterized by lithological peculiarities and by different early metamorphic histories involving early granulite and eclogite facies stages (Kalt et al. 2000). The entire CSGC is interpreted as the lower crust of an upper plate in a Variscan collisional setting (Marschall et al. 2003). The complex experienced a final, high-temperature, low-pressure metamorphism with P,T conditions of around 750°C and 0.4-0.5 GPa (Kalt et al. 2000). This metamorphism marks the transition from a tectonic regime of collisional shortening to horizontal extension (Echtler and Chauvet 1992). The time frame for the transition from shortening to extension is set by U-Pb zircon SHRIMP data at 335 ± 2 Ma for a HP-HT granulitic stage in the northern part of the CSGC (Kober et al. 2004), and age data for the Albtal granite south of the CSGC (334 ± 3 Ma, U-Pb zircon data, Schaltegger 2000). The Albtal granite is interpreted to intrude into a normal fault zone, implying an extensional tectonic regime at the time of intrusion (Echtler and Chauvet 1992). U-Pb monazite data constrain an age of 335-330 Ma for the final Variscan metamorphism of the CSGC (Kalt et al. 1994). The Scharfenstein rhyolite, a volcanic rock overlying the southern parts of the CSGC, has been dated at 333 ± 3 Ma (U-Pb, zircon,

Schaltegger 2000). This consistent dataset implies that the entire CSGC was exhumed to an upper crustal level and largely cooled at or shortly after 330 Ma.

Several generations of hydrothermal veins cut the CSGC gneiss basement. Veins are distinguished into two groups, based on mineralogical, structural and fluid inclusion characteristics (Blüedtner and Martin 1986, Behr and Gerler 1987, Markl et al. 2006). 'Variscan' veins are often quartz-dominated, and relate to late stages of the Variscan thermal evolution or to late-Variscan granitoid intrusions. In contrast, 'post-Variscan' veins are quartz-fluorite-barite-calcite veins, with variable contents and assemblages of base metal phases. The timing of hydrothermal activity is not well constrained, mostly due to a lack of geochronologically useful phases in most veins. According to the published ages of hydrothermal activity in the Schwarzwald, brittle deformation and vein formation occurred repeatedly, from the lower Permian to the Cenozoic. Distinction between hypothetical 'regional hydrothermal events' is difficult with the current database. Nevertheless, the timing of hydrothermal activity in the Schwarzwald appears to conform with the major episodes of hydrothermal mineralization in Variscan Western Europe as identified by Romer et al. (in press): A first, distinct Early Permian (~280-270 Ma) pulse is represented in the Schwarzwald, e.g., by K-Ar data for early adularia of two mining sites in the Kinzigtal (Clara and Friedrich Christian; Lippolt et al. 1986), and by Early Permian ages for uranium mineralizations (Wendt et al. 1979, Hofmann and Eikenberg 1991). Upper Triassic mineralization stages (~230-200 Ma) in the Schwarzwald were found, using K-Ar, Rb-Sr and (U,Th)/He methods, in the Clara mine and for a number of faults in the area (Lippolt et al. 1986, Mertz 1987, Wernicke and Lippolt 1997a). Mineralization events occurred time after time through the Jurassic and Early Cretaceous (Segev et al. 1991, Wernicke and Lippolt 1997b). After a period of near-inactivity, vein formation resumed with the establishment of the Alpine stress field and initiation of faults related to the formation of the Rhine graben in the Cenozoic.

The hydrothermal veins in the Artenberg quarry near Steinach/Kinzigtal have first been investigated in detail by Waldeck (1970). From this quarry exploiting metaquartzdioritic rocks, several types of veins are known. An early set of veins is calcite-dominated. It shows skarn-like mineral reactions indicating P-T conditions near 450°C, 2 kbar, with formation of wollastonite-bearing calcsilicate assemblages (Markl 1999). A later generation of non-metamorphic, quartz-calcite-dominated veins is more abundant. These veins, which form the subject of the present study, show sulphides of Ag, Sb, Zn, Pb, Cu, and As, as well as various carbonate phases, K-feldspar (adularia), TiO₂ phases (predominantly anatase), and fluorite (Waldeck 1970; also observed by the authors). Typical individual vein widths are between 1 and 10 cm. In places, individual veins merge into m-wide mineralized zones with the appearance of hydrothermal breccias. Veins are oriented SW-NE, and presumably are part of a large vein system which can be traced for several km across the Kinzig valley (Fig. 1). The observed absence of crosscutting relationships between different post-Variscan veins, suggests that the veins are the result of a possibly prolonged but single-stage mineralization event. The veins typically show cm- to dm-wide alteration aureolas in the surrounding gneiss, as described below.

Sampling

Samples STE-3, STE-4, and STE-5 were collected from a single huge block of gneiss, almost in-situ, in the southwestern part of the Artenberg quarry near Steinach, Kinzigtal, Schwarzwald (48.292238°N, 8.060199° E; Fig. 1) whereas sample STE-6 originates from an outcrop at ~30 m distance. In this part of the quarry, subparallel veins were tightly spaced forming a continuous belt of locally merging, but not mutually crosscutting fluid pathways. This suggests that all samples belong to the same vein system. STE-3 and STE-4 are cm-wide veins with gneissic host rock. Sample STE-5 is vein material from a local, pocket-like widening of the vein. It shows abundant microcrystalline quartz (chalcedony). Sample STE-6 presents an open cavity lined with calcite, which is decorated by mm-sized, brownish ankerite crystals.

Petrography, and conditions of fluid-rock interaction

Gneiss of the Artenberg area is lithologically fairly homogeneous, medium grained, and shows meta-quartzdioritic bulk composition. Pristine gneiss is composed of plagioclase (An₃₃; ~55 Vol.%), quartz (22%), biotite (17 %), K-feldspar (4 %), chlorite (rare), sericite (rare), apatite (0.4 %), zircon, monazite, and magnetite. Alteration halos, with cm- to dm widths, occur along hydrothermal veins (Fig. 2). The alteration halos are complexly zoned and composed of quartz, chlorite, plagioclase-An₃₃ (relicts), albite, calcite, K-feldspar, sericite, clay minerals, apatite, monazite, hematite, anatase, and very fine grained, Ti-rich aggregates (leucoxene). Sample STE-3 presents typical aspects of a vein-related alteration halo (Fig. 2). Approaching the vein from the domain of pristine gneiss, the earliest noticeable effect of fluid-rock interaction is first incipient chloritization ('bleaching') of biotite, followed by progressive chloritization of biotite combined with growth of hematite and leucoxene. These processes give rise to a propylitization domain as the outermost zone of the alteration halo (Fig. 2). Inwards, complex mineralogical changes are observed involving growth of sericite and albite at the expense of Ca-Na feldspar, crystallization of K-feldspar –sericite intergrowths, progressive impregnation of the rock with calcite and locally sulfides (pyrite predominating), and breakdown of magnetite (schematically shown in Fig. 3). In the interior parts of this sericitization domain, even chlorite is partially replaced by sericite. Towards the vein, the innermost zone of the alteration halo is a domain of potassic alteration characterized by abundant growth of K-feldspar.

Quartz shows increasing abundance of fluid inclusions towards the inner parts of the alteration halo. The only phases that appear to persist unchanged are apatite and zircon. The above zoning is characteristically developed symmetric to veins. However, the zoning is asymmetric in our sample STE-3 (Fig. 2), with intense potassic alteration to the right of the vein, due to the nearby presence of another fluid pathway.

Zoning is similarly observed within the vein itself (Fig. 3). Typically, the salband is formed by coarse-grained quartz, often as mm-sized clear crystals (quartz I). This first precipitate is overgrown by a calcite-rich domain, followed towards the vein interior by a second, later generation of quartz which is often inclusion-rich and cryptocrystalline (quartz II). Etching of vein samples commonly reveals a 'layer-like' appearance of quartz II. Reasons for the different morphologies of quartz I and quartz II remain unclear. Morphological variability possibly reflects different concentrations of SiO₂ in the fluid during precipitation (e.g., Glover and Mrocek 1998)

Latest precipitates are Fe-bearing carbonates (ankerite), which in open cavities decorate both quartz II and calcite.

Alteration conditions can be deduced from the above assemblages and mineral reactions in the alteration zone and in the vein mineralization. The rock alteration zone shows coexistence of chlorite, hematite, pyrite, K-feldspar, sericite (muscovite), and clay minerals (possibly kaolinite). This points to an epithermal, adularia-sericite type of alteration (Heald et al. 1987), which is characterized by near-neutral pH conditions (Fig. 4).

Stable isotope data (C, O, S) on vein minerals of post-Variscan Artenberg veins were interpreted to show that most likely the vein minerals were formed in an open system, at near-hydrostatic pressures, by mixing of fluids equilibrated with the host gneisses at depth (saline brines) with meteoric water (Schwinn et al. 2006, Baatartsogt et al. 2007). According to fluid inclusion data, Artenberg vein minerals were precipitated from highly saline fluids (~20 to 30 wt.% NaCl equivalent), at temperatures of ~90 to 200°C (Baatartsogt et al. 2007). These conditions are characteristic for many other similar vein systems from the Schwarzwald (Behr and Gerler 1987, Behr et al. 1987, Baatartsogt et al. 2007).

Analytical procedures

Mineral separation for Rb–Sr analyses was carried out, after careful mineralogical characterization of the samples, with respect to mineral assemblages (in pristine and altered gneiss) and to mineralization stages within the veins. Gneiss samples used for mineral separation were small (~50 g) in order to minimize the risk of isotopic gradients within the samples. Crushing was performed in a steel mortar followed by mineral enrichment using organic heavy liquids and a FRANTZ magnetic barrier separator. With the exception of one biotite fraction, which was purified only by hand-picking, sheet silicates (biotite, chlorite) were ground in pure ethanol in an agate mortar and then sieved in ethanol to obtain inclusion-free separates. Quartz samples were first treated with concentrated hot HCl to remove carbonate and contaminants. In case of the presence of feldspar in the quartz separates, the quartz was repeatedly leached with hexafluorosilicic acid (cf. Syers et al. 1968) in order to ensure quantitative removal of feldspar prior to analysis. Minerals from vein mineralizations were mechanically isolated, using saws and a microchisel, to control the position of a specific sample in the mineralization sequence. All mineral separates were finally checked and purified by hand-picking under a binocular microscope. Whole rock samples were powdered in a vibratory disc mill with WIDIA inset. For isotopic work, all Rb and Sr concentrations were determined by isotope dilution, using a set of mixed ^{87}Rb – ^{84}Sr spikes. Strontium analytical data were generated on a VG Sector 54 multicollector thermal ionization mass spectrometer (TIMS) at ZLG, Institut für Mineralogie, Münster University, in dynamic multicollection mode. The value obtained for $^{87}\text{Sr}/^{86}\text{Sr}$ of the NBS standard SRM 987 was 0.710254 ± 0.000010 (2σ , $n = 25$). Rb was measured on a TELEDYNE SS 1290 single-collector TIMS instrument. The observed Rb isotopic ratios were corrected for 0.25% per amu mass fractionation. Isotopic data for Rb and Sr are corrected for typical procedural blanks of 0.01 ng (Rb) and 0.05 ng (Sr), respectively. Blank

contributions to sample data are either negligible, or accounted for in the estimates of analytical uncertainties. Quoted errors for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios comprise $2\sigma_m$ analytical errors, uncertainties in the spike composition, and uncertainties introduced by the blank correction. Isochron parameters were calculated using the Isoplot/Ex program of Ludwig (1999), and a decay constant of $1.42 \cdot 10^{-11} \text{ a}^{-1}$ for ^{87}Rb , as recommended by Steiger and Jäger (1977). Standard errors of $\pm 0.007\%$ for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and of $\pm 1.5\%$ for Rb/Sr ratios, as derived from replicate analyses of spiked samples, were applied in isochron age calculations (cf. Kullerød, 1991), except for the rare cases where determined analytical uncertainties were higher than these values. Uncertainties for the isotope and age data are quoted at the 2σ level throughout this work.

X-ray fluorescence (XRF) analyses were carried out at the Institut für Mineralogie, Münster University using standard techniques on fused glass beads prepared by 1:6 dilution with lithiumtetraborate (major elements) and on pressed powder pellets (trace elements). Samples were analysed using a Siemens SRS 200 sequential X-ray spectrometer.

Results

Chemical composition: gneiss and metasomatized zone

Alteration-related changes in chemical rock composition are documented in sample STE-3. Slabs of a profile across that sample (slabs a to h in Fig. 2) were analyzed. Data are presented in Table 1. In general, rock composition varies in line with the visible alteration zones in the sample. In comparison to pristine gneiss, altered gneiss shows significant enrichment in K, Cl, Rb, S, and volatiles (H_2O and CO_2 , measured as loss on ignition; Table 1) as well as depletion of the rock in Na, Sr, and Ca (Fig. 5). Mobility during alteration of all other compounds is not obvious from the bulk chemical data, but cannot be ruled out.

Rb-Sr data: minerals of pristine and altered gneiss

Rb-Sr data for the minerals and pristine gneiss whole rock result in a Rb-Sr isochron age of $327.1 \pm 3.1 \text{ Ma}$ ($n = 5$, MSWD = 1.8; Fig. 6a, Table 2). To calculate this isochron age we used data only for transparent, unaltered feldspar, and discarded the data for turbid (slightly altered) feldspar which is present in small amounts, even in the unaltered gneiss.

Rb-Sr data of minerals separated from strongly altered gneiss show considerable intermineral Sr-isotopic disequilibria, and no conclusive age information for any specific event is obtained (Fig. 6b, Table 2)

Rb-Sr data: hydrothermal vein minerals, and mineralization age constraints

Sr isotopic composition of minerals from the hydrothermal vein turned out to be highly variable, with present-day $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios between ~ 0.7088 and ~ 0.7774 (Table 2). Mineral grains for analysis were sampled from different, well-defined structural positions within the vein. It appears that quartz of the second, 'late' generation partly is characterized by high Rb/Sr ratios. We thus used the Rb-Sr data for that microcrystalline, crust-like, in places pyrite-bearing quartz generation to estimate the age of the mineralization. Three aliquots of second-generation quartz from sample STE-4 define a Rb-Sr isochron age of $279.2 \pm 3.1 \text{ Ma}$ ($n = 3$, MSWD = 0.35; Fig.

6c). Data for similar quartz from sample STE-5 reveal slight Sr-isotopic disequilibria. Nevertheless, STE-5 data define a regression line corresponding to an age of 274 ± 13 Ma ($n = 4$, MSWD = 96, Fig. 6d), consistent with the above 279.2 ± 3.1 Ma isochron age. We therefore adopt an age of ~ 279 Ma as the most reasonable age of vein formation. Assuming that this age estimate is correct, the initial Sr isotopic composition of different vein minerals at the time of crystallization in equilibrium with the fluids can be calculated. The results of this calculation for $t = 279$ Ma are shown in Fig. 7. It appears that the Sr-isotopic composition of the fluid precipitating in the vein mineralization sequence varied drastically during the evolution of the hydrothermal system, with values of $^{87}\text{Sr}/^{86}\text{Sr}$ between <0.7088 (calcite, sample STE-3) and >0.7155 (late-stage ankerite, sample STE-6).

Rb-Sr data: profile across vein-related alteration zone

A profile across sample STE-3, consisting of 26 slabs (see Fig. 2), sliced through the transition from unaltered gneiss to altered gneiss and a hydrothermal vein, was analyzed for Rb-Sr signatures. Results show that fluid-rock interaction had a strong influence on the Rb-Sr systematics of the rock. Alteration resulted in an increase in the Rb concentration and a decrease in the Sr concentration in the altered domains (Table 3, Fig. 8b). Strontium isotopic data, calculated for the time of alteration and metasomatism ($t = 279$ Ma), show that metasomatism also resulted in strongly elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the alteration zone compared to the unaltered gneiss, with maximum values near the contact to the vein. The increase of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios towards the vein is not uniformly continuous but shows an intervening decrease at slabs 17 to 19 (Fig. 8a).

Discussion

Significance of Rb-Sr age data

The Rb-Sr age obtained for pristine gneiss of 327.1 ± 3.1 Ma (Fig. 6a) is, within the limits of uncertainty, identical to the published monazite-derived U-Pb age data of the last Variscan thermal overprint at ~ 335 to 330 Ma (Kalt et al. 1994). This shows that the Rb-Sr system of the minerals analyzed here has not been affected by hydrothermal fluids. The Rb-Sr multimineral age for the pristine gneiss dates cessation of intermineral isotope exchange in the rock during the final stages of Variscan metamorphism.

The two age values obtained for the hydrothermal activity (279.2 ± 3.1 Ma for sample STE-4 and 274 ± 13 Ma for sample STE-5, Fig. 6c, d) are identical within the limits of error, which indicates that the age values are geologically significant. The quartz used for the age calculation was, for each sample, separated from the zone of second-generation quartz (quartz II) in the vein mineralization. The age data are thus based nominally on only one phase (quartz) revealing sample-to-sample differences in the Rb-Sr ratios, which needs to be explained. Quartz II in sample STE-4 is present in two different forms. Massive, microcrystalline, agate-like quartz is characterized by a low $^{87}\text{Rb}/^{86}\text{Sr}$ ratio combined with a fairly high Sr concentration (14.3 ppm, Table 2). In contrast, crust-like, whitish, porous aggregates of quartz II present reproducibly high Rb/Sr ratios, much lower Sr concentrations (near 5 ppm) and very high Rb concentrations (23 to 26 ppm, Table 2). Quartz II from sample STE-5 is present as semitransparent crystals

intergrown with pyrite and rich in fluid inclusions, and again as dense, agate-like masses. Here the agate has high Rb/Sr ratios and very high Rb (near 30 ppm), whereas the crystals contain much less Rb (near 3 ppm) and high Sr (10 to 11 ppm). Quartz has a very stable crystal structure of Si-O bonds that allows for only very limited incorporation of other elements, particularly for 'large' cations. Consequently, published data for Rb and Sr in pure quartz show that both elements are usually present only in sub-ppm amounts (Nash and Crecraft 1985, Götze and Plötze 1997, Götze et al. 2004). If present in larger quantities, Rb and Sr are commonly hosted either in fluid inclusions or in tiny mineral inclusions in quartz (Rossman et al. 1987, Gerler 1990). We therefore hypothesize that the high concentrations of Rb and Sr measured in our quartz samples are predominantly hosted in various types of inclusions. Quartz II from sample STE-5 is visibly rich in fluid inclusions, so that the high Sr content from that quartz may be linked to Ca-Sr-rich brine inclusions. It was not possible to identify Rb-rich inclusions in agate-like quartz II from sample STE-5 and the quartz crusts from STE-4. Nevertheless, the very high Rb concentrations here suggest the presence of a K-Rb-rich inclusion phase, most probably sericite. Differences in Rb-Sr ratios between individual quartz samples can thus be explained by the presence of fluid and mineral inclusions in variable proportions. It appears that the variable abundance of inclusions in quartz can be used as a valuable tool in the geochronology of hydrothermal mineralizations, provided that a) the Sr-isotopic composition of the hydrothermal fluids did not change during quartz precipitation, and b) that no post-crystallization overprints (like fracturing with incorporation of secondary fluid inclusions) occurred.

However, the Sr-isotopic disequilibria between different quartz II samples (Fig. 6d) indicate that the Sr-isotopic composition of the fluid has been slightly variable during precipitation of quartz II. Further, there is a difference between the initial isotopic compositions of quartz II from the two samples (0.71406 ± 0.00008 in sample STE-4 vs. 0.71287 ± 0.00088 in sample STE-5). Quartz II from the two samples is thus not strictly paragenetic, which gives another hint concerning the variability of the fluid composition during crystallization of quartz II in the Artenberg vein system. This finding translates into some degree of uncertainty on the quartz-based age estimate for vein formation. Recalculation of isochron parameters, with allowance for a variability of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ± 0.002 , nevertheless shows that this uncertainty is similar to the error range for the age for sample STE-5 (274 ± 13 Ma) so that we consider the hydrothermal activity as reliably dated to Lower Permian times. Hydrothermal activity thus closely followed in time Variscan post-orogenic, extension-related felsic volcanism in the Schwarzwald which culminated around 286 ± 7 Ma (Lippolt et al. 1983b). The Artenberg hydrothermal system belongs to the Lower Permian episode of hydrothermal vein formation due to post-Variscan crustal extension, a process that affected vast parts of Variscan Central Europe (Romer et al. 2008 and references therein).

Due to intermineral disequilibria, no useful age data was obtained from minerals from the altered gneiss (Fig. 6b). Despite that, it is remarkable that apatite from the altered rock shows an initial Sr isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$ at 327 Ma: ~ 0.7077) identical, within the limits of error, to that of apatite from the unaltered gneiss. It appears that the conditions of hydrothermal alteration did not lead to apatite recrystallization or apatite growth, and that alteration here was mineral-selective. Even partial apatite dissolution appears unlikely, as those elements preferentially hosted in apatite (like REE and P) do not show alteration-related changes in concentration in the whole rock analysis (Table 1). Apatite can thus be considered inert at the given conditions under

which alteration occurred. This is remarkable as it is known that apatite recrystallization or dissolution in presence of fluids may occur even at near-surface conditions (Boudreau and McCallum 1990, Romer 1996).

Sr-isotopic and chemical evolution of fluids

Rb-Sr data for minerals from the hydrothermal vein, with Sr isotopic data calculated for the time of vein formation ($t = 279$ Ma) show a large variability in Sr isotopic compositions (Fig. 7). This variability reflects the Sr-isotopic variability of the mineralizing fluids, because fluid Sr signatures are preserved in the minerals. A more detailed look into the mineralization sequence and isotopic data reveals an evolutionary trend for the isotopic composition of the fluids. The salband-forming quartz I, which is the earliest vein precipitate shows initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to 0.711 (Fig. 7, Fig. 9). Calcite crystals precipitated on quartz I show consistently lower initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, varying between 0.7088 and 0.7108. This strong variability suggests that the calcite mineralization stage either consists of several generations of calcite, or was precipitated from fluids experiencing continuous changes in their Sr-isotopic composition. Optical discrimination between distinct calcite generations was impossible. Detailed insights into this calcite mineralization stage would therefore require additional investigations, like Sr-isotopic characterization of calcite growth zoning. Strontium concentrations of different calcite crystals vary between 67.8 and 502 ppm (Table 2). Because Sr incorporation into calcite at a given temperature is mainly controlled by both the Ca/Sr ratios in the fluid as well as the distribution coefficient for Sr between the fluid and calcite (~ 10 for epithermal hydrous fluids; Kolker and Chou 1994), this points to equally variable Ca/Sr ratios in the mineralizing fluids during calcite precipitation.

Quartz II, which wherever present clearly overgrows calcite, shows much higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7129 and 0.7141 (Figs. 5c, 5d, 6, 8). Initial Sr-isotopic variability between different samples of quartz II is equally high indicating that this quartz either consists of several generations or was precipitated from fluids with a continuously changing Sr-isotopic composition. Ankerite, which is the latest mineral of the vein sequence, shows the highest initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7155; Fig. 7). In summary, the results clearly show that the mineralizing fluids started with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which then went through a minimum, and were later raised to an absolute maximum at the end of the vein mineral precipitation process (Fig. 9). This trend depicts the true isotopic evolution of the fluids in only a schematic and possibly oversimplified way for two reasons. First, from observations of a number of vein precipitates from the Artenberg hydrothermal system it cannot be ruled out that a second calcite generation followed after quartz II. If such calcite II exists and if we did not miss it in sampling this would imply that the fluids went through a second minimum in their $^{87}\text{Sr}/^{86}\text{Sr}$ after quartz II precipitation. Second, the high Sr-isotopic variability during the individual stages of mineralization (e.g., of quartz II) may indicate that the above broad trend even interfered with short-term fluctuations of $^{87}\text{Sr}/^{86}\text{Sr}$ in the fluid.

The Sr isotopic heterogeneity described here is not a unique phenomenon in the Schwarzwald veins. Variable initial Sr-isotopic signatures have been described for other mineralizations e.g. in the Clara mine, Kinzigtal. They have been interpreted as indicating repeated reactivation involving different mineralizing fluids (Lippolt et al. 1986, Baumann and Hofmann 1988). In analogy to our observations, von Gehlen et al. (1984) also reported differences in $^{87}\text{Sr}/^{86}\text{Sr}$

between baryte grains from one single mineralization stage. The ultimate source of the solutes in the fluids from the Artenberg-type veins in the Schwarzwald are the local rocks of the CSGC (von Gehlen et al. 1984, Schwinn and Markl 2005, Markl et al. 2006), among which orthogneiss, paragneiss, and granitoids predominate. The observed Sr-isotopic signatures of the Artenberg vein minerals provide some clues on both the origin and evolution of the hydrothermal fluids. The documented variability in the Sr isotopic composition and the inferred variability of Ca/Sr ratios of the hydrothermal fluids indicate that different sources contributed to the solute budget of the fluids. These sources may be identified with the different lithologies of the area around the Artenberg vein. However, isotopic variability would in this context only be explained by invoking solute contributions in variable proportions from at least two, isotopically highly distinct source rocks. We regard such an explanation as unlikely because isotopic variability within hydrothermal systems appears to be the rule in the Schwarzwald veins, which is incompatible with the fairly invariable (close to granodioritic) country rock composition. Further, it must be stressed that Sr-isotopic signatures of fluids generally do *not* reflect the *bulk* isotopic composition of the rocks from which the solutes were mobilized. This is because in polymineralic rocks epithermal fluid-rock interaction is mineral-selective, meaning that not all minerals of a rock are affected simultaneously and to the same degree. This is evident also from the Artenberg alteration halo, in the outer parts of which biotite is reacted whereas feldspar only shows incipient breakdown, and in which apatite, as a major host of nonradiogenic Sr, remains unaffected. The resulting incongruent release of trace elements and isotopes during fluid-rock interaction has similarly been discussed for REE patterns and Sr-Nd-Pb signatures, which generally differ between solutes and bulk source rocks (e.g., Bach and Irber 1998, Bau et al. 2003).

Instead, the observed mineral-selective reactive decomposition of the Artenberg gneiss suggests that in fact only the phases actually reacting with or being dissolved in a transient fluid are solute sources and influence the Sr-isotopic composition of that fluid. It has been suggested before that most of the material precipitated in post-Variscan veins from the Schwarzwald region originates from the mobilization of elements in the course of local fluid rock interaction, notably from fluid-induced conversion of primary biotite and feldspar to chlorite and various sheet silicates (Schwinn and Markl 2005). Mineral-selective alteration of potential solute source rocks in the CSGC is a common phenomenon. Large volumes of rock, e.g., in the Clara mine, show intense chloritization of biotite associated with only minor feldspar alteration (Huck 1984, Maag 1991). The fluids responsible for this alteration are expected to develop into carriers of the former biotite components, like K, Mg, Fe, and Si, according to the main chlorite-forming reaction

At the time of hydrothermal activity in the Artenberg system, significant Sr-isotopic contrasts already existed between the minerals of unaltered Artenberg gneiss. A calculation of $^{87}\text{Sr}/^{86}\text{Sr}$ at $t = 279 \text{ Ma}$, based on the Rb-Sr data from Table 2, yields $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7081 for feldspar, 0.7077 for apatite, 0.7083 for bulk whole rock, and 0.7867 for biotite.

Fluids carrying a large proportion of former biotite components therefore, when migrating in a vein system, potentially caused wallrock sericitization, K metasomatism, precipitation of quartz,

or precipitation of Mg-Fe carbonates, all with comparatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Conversely, fluids that were involved in plagioclase breakdown should be enriched in Ca and Sr and show low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. We propose that these two 'model fluids', mixed in temporally variable proportions, were responsible for the precipitation of the minerals observed in the Artenberg vein. Fluids predominantly carrying plagioclase breakdown solutes may have precipitated the Sr-rich, low- $^{87}\text{Sr}/^{86}\text{Sr}$ calcite, whereas fluids rich in biotite breakdown products dominated during early and late stages of the hydrothermal system and precipitated, e.g., the low-Sr, high- $^{87}\text{Sr}/^{86}\text{Sr}$ late ankerite. It appears that the Artenberg veins are the result of a dynamically evolving fluid-rock interaction system. In the alteration halo around the Artenberg veins, fluid-rock interaction thus involved the presence of fluids, the Sr-isotopic and chemical composition of which varied through time. This variability can fully be explained by the internal evolution of the fluid-rock reaction system. Although the advection of solutes with the fluids cannot be ruled out, our data do not force us to invoke it. The mineralizing brines may have locally developed from originally solute-poor meteoric water.

Altered gneiss: complex element exchange with transient fluids

The thin slab profile for sample STE-3 (Figs. 2, 3, 7) transects from the zone of unaltered gneiss through the alteration halo around the hydrothermal vein. Chemical zoning in this profile clearly correlates with optically visible, alteration-related mineralogical changes. Enrichment of the altered zone in K and Rb (Figs. 4, 7) is accompanied by the breakdown of biotite and the crystallization of sericite (Fig. 3). Breakdown of biotite should result in K-Rb mobilization and thus potentially in the loss of these elements to the fluid. Results show that if such loss ever occurred, it was overbalanced by K-Rb gain from the transient fluids during sericite and K-feldspar crystallization. In contrast, Ca and Sr mobilization and loss to the fluids during plagioclase breakdown in the altered zone was greater than fixation of these elements by the concurrent growth of carbonates and K-feldspar. It becomes clear that element concentration profiles through alteration zones (like those of Rb and Sr in profile STE-3, Fig. 8b) only record the resulting net effects of metasomatic processes, but do not allow insights into the competing mineralogical processes controlling element release or fixation. More detailed constraints on element mobility require a combination of concentration data, mineralogical observation, and the use of isotopic tracers (cf. Farmer and DePaolo 1987).

The Sr isotopic composition along the profile STE-3 has been calculated for the time of hydrothermal activity ($t = 279$ Ma, Fig. 8a). This calculation corrects the measured Sr-isotopic composition for radiogenic ingrowth since the last geologic overprint. In our case, the result (Fig. 8a) depicts the spatial distribution of Sr isotopic compositions immediately after the end of hydrothermal activity. Details on the rationale of such calculations can be found in Bachmann and Grauert (1986) and Hradetzky and Lippolt (1993). Fig. 8 shows that alteration and metasomatism caused severe disturbance in the original, pre-alteration, Rb/Sr whole rock system. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the altered zone at 279 Ma were in general much higher (up to 0.7113) than in the pristine gneiss (near 0.7085), and show a non-monotonous increase from the pristine gneiss towards the vein with a notable inflection in the slope at slabs 17 to 19 (Fig. 8a). This general picture is robust against potential uncertainties on the age estimate for the alteration – calculations for $t = 300$ Ma and $t = 250$ Ma yield different amplitudes in the isotope distribution curve but give basically the same distribution pattern. This pattern is incompatible

with a simple, non-fractionating bulk leaching of Sr from the alteration zone, because such a scenario is not consistent with the inferred Sr-isotopic gradients in the profile immediately after the alteration event. To explain the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ in the alteration zone, preferential loss of Sr from the feldspar compared to Sr originally residing in the biotite may be invoked. However, such a hypothesis is equally implausible because mineralogical observation shows that biotite breakdown nearly went to completion in the alteration zone and that biotite breakdown is observed at an even greater distance from the vein than feldspar alteration. In the context of fluid-rock interaction and metasomatism in the alteration zone, the observed $^{87}\text{Sr}/^{86}\text{Sr}$ distribution immediately after the alteration event is best explained by a combination of different processes, the most important of which are

- Fluid-mediated mobilization and withdrawal of Sr released by biotite and feldspar breakdown
- Infiltration with fluids carrying Sr with an isotopic composition different from the composition of Sr remaining in the altered bulk rock
- Mixture of locally retained Sr from the rock, with fluid-transported Sr. In our case, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the infiltrating fluid must transiently have exceeded a value of ~ 0.7113 (slab 21 in Fig. 8a) and probably even exceeded the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the highly radiogenic Sr of late ankerite (0.7155, Fig. 7). It is important to note that such high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the local fluids can easily be explained by high proportions of Sr derived from the breakdown of biotite in the gneissic rocks nearby. The local unaltered biotite already had a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~ 0.7867 immediately prior to the alteration event at $t = 279$ Ma.
- Fixation of the isotopic mixture between locally retained and advected Sr in newly formed minerals

The Sr isotope distribution in the vein mineralization (Fig. 9) shows that vein wallrock alteration involved interaction with fluids which changed their isotopic composition through time. We hypothesize that the *spatial* distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the alteration profile correlates with and reflects this isotopic evolution of the fluids. The sequential infiltration into the alteration zone of fluids with first highly radiogenic Sr, followed by less radiogenic Sr and finally again highly radiogenic Sr (Fig. 9) may be mirrored by the outer maximum of $^{87}\text{Sr}/^{86}\text{Sr}$ at 279 Ma around slab 17 (Fig. 8a) followed by the local minimum in $^{87}\text{Sr}/^{86}\text{Sr}$ (slab 19), and the final rise to an absolute maximum in the immediate vicinity of the vein (slab 21). Such a scenario would involve continuous interaction of already altered rocks with subsequently advected fluids, as well as a persistent fluid permeability of both the vein mineralization and the altered wallrock. Irrespective of whether this scenario completely describes element redistribution processes during the metasomatic overprint – it appears that the establishment of the $^{87}\text{Sr}/^{86}\text{Sr}$ distribution during fluid-rock interaction is the result of a sequence of dynamic processes. Individual processes, like selective leaching of Sr from feldspar, can be identified but any quantification is quite difficult. Specifically, the distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the altered rock is not due to a simple two-component mixture between Sr from the fluid and Sr from the rock. Instead this distribution is controlled by a complex and nonlinear interplay between fluid properties, mineral reactions, Sr signatures in the minerals and in the fluid during reaction, rock permeability constraints, and fluid-mineral element distribution coefficients.

Conclusions

The results from this study have shown that Sr-isotopic data from vein minerals and variably metasomatized rock allow, in combination with mineralogical observation, for insights into the evolution of hydrothermal systems that go well beyond the limits of net mass balance. As outlined above, Sr-isotopic data may give hints on the sources of solutes in the fluid, on the fluid-rock interaction history, and on the timing of fluid-rock interaction. From the detailed study of the Artenberg hydrothermal-metasomatic system a number of general and specific conclusions can be drawn:

- The Artenberg hydrothermal system was active in Early Permian times, and thus likely genetically related to the Early Permian, post-Variscan crustal extension episode, which affected large parts of Variscan Central Europe. Rb-Sr data on quartz and its inclusions formed within a hydrothermal vein yield two independent and internally consistent age estimates of 279.2 ± 3.1 Ma and 274 ± 13 Ma, respectively. Unfortunately, constraints on the duration of hydrothermal activity in the Artenberg system are not available.
- Rocks that experienced epithermal fluid-rock interaction cannot be used for isotopic dating using isochron methods (like Rb-Sr or Sm-Nd) because initial isotopic equilibrium among the minerals of the altered rock is unlikely to be attained. The example of the Artenberg alteration zone shows that isotopic relics may persist through the alteration process (like apatite and zircon), that no isochron correlation is obtained for the minerals from an alteration zone (Fig. 6b), and that the initial spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in zones showing metasomatic overprints may be inhomogeneous on any scale.
- Fluids that migrated through the vein system cannot be characterized by a single specific Sr-isotopic signature. Instead, Sr signatures from the minerals precipitated in the hydrothermal vein reveal an isotopic evolution of the fluids through time. Here early fluids with comparatively radiogenic Sr evolved to less radiogenic and finally to very radiogenic Sr bearing fluids. Isotopic changes correlate with compositional changes in the fluid, as evident from the different mineral assemblages precipitated during the different isotopic stages.
- Isotopic data for C, O, and S from post-Variscan Schwarzwald veins have been interpreted to reflect mineral precipitation in the veins due to the mixing of a homogeneous deep saline brine with meteoric waters (Schwinn et al. 2006). The new Sr-isotopic data show that at least in the Artenberg example, fluids had highly variable Sr-isotopic and chemical characteristics. Because a major contribution of Sr to the hydrothermal system by meteoric fluids appears unlikely, the observed Sr-isotopic variations are an argument against the existence of an entirely homogeneous deep saline brine – at least the Sr isotopic composition evolved through time.
- Variable Sr-isotopic and other chemical signatures from the fluids most probably do not reflect different solute source rocks or different fluid sources but can be linked to specific local mineral breakdown reactions dominating during distinct fluid-rock interaction stages. Chemical and Sr-isotopic signatures from early and late stage fluids point to biotite breakdown as a major source of solutes in the fluids, whereas the intervening stage of low- $^{87}\text{Sr}/^{86}\text{Sr}$ fluids can be correlated with the dominance of feldspar (plagioclase)

conversion. The factors actually controlling the mineral-selective reactivity of the fluids and the resulting fluid evolution remain unresolved and are the subject of future research.

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Tables

Table 1 Profile of sample STE-3 (cf. Fig. 2), whole rock composition

Sample Element	STE-3.a	STE-3.b	STE-3.c	STE-3.d	STE-3.e	STE-3.f	STE-3.g	STE-3.h
SiO ₂	64.14	64.90	63.28	63.76	63.62	64.68	63.50	63.96
TiO ₂	0.67	0.64	0.72	0.72	0.74	0.71	0.67	0.72
Al ₂ O ₃	16.79	16.40	16.92	17.01	17.76	17.83	17.06	17.08
Fe ₂ O ₃	4.65	4.47	5.00	5.05	4.78	3.61	5.26	4.71
MnO	0.09	0.08	0.09	0.08	0.073	0.04	0.05	0.06
MgO	2.12	2.07	2.32	2.28	2.32	1.86	2.38	2.19
CaO	3.35	3.13	3.21	2.68	1.11	1.00	1.52	1.03
Na ₂ O	3.29	3.51	3.67	3.31	2.99	2.62	2.77	3.04
K ₂ O	2.12	2.65	2.42	2.37	3.83	3.99	3.41	3.71
P ₂ O ₅	0.16	0.15	0.15	0.17	0.17	0.17	0.17	0.17
LOI	1.83	2.13	2.57	3.08	3.70	3.80	4.07	3.48
sum	100.3	100.1	100.4	100.5	101.1	100.3	100.9	100.1
Sc	17	11	13	13	13	14	11	12
La	64	56	60	62	57	71	58	70
Ce	119	111	116	118	115	127	118	130
V	116	109	115	122	125	123	114	121
S	312	208	488	599	908	296	525	361
Cr	29	25	32	34	38	36	41	45
Cl	59	77	90	102	284	266	281	318
Co	54	57	62	59	50	57	61	49
Ni	11	9	11	11	11	5	8	6
Cu	11	12	15	16	17	10	19	17

<i>Zn</i>	57	74	102	64	70	68	31	34
<i>Th</i>	12	12	13	12	12	14	13	11
<i>Ga</i>	22	22	24	21	23	28	25	27
<i>U</i>	2	3	7	3	4	4	3	4
<i>Y</i>	29	25	29	22	21	18	24	25
<i>Zr</i>	179	162	181	184	203	183	188	189
<i>Nb</i>	11	10	10	13	11	13	10	12
<i>Pb</i>	18	36	47	25	24	24	9	8
<i>Rb</i>	112	95	92	100	197	206	177	192
<i>Sr</i>	356	345	336	294	210	156	156	203
<i>Ba</i>	975	928	790	804	873	904	810	935

XRF data. Major elements in wt-%, trace elements in ppm. LOL: weight loss on ignition (1050°C for 1 h)

Table 2 Rb-Sr mineral data.

Sample No. Analysis No.	Material	Rb [ppm]	Sr [ppm]	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr 2σ _m [%]
STE-3 (unaltered gneiss domain)						
STE-3 (7659)	feldspar, turbid	123	551	0.645	0.71093	0.003
STE-3 (7660)	feldspar, transparent - white	86.7	464	0.541	0.71021	0.003
STE-3 (7661)	apatite	1.18	221	0.0154	0.70776	0.004
STE-3 (7541)	gneiss (whole rock)	87.9	318	0.801	0.71151	0.003
STE-3 (7655)	biotite (picked)	348	12.2	85.6	1.10461	0.004
STE-3 (7656)	biotite (ground in ethanol)	350	9.03	118	1.25491	0.006
STE-3 (strongly altered gneiss)						
STE-3 (7658)	feldspar + sericite	204	322	1.84	0.71739	0.004
STE-3 (8329)	quartz	0.129	0.283	1.32	0.71544	0.010
STE-3 (7662)	apatite	2.02	220	0.0266	0.70784	0.004
STE-3 (7553)	gneiss (whole rock)	198	161	3.56	0.72476	0.003
STE-3 (7654)	biotite + chlorite, intergrown	86.1	44.0	5.67	0.73368	0.003
STE-3 (7657)	,chlorite'	15.6	14.9	3.04	0.72210	0.007
Hydrothermal vein minerals						
STE-3 (7555)	vein whole rock [3a]	20.6	90.3	0.661	0.71201	0.006
STE-3 (7653)	quartz + pyrite [3b]	7.74	5.20	4.11	0.72757	0.003
STE-3 (7666)	calcite [3c]	0.203	502	0.00117	0.70879	0.003
STE-3 (7735)	quartz + pyrite [3d]	7.59	6.09	3.62	0.72536	0.003
STE-4 (8984)	K- feldspar [4a]	293	109	7.80	0.74395	0.003
STE-4 (8989)	coarse grained quartz [4b]	1.02	6.34	0.466	0.71308	0.003
STE-4 (8988)	microcryst. Quartz, late [4c]	3.93	14.3	0.793	0.71721	0.003
STE-4 (8986)	quartz crust, late [4d]	25.9	4.73	15.9	0.77743	0.003
STE-4 (8987)	quartz crust, late [4e]	22.9	4.87	13.7	0.76832	0.003
STE-5 (7663)	calcite [5a]	1.07	440	0.00702	0.70972	0.003
STE-5 (7736)	qtz + py, coarse grained [5b]	2.43	10.1	0.693	0.71519	0.003
STE-5 (7733)	qtz + py, finely ground [5c]	3.33	11.3	0.854	0.71638	0.003
STE-5 (7652)	quartz [5d]	3.35	11.5	0.847	0.71637	0.003
STE-5 (7734)	microcrystalline quartz [5e]	29.6	6.39	13.5	0.76534	0.003

STE-6 (7664)	calcite [6a]	0.0533	67.8	0.00227	0.71081	0.021
STE-6 (7665)	ankerite [6b]	0.0205	78.4	0.00076	0.71550	0.010

An uncertainty of ± 1.5 % is assigned to Rb/Sr ratios. Qtz, quartz; py, pyrite. In [] brackets: as plotted in Fig. 7.

Table 3 Rb/Sr analytical data, whole rock slabs of profile STE-3 (see Fig. 2).

Sample No.	Material	-mm-	Rb [ppm]	Sr [ppm]	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ $2\sigma_m$ [%]
STE-3.1	gneiss	2.7	109	362	0.874	0.71187	0.003
STE-3.2	gneiss	7.5	116	341	0.985	0.71243	0.003
STE-3.3	gneiss	11.5	117	355	0.958	0.71226	0.003
STE-3.4	gneiss	15.5	120	337	1.03	0.71263	0.003
STE-3.5	gneiss	19	115	309	1.07	0.71285	0.003
STE-3.6	gneiss	22.5	108	315	0.991	0.71243	0.003
STE-3.7	gneiss	26	104	321	0.938	0.71219	0.003
STE-3.8	gneiss	30	87.9	318	0.801	0.71151	0.003
STE-3.9	gneiss	33.5	90.6	314	0.836	0.71167	0.003
STE-3.10	gneiss	37	89.4	297	0.870	0.71183	0.003
STE-3.11	gneiss	40.5	86.8	305	0.824	0.71161	0.003
STE-3.12	gneiss	44.5	79.1	326	0.702	0.71100	0.004
STE-3.13	gneiss	48	79.5	303	0.760	0.71131	0.003
STE-3.14	gneiss, altered	51	81.2	302	0.779	0.71143	0.003
STE-3.15	gneiss, altered	54.5	105	264	1.15	0.71334	0.003
STE-3.15-2	gneiss, altered	54.5	107	268	1.15	0.71337	0.003
STE-3.16	gneiss, altered	58	144	202	2.06	0.71767	0.003
STE-3.17	gneiss, altered	62	176	191	2.67	0.72084	0.003
STE-3.18	gneiss, altered	66	194	180	3.12	0.72254	0.003
STE-3.19	gneiss, altered	71	179	159	3.26	0.72293	0.003
STE-3.20	gneiss, altered	75.5	198	161	3.56	0.72476	0.003
STE-3.20-2	gneiss, altered	75.5	198	161	3.55	0.72478	0.003
STE-3.21	gneiss, altered	80	192	159	3.50	0.72509	0.003
STE-3.22	vein material	84	20.6	90.3	0.661	0.71201	0.006
STE-3.23	gneiss, altered	89	161	157	2.98	0.72242	0.003
STE-3.24	gneiss, altered	94	175	142	3.56	0.72470	0.003
STE-3.25	gneiss, altered	98.5	186	178	3.04	0.72211	0.003
STE-3.26	gneiss, altered	103.5	181	196	2.68	0.72035	0.003

An uncertainty of $\pm 1.5\%$ is assigned to Rb/Sr ratios. mm: distance (in mm) from profile origin (cf. Fig. 2). Samples 3.15-2 and 3.20-2 are replicate analyses.

Figures

Fig. 1 Geological map of the Kinzig valley near Haslach / Steinach, Schwarzwald. Map after Klein and Stenger (1987). Position of hydrothermal veins after Bliedtner and Martin (1986). Samples originate from the Artenberg quarry near Steinach. Below: remnants of the Variscan orogen in Central and Western Europe. Arrow indicates location of the study area.

Fig. 2 Sample STE-3, with position of Rb-Sr thin slab profile (slabs 1 – 26) and profile for chemical composition (slabs a-h). Zoned fluid-rock interaction halo to the left of the vein is ~5 cm wide.

Fig. 3 Schematic illustration of distribution and relative abundance of minerals in the hydrothermal vein and surrounding rock, sample STE-3 (see Fig. 2)

Fig. 4 $\log a_{O_2}$ -pH diagram showing the most likely physicochemical environment for the Artenberg fluid-rock reaction system. The alteration assemblage includes hematite, pyrite, chlorite, K-feldspar, muscovite, and clay minerals, as characteristic for epithermal adularia-sericite-type alteration. Diagram conditions ($t = 250^\circ\text{C}$, total $S = 0.02$ molal, salinity = 1 molal, $\text{Na/K} = 9$) reflect typical conditions of formation of adularia-sericite-type alterations. See text for specific P, T, X conditions of the Artenberg hydrothermal system.

Fig. 5 Distribution of selected main elements, trace elements, and volatiles (measured as LOI, loss on ignition) in profile across sample STE-3 (cf. Fig. 2)

Fig. 6 Rb-Sr isotopic ages for rocks and minerals of the Artenberg hydrothermal system. Analytical data: see Table 2. qtz, quartz; py, pyrite; fsp, feldspar.

Fig. 7 Rb-Sr data for minerals precipitated in the Artenberg veins. Strontium isotopic compositions calculated for $t = 279$ Ma, which is the age of mineral crystallization. Note large spread of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and distinct fields for specific minerals. Analytical data taken from Tab. 2.

Fig. 8 Profile STE-3 (see Fig. 2). Concentrations of Rb, Sr, and isotopic composition of Sr calculated for the time of vein formation and metasomatism (279 Ma). Numbers 1-26 refer to profile slab numbers in Fig. 2.

Fig. 9 Schematic crystallization sequence of minerals in the Artenberg hydrothermal veins, and characteristic isotopic mineral signatures. $^{87}\text{Sr}/^{86}\text{Sr}$ data (see Table 2, Fig. 7) calculated for $t = 279$ Ma. The Sr-isotopic signature of the mineralizing fluids changed drastically with time.