Sulfate brines in fluid inclusions of hydrothermal veins:

Compositional determinations in the system H₂O-Na-Ca-Cl-SO₄

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ABSTRACT

Sulfate is among the most abundant ions in seawater and sulfate-bearing brines are common in sedimentary basins, among other environments. However, the properties of sulfate-bearing fluid inclusions during microthermometry are as yet poorly constrained, restricting the interpretation of fluid-inclusion compositions where sulfate is a major ion. The Schwarzwald mining district on the eastern shoulder of the Upper Rhinegraben rift is an example of a geologic system characterized by sulfate-bearing brines, and constraints on the anion abundances (chloride versus sulfate) would be desirable as a potential means to differentiate fluid sources in hydrothermal veins in these regions. Here, we use the Pitzer-type formalism to calculate equilibrium conditions along the vapor-saturated liquidus of the system H₂O-Na-Ca-Cl-SO₄, and construct phase diagrams displaying the predicted phase equilibria. We combine these predicted phase relations with microthermometric and crush-leach
analyses of fluid inclusions from veins in the Schwarzwald and Upper Rhinegraben, to estimate the compositions of these brines in terms of bulk salinity as well as cation and anion loads (sodium versus calcium, and chloride versus sulfate). These data indicate systematic differences in fluid compositions recorded by fluid inclusions, and demonstrate the application of detailed low-temperature microthermometry to determine compositions of sulfate-bearing brines. Thus, these data provide new constraints on fluid sources and paleo-hydrology of these classic basin-hosted ore-forming systems. Moreover, the phase diagrams presented herein can be applied directly to compositional determinations in other systems.

Keywords: hydrothermal fluid; ore deposition; sedimentary basin, fluid mixing, basinal brine, sulfate
Continental rift systems and large sedimentary basins commonly exhibit pronounced compositional heterogeneity between crystalline and sedimentary rocks. Clastic (arkoses, sandstones, conglomerates, claystones) and chemical sediments (limestones, dolostones, gypsum rock, and halides) commonly reach formation thicknesses of thousands of meters in such basins. Examples include the South East Basin, France (Aquilina et al., 2011), the Maestrat basin, Spain (Boiron et al., 2010), the St. Lawrence rift, Canada (Carignan et al., 1997) and the North German basin, Germany (Lüders et al., 2010). These are large-scale systems containing diverse lithologies of source rocks, typically characterized by notable compositional variability among formation fluids (e.g. Carpenter et al., 1974; Lüders et al., 2010; Göb et al., 2013; Kolchugin et al., 2016; Walter et al., 2016). To understand the chemical evolution, modification and migration of the different fluids is of both fundamental and economic interest. Migration of fluids in these systems is of relevance to geothermal energy production, mobilization and transport of chemical components, and the genesis of ore deposits (Kendrick et al., 2002; Heijlen et al., 2008; Mercandier et al., 2010; Richard et al., 2010; Fusswinkel et al., 2013). Nevertheless, at present the diversity, circulation and chemical evolution of different fluids in such basins is still only partially understood (e.g. Lorenz, 2002 and references therein).

Over the last decades, numerous publications have dealt with fluid modification and provenance based on measured fluid composition especially on source tracers like metal contents and mass ratios Ca/Na, Cl/Br, Rb/Cs etc. (e.g. Stober & Bucher 1999, Möller et al. 1997; Bucher and Stober; 2010; Loges et al., 2012; Fusswinkel et al., 2013; Göb et al., 2013; Burisch et al., 2016a; Walter et al., 2016). One of the most widely used source tracers is the Cl/Br mass ratio. Highly saline basement brines typically show Cl/Br mass ratios <100. In contrast, brines that acquired their salinity by halite dissolution show Cl/Br mass ratios much higher than that those of seawater (Cl/Br = 288). During surficial halite precipitation in evaporitic settings, the residual bittern brines show progressively decreasing Cl/Br ratios (288-34) with increasing degree of evaporation (Frape and Fritz, 1987; McCaffrey et al., 1987; Edmunds and Savage, 1991; Banks et al., 2000; Stober and Bucher, 2004; Möller et al., 2005; Yardley, 2005; Walter et al., 2016). Furthermore, water-rock interaction with crystalline rocks can result in low Cl/Br mass ratios (Bucher and Stober, 2002). In addition,
Burisch et al. (2016b) showed that fluids with salinities above 20 wt.% and low Cl/Br ratios can only be formed by involving an externally derived bittern brine. Hence, the Cl/Br mass ratio is an effective tool for defining the provenance of basement and formation fluids. Analogously, for modern fluids it is possible to distinguish between different sources according to Cl/Br, Ca/Na and SO$_4$/Cl ratios (e.g. Göb et al., 2013 and references therein). However, for paleofluids in geologic formations, methods are required to estimate SO$_4$/Cl ratios of the paleofluids for provenance studies.

Microthermometry of fluid inclusions trapped in veins is an important tool to study the physical and chemical properties of paleofluids (Roedder, 1984). Commonly, the microthermometric properties of basinal fluids trapped as inclusions are interpreted according to the phase equilibria of the binary NaCl-H$_2$O system, or less commonly the ternary NaCl-CaCl$_2$-H$_2$O or NaCl-H$_2$O-CH$_4$ systems (Goldstein and Reynolds, 1994; Becker et al., 2010; Fall et al., 2015; Steele-MacInnis et al., 2011; Steele-MacInnis et al., 2016). Quaternary systems are much less characterized, but compositions in the system H$_2$O-NaCl-CaCl$_2$-MgCl$_2$ have been deduced in few studies in order to interpret saline groundwaters and basinal brines (Crawford et al., 1979; Steele-MacInnis et al., 2016).

In contrast to the aforementioned systems, very little has been published regarding the concentrations and effects of sulfate in aqueous fluid inclusions by microthermometry (Steele-MacInnis et al., 2016), despite the recognition by Roedder (1984) that SO$_4^{2-}$ is commonly one of the most abundant solutes in natural inclusions. Sulfate is the second most abundant anion in modern seawater, and becomes enriched in the liquid during seawater evaporation (McCaffrey et al., 1987). Sulfate is also among the most abundant ions in saline groundwater in some, but not all environments (Hem, 1985). Thus, we expect that sulfate may reach significant concentrations in fluid inclusions from some environments, but solidus-liquidus relations appropriate for interpreting sulfate-bearing fluid compositions from microthermometry are mostly lacking. The liquidus phase diagram for the system H$_2$O-NaCl-Na$_2$SO$_4$ was perhaps first constructed by Borisenko (1977; see also Hurai et al., 2015, p. 36). Samson et al. (1995) constructed a liquidus phase diagram for the system H$_2$O-NaCl-Na$_2$SO$_4$ based on experimental data from Linke (1958) and Seshadri and Lobo (1957). Zen (1960) also constructed a partially schematic, partially quantitative liquidus projection of the system H$_2$O-NaCl-
CaSO₄. Harvie and Weare (1980) used a Pitzer-type approach to model solubilities of various minerals in aqueous solution from 0-25 °C, including sulfate minerals.

Sulfate in fluid inclusions has been previously detected by various microanalytical techniques such as Raman spectroscopy (Frezzotti et al., 2012 and references therein; Hurai et al., 2017) and crush-leach analysis (e.g. Meere & Banks, 1997; Vandeginste et al., 2009; Burisch et al., 2017, Walter et al., 2016). Sulfur, likely in the form of sulfate, has also been analyzed by decrepitate-mound analysis (e.g., Pandur et al., 2014), and laser ablation (LA)-ICPMS (e.g. Burisch et al., 2016a, Prokopyev et al., 2016). Nevertheless, the effect(s) of sulfate during microthermometric measurements remain of key interest for several reasons. Firstly, microthermometry remains the most commonly employed, routine method for analyzing aqueous inclusions (Steele-MacInnis et al., 2016). Secondly, methods such as LA-ICPMS of individual fluid inclusions and crush leach (IC and TXRF) rely on an accurate value of a known, internal-standard concentration (typically [Na⁺] or chlorinity) to convert element ratios into absolute concentrations, and the internal-standard concentration is most commonly inferred via microthermometry (Allan et al., 2005; Leisen et al., 2012; Steele-MacInnis et al., 2016). This remains a significant challenge for fluids that contain sulfate, as the potential effects of sulfate on microthermometric properties are commonly ignored. Furthermore, inclusions containing appreciable sulfate apparently exhibit a tendency to metastable behavior (Kotel’nikova and Kotel’nikov, 2007).

For this contribution we focus on fluid inclusions in hydrothermal veins from the Schwarzwald mining district in SW Germany. The Schwarzwald is a well-investigated area. Numerous previous studies include: studies of the regional geology (Ziegler, 1990, Geyer and Gwinner, 2011 and references therein); detailed mineralogical and fluid inclusion microthermometric studies of specific ore deposits (e.g. Baatartsogt, 2006, 2007; Fußwinkel et al., 2013; Markl et al., 2006; Pfaff et al., 2010; Schwinn et al., 2006; Staude et al., 2007, 2009, 2010a, 2011a, 2012a, b; Ströbele et al., 2012; Walter et al., 2015, 2016); trace-element studies of common ore minerals of the district, such as fahlore (tetrahedrite-tennantite) and sphalerite (Staude et al., 2010b; Pfaff et al., 2011); stable isotope analyses (Staude et al., 2011a, 2012a, 2012b; Walter et al., 2015) and age-dating (Pfaff et al., 2009, and references therein); studies on the composition of modern thermal, mineral and formation waters (Stober & Bucher 1999, 2010; Möller et al. 1997; Loges et al., 2012; Göb et al.,
2013); paleo-hydrological modeling (Pfaff et al., 2010; Staude et al., 2011a; Bons et al., 2014; Walter et al., 2015, 2016) and also hydrogeological/hydraulic investigations (Stober & Bucher 2004) as well as experimental rock leaching studies (Bucher and Stober, 2002; Burisch et al., 2016a). Recently, Walter et al. (2016) reported that fluid inclusions in certain vein generations and host minerals contain appreciable sulfate, which may reflect fluid source. Sulfate containing inclusions were recognized on primary growth zones. These fluid signature alternates with NaCl-CaCl₂-H₂O type fluids on several growth zones within one host mineral crystal. They were recognized by the present of three solid phases. Beside of ice, one of these solids show an incongruent dissolution at about -22°C and two other greenish solids were still present at positive temperatures, which make it easy to detect this fluid type.

In this study, we document the predicted liquidus relations in the quaternary system H₂O-Na-Ca-Cl-SO₄ and its sub-systems, with application to estimating compositions of saline, sulfate-bearing brine inclusions in hydrothermal veins and hence, with attention to the chloride/sulfate endowments of these fluids.

2. GEOLOGICAL SETTING

The Schwarzwald (Fig. 1) in SW-Germany mainly consists of crystalline basement rocks, dominantly metasedimentary gneisses, migmatites and granites, that were metamorphosed during Carboniferous (Variscan) collisional processes (Geyer and Gwinner, 2011). These metamorphic rocks were intruded between 335 and 315 Ma by post-collisional granites (Todt, 1976; Altherr et al., 2000; Hann, 2003). These crystalline basement rocks were covered by a Paleozoic and Mesozoic sedimentary sequence atop the Permian erosion surface (Geyer and Gwinner, 2011; and references therein).

During the Permian (Rotliegend), the basins (thickness ≤500m) received sedimentation of redbeds (arkoses, conglomerates, evaporites; Jenkner, 1986; Nitsch and Zedler, 2009; Geyer and Gwinner, 2011). Since Lower Triassic, distal quartzitic Buntsandstein units were deposited and reached a thickness of ≤400m in the northern and <50 m in the southern Schwarzwald. The
Buntsandstein is locally separated from the Middle Triassic by the Rötton clay aquitard in the north. Middle Triassic (Muschelkalk) units, including limestones, shales and evaporites (carbonates, anhydrite, gypsum and halite) reach thicknesses from 160 to 220 m (Stober & Bucher, 2014) in SW Germany. During the Upper Triassic (Keuper), dominantly clastic sediments and evaporitic gypsum formations were deposited, with thickness varying between about 300 m in the north to <100 m in the south. During the Jurassic, an approximately 1100 m thick unit of mostly marine carbonates and claystones was deposited (Geyer and Gwinner, 2011). No Cretaceous sediments are preserved owing to tectonic uplift and erosion.

Since the breakup of the Upper Rhinegraben rifting (see Fig 1), Paleogene to Quaternary sediments of locally up to 4000 m thickness were deposited in the Upper Rhinegraben, including Oligocene halite-sylvite bearing evaporates, anhydrite, gypsum and organic-rich claystones (Geyer and Gwinner, 2011 and references therein, Stober & Bucher, 2014).

### 2.1. Hydrothermal veins in the Schwarzwald

About 1000 hydrothermal veins are known in the Schwarzwald (Metz et al., 1957; Bliedner & Martin, 1986; Staude et al., 2009, Walter et al., 2016). Most of the veins consist of quartz, fluorite, barite and carbonates with a wide range in modal amounts of base and precious metal oxides, sulfides and arsenides (Fe-Mn, Cu-Pb-Zn and Ag-Bi-Co-Ni-U) (Metz et al., 1957). Five maxima of hydrothermal activity which are related to events of vein formation are known in the Schwarzwald, starting in late-Carboniferous with quartz-tourmaline veins; followed by Permian quartz veins with rare Au-Sb mineralization; then barren Triassic-Jurassic quartz-hematite veins; then Jurassic-Cretaceous fluorite-barite-quartz-carbonate veins with (sub-) economic amounts of Pb-Zn-Cu, Fe-Mn and or rarely Ag-Bi-Co-Ni-U ores; and finally post-Cretaceous quartz-barite-fluorite ± carbonate veins with variable mineralogy and Pb±Zn±Cu± (As) mineralization (Staude et al., 2012; Pfaff et al., 2009, Walter et al., 2016). All the veins studied herein belong to the latter, post-Cretaceous group and are related to the opening of the Upper Rhinegraben.
### 2.2. Hydrology of the Schwarzwald and Upper Rhinegraben

Data on water chemistry from numerous drill holes and wells show that a vertical fluid stratification is present in the Schwarzwald basement (Bucher & Stober, 2010). Representative fluid data is presented in table 1. Shallow bore holes (<1 km depth) contain Ca-Na-HCO₃ type fluids with low TDS of <2 wt.%. Below 3 km, the fluid composition changes to CO₂-bearing Ca-Na-HCO₃-SO₄ type fluids, in which the high SO₄ content probably relates to oxidation of sulfides in the host rock. In the transition zone between oxidized to reduced fluid conditions, the sulfate and CO₂ content in the fluid decreases continuously with increasing chlorinity. The deepest fluids known today (down to about 8 km depth in the Urach HDR drilling) are high-TDS (total dissolved solids) Na-Ca-Cl fluids (~200 g/L) with Cl/Br mass ratios ~80-100 and a low SO₄/Cl mole ratio of ~0.014 typical of deep seated brines worldwide (Bucher and Stober, 2010; Edmunds and Savage, 1991; Emmermann et al., 1995; Frape and Fritz, 1987; Frape et al., 1984; Köhler, 1992; Kozlovsky, 1984; Sanjuan et al., 2010). This vertical fluid stratification is interpreted to be a result of successive infiltration of surface derived waters into the crust over time (Agemar et al., 2013; Bons et al., 2014; Walter et al., 2016 and references therein).

#### 2.2.1. Sedimentary cover (Permian-Jurassic)

The various sedimentary cover rocks show a wide range in compositions and permeabilities that are reflected by variable fluid compositions. Fluids from Permian redbeds are typically Na-Ca-(K)-Cl fluids with a maximum TDS of 124 g/L (Pauwels et al., 1993). The Permian sedimentary basins are only locally present and hence, not significant aquifers in the study area (Geyer & Gwinner, 2011).

Lower Triassic (Buntsandstein) formation waters are Na-Ca-HCO₃-Cl-(SO₄) type fluids with a maximum TDS of 207 g/L and Cl/Br mass ratios of 165-327 and SO₄/Cl mole ratios ([SO₄]/[SO₄] + [Cl]) of 0.009-0.010 (Pauwels et al., 1993, Ludwig et al., 2011). Formation waters in the middle Triassic (Muschelkalk) limestone-gypsum-halite formation show a wide range in composition, depending on the specific lithological facies. Those from the dolomite and sulfate (gypsum/anhydrite)
lithologies are Na-Ca-(Mg)-Cl-HCO$_3$-SO$_4$ and Ca-Mg-Na-HCO$_3$-SO$_4$-Cl fluids of low to moderate TDS (6 g/L), a Cl/Br mass ratio of 25-725 and a SO$_4$/Cl mole ratio of 0.2 – 0.77 (He et al., 1999; Göb et al., 2013). However, those which interacted with the halite formation are Na-(Ca)-Cl fluids with a TDS up to 246 g/L (He et al., 1999; Göb et al., 2013) and show high chlorinity and high Cl/Br mass ratios up to 9900 with a SO$_4$/Cl mole ratios of 0.015-0.017 (Stober and Bucher, 1999; Göb et al., 2013).

Fluids in the upper Triassic (Keuper) clay-, sand- and marlstone formations are of the Ca-Na-HCO$_3$-SO$_4$-Cl type with TDS (≤2.5 g/L), high Cl/Br mass ratios of 405-533 and SO$_4$/Cl mole ratios of 0.375-0.875 (Göb et al., 2013) (Köhler et al., 1992; Göb et al., 2013). Previous studies show that the Keuper rocks are of minor importance as aquifers (Stober and Bucher, 2014).

The Lower Jurassic (Lias) clay formation is an aquitard rather than an aquifer and the pore fluids of this strata are negligible. In the Rhinegraben valley, the Middle Jurassic (Dogger, Hauptrogenstein Fe-rich limestones) contains a karst aquifer for thermal waters with two different types of fluids: a Na-Ca-Cl fluid with SO$_4$/Cl mole ratios of 0.077-0.933 with Cl/Br mass ratios of 234-338 and a Ca-Mg-HCO$_3$-SO$_4$ water with a SO$_4$/Cl mole ratio of 0.777 and a Cl/Br mass ratio of 72 (He et al., 1999).

2.2.2. Tertiary and Quaternary sediment fillings in the Upper Rhinegraben

The Tertiary filling above the Jurassic strata in the Upper Rhinegraben dominantly consists of evaporite sequences (sulfates and halides) that are interlayered with limestone and locally occurring organic-rich shales (Pechelbronn formation). Quaternary sediments on the Tertiary surface are mainly gravel formations. Below the Tertiary sediments in the Upper Rhinegraben, tilted blocks of the former sedimentary cover (Triassic-Jurassic) are known. Fluids hosted in these lithologies are discussed above. Hydrothermal sulfates in fractures (dominantly anhydrite and gypsum,) are related to Ca-SO$_4$-rich fluids of presumably high SO$_4$/Cl ratio, derived from an about 400 m thick sulfate-bearing formation in the rift (Lorenz, 2002). Fluids that have interacted with Oligocene halite are Na-dominated, have a high TDS and high Cl/Br ratios up to 2400 (Stober and Bucher, 1999) and a
presumably low SO$_4$/Cl mole ratio. Furthermore, fluids that are related to the 600m thick Oligocene
gypsum-anhydrite-halite-sylvite Pechelbronn formation in the rift are expected to have a CaSO$_4$-NaCl-
KCl signature with a high SO$_4$/Cl mole ratio (Borchert, 1959).

2.3. Sample material

To investigate the sulfate-bearing brines that were involved in ore formation, five locations
have been investigated in detail. All of these five veins are situated in fractures of the Upper
Rhinegraben fault system (SSW-NNE and NW-SE trending). Hence, all veins are of post-Cretaceous
age and belong to the same hydrothermal maximum (Walter et al., 2015; 2016). The centimetre-sized
quartz samples (Fig. 2A-E) contain primary fluid inclusions which decorate macroscopically visible
growth zones (defined by fluid inclusions and clay minerals on the former crystal surfaces). In two
localities the selected euhedral quartz crystals represent the youngest precipitates. The Böschlisgrund
(Fig. 2A) Karl August Mine (Fig. 2B) and Kropbach Hof (Fig. 2D) samples contain primary fluid
inclusions in the ore-stage quartz. All the localities are located within a few kilometres (<5km) of each
other.

The Karl-August quartz vein (sample BO66, see Fig. 2B) is situated 2 km east of the
Rhinegraben boundary fault in the Münstertal. The vein follows the boundary of a granitic dyke in the
paragneiss unit and contains massive sphalerite associated with grey fine-grained quartz overgrown by
large euhedral quartz crystals.

The Riggenbach (samples BO29, Fig. 2C) and Böschlisgrund veins (Fig. 2A, BO98) show an
early quartz-galena-sphalerite stage followed by a younger siderite stage with massive Cu-Ni ores.
Euhedral, large quartz crystals are the latest assemblage and overgrow the former paragenetic
sequence (Pb-Zn and Ni-Cu stages). The Riggenbach mine (Fig. 2C) is situated in the Münstertal,
about 4 km East of the Rhinegraben boundary fault, whereas the Böschlisgrund vein (Fig. 2A) crops
out northeast of the town of Sulzburg about 5 km east of the Rhinegraben boundary fault.
The Wildsbach West (Fig. 2D) and Kropbach Hof mines (Fig. 2E) are mined a few hundred meters to the east and west of the Karl-August Mine (Fig. 2B) respectively in the Münstertal. An early galena-sphalerite-fahlore quartz stage is overgrown by barren euhedral, centimetre-sized quartz crystals.

3. METHODS

3.1. Microthermometry

Cross sections through selected hydrothermal quartz crystals with up to two doubly polished thick sections (150 to 350µm) were prepared. The chronological sequence of fluid inclusions (fluid inclusion assemblages, FIA, Goldstein and Reynolds, 1994) was determined by optical microscopy. Fluid inclusions were classified as primary (p), pseudo-secondary (ps), secondary (s), isolated inclusions (iso) and clusters of inclusions with no geometrical relation to former crystal surfaces or fractures (c) (Walter et al., 2015). Microthermometric analyses were performed using a Linkam stage (model THMS600). Each fluid inclusion was analyzed by low-temperature microthermometry to determine the final melting temperature of various solids: ice \(T_{m,\text{ice}}\), hydrohalite \(T_{m,\text{hh}}\), halite \(T_{m,\text{hal}}\), mirabilite \(T_{m,\text{mir}}\) as well as an additional sulfate phase (presumably gypsum, \(T_{m,\text{gyp}}\)) and the homogenization temperature \(T_h\). Synthetic \(H_2O\), \(H_2O-NaCl\) and \(H_2O-CO_2\) standards were used for calibration. The precision of the measurements is less than 0.1°C. Fluid inclusion assemblages with strong deviation in salinity (\(>\pm 2\text{wt.} \% \text{NaCl + CaCl}_2\)) within a homogeneous trail were excluded for discussion, since this behavior suggests that the inclusions may have been modified by post-entrapment processes. Volume fractions were estimated by optical microscopy (Shepherd et al., 1985; Bakker and Diamond, 2006) and were described in the volume fraction notation based on their phase assemblage at room temperature \(L_x\), numerical subscription refers to the volume percentage of aqueous liquid), carbonic liquid \(L_c\), vapor \(V\) and solid \(S\). A pressure correction (Bodnar and Vityk, 1994) was applied assuming hydrostatic conditions with a depth of the water column inferred from paleo-depth. Uncertainties of this approach are discussed in Walter et al. (2015). For the high salinity fluid inclusions of the Schwarzwald, pressure corrections have only a negligible effect on the
estimated trapping temperature.

3.2. Micro-Raman spectroscopy

Micro-Raman measurements were performed with a Renishaw InVia Reflex confocal Raman spectrometer at the University of Tübingen to detect and identify volatile components and sulfate in representative fluid inclusion assemblages. All measurements were carried out with a laser wavelength of 532nm using a laser output of 50%. The x50 objective used has a numerical aperture of 0.55 with an opening angle of 66.7°. The slit diaphragm was regulated and corrected automatically. The focus diameter was approximately 2µm, the measurement time was 30 seconds with three accumulations. To correct any influence from the matrix, measurements in the host mineral were performed under identical conditions and orientation. As far as possible (depending on inclusion size), separate measurements focusing on liquid and on vapour were performed. For qualitative evaluation, the Raman database for fluid inclusions of Frezzotti et al. (2012) was used.

3.3. Crush-leach analysis

From 6 samples that contained only one fluid type (as determined by petrography and microthermometry prior to crush-leach analysis), about 3 g of quartz, (grain size of 2.5 to 5 mm) were separated by hand to avoid visible impurities. The analyses were performed at the University of Tübingen following the method of Köhler et al. (2009) and Walter et al. (2016). These separates were first washed for 3.5 hours in HNO₃ at 60-70°C and subsequently washed for one week with ultrapure water, changing the water twice a day. These samples were then dried and crushed in an agate mortar. Subsequently, 10 ml of ultrapure water were added, which was acidified with suprapure HNO₃ to suppress adsorption of doubly-charged cations (especially Ca²⁺; Köhler et al., 2009). The loaded solutions were injected into a Dionex ICS 1000 ion chromatography systems, equipped with an IonPac AS 9-HC 2mm column for quantification of anions (F, Cl, Br, PO₄ and SO₄) and an IonPac CS 12-A column for cations (Li, Na, K, Mg, Ca, Ba, Sr). For injection of the solutions, disposable syringe filters CROMAFILE® Xtra RC-20/25 and CROMAFILE® Xtra PVDF-20/25 for anions and cations,
respectively, were used (Ladenburger 2012, and Ladenburger et al., 2012). Blank runs were carried out after each analysis, and standard solutions were regularly analyses to monitor the reproducibility and precision of the measurements. Uncertainties were usually smaller than 15% (thus, <30% for the element ratios) and effective detection limits were generally <10 mg/L. Absolute concentrations were calculated based on the salinity determined by microthermometry using Cl as internal standard (Allan et al., 2005).

The complete dataset is presented in the electronic supplement. All of the crush-leach solutions contain dissolved carbonate (presumably HCO$_3^-$) from fluid inclusions (as indicated by the presence of CO$_2$ based on Raman spectroscopy) and we assume that the positive deviations from electrical neutrality can be ascribed to carbonate species (e.g. Bottrell et al., 1988; Banks et al., 2000; Dolnischek et al. 2014). Contamination of the leachates by dissolution of host minerals is not relevant for quartz.

3.4. Numerical modeling: The system Na-Ca-Cl-SO$_4$

The solidus-liquidus phase equilibria were calculated in binary, ternary and quaternary compositional space within the system H$_2$O-Na-Ca-Cl-SO$_4$ using procedures similar to those described by Steele-MacInnis et al. (2016). Briefly, we used the Pitzer-type ion interaction model to compute the activities of solutes and H$_2$O, using interaction parameters tabulated by Marion and Kargel (2008). The model of Pitzer (1973) and Pitzer and Mayorga (1974) allows computation of the activities of ions (as well as non-electrolyte solutes) and solvent by parameterizing and invoking all potential two-way (binary) and three-way (ternary) interactions in a solution. The parameters for ion interactions are temperature functions (Marion and Kargel, 2008). Equilibrium between liquid and solid is attained with the appropriate ion activity product is equal to the solubility product of a given mineral. The solubility products are also described by temperature functions (Marion and Kargel, 2008), permitting calculation of solid-liquid equilibria over a range of temperatures. This model has been previously applied to compute solidus-liquidus phase diagrams for some binary systems by Spencer et al. (1990), and for binary, ternary and quaternary systems in which chloride is the only anion by Williams-Jones and Samson (1990) and Steele-MacInnis et al. (2016).
In this study, we focus on solidus-liquidus equilibria at vapor saturation of binary and ternary subsystems, and one quaternary (reciprocal) system, described in detail below. For the binary systems, Gibbs' phase rule specifies that three-phase coexistence (solid-liquid-vapor) is univariant, thus forming liquidus lines in temperature-composition space. The univariant lines intersect at invariant four-phase point(s). The locus of points along the three-phase univariant lines are determined by solving, at each temperature, the concentration of salt that satisfies equality between the ion activity product and the solubility product for the given mineral. Invariant points are determined by the intersections of univariant lines. For the ternary systems, the univariant lines represent the four-phase coexistence of liquid, vapor and two solids. As such, these lines are determined by adjusting the concentrations of two solutes at each temperature, to satisfy the equality of ion-activity product and solubility product of two solids simultaneously. Ternary invariant points occur at the intersection of four-phase curves, and five phases (liquid, vapor and three solids) are in equilibrium at these points, which also represent the intersection between the liquidus and solidus. In the quaternary system the univariant lines represent equilibrium of five phases (liquid, vapor and three solids), and thus three solid-liquid equilibria must be satisfied simultaneously.

The systems modeled here are as follows: Binary systems modeled are H$_2$O-NaCl and H$_2$O-CaCl$_2$ (from Steele-MacInnis et al., 2016), plus H$_2$O-Na$_2$SO$_4$ and H$_2$O-CaSO$_4$. Ternary systems modeled are H$_2$O-NaCl-CaCl$_2$ (from Steele-MacInnis et al., 2016), H$_2$O-NaCl-Na$_2$SO$_4$, H$_2$O-CaCl$_2$-CaSO$_4$, and H$_2$O-Na$_2$SO$_4$-CaSO$_4$. Notice that the ternary systems included here always contain either a common cation or a common anion between the two salt components. This ensures that the compositional space sampled is strictly ternary, i.e. not involving precipitation of solid phases whose compositions lie outside of the compositional space. For example, the system H$_2$O-Na$_2$SO$_4$-CaCl$_2$ is not a true ternary system, but rather pseudoternary (quaternary) because of gypsum/anhydrite precipitation – as these two minerals lie outside of the H$_2$O-Na$_2$SO$_4$-CaCl$_2$ compositional space. The quaternary system modeled here is the reciprocal system H$_2$O-Na-Ca-Cl-SO$_4$. Although this notation suggests that the latter is a system of five components, the system occupies quaternary compositional space because we can only specify the amount of H$_2$O plus three ions independently, whereas the concentration of the remaining (fourth) ion is always constrained by the requirement of charge...
balance. Stated differently, we can fully describe any composition in this system terms of H$_2$O plus three salts by writing the fourth salt as a linear combination of the other three (albeit with negative stoichiometries; Clibbens, 1920) such as: CaCl$_2$ = CaSO$_4$ + 2NaCl – Na$_2$SO$_4$. For convenience, we can also describe compositions in this quaternary system in terms of coordinates within a square-based pyramid of compositional space (rather than a tetrahedron, as used for quaternary systems involving three salts of a common ion; Steele-MacInnis et al., 2016). Importantly, by projecting from the H$_2$O apex of the compositional pyramid onto the plane of four salts, we can represent the ice+vapor-saturated liquidus surfaces on a two-dimensional plane (Clibbens, 1920; Crawford et al., 1979; Steele-MacInnis et al., 2016). In the case of a reciprocal system such as H$_2$O-Na-Ca-Cl-SO$_4$, the projection from the H$_2$O apex can be represented as a compositional square, of which one axis represents mole fraction of anions (e.g., [SO$_4^{2-}$] / ([Cl]$^+$+[SO$_4^{2-}$]) and the other axis represents mole fraction of cations (e.g., [Na$^+$] / ([Na$^+$]+[Ca$^{2+}$]). This projection is sometimes referred to as Jänecke's method (Clibbens, 1920).

4. RESULTS

4.1. Microthermometry

Detailed petrography (optical microscopy and microthermometry) of fluid inclusion assemblages (FIAs) enables their classification according to their relative age. Major differences between primary and secondary fluid inclusions analyzed in this study can be summarized as follows: Primary inclusions along crystal growth zones are typically smaller (<5-15 $\mu$m) than secondary inclusions and pseudosecondary assemblages (<5-80 $\mu$m), which mostly occur along (partly) sealed fractures and crosscut the primary structures often exhibiting angular shapes. We used the temporal relationships between FIAs to construct the relative temporal sequence of fluid inclusions (p, s, ps, iso) analyzed here.

In general, veins situated directly on the Rhinegraben boundary fault or on conjugate faults (related to the boundary fault) show complex, temporally alternating fluid signatures within one host mineral crystal involving low-, medium- and high-salinity fluid inclusion assemblages of variable temperatures (Walter et al., 2015, 2016). Figure 3A illustrates the primary occurrence of sulfate
bearing fluids on a growth zone. Veins situated on faults farther away from the Rhinegraben boundary
fault typically do not show such complex sequences. For this study only the sulfate bearing fluids are
reported, because the focus is on these fluids. The complete raw data is presented in the electronic
supplement. The following section deals with the characteristics of the natural sulfate-bearing fluids
from the Münstertal mining district in SW-Germany, which serves as a representative example of the
types of microthermometric observations characteristic of sulfate brines.

Two types of sulfate-bearing fluids were recognized, hereafter referred to as type A and type
B. The type A inclusions show a freezing point depression between -40 and -80°C and final melting of
ice from -0.1 to -12.9°C. In many inclusions, an equant dark green solid phase dissolves between
+22.3 and +24.0°C. In some inclusions, a long prismatic, lime green solid SO_4-phase melts between
+44.2 and +66.8°C. One distinguishing characteristic of these type B inclusions is the observation of
hydrohalite (NaCl·2H_2O) dissolution between -22.3 and -26°C which is identified by a peritectic
reaction to XXX. Homogenization temperatures show variations between 107°C and 223°C with
L_{90}(LV)_{10} to L_{90}(LV)_{20}. The main defining attribute of type B is a clearly visible double bubble,
suggesting a CO_2-bearing fluid. Melting of solid CO_2 in these inclusions occurs between -56.4 and -
56.8°C. The CO_2-rich phases within the inclusions homogenizes to the vapor phase (L_\text{aq}L_\text{car}V \rightarrow L_\text{aq}V)
between +21.3 and +31°C. Clathrate is observed in some FIAst, finally melting at +1.4°C to +6.4°C.
Micro-Raman data confirm both SO_4 and CO_2 bands. Based on the measured CO_2 homogenization
temperature (to the vapor phase, indicating low CO_2 density) and the visually estimated volume
fractions, we infer that the CO_2 mole fraction, X_{CO_2}, is between about 2 to 5 mol% in the inclusions
Figure 3B-E illustrates the microthermometric observations of this fluid type within a large fluid
inclusion. Figure 3F and G report the presence of SO_4 in the fluid phase by Micro-Raman and LA-
ICPMS.

Fluids of type B were found in one sample only: BO66. These inclusions solidified around -70
to -100 °C. First melting occurred above -45°C. Final ice melting was detected between -10.9 and -
15°C, at which temperature the inclusions were observed to contain a mixture of two greenish solids
(plus liquid plus vapour). Final dissolution of the first of these, an equant, dark green solid phase, was
reached at +21.8 to +24°C. Final dissolution of the second greenish solid, a lime green, long prismatic
solid phase occurred at +44.2° to +66.8°C (see green solids in Fig. 3B-E). Homogenization temperatures vary within an assemblage (between 8° and 40°C) and range from 107 °C to 220 °C between different assemblages. Inclusion sizes vary from <5 µm to >100 µm with volume fractions of L₉₀V₁₀ to L₉₀V₅ (i.e., 5-10 vol% vapour).

4.2. Crush-leach analyses

In total, 6 crush leach analyses of 6 veins were performed. The complete dataset is presented in the electronic supplement (HCO₃ is derived by charge balance). In accordance with the microthermometric results, these analyses record the presence of SO₄, with SO₄/Cl mole ratios of 0.192-0.594 in the two recognized fluid types: Na-Ca-Cl-SO₄, and Na-Ca-Cl-SO₄-HCO₃. The calculated HCO₃ content (based on charge balance) is in the range of 435-3800 (meq/l).

4.3. Phase relations on the vapor-saturated liquidus

4.3.1. Binary systems

For compositional determinations based on microthermometric observations, it is instructive to start by interpreting binary phase diagrams, and subsequently combine these systems to investigate higher-order systems. Therefore Fig. 4 shows the vapor-saturated liquidus relations for four binary systems: H₂O-NaCl, H₂O-CaCl₂, H₂O-Na₂SO₄ and H₂O-CaSO₄. The two former, chloride-bearing systems have been described in detail previously (Spencer et al., 1990; Bodnar and Vityk, 1994; Oakes et al., 1990; Baumgartner and Bakker, 2000; Steele-MacInnis et al., 2016). Briefly, both systems are characterized by eutectic points separating the ice-stable liquidus from the liquidus of salt hydrate (hydrohalite in the system H₂O-NaCl, and antarcticite, CaCl₂·8H₂O, in the system H₂O-CaCl₂). Peritectic points separate the liquidus lines of hydrohalite from halite in the former system (Fig. 4A), and separate three hydrates of calcium chloride (antarcticite, sinjarite, and Ca-dihydrate) as well as anhydrous calcium chloride (not shown on Fig. 4B). The eutectic temperature in the system H₂O-NaCl is approximately -21.2 °C, and the eutectic liquid composition 23.3 wt% NaCl (Hall et al., 1988). The
eutectic temperature in the system H₂O-CaCl₂ is approximately -50 °C, and the eutectic liquid composition ~31 wt% CaCl₂ (Yanatieva, 1946).

Binary phase diagrams of sulfate-bearing systems are shown in Fig. 4C and 4D, and differ markedly from the chloride-bearing systems in several ways. Firstly, both systems, H₂O-Na₂SO₄ and H₂O-CaSO₄, exhibit only modest freezing-point depression of ice to the eutectic temperature (and concomitantly, relatively dilute eutectic liquid compositions), as well as retrograde solubility of salts and/or salt hydrates (Fig. 4C and 4D). In the system H₂O-Na₂SO₄, the predicted eutectic temperature is approximately -1.1 °C, with a liquid of 3.9 wt% Na₂SO₄ coexisting with ice plus mirabilite. Mirabilite decomposes to thenardite (anhydrous Na₂SO₄) plus liquid at a peritectic point located at about +32.5 °C and a liquid composition of 31.8 wt% Na₂SO₄. Thenardite exhibits retrograde solubility on the liquidus over the range of temperature investigated here, such that by +55 °C, the liquid salinity in equilibrium with thenardite has decreased to 24.7 wt% Na₂SO₄ (Fig. 4C).

The liquidus in the system H₂O-CaSO₄ is notably different from both the chloride-bearing binaries and from the system H₂O-Na₂SO₄, as a consequence of the exceptionally low solubilities of both gypsum and anhydrite (Fig. 4D). The predicted eutectic point, at which ice is in equilibrium with gypsum, occurs at approximately -0.02 °C and a liquid composition of 0.13 wt% CaSO₄. The gypsum liquidus is nearly vertical (i.e., solubility shows little temperature dependence) over the range of temperature investigated here. In detail, gypsum shows prograde solubility up to approximately +33 °C, above which the solubility is retrograde. Over the range of temperature analyzed here, anhydrite is always metastable (Fig. 4D). The predicted metastable eutectic between ice and anhydrite is located at -0.07 °C at a liquid salinity of 0.38 wt% CaSO₄. The metastable anhydrite liquidus shows retrograde solubility, such that this curve will intersect the gypsum liquidus at just above +55 °C (just beyond the maximum on the y-axis of Fig. 4D). The crossover point between the liquidi of gypsum and anhydrite is a peritectic point, at which gypsum decomposes to anhydrite plus liquid during heating.

### 4.3.2. Ternary systems

Figure 5 shows the vapor-saturated liquidus relations of the system H₂O-NaCl-CaCl₂ (Vanko et al., 1988; Schiffries et al., 1990; Oakes et al., 1990; Steele-MacInnis et al., 2011; Steele-MacInnis et
This system is characterized by wide stability fields of ice and halite on the liquidus, separated by a swath of hydrohalite stability. The stability fields of antarcticite and other calcium salts are limited to a thin sliver at very Ca-rich compositions, owing to the salting-out of halite by soluble calcium salts (Steele-MacInnis et al., 2016). These features of the liquidus phase diagram for H₂O-NaCl-CaCl₂ are nearly identical to those of other systems of H₂O, NaCl and divalent-cation chlorides (e.g., MgCl₂ and FeCl₂; Lecumberri-Sanchez et al., 2015; Steele-MacInnis et al., 2016). The eutectic in this system is located at approximately -50 °C, at which point a very CaCl₂-rich liquid is in equilibrium with ice, hydrohalite and antarcticite. For most geologic fluid compositions, antarcticite is the first solid to melt, followed by hydrohalite, with ice melting last; in this case, the hydrohalite melting temperature provides a constraint on the NaCl:CaCl₂ ratio, whereas the ice melting temperature constrains the bulk salinity (Steele-MacInnis et al., 2011; Schlegel et al., 2012; Steele-MacInnis et al., 2016).

Figure 6 shows the vapor-saturated liquidus surface in the system H₂O-NaCl-Na₂SO₄, predicted in the present study. This diagram is consistent with the phase diagram constructed by Samson et al. (1995) using the empirical data of Seshadri and Lobo (1957) and Linke (1958). The first most obvious difference in this system, compared to the systems with NaCl and divalent cation chlorides such as CaCl₂ (Fig. 5), is the large stability field of mirabilite and the concomitant collapse of the ice-liquidus field to a thin wedge near the H₂O-NaCl join. The hydrohalite field is also reduced to a thin sliver near the H₂O-NaCl join, and as such, the eutectic point in this system (at which ice, hydrohalite and mirabilite are in equilibrium) is located very close to the binary H₂O-NaCl eutectic at -21.5 °C. The stability field of thenardite also encroaches on the formerly extensive halite liquidus. All of these features can be rationalized in terms of the relatively low solubility of sulfate salts. The reduced extent of the ice and hydrohalite fields imply significantly different sequence of melting temperatures for inclusions containing even modest sulfate concentrations: Firstly, hydrohalite is unlikely to be the second-to-last solid phase to melt in such inclusions and, rather, hydrohalite is commonly the first phase consumed at the eutectic. Secondly, for a wide range of compositions, ice is the second-to-last (rather than last) phase to melt, followed by mirabilite as the last phase to melt.
Systems containing CaSO$_4$ (Figs. 7 and 8) exhibit liquidus relations dominated by the stability field of gypsum, owing to the very low solubility of the latter phase. As such, all of the univariant curves are compressed towards the CaSO$_4$-free binary join when plotted in ternary mass-fraction space. In order to better display the unvariant boundaries, we therefore recast the projection by multiplying the CaSO$_4$ concentration (wt%) by 50x, and renormalizing to 100% with respect to the sum of H$_2$O, CaCl$_2$ and 50xCaSO$_4$ (Fig. 7) or with respect to the sum of H$_2$O, Na$_2$SO$_4$ and 50xCaSO$_4$ (Fig. 8).

The liquidus of the system H$_2$O-CaCl$_2$-CaSO$_4$ is dominated by the stability field of gypsum, with the ice liquidus and antarcticite liquidus each occupying a relatively thin sliver near the H$_2$O-CaCl$_2$ join. The eutectic in this ternary system is thus approximately coincident with that in the H$_2$O-CaCl$_2$ system. The gypsum liquidus surface exhibits a very steep temperature-salinity trajectory, analogous to that in the binary system H$_2$O-CaSO$_4$. As such, the isotherms on the gypsum liquidus cluster very close to the ice-gypsum cotectic curve (Fig. 7).

The liquidus of the system H$_2$O-Na$_2$SO$_4$-CaSO$_4$ is also dominated by the gypsum stability field, but although not as much as in the system H$_2$O-CaCl$_2$-CaSO$_4$ because of the competing mirabilite stability field (Fig. 8). The ice liquidus is restricted to very close to the H$_2$O apex, and the eutectic point between ice, mirabilite and gypsum is located at just above -1 °C, with a liquid composition of ca. 1.3 wt% Na$_2$SO$_4$ and 0.1 wt% CaSO$_4$. These data suggest that for wide ranges of composition in this system, ice will be the first phase consumed at the eutectic. The liquid composition will then evolve along the mirabilite plus gypsum cotectic curve until one of those two phases is consumed second-to-last, and the other will melt last. The H$_2$O-Na$_2$SO$_4$-CaSO$_4$ system also differs from the preceding systems in that an intermediate salt appears on the liquidus: glauberite, Na$_2$Ca(SO$_4$)$_2$. The glauberite stability field appears to be limited to relatively high salinities and intermediate salt ratios, between the stability of thenardite and gypsum.

4.3.3. Quaternary system

Figure 9 shows a projection from the H$_2$O apex onto the ice+vapor saturated liquidus of the system H$_2$O-Na-Ca-Cl-SO$_4$, plotted in a compositional square according to Jänecke's method.
(Clibbens, 1920). Ion fractions in this diagram are reported based on molal concentrations. In this projection, similarly to in the ternary systems involving CaSO₄, we have multiplied the sulfate concentration by 50x, and we have multiplied the calcium concentration by 10x, in order to better display the main features. Each divariant field represents the mutual stability of ice plus one other solid phase, in equilibrium with liquid plus vapor. Three solid phases are in equilibrium on the cotectic curves, and the invariant points represent the equilibrium of four solid phases plus liquid plus vapor.

The cotectic surfaces of ice plus sulfate minerals are the dominant features on the H₂O-Na-Ca-Ca-SO₄ quaternary diagram, when projected from H₂O onto the plane of four salts (Fig. 9). The field of gypsum occupies almost half of the diagram, for compositions to the calcium-rich side of the diagram (if the multiplication factors 50x and 10x are omitted from the y- and x-axes, then the ice+gypsum field takes up almost the entire diagram). The field of mirabilite occupies the majority of the sodium-rich side. The fields of sodium and calcium chlorides (hydrohalite and antarcticite, respectively) are comparatively smaller, again owing to the low solubilities of sulfate minerals compared to chlorides. The subsolidus assemblage in low-salinity H₂O-Na-Ca-Ca-SO₄ fluids is either ice+hydrohalite+antarcticite+gypsum, or ice+hydrohalite+mirabilite+gypsum, depending on the bulk composition. Assemblages containing both mirabilite and antarcticite are forbidden, according to the phase equilibria (Fig. 9). This feature is typical of reciprocal quaternary phase diagrams, in which two salts or salt hydrates are referred to as the "stable pair" (in this case, gypsum plus hydrohalite) whereas two are referred to as the "unstable pair" (here, mirabilite plus antarcticite; Clibbens, 1920). Incidentally, the fact that mirabilite plus antarcticite is the unstable pair furthermore confirms that the system H₂O-Na₂SO₄-CaCl₂ is not ternary, but rather quaternary, owing to gypsum precipitation.

Arrows on the univariant curves in Fig. 9 point down temperature, and the estimated temperatures at the invariant points are labelled. According to these results, the invariant point p is a peritectic point, at which hydrohalite and mirabilite/gypsum melt incongruently. Specifically, during heating, inclusions that contain ice+hydrohalite+gypsum will undergo incongruent dissolution of hydrohalite to produce mirabilite+liquid at point p. Also note that during cooling, mirabilite initially precipitated along the liquidus must be re-dissolved in order for the liquid composition to depart from point p along the ice+hydrohalite+gypsum cotectic line. The predicted temperature of this peritectic
point is -22 °C. The invariant point of ice+hydrohalite+gypsum+antarcticite is a eutectic point, with
the estimated eutectic temperature of -52 °C (similar to that in the H₂O-NaCl-CaCl₂ system).

In practice, unlike the case for ice-saturated cotectic surfaces, it is not straightforward to
project the relevant phase relations onto a convenient 2D plane at saturation of a specific salt or salt-
hydrate. In the present study, most of our inclusions have gypsum as the last solid phase to melt, and
thus it would be of interest to project from the composition of gypsum onto a 2D plane. Options
include projecting from of gypsum onto the H₂O-Na₂SO₄-CaCl₂ plane, or onto the NaCl-Na₂SO₄-
CaCl₂ plane, but both of these projections yield incomplete information on salt ratios and salinity, and
therefore these projections are not included here.

5. DISCUSSION

5.1. Fluid chemistry of the sulfate bearing brines

The modeled phase equilibria described in Section 4.3 provide a guide for our interpretations
of the microthermometric observations of fluid inclusions from the Schwarzwald and Upper
Rhinegraben veins. Specifically, these calculations permit us to tentatively identify the unknown,
sulfate-bearing phases in the fluid inclusions, to rationalize the relative sequence of phase changes
observed, and to estimate bulk compositions of the fluid inclusions based on the measured melting
temperatures. In this section, we combine these data in order to derive compositional estimates, and
especially to compare/contrast the Type A and Type B inclusions in the Schwarzwald and Upper
Rhinegraben samples.

Not surprisingly, the predicted phase equilibria corroborate that a calcium sulfate mineral –
either gypsum or anhydrite – is the most likely solid phase to melt last during heating, for a wide range
of compositions. At thermodynamic equilibrium, gypsum would be the expected calcium-sulfate phase
on the liquidus up to ca. +60°C (Fig. 4D), whereas anhydrite would be metastable. Hardie (1967)
reported that at ambient pressure, gypsum is the first solid phase to precipitate throughout a range of
temperatures, including both the gypsum-stable part of the liquidus up to the anhydrite-stable part of the liquidus. In the experiments of Hardie (1967), formation of metastable gypsum rather than stable anhydrite was common, whereas formation of metastable anhydrite rather than stable gypsum was not. As such, we suspect that the calcium sulfate daughter mineral observed in our inclusions is gypsum – the stable calcium sulfate phase at the conditions of our microthermometric observations. The melting temperature of this phase is on the order of +40 to +70°C in both the Type A and the Type B inclusions, which near the crossover temperature between the gypsum and anhydrite portions of the liquidus (i.e., the gypsum-anhydrite peritectic point; Fig. 4D).

In all inclusions analyzed here, the last melting of a calcium sulfate phase (presumably gypsum) is preceded by second-to-last melting of an equant, greenish solid phase at around +19 to +25°C. According to the predicted liquidus relations described above, this solid is most likely mirabilite. Mirabilite is a monoclinic phase, but forms crystals "like pyroxene in habit and angles" (Winchell, 1927). Thus, the appearance of this phase in our inclusions –equant, apparently cubic – is consistent with the habit of monoclinic mirabilite. We would expect that mirabilite would show birefringence (in fact, anomalous interference colors without extinction; Winchell, 1927), which is not observed in our samples, but this may be a consequence of the very small crystal size within the inclusions. The range of melting temperatures of this phase is consistent with the mirabilite liquidus (Figs. 1C, 3).

Thenardite (orthorhombic) may also be an option, stable down to 15°C in NaCl-bearing solutions (Fig. 6), but is less likely as a second-to-last phase to melt before gypsum (Fig. 6).

Excluding CO₂-clathrate, which is present in the Type B inclusions, ice is the third-to-last solid phase to melt in our inclusions. Ice melting temperatures are on the order of -15 to -10 °C for inclusions of Type A, and -13 to -0.1 for inclusions of Type B. In both inclusion types, ice melting represents the departure from the ice-saturated quaternary cotectic surface shown in Fig. 9.

Prior to ice melting, inclusions of Type A show only the first melting, or eutectic event, which occurs at >-45°C. The fact that first melting occurs at temperatures greater than -52°C suggests that these inclusions do not contain antarcticite in the subsolidus assemblage. Thus, based on this observation, we infer that the likely subsolidus assemblage in these inclusions is
ice+hydrohalite+mirabilite+gypsum. In this case, hydrohalite is the first solid phase to be fully consumed at the first-melting temperature (predicted to be ca. -27°C), which also explains why we did not measure a hydrohalite melting temperature in these inclusions. Upon hydrohalite melting, the liquid phase in these inclusions of Type A would evolve along the ice+mirabilite+gypsum cotectic line, until ice is consumed at -15 to -10 °C, after which the liquid composition moves onto the mirabilite+gypsum plane (not shown in Fig. 9, but extending from the mirabilite+gypsum cotectic in Fig. 8). Mirabilite is consumed at ca. +19 to +25 °C, after which the liquid composition evolves towards gypsum dissolution until gypsum is consumed.

Inclusions of Type B undergo a different sequence of melting events compared to inclusions of Type A. Firstly, of the observations of hydrohalite dissolution implies that hydrohalite is not the first phase consumed at the eutectic temperature in these inclusions. Therefore, we infer that the subsolidus assemblage in these inclusions is probably ice+hydrohalite+antarcticite+gypsum, and that antarcticite is the first solid phase consumed at the eutectic. This inference further implies that these inclusions are more enriched in Ca than the Type A inclusions (Fig. 9). After antarcticite dissolution, the liquid composition will evolve along the ice+hydrohalite+gypsum cotectic line until hydrohalite is consumed at -22.3 to -26 °C. Among these Type B inclusions, after hydrohalite is fully consumed, some inclusions exhibit two remaining solid phases, mirabilite+gypsum, whereas some have only mirabilite and lack gypsum. For the inclusions of Type B that exhibit mirabilite as second-to-last to melt, and gypsum last, we infer that hydrohalite is consumed at the peritectic point (ca. -22 °C in the model system) by reaction to form mirabilite, either in the presence or absence of excess gypsum. For the inclusions of Type B that exhibit mirabilite as the last phase to melt, we infer either that gypsum never formed in these inclusions, or that gypsum was consumed prior to hydrohalite at the peritectic point.

Based on the interpretations described above, we estimated the compositions of the Type A and Type B inclusions from the Schwarzwald and Upper Rhinegraben samples as follows. Firstly, for Type A inclusions, lack of detectable hydrohalite dissolution suggests first melting at the quaternary peritectic point as noted above, which implies that the bulk composition falls within the ice+hydrohalite+mirabilite+gypsum tetrahedron (i.e., the composition is antarcticite undersaturated).
For inclusions of Type B, first melting appears to occur at the quaternary eutectic point, suggesting that the bulk composition is more Ca-rich than for the Type A inclusions. In principle, third-to-last melting of ice and second-to-last melting of mirabilite constrain the ratios of salts, whereas last melting of gypsum constrains the bulk salinity. However, in practice, the precise last melting temperature of gypsum has little effect on the estimated salinity because the gypsum liquidus surface has an extremely steep temperature-salinity slope (see Fig. 4D). Furthermore, salt ratios from third-to-last and second-to-last melting temperatures are difficult to portray graphically for inclusions in which ice is not the last solid phase to melt (as in the case of our inclusions), because the ice-saturated projection is no longer suitable and because the salt ratios vary continuously from first to last melting. As such, the salinity determination is best accomplished numerically, by solving for the bulk fluid composition that yields the correct sequence and temperatures of equilibrium freezing/melting events. This was done using the same numerical methods as described above for computing phase relations for the phase diagram constructions, using Pitzer's equations. Results are shown in Figure 10 and tabulated in the Supplementary Materials.

Bulk compositions of both the Type A and Type B inclusions indicate salinities of broadly ~20-30 wt% total salt. Type A inclusions are significantly enriched in sodium with respect to calcium but show somewhat variable sulfate/chloride ratios, the latter of which appears to vary systematically according to location: The most sulfate-rich inclusions are from the Kropbach Hof samples, and the most chloride rich are from Riggenbach. The sublinear trend exhibited by the Type A inclusions on Figure 10 roughly corresponds to the projection of the mirabilite-gypsum cotectic surface onto the plane of four salts. The Type B inclusions show a different overall trend, limited to more modest sulfate fraction and extending to significantly higher calcium-to-sodium ratios. This trend is expected based on the measured hydrohalite melting temperatures, which suggest that the Type B inclusions undergo first melting at the antarcticite-bearing quaternary eutectic point. Notice that these results indicate enrichment in sulfate only in the calcium-poor (Type A) inclusions, and calcium-enrichment only in inclusions (Type B) containing relatively modest sulfate fractions (Fig. 10). This observation likely reflects that calcium and sulfate enrichments are mutually exclusive, owing to the low solubility of gypsum and anhydrite.
It must be noted that from the crush-leach analyses, we know that these inclusions also contain some bicarbonate ion. It is likely that the Type B inclusions, especially, contain some significant bicarbonate concentrations. This in turn is also consistent with the observation of double bubbles in the inclusions, as well as melting of solid CO$_2$ and CO$_2$-clathrate. Thus, the Type B inclusions would likely be better represented by the quinary H$_2$O-Na-Ca-Cl-SO$_4$-HCO$_3$ system. Nevertheless, the liquidus relations modeled here provide reasonable constraints on the Na/Ca and Cl/SO$_4$ ratios in these inclusions, and indicate significant differences from the Type A inclusions.

5.2 Mole fractions as indicators of fluid sources

Based on our model, which allows to calculate ion SO$_4$/Cl mole ratios from microthermometric data, we are able to compare our calculated fluid compositions to modern fluids in the Upper Rhinegraben rift. Walter et al. (2016) showed that fluids and related aquifers get modified by water/rock interaction over time. However, the fluids in this study are archived in very young veins that are situated on fractures that are related to the Neogene strike-slip tectonics of the Upper Rhinegraben rift (Werner and Franzke, 2001). The work of Walter et al. (2016, 2017) indicates that the primary fluid composition of the original aquifers is archived over a time period of millions years. Hence, we assume that effect of fluid-rock interaction by short living aquifers is negligible. Furthermore, the modern fluids show typical signatures (e.g. Na/Ca ratios, TDS, Cl/Br ratios, Cl/SO$_4$ ratios) which are directly related to their source rocks (Göb et al., 2013 and references therein). For example, the middle Triassic Muschelkalk halite formation has a high TDS, high Cl/Br ratios and very high Na/Ca ratios. In addition, numerous authors have concluded that fluid mixing was important for the hydrothermal vein mineralization in the Schwarzwald mining district (e.g. Baatartsogt et al., 2007, Staude et al., 2009; Fusswinkel et al., 2013; Bons et al., 2014; Burisch et al., 2016a; Walter et al., 2015, 2016). Hence, the previous work allows us to discuss the measured fluid composition (in hydrothermal veins) as a mixed hydrothermal fluid from different aquifers that are similar to the observed fluids in modern aquifers in the Schwarzwald and Upper Rhinegraben.
Fluid type A that is observed in the Böschlisgrund, Kropbach Hof, Wildsbach West, Riggenbach and Karl August mine and shows an absolute salinity of 24.3-27.9 wt% which requires high-salinity sources. The fluid signature shows a dominance of Na with very low Ca contents ([Ca]/([Ca] + [Na]) of 0.03-0.04. Hence, a sodium rich fluid source is required. The observed Cl/Br mass ratios of 88-120 show that the NaCl-rich fluids from the middle Triassic halite formation (Cl/Br 9900) are an unlikely source. The high SO4/Cl mole ratio of 0.22 to 0.60 in our samples imply fluid mixing between a sulfate dominated aquifer and a Cl rich source.

The high-salinity Na-Cl rich, SO4-depleted fluid is presumably a continental basement brine, which is the most important fluid source and base-metal carrier for all veins in the Schwarzwald mining district (Staude et al., 2009; Fußwinkel et al., 2013; Bons et al., 2014; Walter et al., 2015, 2016 and references therein). The second mixing endmember is presumably derived from the Middle Triassic sulfate facies aquifer which contains fluids that show high SO4/Cl mole ratios up to 0.77 with a low Cl/Br mass ratio and a moderate salinity. In addition, one fluid signature was observed by He et al., (1999) in the Hauptrogenstein with a SO4/Cl mole ratio up to 0.77 and a low Cl/Br mass ratio with moderate salinity that could be a possible source. All the other aquifers are either depleted in SO4 like the Buntsandstein or are significantly elevated in Cl/Br and Ca content like the Keuper fluids (Göb et al., 2013).

In contrast to fluid type A, the similar fluid type B is only present in the Karl August vein and shows an equal salinity to fluid type A. However it has a relative depletion in SO4 and an higher Ca content related to low Cl/Br mass ratios. Again the high Cl/Br reservoirs seemed not to have been an important source. There are two models that could explain the variation relative to fluid type A, by changes in the fluid mixing ratio or by an additional Ca-enriched fluid source (Fig. 10), which is also described for the Karl August vein (Walter et al. 2016).

For both fluid types, the high SO4 content implies a dominant fluid influx from the Muschelkalk sulfate-facies aquifer and requires high mixing ratios of sedimentary brine over basement brine. This correlation was also recognized by Walter et al. (2017) in Jurassic-Cretaceous veins of the Schwarzwald mining district. Furthermore, this inference is consistent with the regional
geology (Fig. 1). All these veins are situated on conjugate faults of the Upper Rhinegraben rift in the
paragneiss unit close to the main offset fault (Schwarzwaldrandverwerfung) that borders the plains of
the rift against the rift shoulders. Furthermore, tilted blocks of the former sedimentary overburden
(with the significant Muschelkalk-sulfate-facies and Hauptrogenstein thermal aquifer) are directly
juxtaposed at the Schwarzwaldrandverwerfung to the gneiss unit that hosts the veins. Additionally, no
clays can be recognized in the veins, which, if present, would have sealed the fluid pathways. Hence,
fluid migration from Muschelkalk and Hauptrogenstein aquifers in the Upper Rhinegraben into the
first km of the gneiss unit of the rift shoulder seems to be plausible. The fact that there are several spas
with thermal waters along the Schwarzwaldrandverwerfung that are derived from Muschelkalk and
Hauptrogenstein also supports the argument for a Muschelkalk and Hauptrogenstein provenance for
the SO₄ fluid endmember in our mixed fluid.

In summary, the numerical model based on the Pitzer-type ion interaction theory for
computing the activities of solutes especially for SO₄ and H₂O that is presented in this study improved
the ability to interpret microthermometric data of SO₄-containing fluid inclusions and has the capacity
to significantly improve the knowledge of fluid provenance.

6. CONCLUSIONS

The new thermodynamic model for microthermometry that is presented in this contribution for the
system H₂O-Na-Ca-Cl-SO₄ shows a significant potential in the investigation of sulfate brines that are
common in numerous sedimentary basins worldwide. This model allows to calculate accurate
corrections for further major and trace element methods in fluid research like LA-ICPMS on single
inclusions and/or crush-leach analyses, that will help to illuminate sulfate concentrations of brines.
Furthermore, the model yields SO₄/Cl mole ratios and Ca/Na mole ratios that are an effective tool as
source tracers. As discussed above, the combination of fluid tracers like Ca/Na, Cl/Br and SO₄/Cl
permits differentiation between several natural aquifers.
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FIGURE CAPTIONS

Figure 1

Figure 2
Samples: A) siderite-quartz-chalcopyrite Böschlisgrund vein, B) zoned quartz I is overgrown by a quartz + sphalerite generation from the Karl August mine, C) euhedral zoned quartz overgrows clast of gneiss, D and E) zoned quartz II contains galena from the Kropbach Hof and Wildsbach West mine.

Figure 3
A) image illustrates primary occurrence of sulfate bearing fluid inclusions on a quartz growth zone. B-E) microthermometry of sulfate brine bearing fluid inclusions from the Karl August mine near Kropbach. Note green equant and green acicular solids that finally dissolve at positive temperatures. B) At -24.1°C three solids (ice + two green solids) are present with H2O liquid and vapor. C) At -13.7°C ice is closely to final melting. An incongruent melting of one green solid happened at about -22°C. D) At + 24.4°C two green solids (probably mirabilite and gypsum) with liquid and vapor is present. E) above +36°C only one green (acicular) solid is present with liquid and vapor. F) Microraman analyses of the fluid inclusion in figure B-E at room temperature indicate high sulfate contents in the liquid. Signals of the
two greenish solids are two low for doubtless phases determinations. G) LA-ICPMS signals
of single fluid inclusion (not detailed in this study) show the temporal distribution of S, Cl
and Na. During ablation several inclusions were ablated on the growth zone. Note that S, Cl
and Na simultaneously crest when the inclusion is ablated and hence, S was inside the fluid
inclusion and not a contamination by host mineral solid inclusions.

Figure 4

Binary vapor-saturated liquidus diagrams for H₂O-NaCl (A), H₂O-CaCl₂ (B), H₂O-Na₂SO₄
(C) and H₂O-CaSO₄ (D). I = ice; HH = hydrohalite; H = halite; Ant = antarcticite; Mb =
mirabilite; Th = thenardite; Gp = gypsum; Anh = anhydrite; L = liquid.

Figure 5

Ternary vapor-saturated liquidus diagram for the system H₂O-NaCl-CaCl₂, after Steele-
MacInnis et al. (2016). Axes are in mass fraction (wt%). Isotherms (grey lines) are in 5°C
increments.

Figure 6

Ternary vapor-saturated liquidus diagram for the system H₂O-NaCl-Na₂SO₄. Axes in mass
fraction (wt%). Isotherms (grey lines) are in 5°C increments.

Figure 7

Ternary vapor-saturated liquidus diagram for the system H₂O-NaCl-CaSO₄. Axes in mass
fraction (wt%), with CaSO₄ concentration multiplied by a factor of 50x. Isotherms (grey lines)
are in 5°C increments. Dotted isotherms represent the projection of the gypsum field to
higher temperature, but plot above the ice field owing to the retrograde solubility of gypsum. The dotted cotectic curve between ice and anhydrite is metastable (projected from below the gypsum liquidus surface).

**Figure 8**

Ternary vapor-saturated liquidus diagram for the system H$_2$O-Na$_2$SO$_4$-CaSO$_4$. Axes in mass fraction (wt%), with CaSO$_4$ concentration multiplied by a factor of 50x. Isotherms (grey lines) are in 5 °C increments. Dotted isotherms represent the projection of the gypsum field to higher temperature, but plot above the mirabilite field owing to the retrograde solubility of gypsum. The dotted cotectic curves between ice, mirabilite and anhydrite are metastable (projected from below the gypsum liquidus surface).

**Figure 9**

Ice-bearing, vapor-saturated liquidus projection of the quaternary system H$_2$O-Na-Ca-Cl-SO$_4$, projected from the H$_2$O apex onto the plane of reciprocal salt pairs (Jänecke's method; Clibbens, 1920). Axes in mole fraction (mol%), with [SO$_4$] multiplied by 50x and [Ca] multiplied by 10x. Arrows on the cotectic curves point down temperature, and temperatures of the invariant points are labelled in °C in the ellipses. I = ice; HH = hydrohalite; Mb = mirabilite; A = antarcticite; e = eutectic; p = peritectic.

**Figure 10**

Cation and anion charge fractions of fluid inclusions in the Schwarzwald samples, calculated according to the quaternary liquidus relations described in this study. See text for details.