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# Late-metamorphic veins record deep ingression of meteoric water: A LA-ICPMS fluid inclusion study from the fold-and-thrust belt of the Rhenish Massif, Germany

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ABSTRACT

The fluid evolution of late-metamorphic quartz vein systems in the fold-and-thrust belt of the Rhenish Massif has been studied by microthermometry and LA-ICPMS microanalysis. The quartz veins are hosted by very low-grade organic-matter-rich metasiltstones and metapelites of the Hunsrück nappe complex. The veins record two major stages of textural evolution, a massive vein filling assemblage with elongate-blocky quartz, chlorite, albite and apatite, and a later open space filling assemblage with euhedral crystals of quartz, ankerite/dolomite and minor calcite and sulfides. The euhedral quartz crystals host well-preserved fluid inclusion assemblages, which made it possible to reconstruct the chemical evolution of the fluid system with time. The fluid inclusions are all aqueous two-phase with low salinity, and three successive fluid generations record a systematic decrease in salinity from 4.7–5.3 to 3.1–3.9 and then to 1.4–1.7 wt.% eqv. NaCl. The salinity decrease is paralleled by a decrease in homogenization temperatures from 210–225 °C to 148–164 °C and 124–139 °C. Using LA-ICPMS microanalysis of individual fluid inclusions, reproducible elemental concentrations of Li, Na, K, Rb, Cs, Mg, Ca, Ba, Sr, B, Al, As, Sb, S, Cl and Br could be determined. The concentrations of the alkali metals and of boron, arsenic and antimony are correlated with the fluid salinity. Element concentrations are highest in the early fluid generation and decrease systematically in the latter two generations. The systematic changes in fluid composition (salinity, homogenization temperature and elemental concentrations) are best explained by fluid mixing between a hot metamorphic fluid of moderate salinity (that carried elevated concentrations of B, As and Sb) and a cooler dilute fluid that was of meteoric origin. The fluid evolution therefore signals deep ingression of meteoric water during late-metamorphic exhumation and uplift. The molar Cl/Br ratios of the fluid inclusions lie on a linear array that extends from close to seawater to values that are substantially below seawater. Because evaporitic sources are conspicuously absent in the shallow-water marine sequence of the Rhenish Massif, the elevated Br concentrations (and Cl/Br ratios below seawater) are best explained by fluid–rock interaction and liberation of Br from the organic matter in the metasediments.

## 1. Introduction

Fluids play an important role in the structural and chemical evolution of orogenic belts, because advection of metamorphic fluids affects the distribution of heat and mass, and influences mineral reactions and deformation (Bickle and Mckenzie, 1987; Connolly and Thompson, 1989; Ferry and Dipple, 1991; Ferry, 1994). Evidence for extensive fluid flow during metamorphic processes is provided by abundant quartz vein arrays in regionally metamorphosed terranes in the upper crust (Yardley, 1983; Mullis et al., 1994; Cartwright and Buick, 2000; Oliver and Bons, 2001). Quartz vein systems record information about the pressure–temperature conditions and the composition of metamorphic fluids generated along the metamorphic path (Cox et al., 1987; Evans, 1995; Nesbitt and Muehlenbachs, 1995; Schroyen and Muchez, 2000; Ague, 2003; Sindern et al., 2012). Production of metamorphic fluids is related to dehydration and decarbonation of hydrous minerals and carbonates in sedimentary and volcanic rocks as they are subjected to increasing temperatures and pressures. Devolatilization and expulsion of fluids during orogen-scale deformation cause focused fluid flow through major shear and fault zones, and facilitates transfer of large volumes of fluid from deeper to shallower levels of the crust (Baumgartner and Ferry, 1991; Yardley and Bottrell, 1992; Oliver, 1996; Connolly, 1997; Bons, 2001; Oliver and Bons, 2001; Cox, 2007). Focusing of deep and hot fluids through veins and shear zones in the upper crust may cause local thermal anomalies (Kerrich, 1986; Chamberlain and Rumble, 1988) and major changes in bulk rock composition including the formation of economic ore deposits (Sibson et al., 1988; Cox et al., 1991; Ridley, 1993; Groves et al., 1995). Fluid systems during the late retrograde

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stage of the metamorphic cycle may also experience deep ingression of meteoric water down to several kilometers depth (Templeton et al., 1998; Gleeson et al., 2000; Boiron et al., 2003; Sharp et al., 2005) and arguably even into the lower crust (Wickham and Taylor, 1985, 1987; McCaig et al., 1990).

The formation of metamorphic veins and development of related alteration selvages can be rather complex, involving mineral precipitation from advecting fluids, and fluid–rock interaction and element mobility during several successive stages (Cox et al., 1987; Baumgartner and Ferry, 1991; Cartwright and Buick, 2000; Penniston-Dorland and Ferry, 2008). Reflecting this complexity, quantitative understanding of vein formation processes requires investigation by interconnected methods that encompass structural geology, metamorphic petrology, isotope geochemistry, fluid inclusion studies, alteration geochemistry, and numerical modeling of deformation, fluid flow and reactive transport (Ramsay, 1980; Cox and Etheridge, 1983; Yardley, 1983; Etheridge et al., 1984; Yardley, 1986; Bickle and Mckenzie, 1987; Connolly and Thompson, 1989; Bottrell et al., 1990; Ferry and Dipple, 1991; Dipple and Ferry, 1992; Ferry, 1994; Oliver, 1996; Oliver and Bons, 2001; Ague, 2003; Dipple et al., 2005; Cox, 2007; Yardley, 2009; Wagner et al., 2010; Ague, 2011). Numerical models for reactive fluid flow, mass transfer and vein formation in metamorphic belts require data for the composition of paleofluids, in particular concentration data for major cations, ligands and trace ore metals. Recent advances in microanalytical techniques such as laser-ablation inductively-coupled plasma-mass spectrometry (LA-ICPMS) and synchrotron X-ray fluorescence (SXRF) analysis of individual fluid inclusions have provided much insight into the composition of fluids involved in magmatic-hydrothermal and sediment-hosted ore-forming systems (Audétat et al., 2000; Heijlen et al., 2008; Stoffell et al., 2008; Catchpole et al., 2011; Seo et al., 2012), but only few studies that employed these techniques have addressed the composition of metamorphic fluids (Thébaud et al., 2006; Miron et al., 2013). The vast majority of composition data for metamorphic fluids are based on bulk analysis that yields little information about the time–space evolution of the fluid systems (Bottrell et al., 1988; Banks et al., 1991; Yardley et al., 1993; Meere and Banks, 1997; Marshall et al., 1998; McCaig et al., 2000; Neumayr et al., 2007). Detailed texturally-resolved microanalysis of individual fluid inclusions is critical for resolving internal and external contributions to metamorphic fluid–rock systems (Boiron et al., 1992; Touret, 2001), and recognizing pulses of advective fluid flow that might relate to enhanced devolatilization at depth or deep ingression of surface-derived fluids (Boiron et al., 2003).

This study reports the results of a fluid inclusion study of quartz vein systems in very low-grade metasediments along a cross section through the Hunsrück nappe, located in the southern part of the Variscan fold-and-thrust-belt of the Rhenish Massif (Germany). The study combines detailed fluid inclusion petrography with microthermometry and LA-ICPMS microanalysis of fluid inclusion assemblages that record successive stages of vein growth and fluid trapping. The dataset comprises the concentrations of major elements, trace metals and sulfur, and the Cl/Br ratios, and is used to constrain the fluid evolution, fluid–rock equilibria and the fluid source signature. The fluid inclusion data demonstrate that salinities and concentrations of fluid volatile elements such as boron decrease systematically with time. In conjunction with information on the relative timing of vein formation and pressure–temperature constraints, the dilution of the fluid system is interpreted as signal of deep ingression of meteoric water during late-orogenic exhumation and uplift.

## 2. Geological setting

The studied quartz vein systems (Kaub, Werlau, Gründelbach and Wispertal) are situated in very low-grade metasedimentary rocks of the Hunsrück nappe, a tectono-stratigraphic unit located in the southeastern part of the Rhenish Massif (Fig. 1). The Rhenish Massif is a typical example of a thin-skinned fold-and-thrust belt and forms part of the external Rhenohercynian zone of the Central European Variscan orogenic belt (Oncken et al., 1999). The Rhenish Massif is composed of metamorphosed sedimentary and volcano-sedimentary rock units of Lower Devonian to Upper Carboniferous age, which formed during basin development in a passive continental margin setting (Matte, 1991; Oncken et al., 1999). The Lower Devonian rocks are rather homogeneous sandstones, siltstones and pelites with only very few thin intercalated tuffitic horizons (Franke et al., 1978), whereas Middle–Upper Devonian to Lower Carboniferous units comprise more heterogeneous lithologies such as shallow-marine platform carbonates, volcano-sedimentary rocks, submarine volcanics, pelites and black shales (Franke et al., 1978).

The Rhenish Massif was affected by progressive deformation during the Upper Carboniferous under predominantly NW-SE directed compression, resulting in a SW-NE strike of the first-order structural features (major folds, pervasive foliation, fault and thrust zones). The resulting structural style is characterized by stacks of imbricate nappes that are separated by major thrust zones (Fig. 2). The northernmost Midi-Aachen thrust forms the basal detachment between the fold-and-thrust belt and the underlying basement. The main tectono-stratigraphic units are separated by the Siegen, Boppard and Taunus thrust systems, with the Boppard thrust forming the boundary between the Hunsrück nappe complex and the tectonically lower Mosel syncline (Fig. 2). Progressive deformation resulted in development of a first pervasive cleavage ($S_1$) related to the major folding and thermal peak, which was partially overprinted by two subsequent generations of incipient crenulation cleavage ($S_2$ and $S_3$) (Oncken, 1984, 1988). The major fold structures are partly cut by SW-NE striking fault and thrust zones, which developed during increasing convergence under an essentially similar large-scale stress field. The deformation ages are constrained from K–Ar and Ar–Ar dating of syndeformational phyllosilicates, which show a systematic decrease from 325 to 300 Ma across the belt. This indicates that the deformation propagated steadily from south towards the Variscan front in the north (Ahrendt et al., 1983; Plesch and Oncken, 1999).

The peak metamorphic conditions were estimated from deformation microtextures, mineral assemblages, coal rank and illite crystallinity, and do not generally exceed very low-grade (sub-greenschist facies) conditions (Oncken, 1991; Oncken et al., 1995). Only the southernmost tectono-stratigraphic unit experienced slightly higher peak metamorphic conditions up to lower greenschist facies (Oncken, 1991; Dittmar et al., 1994), with temperature and pressure estimated at 320–350 °C and 4–6 kbar (Massone, 1995; Oncken et al., 1995). Metamorphic conditions in the Hunsrück nappe have been estimated from mineral chemistry, vitrinite reflectance and illite crystallinity data, and the resulting temperature and pressure conditions are 270–300 °C and 2–4 kbar (Wolf, 1978; Oncken, 1991). Deformation outlasted the metamorphic peak and caused the formation of crenulation cleavages which partially overprint the pervasive $S_1$ cleavage, together with back-rotation structures and re-activation of fault zones at the transition from syn-orogenic compression to late-orogenic uplift (Oncken, 1991). This event is related to the rotation of the regional stress field from NW-SE towards E-W direction (Oncken et al., 1999), reflecting the rearrangement of the plate-boundary interactions at the onset of the Late-Paleozoic strike-slip regime in Central Europe (Arthaud and Matte, 1977; Henk, 1997). The formation of widespread late-metamorphic quartz vein systems in the Hunsrück nappe complex is closely related to late-orogenic brittle overprinting structures. The maximum temperature–pressure conditions during vein formation were estimated as 370–420 °C and 0.2–0.7 kbar from chlorite thermometry, oxygen isotope geothermometry and fluid inclusion data. The veins record a systematic decrease in temperature down to about 140–190 °C (Wagner and Cook, 2000; Wagner et al., 2010). Stable isotope data show that the fluid system involved both internal and external contributions, and that the veins formed in a continuum between rock-buffered and more fluid-buffered conditions (Wagner et al., 2010).