Origin of lithium in deep brines of SW-Germany – first results

Jens C. Grimmer[1], Kirsten Drüppel[1], Ingrid Stober[1]

[1] Institute of Applied Geosciences, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, 76131 Karlsruhe, Germany

jens.grimmer@kit.edu

Keywords: lithium, basement brines, leaching experiments, crystalline basement rocks.

ABSTRACT

We focus on the origin of the commonly high lithium (Li) concentrations in continental brines that are characterized by high total dissolved solids (TDS). Our approach comprises geochemical bulk rock analyses to constrain available Li contents and simple leaching experiments on pulverized granitoids and rhyolites of the Schwarzwald. Hydrochemical analyses of the leachates are used to constrain leached Li concentrations. The granitoids indicate a correlation between leached Li and the anorthite content and modal abundance of feldspars, whereas leaching of Li from post-Variscan rhyolites additionally suggests a dependence on grain size and abundance of fluid inclusions. The next steps require a refinement of our experimental approaches and a focus on specific parameters such as alteration, grain size, temperature, and fluid inclusions. Additionally, Li-isotope analyses will be carried out on key samples.

1. INTRODUCTION

Deep buried sedimentary and crystalline basement rocks in the Upper Rhine Graben contain and conduct water in several km depths. Na-(Ca)-Cl brines of about 100 g/kg TDS are the prevailing fluids irrespective of reservoir lithology and often display high Li concentrations (Pauwels et al. 1993, Stober and Bucher 2014). Li is a conservative tracer that, due to its high solubility, is enriched in most of these brines and originated either from i) dissolved evaporates, ii) trapped marine water in the crystalline basement during Mesozoic transgressions, or iii) was leached from crystalline basement rocks during hydrothermal alteration. The c. 500-1500 m high eastern graben shoulder of the Schwarzwald exposes Variscan Carboniferous granites and gneisses and post-Variscan Permian rhyolitic rocks (Fig. 1). Surface exposure and topography are important boundary conditions for i) the entrance of meteoric fluids into crystalline basement rocks along permeable fault and fracture zones and ii) for the formation of a hydraulic gradient that can drive fluids into geothermal reservoirs of the Upper Rhine Graben and deeper parts of the crystalline basement rocks.

In order to elucidate the source of Li in the brines we studied Li contents in granitoids and rhyolites of the northern Schwarzwald and the leaching behavior of these rocks.

2. RESULTS

2.1. Petrography and geochemistry

Granites mainly comprise medium grained biotite and two-mica granites with megacrysts of K-feldspar. Some of the samples display a weak foliation, defined by phyllosilicates. The modes of the granites are variable, with increasing amounts of biotite and plagioclase being accompanied by decreasing amounts of quartz, K-feldspar, and white mica. Plagioclase displays normal zoning with anorthite contents ranging from 36 to 1 mol%, increasing with increasing amounts of biotite and plagioclase.

Rare medium grained, equigranular monzonites are mainly composed of plagioclase (An_{5-15}), amphibole, biotite, and quartz. In all granitoid samples, apatite, zircon, Fe-Ti oxides, and hematite are common accessory phases. Alteration is extensive in most of the samples, mainly accompanied by strong sericitization of plagioclase and formation of both chlorite and hematite at the expense of biotite.

The SiO_2 contents of the granites range between 70 wt.% and 78 wt.%, whereas those of the monzonites are distinctly lower (55–65 wt.%). Li varies between 50-195 ppm and 45-185 ppm in the granites and monzonites, respectively, with the amount of Li increasing with increasing modes of phyllosilicates. The ratio $FeO^{tot}/(MgO + FeO^{tot})$ of the granites and monzonites is constantly low, thus plotting in the magnesian field of Frost et al. (2001). The granites are calc-alkaline to alkali-calcic in composition, whereas the monzonites are alkali-calcic to alkalic. All granitoids are strongly peraluminous S-type granites. They plot in the field of syn- to post-collisional granites in the discrimination diagrams of Pearce et al. (1984) and display LREE enriched chondrite-normalized REE patterns with accentuated negative Eu anomalies, which are almost absent in the monzonites.

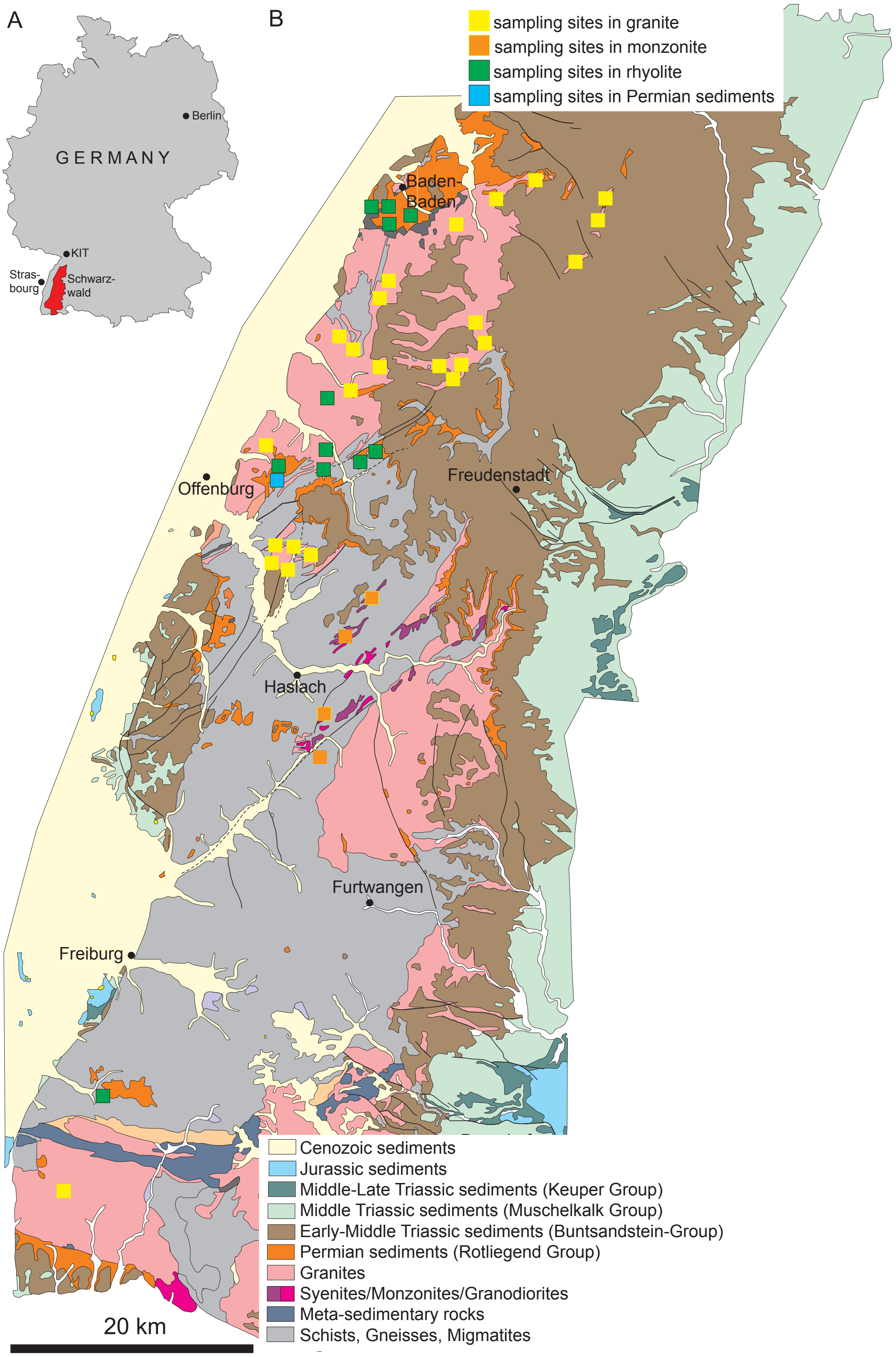

Figure 1: A) Index map showing the Schwarzwald crystalline basement rocks in SW Germany. B) Geological map showing sampling sites. Map modified from LGRB (2006).

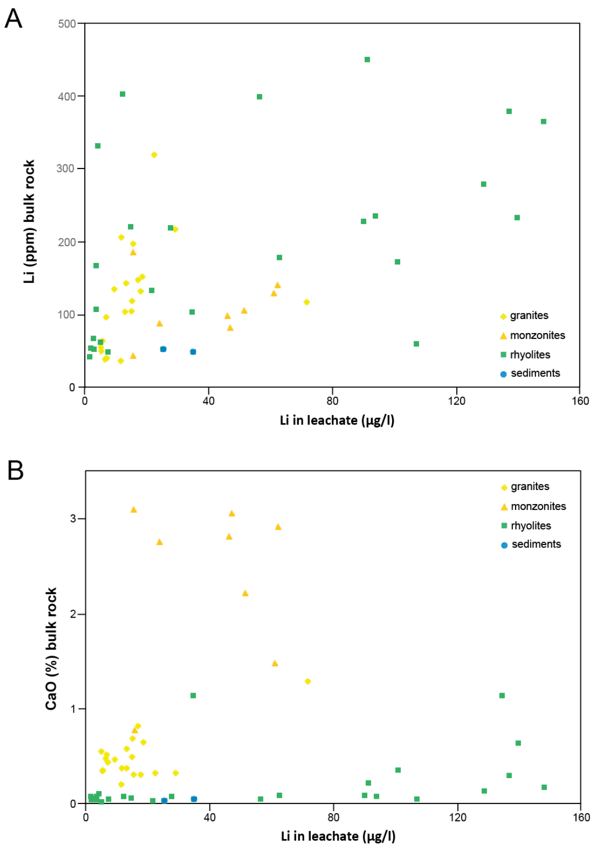

Figure 2: A) Diagram showing Li concentrations in leachate versus Li concentrations of the bulk rock (Li-Li-diagram). The Li-Li-diagram shows no systematic correlation of Li concentrations in the leachate with rhyolites, but there seems to be a correlation with monzonites and granites. B) Diagram showing Li concentrations in leachate versus CaO concentrations of the bulk rock (Li-CaO-diagram). The Li-CaO-diagram shows a positive correlation for the granitic and monzonitic rocks, indicating a correlation with the anorthite component in the plagioclases and modal plagioclase content.

Rhyolites (including both solidified lava flows and tuffs) show fine- to medium grained phenocrysts of dihexahedric quartz and euhedral K-feldspar and albite (An_{0-5}), set in a very fine grained to vitreous matrix of quartz, feldspar, and biotite. Cavities in the porous matrix are filled with microcrystalline quartz. Hematite, apatite, zircon, and pyrite are accessory phases. A flow structure is common. Postmagmatic alteration of the rhyolites resulted in the partial replacement of feldspar by sericite and iron oxide, alteration of hematite to Fe-hydroxides, and devitrification of the glassy groundmass. In abundant hydrous fluid inclusions in quartz, small crystals of KCl are recognized. Like the granites, the rhyolites are SiO_2-rich (74-78 wt.%), calc-alkaline, magnesian and strongly peraluminous in composition. All rhyolites display LREE enriched patterns and a pronounced Eu-anomaly in chondrite-normalized REE plots. The rhyolites are characterized by significantly higher Li values (170-450 ppm) than both granites and monzonites.

2.2. Leaching experiments

Leaching experiments were carried out in a glass batch reactor at a constant temperature of 70 °C with 20 g of rock powder (<40 µm) in 160 ml bi-distilled water, to study the water-rock-interaction. We grinded the rock samples very carefully to a grain size <150 µm in order to open fluid inclusions in quartz. Electrical conductivity and pH were continuously measured during the experiments. Leaching experiments with granites yielded Li concentrations <70 µg/l. Leaching experiments with rhyolites yielded Li concentrations between 28 µg/l and 140 µg/l.

3. CONCLUSIONS AND OUTLOOK

While we observe no correlation between Li concentration in bulk rock and leachates of rhyolites, there seems to be a correlation for granites and monzonites (Fig. 2). Additionally we observe a correlation with the anorthite-component of plagioclase, expressed as CaO (%) (Fig. 2B), and the abundance and composition of fluid inclusions. Li concentrations of the bulk rocks, on the other hand, do not seem to play a major role (Fig. 2) at the given experimental boundary conditions and may become a more important controlling parameter at higher temperatures and longer reaction times as indicated by the study of Bucher and Stober (2002). The next steps of our investigations will focus on understanding and constraining the parameters and processes that control concentration of Li in the leachate. Our future investigation will focus on texture, grain size, fluid inclusions, as well as mineral and water major and trace element compositions. Li isotope analyses may further help to constrain its origin.

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