Chemical Geology 433 (2016) 24–35

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

The effect of temperature and cataclastic deformation on the composition of upper crustal fluids — An experimental approach

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ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form 30 March 2016
Accepted 31 March 2016
Available online 11 April 2016

Keywords:
Halogen systematic
Hydrothermal ore
Metals
Brittle deformation
Cl/Br
Cataclasis
Water–rock interaction

ABSTRACT

We investigated the potential of common crystalline rocks to facilitate the geochemical evolution of continental basement brines and to serve as a metal source for hydrothermal ore deposits. We performed leaching experiments on typical crystalline basement rocks (granite and gneiss), a redbed sandstone and their mineral separates (feldspar, quartz and biotite) at variable T (25, 180, 275 and 350 °C), P (ambient pressure, 0.9, 1.4 and 1.9 kbar), grain-size fractions (<0.01 mm, 0.063–0.125 and 2–4 mm) and variable fluid/rock ratios (10 to 1.1) with ultra-pure water and 25 wt.% NaCl solution as solvents.

The modification of the fluid chemistry during water–rock interaction strongly depends on grain-size: leachates (using pure H_2O) of fine-grained rock powders have lower Na/Cl and Cl/Br ratios but much higher chlorinities (by a factor of up to 40) compared to leachates from coarse-grained rock powders. The Cl/Br ratios of all leachates are lower than that of their respective whole-rocks. Smaller grain-sizes of the starting materials yield element ratios (Cl/Br and Na/Cl) similar to those found in natural fluids, emphasizing the influence of cataclastic deformation on the fluid chemistry of crustal fluids. During our leaching experiments, Pb, Zn, Cu and W are released by felsic minerals, while biotite alteration releases Ni, As and additional Zn and Cu.

Our experiments confirm that crystalline rocks may serve as metal source for hydrothermal ore deposits. Short-term water–rock interactions along cataclastic fault zones in the brittle crust may influence the geochemical evolution of upper crustal fluids. This is further suggested by low F/Cl and Cl/Br ratios in some of the leachates being very similar to halogen systematics in natural fluid samples.

1. Introduction

Fluids are of major importance during most geological transport processes related to magmatism, metamorphism or formation of ore deposits. Hence, understanding the nature and evolution of their chemistry has been the focus of many studies in the last decades (Frape et al., 1984; Vovk, 1987; Nurmi et al., 1988; Lodemann et al., 1997; Markl et al., 1998; Savoye et al., 1998; Frape et al., 2003; Gleeson et al., 2003; Stober and Bucher, 2004; Gleeson and Turner, 2007; Piribauer et al., 2011).

Fluids with high salinity (up to 26 wt.% NaCl equivalent) appear to be typical of the middle and lower parts of the upper continental crust (Lodemann et al., 1997; Stober and Bucher, 1999a; Frape et al., 2003). Such deep-seated fluids represent a large halogen reservoir and influence the redistribution of metals in the crust (e.g. Yardley, 2005). The major cations in crustal fluids are Na or Ca, the dominant anion is invariably Cl, resulting in Na/Cl ratios of around one (or lower for Ca-dominated basement fluids). Deep-seated fluids show relatively high Br concentrations, resulting in low Cl/Br mass ratios (Cl/Br is given as mass ratio in this work) below the seawater ratio of 288 (Frape et al., 1984; Stober and Bucher, 1999a).

At shallow crustal depths, however, fluids are typically Ca and HCO_3-rich (Frape et al., 2003), except for fluids being derived from evaporite-bearing (mostly halite) aquifers having high Na and Cl concentrations (Stober and Bucher, 1999a). However, halite dissolution brines typically contain significant amounts of HCO_3 and very low Br (Stober and Bucher, 1999b), since halite incorporates only minor amounts of Br (Cl/Br ~2000–10,000; Siemann and Schramm, 2000). Hence, the Cl/Br ratio is often used to discriminate between halite dissolution brines (often shallow origin) and deep fluids and/or fluids derived by seawater evaporation (Chi and Savard, 1997; Savoye et al., 1998; Stober and Bucher, 1999b; Leisen et al., 2012; Fusswinkel et al., 2013), without specifically knowing what causes low Cl/Br ratios in deep crustal fluids.

Although highly saline basement fluids have been known for decades, the processes causing their extreme chlorinities combined with low Cl/Br and Na/Cl ratios are not understood in detail: some authors propose an in-situ source for halogens (e.g., Cl and Br being leached from hydrous silicates), which increases during mineral hydration reactions (e.g. Kullerud, 1996; Markl and Bucher, 1998), or may be

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http://dx.doi.org/10.1016/j.chemgeo.2016.03.031
0009-2541/

inherited and pre-enriched from fluid inclusion leakage (Nordstrom et al., 1989). On the contrary, others propose that the dominant source of the salinity is not within the crystalline basement itself but is related to evaporation (Bottomley et al., 1999; Boiron et al., 2010; Richard et al., 2011) or freezing of large amounts of seawater during glacial periods (Herut et al., 1990). Once halite saturation is reached, the Cl/Br ratio decreases because of the strong incompatibility of Br in halite (McCaffrey et al., 1987; Siemann and Schramm, 2000) and is thereby passively enriched in the residual brine, which migrates subsequently downwards (Spencer, 1987; Bons et al., 2014).

Basement brines are often invoked as an important source for metals such as Pb, Zn, Cu, Co, Ni, U or Ag, typically found in hydrothermal vein-type deposits (basement-, unconformity-, and basin-hosted) (Wilkinson et al., 2005; Yardley, 2005; Gleeson and Turner, 2007; Boiron et al., 2010; Richard et al., 2011; Fusswinkel et al., 2013). Whether these metal-rich continental basement brines are a ubiquitous phenomenon (Yardley, 2005) or if they reflect local exceptions, having anomalous high metal concentrations (Wilkinson et al., 2009) is poorly constrained.

Here, we report the results of leaching experiments performed with Variscan basement rocks (granite and gneiss) and Triassic sandstone of the Schwarzwald, SW Germany. Compared to previous leaching experiments on rocks from the Schwarzwald (Bucher and Stober, 2002), our experiments cover much larger time (t) and temperature (T) intervals and include experiments with 25 wt.% NaCl solution (s25) and variable fluid/rock ratios. The experiments represent an undisturbed internal geochemical signal, without an external element source and therefore show if interaction with granite and gneiss is able to explain the geochemical characteristics of basement fluids. Furthermore, we consider the modes of fluid modification during water–rock interaction of externally derived fluids, being introduced into the crystalline basement.

2. Starting materials and analytical methods

2.1. Samples

Granite, gneiss and sandstone samples used for this study were collected in the central Schwarzwald, Germany, which are taken here as a type example of a Variscan upper crustal section (as has been done in several studies before, see e.g. Bucher and Stober, 2002; Fusswinkel et al., 2013; Walter et al., 2015). Paragneiss (MB2) was collected from the Hechtsberg quarry near Hausach, granite (MB3) from the Eselsbach near Schramberg and Triassic redbed sandstone (MB5) from Kuhbach near Lahr. The paragneiss has an average grain-size of 5 mm and consists of about 42 vol.% biotite, 32 vol.% plagioclase, 14 vol.% quartz, 7 vol.% K-feldspar, 1 vol.% garnet and accessory apatite and titanite (determined by image analysis). The granite has an average grain-size of 10–15 mm and contains about 44 vol.% K-feldspar, 31 vol.% quartz, 14 vol.% plagioclase, 7 vol.% biotite, 1 vol.% muscovite and accessory apatite, ilmenite, magnetite, monazite and zircon. In both basement rocks, plagioclase is partly sericitizied (the degree of sericitization being stronger in the granite), while K-feldspar is almost unaltered. Around 10 vol.% of the granite's primary biotite is replaced by fine-grained intergrowths of hematite, orthoclase and muscovite. The sandstone has an average grain-size of 0.5–1 mm, a porosity of 3 vol.% and consists of around 90 vol.% quartz, 6 vol.% K-feldspar and minor amounts of illitisized plagioclase and apatite. The cement is of argillic type and contains clay minerals and euhedral hematite (photomicrographs and microprobe data of the rock-forming minerals are included in the electronic supplement).

2.2. Sample preparation

Alteration crusts and secondary mineral veins were carefully removed. After coarse crushing, three aliquots of each sample (around 5 kg each) were crushed, ground and sieved until the whole aliquot was entirely processed. Thereby, a fine-grained fraction FG (<10 μm), a medium-grained fraction MG (63–125 μm) and a coarse-grained fraction CG (2–4 mm) of each sample were produced. A fourth aliquot (~5 kg) of gneiss and granite was used for mineral separation, which resulted in a felsic (quartz and feldspar) and a biotite fraction. No significant loss of mass during processing of the whole-rock samples could be recognized. 0.4 kg of felsic granite and gneiss separates, 0.3 kg of gneissic biotite and 0.2 kg of granitic biotite could be derived from 5 kg starting material.

2.3. Leaching experiments

Batch experiments at 25 °C with different grain-sizes and at various P–T, as well as multi-step experiments with changing fluid/rock ratios were carried out (Table 1).

2.3.1. Batch experiments at 25 °C (I)

Whole rock powders (FG, MG, CG) (Ia and c) and mineral separates (Ib and d) of gneiss and granite (FG) were leached in ultrapure water (pw) and 25 wt.% NaCl solution (s25) for 1 (t_1), 10^3 (t_2) and 4.5×10^4 (t_3) min, using an individual beaker (pure quartz glass) for each time interval t to maintain a constant fluid/rock ratio of 10 (10 g sample) (Table 1). The beakers were manually shaken three times a day.

2.3.2. Batch experiments at elevated P and T (II)

Gold capsules of 6 cm length and 5 mm diameter were used in horizontal autoclaves with H_2O as pressure medium. To avoid fluid loss and reduce the amount of encapsulated air during welding, the filled unsealed capsules were frozen in liquid nitrogen before sealing. MG whole rock was leached with a fluid/rock ratio of 10 (between 88 and 94 mg of rock material) at 180 °C/0.9 kbar, 275 °C/1.4 kbar and 350 °C/1.9 kbar for 4.5×10^4 min (Table 1).

2.3.3. Multistep experiments at 25 °C (III)

CG of gneiss and granite were leached in pw for 4.5×10^4 min at a fluid/rock ratio of 3.33 (120 g of sample material). These leachates were separated from the slurry, transferred into new beakers and MG of the respective lithologies was added using a fluid/rock ratio of 10. This was repeated three times after 10^3 min, resulting in a subsequent decrease of the fluid/rock ratio to 1.1 (Table 1). With this setup we try to mimic a migration path of a fluid batch, which is successively modified by the reaction with fresh cataclastic material.

2.4. Analytical procedures

All analyses were carried out at the Institut für Geowissenschaften, University of Tübingen, Germany.

2.4.1. Rocks

Major and trace elements of whole-rocks (triplicates) and mineral separates were determined by X-ray fluorescence (XRF) and total reflection X-ray fluorescence (TXRF). Fluorine, Cl and Br were extracted from whole-rock powders by pyrohydrolysis and quantified by ion chromatography (IC), using a similar setup as described by (Köhler et al., 2009). The effective detection limits for whole rocks are about 5 μg/g for F and Cl and 0.1–0.15 μg/g for Br (depending on the F concentration of the sample). Based on the frequent analyses of standard solutions, the relative uncertainty is ≤7%.

All leachates were filtered with a 0.2 μm Chromafile Xtra PVDF-20/25 for cations and a Xtra RC-20/25 for anions, which were analysed with a Dionex ICS 1000 ion chromatography system (CS12-A- and AS9-HC columns). Uncertainties are about 7% with detection limits of below 10 μg/l for Na^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^- and NO_3^-, and 2 μg/l for Br^-, PO_4^{3-} and SO_4^{2-}. Ni, Zn, Cu, Pb, W and As were determined