Sulfate brines in fluid inclusions of hydrothermal veins: Compositional determinations in the system H_2O-Na-Ca-Cl-SO_4

Benjamin F. Walter[1*], Matthew Steele-MacInnis[2], Gregor Markl[1]

[1]Department of Geosciences, University of Tübingen, Wilhelmstrasse 56, 72074 Tübingen, Germany

[2]Department of Geosciences, The University of Arizona, 1040 E 4th St., Tucson AZ 85721 USA

*Corresponding author: benjamin.walter@uni-tuebingen.de, Tel: 004972072/2973155

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 H_2O-Na-Ca-Cl-SO_4, 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*

1. INTRODUCTION:

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,

66 Burisch et al. (2016b) showed that fluids with salinities above 20 wt.% and low Cl/Br ratios can only
67 be formed by involving an externally derived bittern brine. Hence, the Cl/Br mass ratio is an effective
68 tool for defining the provenance of basement and formation fluids. Analogously, for modern fluids it
69 is possible to distinguish between different sources according to Cl/Br, Ca/Na and SO_4/Cl ratios (e.g.
70 Göb et al., 2013 and references therein). However, for paleofluids in geologic formations, methods are
71 required to estimate SO_4/Cl ratios of the paleofluids for provenance studies.

72 Microthermometry of fluid inclusions trapped in veins is an important tool to study the
73 physical and chemical properties of paleofluids (Roedder, 1984). Commonly, the microthermometric
74 properties of basinal fluids trapped as inclusions are interpreted according to the phase equilibria of
75 the binary NaCl-H_2O system, or less commonly the ternary NaCl-$CaCl_2$-H_2O or NaCl-H_2O-CH_4
76 systems (Goldstein and Reynolds, 1994; Becker et al., 2010; Fall et al., 2015; Steele-MacInnis et al.,
77 2011; Steele-MacInnis et al., 2016). Quaternary systems are much less characterized, but compositions
78 in the system H_2O-NaCl-$CaCl_2$-$MgCl_2$ have been deduced in few studies in order to interpret saline
79 groundwaters and basinal brines (Crawford et al., 1979; Steele-MacInnis et al., 2016).

80 In contrast to the aforementioned systems, very little has been published regarding the
81 concentrations and effects of sulfate in aqueous fluid inclusions by microthermometry (Steele-
82 MacInnis et al., 2016), despite the recognition by Roedder (1984) that SO_4^{2-} is commonly one of the
83 most abundant solutes in natural inclusions. Sulfate is the second most abundant anion in modern
84 seawater, and becomes enriched in the liquid during seawater evaporation (McCaffrey et al., 1987).
85 Sulfate is also among the most abundant ions in saline groundwater in some, but not all environments
86 (Hem, 1985). Thus, we expect that sulfate may reach significant concentrations in fluid inclusions
87 from some environments, but solidus-liquidus relations appropriate for interpreting sulfate-bearing
88 fluid compositions from microthermometry are mostly lacking. The liquidus phase diagram for the
89 system H_2O-NaCl-Na_2SO_4 was perhaps first constructed by Borisenko (1977; see also Hurai et al.,
90 2015, p. 36). Samson et al. (1995) constructed a liquidus phase diagram for the system H_2O-NaCl-
91 Na_2SO_4 based on experimental data from Linke (1958) and Seshadri and Lobo (1957). Zen (1960) also
92 constructed a partially schematic, partially quantitative liquidus projection of the system H_2O-NaCl-

93 $CaSO_4$. Harvie and Weare (1980) used a Pitzer-type approach to model solubilities of various minerals
94 in aqueous solution from 0-25 °C, including sulfate minerals.

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

110 For this contribution we focus on fluid inclusions in hydrothermal veins from the
111 Schwarzwald mining district in SW Germany. The Schwarzwald is a well-investigated area.
112 Numerous previous studies include: studies of the regional geology (Ziegler, 1990, Geyer and
113 Gwinner, 2011 and references therein); detailed mineralogical and fluid inclusion microthermometric
114 studies of specific ore deposits (e.g. Baatartsogt, 2006, 2007; Fußwinkel et al., 2013; Markl et al.,
115 2006; Pfaff et al., 2010; Schwinn et al., 2006; Staude et al., 2007, 2009, 2010a, 2011a, 2012a, b;
116 Ströbele et al., 2012; Walter et al., 2015, 2016); trace-element studies of common ore minerals of the
117 district, such as fahlore (tetrahedrite-tennantite) and sphalerite (Staude et al., 2010b; Pfaff et al., 2011);
118 stable isotope analyses (Staude et al., 2011a, 2012a, 2012b; Walter et al., 2015) and age-dating (Pfaff
119 et al., 2009, and references therein); studies on the composition of modern thermal, mineral and
120 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-$CaCl_2$-H_2O 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 H_2O-Na-Ca-Cl-SO_4 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

148 Buntsandstein is locally separated from the Middle Triassic by the Rötton clay aquitard in the north.
149 Middle Triassic (Muschelkalk) units, including limestones, shales and evaporites (carbonates,
150 anhydrite, gypsum and halite) reach thicknesses from 160 to 220 m (Stober & Bucher, 2014) in SW
151 Germany. During the Upper Triassic (Keuper), dominantly clastic sediments and evaporitic gypsum
152 formations were deposited, with thickness varying between about 300 m in the north to <100 m in the
153 south. During the Jurassic, an approximately 1100 m thick unit of mostly marine carbonates and
154 claystones was deposited (Geyer and Gwinner, 2011). No Cretaceous sediments are preserved owing
155 to tectonic uplift and erosion.

156 Since the breakup of the Upper Rhinegraben rifting (see Fig 1), Paleogene to Quaternary
157 sediments of locally up to 4000 m thickness were deposited in the Upper Rhinegraben, including
158 Oligocene halite-sylvite bearing evaporates, anhydrite, gypsum and organic-rich claystones (Geyer
159 and Gwinner, 2011 and references therein, Stober & Bucher, 2014).
160

161 **2.1. Hydrothermal veins in the Schwarzwald**

162 About 1000 hydrothermal veins are known in the Schwarzwald (Metz et al., 1957; Bliedner &
163 Martin, 1986; Staude et al., 2009, Walter et al., 2016). Most of the veins consist of quartz, fluorite,
164 barite and carbonates with a wide range in modal amounts of base and precious metal oxides, sulfides
165 and arsenides (Fe-Mn, Cu-Pb-Zn and Ag-Bi-Co-Ni-U) (Metz et al., 1957). Five maxima of
166 hydrothermal activity which are related to events of vein formation are known in the Schwarzwald,
167 starting in late-Carboniferous with quartz-tourmaline veins; followed by Permian quartz veins with
168 rare Au-Sb mineralization; then barren Triassic-Jurassic quartz-hematite veins; then Jurassic-
169 Cretaceous fluorite-barite-quartz-carbonate veins with (sub-) economic amounts of Pb-Zn-Cu, Fe-Mn
170 and or rarely Ag-Bi-Co-Ni-U ores; and finally post-Cretaceous quartz-barite-fluorite ± carbonate veins
171 with variable mineralogy and Pb±Zn±Cu± (As) mineralization (Staude et al., 2012; Pfaff et al., 2009,
172 Walter et al., 2016). All the veins studied herein belong to the latter, post-Cretaceous group and are
173 related to the opening of the Upper Rhinegraben.
174

175 **2.2. Hydrology of the Schwarzwald and Upper Rhinegraben**

176 Data on water chemistry from numerous drill holes and wells show that a vertical fluid
177 stratification is present in the Schwarzwald basement (Bucher & Stober, 2010). Representative fluid
178 data is presented in table 1. Shallow bore holes (<1 km depth) contain Ca-Na-HCO_3 type fluids with
179 low TDS of <2 wt.%. Below 3 km, the fluid composition changes to CO_2-bearing Ca-Na-HCO_3-SO_4
180 type fluids, in which the high SO_4 content probably relates to oxidation of sulfides in the host rock. In
181 the transition zone between oxidized to reduced fluid conditions, the sulfate and CO_2 content in the
182 fluid decreases continuously with increasing chlorinity. The deepest fluids known today (down to
183 about 8 km depth in the Urach HDR drilling) are high-TDS (total dissolved solids) Na-Ca-Cl fluids
184 (~200 g/L) with Cl/Br mass ratios ~80-100 and a low SO_4/Cl mole ratio of ~0.014 typical of deep
185 seated brines worldwide (Bucher and Stober, 2010; Edmunds and Savage, 1991; Emmermann et al.,
186 1995; Frape and Fritz, 1987; Frape et al., 1984; Köhler, 1992; Kozlovsky, 1984; Sanjuan et al., 2010).
187 This vertical fluid stratification is interpreted to be a result of successive infiltration of surface derived
188 waters into the crust over time (Agemar et al., 2013; Bons et al., 2014; Walter et al., 2016 and
189 references therein).

190

191 *2.2.1.Sedimentary cover (Permian-Jurassic)*

192 The various sedimentary cover rocks show a wide range in compositions and permeabilities
193 that are reflected by variable fluid compositions. Fluids from Permian redbeds are typically Na-Ca-
194 (K)-Cl fluids with a maximum TDS of 124 g/L (Pauwels et al., 1993). The Permian sedimentary
195 basins are only locally present and hence, not significant aquifers in the study area (Geyer & Gwinner,
196 2011).

197 Lower Triassic (Buntsandstein) formation waters are Na-Ca-HCO_3-Cl-(SO_4) type fluids with a
198 maximum TDS of 207 g/L and Cl/Br mass ratios of 165-327 and SO_4/Cl mole ratios ($[SO_4]/[SO_4] + [Cl]$) of 0.009-0.010 (Pauwels et al., 1993, Ludwig et al., 2011). Formation waters in the middle
200 Triassic (Muschelkalk) limestone-gypsum-halite formation show a wide range in composition,
201 depending of 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 meterto 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 ($T_{m,ice}$), hydrohalite ($T_{m,hh}$), halite ($T_{m,hal}$), mirabilite ($T_{m,mir}$) as well as an additional sulfate phase (presumably gypsum, $T_{m,gyp}$) 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 (> ±2wt.% 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

281 estimated trapping temperature.

282

283 **3.2. Micro-Raman spectroscopy**

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

294

295 **3.3. Crush-leach analysis**

296 From 6 samples that contained only one fluid type (as determined by petrography and
297 microthermometry prior to crush-leach analysis), about 3 g of quartz, (grain size of 2.5 to 5 mm) were
298 separated by hand to avoid visible impurities. The analyses were performed at the University of
299 Tübingen following the method of Köhler et al. (2009) and Walter et al. (2016). These separates were
300 first washed for 3.5 hours in HNO_3 at 60-70°C and subsequently washed for one week with ultrapure
301 water, changing the water twice a day. These samples were then dried and crushed in an agate mortar.
302 Subsequently, 10 ml of ultrapure water were added, which was acidified with suprapure HNO_3 to
303 suppress adsorption of doubly-charged cations (especially Ca^{2+}; Köhler et al., 2009). The loaded
304 solutions were injected into a Dionex ICS 1000 ion chromatography systems, equipped with an IonPac
305 AS 9-HC 2mm column for quantification of anions (F, Cl, Br, PO_4 and SO_4) and an IonPac CS 12-A
306 column for cations (Li, Na, K, Mg, Ca, Ba, Sr). For injection of the solutions, disposable syringe
307 filters CROMAFILE® Xtra RC-20/25 and CROMAFILE® Xtra PVDF-20/25 for anions and cations,

308 respectively, were used (Ladenburger 2012, and Ladenburger et al., 2012). Blank runs were carried out
309 after each analysis, and standard solutions were regularly analyses to monitor the reproducibility and
310 precision of the measurements. Uncertainties were usually smaller than 15% (thus, <30% for the
311 element ratios) and effective detection limits were generally <10 mg/L. Absolute concentrations were
312 calculated based on the salinity determined by microthermometry using Cl as internal standard (Allan
313 et al., 2005).

314 The complete dataset is presented in the electronic supplement. All of the crush-leach
315 solutions contain dissolved carbonate (presumably HCO_3^-) from fluid inclusions (as indicated by the
316 presence of CO_2 based on Raman spectroscopy) and we assume that the positive deviations from
317 electrical neutrality can be ascribed to carbonate species (e.g. Bottrell et al., 1988; Banks et al., 2000;
318 Dolnischek et al. 2014). Contamination of the leachates by dissolution of host minerals is not relevant
319 for quartz.
320

321 **3.4. Numerical modeling: The system Na-Ca-Cl-SO_4**

322 The solidus-liquidus phase equilibria were calculated in binary, ternary and quaternary
323 compositional space within the system H_2O-Na-Ca-Cl-SO_4 using procedures similar to those described
324 by Steele-MacInnis et al. (2016). Briefly, we used the Pitzer-type ion interaction model to compute the
325 activities of solutes and H_2O, using interaction parameters tabulated by Marion and Kargel (2008).
326 The model of Pitzer (1973) and Pitzer and Mayorga (1974) allows computation of the activities of ions
327 (as well as non-electrolyte solutes) and solvent by parameterizing and invoking all potential two-way
328 (binary) and three-way (ternary) interactions in a solution. The parameters for ion interactions are
329 temperature functions (Marion and Kargel, 2008). Equilibrium between liquid and solid is attained
330 with the appropriate ion activity product is equal to the solubility product of a given mineral. The
331 solubility products are also described by temperature functions (Marion and Kargel, 2008), permitting
332 calculation of solid-liquid equilibria over a range of temperatures. This model has been previously
333 applied to compute solidus-liquidus phase diagrams for some binary systems by Spencer et al. (1990),
334 and for binary, ternary and quaternary systems in which chloride is the only anion by Williams-Jones
335 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_2O-NaCl and H_2O-$CaCl_2$ (from Steele-MacInnis et al., 2016), plus H_2O-Na_2SO_4 and H_2O-$CaSO_4$. Ternary systems modeled are H_2O-NaCl-$CaCl_2$ (from Steele-MacInnis et al., 2016), H_2O-NaCl-Na_2SO_4, H_2O-$CaCl_2$-$CaSO_4$, and H_2O-Na_2SO_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_2O-Na_2SO_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_2O-Na_2SO_4-$CaCl_2$ compositional space. The quaternary system modeled here is the reciprocal system H_2O-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_2O plus three ions independently, whereas the concentration of the remaining (fourth) ion is always constrained by the requirement of charge

364 balance. Stated differently, we can fully describe any composition in this system terms of H_2O plus
365 three salts by writing the fourth salt as a linear combination of the other three (albeit with negative
366 stoichiometries; Clibbens, 1920) such as: $CaCl_2 = CaSO_4 + 2NaCl – Na_2SO_4$. For convenience, we can
367 also describe compositions in this quaternary system in terms of coordinates within a square-based
368 pyramid of compositional space (rather than a tetrahedron, as used for quaternary systems involving
369 three salts of a common ion; Steele-MacInnis et al., 2016). Importantly, by projecting from the H_2O
370 apex of the compositional pyramid onto the plane of four salts, we can represent the ice+vapor-
371 saturated liquidus surfaces on a two-dimensional plane (Clibbens, 1920; Crawford et al., 1979; Steele-
372 MacInnis et al., 2016). In the case of a reciprocal system such as H_2O-Na-Ca-Cl-SO_4, the projection
373 from the H_2O apex can be represented as a compositional square, of which one axis represents mole
374 fraction of anions (e.g., $[SO_4^{2-}] / ([Cl^-]+[SO_4^{2-}])$ and the other axis represents mole fraction of cations
375 (e.g., $[Na^+] / ([Na^+]+[Ca^{2+}])$. This projection is sometimes referred to as Jänecke's method (Clibbens,
376 1920).
377
378 ## 4. RESULTS
379 ### 4.1. Microthermometry
380 Detailed petrography (optical microscopy and microthermometry) of fluid inclusion
381 assemblages (FIAs) enables their classification according to their relative age. Major differences
382 between primary and secondary fluid inclusions analyzed in this study can be summarized as follows:
383 Primary inclusions along crystal growth zones are typically smaller (<5-15 µm) than secondary
384 inclusions and pseudosecondary assemblages (<5-80 µm), which mostly occur along (partly) sealed
385 fractures and crosscut the primary structures often exhibiting angular shapes. We used the temporal
386 relationships between FIAs to construct the relative temporal sequence of fluid inclusions (p, s, ps, iso)
387 analyzed here.
388 In general, veins situated directly on the Rhinegraben boundary fault or on conjugate faults
389 (related to the boundary fault) show complex, temporally alternating fluid signatures within one host
390 mineral crystal involving low-, medium- and high-salinity fluid inclusion assemblages of variable
391 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 ($NaCl \cdot 2H_2O$) 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 $L_{80}(LV)_{20}$. 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 ($L_{aq}L_{car}V \rightarrow L_{aq}V$) between +21.3 and +31°C. Clathrate is observed in some FIAs, 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_{CO2}, 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

420 solid phase occurred at +44.2° to +66.8°C (see green solids in Fig. 3B-E).Homogenization
421 temperatures vary within an assemblage (between 8° and 40°C) and range from 107 °C to 220 °C
422 between different assemblages. Inclusion sizes vary from <5 μm to >100 μm with volume fractions of
423 $L_{90}V_{10}$ to $L_{90}V_5$ (i.e., 5-10 vol% vapour).
424
425 **4.2. Crush-leach analyses**
426 In total, 6 crush leach analyses of 6 veins were performed. The complete dataset is presented in the
427 electronic supplement (HCO_3 is derived by charge balance). In accordance with the
428 microthermometric results, these analyses record the presence of SO_4, with SO_4/Cl mole ratios of
429 0.192-0.594 in the two recognized fluid types: Na-Ca-Cl-SO_4, and Na-Ca-Cl-SO_4-HCO_3. The
430 calculated HCO_3 content (based on charge balance) is in the range of 435-3800 (meq/l).
431
432 **4.3. Phase relations on the vapor-saturated liquidus**
433 *4.3.1. Binary systems*
434 For compositional determinations based on microthermometric observations, it is instructive
435 to start by interpreting binary phase diagrams, and subsequently combine these systems to investigate
436 higher-order systems. Therefore Fig. 4 shows the vapor-saturated liquidus relations for four binary
437 systems: H_2O-NaCl, H_2O-$CaCl_2$, H_2O-Na_2SO_4 and H_2O-$CaSO_4$. The two former, chloride-bearing
438 systems have been described in detail previously (Spencer et al., 1990; Bodnar and Vityk, 1994; Oakes
439 et al., 1990; Baumgartner and Bakker, 2000; Steele-MacInnis et al., 2016). Briefly, both systems are
440 characterized by eutectic points separating the ice-stable liquidus from the liquidus of salt hydrate
441 (hydrohalite in the system H_2O-NaCl, and antarcticite, $CaCl_2 \cdot 8H_2O$, in the system H_2O-$CaCl_2$).
442 Peritectic points separate the liquidus lines of hydrohalite from halite in the former system (Fig. 4A),
443 and separate three hydrates of calcium chloride (antarcticite, sinjarite, and Ca-dihydrate) as well as
444 anhydrous calcium chloride (not shown on Fig. 4B). The eutectic temperature in the system H_2O-NaCl
445 is approximately -21.2 °C, and the eutectic liquid composition 23.3 wt% NaCl (Hall et al., 1988). The

446 eutectic temperature in the system H_2O-$CaCl_2$ is approximately -50 °C, and the eutectic liquid
447 composition ~31 wt% $CaCl_2$ (Yanatieva, 1946).

448 Binary phase diagrams of sulfate-bearing systems are shown in Fig. 4C and 4D, and differ
449 markedly from the chloride-bearing systems in several ways. Firstly, both systems, H_2O-Na_2SO_4 and
450 H_2O-$CaSO_4$, exhibit only modest freezing-point depression of ice to the eutectic temperature (and
451 concomitantly, relatively dilute eutectic liquid compositions), as well as retrograde solubility of salts
452 and/or salt hydrates (Fig. 4C and 4D). In the system H_2O-Na_2SO_4, the predicted eutectic temperature is
453 approximately -1.1 °C, with a liquid of 3.9 wt% Na_2SO_4 coexisting with ice plus mirabilite. Mirabilite
454 decomposes to thenardite (anhydrous Na_2SO_4) plus liquid at a peritectic point located at about +32.5
455 °C and a liquid composition of 31.8 wt% Na_2SO_4. Thenardite exhibits retrograde solubility on the
456 liquidus over the range of temperature investigated here, such that by +55 °C, the liquid salinity in
457 equilibrium with thenardite has decreased to 24.7 wt% Na_2SO_4 (Fig. 4C).

458 The liquidus in the system H_2O-$CaSO_4$ is notably different from both the chloride-bearing
459 binaries and from the system H_2O-Na_2SO_4, as a consequence of the exceptionally low solubilities of
460 both gypsum and anhydrite (Fig. 4D). The predicted eutectic point, at which ice is in equilibrium with
461 gypsum, occurs at approximately -0.02 °C and a liquid composition of 0.13 wt% $CaSO_4$. The gypsum
462 liquidus is nearly vertical (i.e., solubility shows little temperature dependence) over the range of
463 temperature investigated here. In detail, gypsum shows prograde solubility up to approximately +33
464 °C, above which the solubility is retrograde. Over the range of temperature analyzed here, anhydrite is
465 always metastable (Fig. 4D). The predicted metastable eutectic between ice and anhydrite is located at
466 -0.07 °C at a liquid salinity of 0.38 wt% $CaSO_4$. The metastable anhydrite liquidus shows retrograde
467 solubility, such that this curve will intersect the gypsum liquidus at just above +55 °C (just beyond the
468 maximum on the y-axis of Fig. 4D). The crossover point between the liquidi of gypsum and anhydrite
469 is a peritectic point, at which gypsum decomposes to anhydrite plus liquid during heating.

470 *4.3.2. Ternary systems*

471 Figure 5 shows the vapor-saturated liquidus relations of the system H_2O-NaCl-$CaCl_2$ (Vanko
472 et al., 1988; Schiffries et al., 1990; Oakes et al., 1990; Steele-MacInnis et al., 2011; Steele-MacInnis et

al., 2016). 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 H_2O-NaCl-$CaCl_2$ are nearly identical to those of other systems of H_2O, NaCl and divalent-cation chlorides (e.g., $MgCl_2$ and $FeCl_2$; 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 $CaCl_2$-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:$CaCl_2$ 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 H_2O-NaCl-Na_2SO_4, 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 $CaCl_2$ (Fig. 5), is the large stability field of mirabilite and the concomitant collapse of the ice-liquidus field to a thin wedge near the H_2O-NaCl join. The hydrohalite field is also reduced to a thin sliver near the H_2O-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 H_2O-NaCl eutectic at -21.5 °C. The stability field of thenardite also encroaches on the formery 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.

500 Systems containing $CaSO_4$ (Figs. 7 and 8) exhibit liquidus relations dominated by the stability
501 field of gypsum, owing to the very low solubility of the latter phase. As such, all of the univariant
502 curves are compressed towards the $CaSO_4$-free binary join when plotted in ternary mass-fraction
503 space. In order to better display the unvariant boundaries, we therefore recast the projection by
504 multiplying the $CaSO_4$ concentration (wt%) by 50x, and renormalizing to 100% with respect to the
505 sum of H_2O, $CaCl_2$ and 50x$CaSO_4$ (Fig. 7) or with respect to the sum of H_2O, Na_2SO_4 and 50x$CaSO_4$
506 (Fig. 8).

507 The liquidus of the system H_2O-$CaCl_2$-$CaSO_4$ is dominated by the stability field of gypsum,
508 with the ice liquidus and antarcticite liquidus each occupying a relatively thin sliver near the H_2O-
509 $CaCl_2$ join. The eutectic in this ternary system is thus approximately coincident with that in the H_2O-
510 $CaCl_2$ system. The gypsum liquidus surface exhibits a very steep temperature-salinity trajectory,
511 analogous to that in the binary system H_2O-$CaSO_4$. As such, the isotherms on the gypsum liquidus
512 cluster very close to the ice-gypsum cotectic curve (Fig. 7)

513 The liquidus of the system H_2O-Na_2SO_4-$CaSO_4$ is also dominated by the gypsum stability
514 field, but although not as much as in the system H_2O-$CaCl_2$-$CaSO_4$ because of the competing
515 mirabilite stability field (Fig. 8). The ice liquidus is restricted to very close to the H_2O apex, and the
516 eutectic point between ice, mirabilite and gypsum is located at just above -1 °C, with a liquid
517 composition of ca. 1.3 wt% Na_2SO_4 and 0.1 wt% $CaSO_4$. These data suggest that for wide ranges of
518 composition in this system, ice will be the first phase consumed at the eutectic. The liquid composition
519 will then evolve along the mirabilite plus gypsum cotectic curve until one of those two phases is
520 consumed second-to-last, and the other will melt last. The H_2O-Na_2SO_4-$CaSO_4$ system also differs
521 from the preceding systems in that an intermediate salt appears on the liquidus: glauberite,
522 $Na_2Ca(SO_4)_2$. The glauberite stability field appears to be limited to relatively high salinities and
523 intermediate salt ratios, between the stability of thenardite and gypsum.

524 *4.3.3. Quaternary system*

525 Figure 9 shows a projection from the H_2O apex onto the ice+vapor saturated liquidus of the
526 system H_2O-Na-Ca-Cl-SO_4, plotted in a compositional square according to Jänecke's method

527 (Clibbens, 1920). Ion fractions in this diagram are reported based on molal concentrations. In this
528 projection, similarly to in the ternary systems involving $CaSO_4$, we have multiplied the sulfate
529 concentration by 50x, and we have multiplied the calcium concentration by 10x, in order to better
530 displaythe main features. Each divariant field represents the mutual stability of ice plus one other solid
531 phase, in equilibrium with liquid plus vapor. Three solid phases are in equilibrium on the cotectic
532 curves, and the invariant points represent the equilibrium of four solid phases plus liquid plus vapor.

533 The cotectic surfaces of ice plus sulfate minerals are the dominant features on the H_2O-Na-Ca-
534 Ca-SO_4 quaternary diagram, when projected from H_2O onto the plane of four salts (Fig. 9). The field
535 of gypsum occupies almost half of the diagram, for compositions to the calcium-rich side of the
536 diagram (if the multiplication factors 50x and 10x are omitted from the *y*- and *x*-axes, then the
537 ice+gypsum field takes up almost the entire diagram). The field of mirabilite occupies the majority of
538 the sodium-rich side. The fields of sodium and calcium chlorides (hydrohalite and antarcticite,
539 respectively) are comparatively smaller, again owing to the low solubilities of sulfate minerals
540 compared to chlorides. The subsolidus assemblage in low-salinity H_2O-Na-Ca-Ca-SO_4 fluids is either
541 ice+hydrohalite+antarcticite+gypsum, or ice+hydrohalite+mirabilite+gypsum, depending on the bulk
542 composition. Assemblages containing both mirabilite and antarcticite are forbidden, according to the
543 phase equilibria (Fig. 9). This feature is typical of reciprocal quaternary phase diagrams, in which two
544 salts or salt hydrates are referred to as the "stable pair" (in this case, gypsum plus hydrohalite) whereas
545 two are referred to as the "unstable pair" (here, mirabilite plus antarcticite; Clibbens, 1920).
546 Incidentally, the fact that mirabilite plus antarcticite is the unstable pair furthermore confirms that the
547 system H_2O-Na_2SO_4-$CaCl_2$ is not ternary, but rather quaternary, owing to gypsum precipitation.

548 Arrows on the univariant curves in Fig. 9 point down temperature, and the estimated
549 temperatures at the invariant points are labelled. According to these results, the invariant point *p* is a
550 peritectic point, at which hydrohalite and mirabilite/gypsum melt incongruently. Specifically, during
551 heating, inclusions that contain ice+hydrohalite+gypsum will undergo incongruent dissolution of
552 hydrohalite to produce mirabilite+liquid at point *p*. Also note that during cooling, mirabilite initially
553 precipitated along the liquidus must be re-dissolved in order for the liquid composition to depart from
554 point *p* along the ice+hydrohalite+gypsum cotectic line. The predicted temperature of this peritectic

555 point is -22 °C. The invariant point of ice+hydrohalite+gypsum+antarcticite is a eutectic point, with
556 the estimated eutectic temperature of -52 °C (similar to that in the H_2O-NaCl-$CaCl_2$ system).

557 In practice, unlike the case for ice-saturated cotectic surfaces, it is not straightforward to
558 project the relevant phase relations onto a convenient 2D plane at saturation of a specific salt or salt-
559 hydrate. In the present study, most of our inclusions have gypsum as the last solid phase to melt, and
560 thus it would be of interest to project from the composition of gypsum onto a 2D plane. Options
561 include projecting from of gypsum onto the H_2O-Na_2SO_4-$CaCl_2$ plane, or onto the NaCl-Na_2SO_4-
562 $CaCl_2$ plane, but both of these projections yield incomplete information on salt ratios and salinity, and
563 therefore these projections are not included here.

564

565 # 5. DISCUSSION

566

567 ## 5.1. Fluid chemistry of the sulfate bearing brines

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

576 Not surprisingly, the predicted phase equilibria corroborate that a calcium sulfate mineral –
577 either gypsum or anhydrite – is the most likely solid phase to melt last during heating, for a wide range
578 of compositions. At thermodynamic equilibrium, gypsum would be the expected calcium-sulfate phase
579 on the liquidus up to ca. +60°C (Fig. 4D), whereas anhydrite would be metastable. Hardie (1967)
580 reported that at ambient pressure, gypsum is the first solid phase to precipitate throughout a range of

581 temperatures, including both the gypsum-stable part of the liquidus up to the anhydrite-stable part of
582 the liquidus. In the experiments of Hardie (1967), formation of metastable gypsum rather than stable
583 anhydrite was common, whereas formation of metastable anhydrite rather than stable gypsum was not.
584 As such, we suspect that the calcium sulfate daughter mineral observed in our inclusions is gypsum –
585 the stable calcium sulfate phase at the conditions of our microthermometric observations. The melting
586 temperature of this phase is on the order of +40 to +70°C in both the Type A and the Type B
587 inclusions, which near the crossover temperature between the gypsum and anhydrite portions of the
588 liquidus (i.e., the gypsum-anhydrite peritectic point; Fig. 4D).

589 In all inclusions analyzed here, the last melting of a calcium sulfate phase (presumably
590 gypsum) is preceded by second-to-last melting of an equant, greenish solid phase at around +19 to +25
591 °C. According to the predicted liquidus relations described above, this solid is most likely mirabilite.
592 Mirabilite is a monoclinic phase, but forms crystals "like pyroxene in habit and angles" (Winchell,
593 1927). Thus, the appearance of this phase in our inclusions –equant, apparently cubic – is consistent
594 with the habit of monoclinic mirabilite. We would expect that mirabilite would show birefringence (in
595 fact, anomalous interference colors without extinction; Winchell, 1927), which is not observed in our
596 samples, but this may be a consequence of the very small crystal size within the inclusions. The range
597 of melting temperatures of this phase is consistent with the mirabilite liquidus (Figs. 1C, 3).
598 Thenardite (orthorhombic) may also be an option, stable down to 15°C in NaCl-bearing solutions (Fig.
599 6), but is less likely as a second-to-last phase to melt before gypsum (Fig. 6).

600 Excluding CO_2-clathrate, which is present in the Type B inclusions, ice is the third-to-last
601 solid phase to melt in our inclusions. Ice melting temperatures are on the order of -15 to -10 °C for
602 inclusions of Type A, and -13 to -0.1 for inclusions of Type B. In both inclusion types, ice melting
603 represents the departure from the ice-saturated quaternary cotectic surface shown in Fig. 9.

604 Prior to ice melting, inclusions of Type A show only the first melting, or eutectic event, which
605 occurs at >-45°C. The fact that first melting occurs at temperatures greater than -52°C suggests that
606 these inclusions do not contain antarcticite in the subsolidus assembalge. Thus, based on this
607 observation, we infer that the likely subsolidus assemblage in these inclusions is

608 ice+hydrohalite+mirabilite+gypsum. In this case, hydrohalite is the first solid phase to be fully
609 consumed at the first-melting temperature (predicted to be ca. -27°C), which also explains why we did
610 not measure a hydrohalite melting temperature in these inclusions. Upon hydrohalite melting, the
611 liquid phase in these inclusions of Type A would evolve along the ice+mirabilite+gypsum cotectic
612 line, until ice is consumed at -15 to -10 °C, after which the liquid composition moves onto the
613 mirabilite+gypsum plane (not shown in Fig. 9, but extending from the mirabilite+gypsum cotectic in
614 Fig. 8). Mirabilite is consumed at ca. +19 to +25 °C, after which the liquid composition evolves
615 towards gypsum dissolution until gypsum is consumed.

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

631 Based on the interpretations described above, we estimated the compositions of the Type A
632 and Type B inclusions from the Schwarzwald and Upper Rhinegraben samples as follows. Firstly, for
633 Type A inclusions, lack of detectable hydrohalite dissolution suggests first melting at the quaternary
634 peritectic point as noted above, which implies that the bulk composition falls within the
635 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.

664 It must be noted that from the crush-leach analyses, we know that these inclusions also contain
665 some bicarbonate ion. It is likely that the Type B inclusions, especially, contain some significant
666 bicarbonate concentrations. This in turn is also consistent with the observation of double bubbles in
667 the inclusions, as well as melting of solid CO_2 and CO_2-clathrate. Thus, the Type B inclusions would
668 likely be better represented by the quinary H_2O-Na-Ca-Cl-SO_4-HCO_3 system. Nevertheless, the
669 liquidus relations modeled here provide reasonable constraints on the Na/Ca and Cl/SO_4 ratios in these
670 inclusions, and indicate significant differences from the Type A inclusions.

671

672 **5.2 Mole fractions as indicators of fluid sources**

673

674 Based on our model, which allows to calculate ion SO_4/Cl mole ratios from
675 microthermometric data, we are able to compare our calculated fluid compositions to modern fluids in
676 the Upper Rhinegraben rift. Walter et al. (2016) showed that fluids and related aquifers get modified
677 by water/rock interaction over time. However, the fluids in this study are archived in very young veins
678 that are situated on fractures that are related to the Neogene strike-slip tectonics of the Upper
679 Rhinegraben rift (Werner and Franzke, 2001). The work of Walter et al. (2016, 2017) indicates that the
680 primary fluid composition of the original aquifers is archived over a time period of millions years.
681 Hence, we assume that effect of fluid-rock interaction by short living aquifers is negligible.
682 Furthermore, the modern fluids show typical signatures (e.g. Na/Ca ratios, TDS, Cl/Br ratios, Cl/SO_4
683 ratios) which are directly related to their source rocks (Göb et al., 2013 and references therein). For
684 example, the middle Triassic Muschelkalk halite formation has a high TDS, high Cl/Br ratios and very
685 high Na/Ca ratios. In addition, numerous authors have concluded that fluid mixing was important for
686 the hydrothermal vein mineralization in the Schwarzwald mining district (e.g. Baatartsogt et al., 2007,
687 Staude et al., 2009; Fusswinkel et al., 2013; Bons et al., 2014; Burisch et al., 2016a; Walter et al.,
688 2015, 2016). Hence, the previous work allows us to discuss the measured fluid composition (in
689 hydrothermal veins) as a mixed hydrothermal fluid from different aquifers that are similar to the
690 observed fluids in modern aquifers in the Schwarzwald and Upper Rhinegraben.

691 Fluid type A that is observed in the Böschlisgrund, Kropbach Hof, Wildsbach West,
692 Riggenbach and Karl August mine and shows an absolute salinity of 24.3-27.9 wt% which requires
693 high-salinity sources. The fluid signature shows a dominance of Na with very low Ca contents
694 ([Ca]/[Ca] + [Na]) of 0.03-0.04. Hence, a sodium rich fluid source is required. The observed Cl/Br
695 mass ratios of 88-120 show that the NaCl-rich fluids from the middle Triassic halite formation (Cl/Br
696 9900) are an unlikely source. The high SO_4/Cl mole ratio of 0.22 to 0.60 in our samples imply fluid
697 mixing between a sulfate dominated aquifer and a Cl rich source.

698 The high-salinity Na-Cl rich, SO_4-depleted fluid is presumably a continental basement brine,
699 which is the most important fluid source and base-metal carrier for all veins in the Schwarzwald
700 mining district (Staude et al., 2009; Fußwinkel et al., 2013; Bons et al., 2014; Walter et al., 2015, 2016
701 and references therein). The second mixing endmember is presumably derived from the Middle
702 Triassic sulfate facies aquifer which contains fluids that show high SO_4/Cl mole ratios up to 0.77 with
703 a low Cl/Br mass ratio and a moderate salinity. In addition, one fluid signature was observed by He et
704 al., (1999) in the Hauptrogenstein with a SO_4/Cl mole ratio up to 0.77 and a low Cl/Br mass ratio with
705 moderate salinity that could be a possible source . All the other aquifers are either depleted in SO_4 like
706 the Buntsandstein or are significantly elevated in Cl/Br and Ca content like the Keuper fluids (Göb et
707 al., 2013).

708 In contrast to fluid type A, the similar fluid type B is only present in the Karl August vein and
709 shows an equal salinity to fluid type A. However it has a relative depletion in SO_4 and an higher Ca
710 content related to low Cl/Br mass ratios. Again the high Cl/Br reservoirs seemed not to have been an
711 important source. There are two models that could explain the variation relative to fluid type A ,by
712 changes in the fluid mixing ratio or by an additional Ca-enriched fluid source (Fig. 10), which is also
713 described for the Karl August vein (Walter et al. 2016).

714 For both fluid types, the high SO_4 content implies a dominant fluid influx from the
715 Muschelkalk sulfate-facies aquifer and requires high mixing ratios of sedimentary brine over
716 basement brine. This correlation was also recognized by Walter et al. (2017) in Jurassic-Cretaceous
717 veins of the Schwarzwald mining district. Furthermore, this inference is consistent with the regional

718 geology (Fig. 1). All these veins are situated on conjugate faults of the Upper Rhinegraben rift in the
719 paragneiss unit close to the main offset fault (Schwarzwaldrandverwerfung) that borders the plains of
720 the rift against the rift shoulders. Furthermore, tilted blocks of the former sedimentary overburden
721 (with the significant Muschelkalk-sulfate-facies and Hauptrogenstein thermal aquifer) are directly
722 juxtaposed at the Schwarzwaldrandverwerfung to the gneiss unit that hosts the veins. Additionally, no
723 clays can be recognized in the veins, which, if present ,would have sealed the fluid pathways. Hence,
724 fluid migration from Muschelkalk and Hauptrogenstein aquifers in the Upper Rhinegraben into the
725 first km of the gneiss unit of the rift shoulder seems to be plausible. The fact that there are several spas
726 with thermal waters along the Schwarzwaldrandverwerfung that are derived from Muschelkalk and
727 Hauptrogenstein also supports the argument for a Muschelkalk and Hauptrogenstein provenance for
728 the SO_4 fluid endmember in our mixed fluid.

729 In summary, the numerical model based on the Pitzer-type ion interaction theory for
730 computing the activities of solutes especially for SO_4 and H_2O that is presented in this study improved
731 the ability to interpret microthermometric data of SO_4-containing fluid inclusions and has the capacity
732 to significantly improve the knowledge of fluid provenance.

733

734 ## 6. CONCLUSIONS

735 The new thermodynamic model for microthermometry that is presented in this contribution for the
736 system H_2O-Na-Ca-Cl-SO_4 shows a significant potential in the investigation of sulfate brines that are
737 common in numerous sedimentary basins worldwide. This model allows to calculate accurate
738 corrections for further major and trace element methods in fluid research like LA-ICPMS on single
739 inclusions and/or crush-leach analyses, that will help to illuminate sulfate concentrations of brines.
740 Furthermore, the model yields SO_4/Cl mole ratios and Ca/Na mole ratios that are an effective tool as
741 source tracers. As discussed above, the combination of fluid tracers like Ca/Na, Cl/Br and SO_4/Cl
742 permits differentiation between several natural aquifers.

743

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FIGURE CAPTIONS

Figure 1

Geological map of the study area, showing the Rhinegraben rift shoulders and the rifting related hydrothermal veins . Based in part on GeoRG data after Beccaletto et al. (2010). The numbers refer to the mineralizations: 1. Karl August mine near Kropbach, 2. Böschlisgrund, 3. Riggenbach, 4. Kropbach Hof and 5. Wildsbach West.

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 (proably 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 H_2O-NaCl (A), H_2O-$CaCl_2$ (B), H_2O-Na_2SO_4 (C) and H_2O-$CaSO_4$ (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 H_2O-NaCl-$CaCl_2$, 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 H_2O-NaCl-Na_2SO_4. Axes in mass fraction (wt%). Isotherms (grey lines) are in 5 °C increments.

Figure 7

Ternary vapor-saturated liquidus diagram for the system H_2O-NaCl-$CaSO_4$. 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 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_2O-Na_2SO_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_2O-Na-Ca-Cl-SO_4, projected from the H_2O 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.

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