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Reservoir Characterization by Sr Isotopes – A Case Study from the Upper Rhine Valley, Germany

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ABSTRACT

Understanding geochemical processes in deep geo-reservoirs is of significance for sustainable exploitation of geothermal resources and an important economic parameter for the operation of geothermal power plants. The isotopic composition of Sr provides a powerful tool to investigate water-rock interaction and is a natural tracer for the study of the origin of fluids and hydrodynamic processes in reservoirs. In this paper we present preliminary results from $^{87}Sr/^{86}Sr$ ratios in mineral and thermal water collected in the continental rift system of the Upper Rhine Valley and adjacent Black Forest area in southwestern Germany. By comparing $^{87}Sr/^{86}Sr$ ratios from water samples and mineral separates, sources of solutes were determined for the main producing aquifers. The results show that weathering of feldspars from crystalline rocks and siliciclastic sedimentary deposits as well as the dissolution of calcium carbonate from calcareous rocks predominate the isotopic composition of dissolved Sr in mineral and thermal water. The variability of water types associated with different Sr isotope ratios argues for complex mixing processes likely induced by groundwater flow along permeable fractures and fault zones.

1. INTRODUCTION

The Upper Rhine Graben (URG) located in southwestern Germany is part of the European Cenozoic rift system and has been the target for intensive research throughout the past decades, especially in the context of hydrocarbon exploration and because of its high geothermal potential (e.g. Lutz and Cleintuar, 1999; Rybach, 2007). Thermal water sources were exploited since historic times and are today an important economic factor in the region for spa operation and heat mining. While most operations target aquifer depths of less than 1000 meters below the surface, exploitation of deep geothermal sources is focused on areas of enhanced geothermal gradients, e.g. at the Soultz-sous-Forêts site (Clauser et al. 2002). Geothermal gradients in the URG are generally between 45°C and 50°C km^{-1} and reservoir temperatures reach up to 150 °C at depths of 2500 to 4000 m (e.g. Rybach 2007; Stober and Bucher, 2015). Heat anomalies are considered to be produced by upwelling of deep thermal groundwater as a result of high hydraulic conductivity of reservoir rocks and existing fault and fracture zones (Stober and Bucher, 2015).

Fluids produced from deep geothermal wells in the URG consist of high-mineralized Na-Cl-dominated brine. The origin of brine and sources of solutes in thermal waters are important parameters for the characterization of geochemical processes in the reservoir of the URG. Based on the chemical composition of a large number of water samples Stober and Bucher (1999a) emphasized a vertical stratification of water types of $Ca-HCO_3$ type groundwater close to the surface, $Na-Ca-HCO_3-SO_4$ type groundwater at intermediate depths, and Na-Ca-Cl type water at greater depths. For the origin of saline thermal water, a reservoir in depths of 3-4 km and development of mixtures from three components: freshwater from the surface, saline water of marine origin, and water-rock interaction was considered. Solutes in CO_2-rich mineral water of shallow aquifers were assumed to be solely derived by water-rock interaction including plagioclase, calcite, and mica dissolution (Stober and Bucher, 1999a/b).

The present study presents preliminary Sr isotope data from mineral and thermal water as well as rock samples to elucidate water-mineral interaction, sources of solutes, and potential mixing of fluids from different aquifers in the URG. The study was performed within the ANEMONA project, funded by the Federal Ministry for Economic Affairs and Energy (BMWi), Germany, under the Energy Research Program.

2. GEOLOGICAL SETTING

The European Cenozoic Rift System extends between the Mediterranean and the North Sea in western and central Europe over a distance of more than 1000 km. Formation of the rift system by extensional deformation in the northern Alpine foreland in the course of compressional tectonics, related to the Alpine orogeny, started in the late Eocene, while it continues until today (Ziegler 1992; Dèzes et al. 2004). The horst and graben structure of the URG is located between the Black Forest and the Vosges Mountains and constitutes a prominent segment of the European Cenozoic Rift System (Fig. 1). The graben is between 30 km and 40 km wide and about 300 km long. During crustal extension, Late Variscan and Permo-Carboniferous crustal discontinuities were reactivated within the URG (Schumacher, 2002; Ziegler et al. 2006). Prominent NNE oriented sinistral fault zones are associated with Lower Carboniferous to Permian intrusive complexes. These fault zones are considered to be important hydraulic pathways for geothermal fluids in the URG (Meixner et al. 2016).

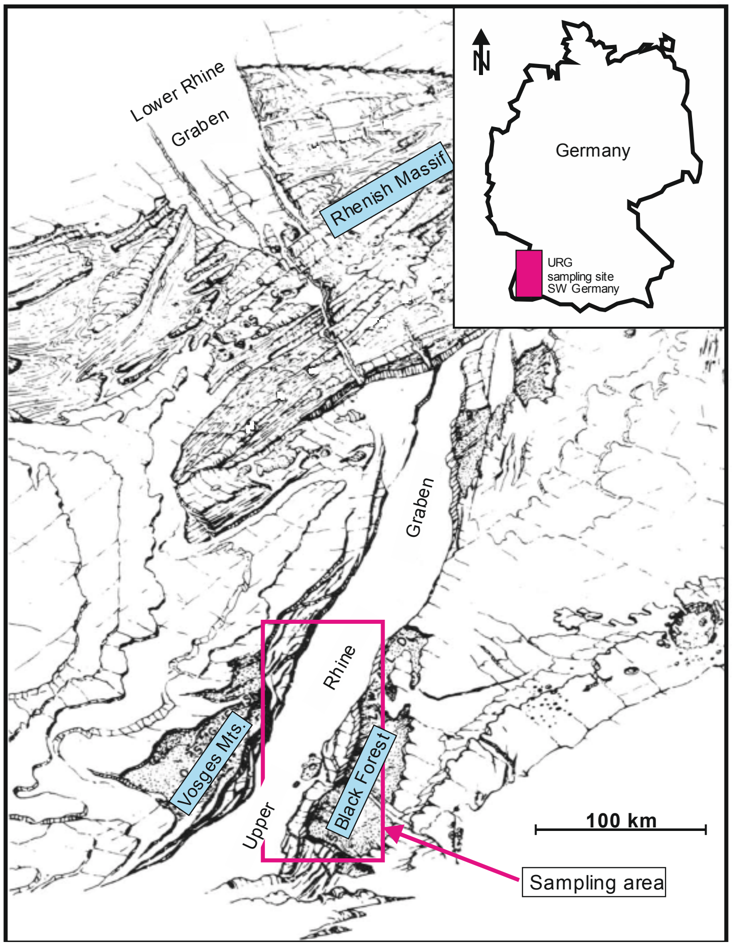

Figure 1: Sketch map of the Upper Rhine Graben with sampling area (Modified after Sittler 1969 and Cloos 1955).

While the graben shoulders of the Black Forest and Vosges Mountains largely expose granites and gneisses of the Variscan basement, which are partly covered by Mesozoic sediments, the graben structure was filled by up to 3 km of Mesozoic and Cenozoic sediments that were deposited on crystalline rocks and unconformably overlie Permo-Carboniferous series (e.g. Pflug, 1982). Producing aquifers in the URG are mainly formed by Permian, Triassic, and Tertiary sandstones and Triassic and Jurassic limestones (Stober and Bucher, 2015). Hydraulic conditions of the rock formations are considered responsible for heat transfer (Pribnow and Schellschmidt, 2000). Hydraulic and hydrochemical properties of sedimentary reservoir rocks and fluids in the URG were compiled by Stober and Bucher (2015). Generally, hydraulic conductivities are high in sandstone and limestone reservoir rocks, reaching values in the range of 10^{-7} to 10^{-9} m s^{-1}. The concentration of total dissolved solids (TDS) in thermal groundwater increases with depth and shows high values of >5 g/kg below 800 m depth, while brines in deep aquifers can reach concentrations of up to 300 g/kg.

3. METHODS

Mineral and thermal water and rock samples were collected in the Upper Rhine Valley and in the adjacent Black Forest (Fig. 1). Water samples were either collected from natural springs or from wells in different depths. The investigation of rocks and mineral samples was focused on the main producing aquifers in the URG. Rock samples of potential reservoir rocks were collected from equivalent outcrops at the Earth's surface. Water samples were analyzed for major cations and anions using conventional ion-chromatography technique (Dionex DX320/500), trace elements were analyzed by ICP-MS (Perkin Elmer - ELAN DRC II), and Sr isotopes analysis of water and mineral samples was performed on a Finnigan MAT 262 thermal ionization mass spectrometer at the University of Goettingen, Germany.

Water samples were filtered through 0.45µm nylon filter prior to chemical analysis. For Sr isotope analysis, about 10 mL of the fluid samples were evaporated and dissolved in 1 mL of 2.5 N hydrochloric acid. Separation of Sr from other ions in the sample solution was carried out on ion-chromatography columns using Biorad AG 50x8 (200-400 mesh) resin and 2.5 N hydrochloric acid as eluent. Purified Sr fractions were loaded onto outgassed Re filaments (double-filament technique) with 0.25N H_3PO_4 (ultrapure). $^{87}Sr/^{86}Sr$ ratios were corrected for instrumental fractionation using the natural $^{88}Sr/^{86}Sr$ ratio of 8.375209. The analytical precision for the analyzed $^{87}Sr/^{86}Sr$ ratios is 0.003% (2σ) or less. Routine standard measurements yielded an average $^{87}Sr/^{86}Sr$ ratio of 0.71039 ± 0.00001 (2σ: n=40) for the NBS987 Sr standard. Blanks for the chemical procedures were less than 0.5 ng for strontium.

For the analysis of mineral samples, rocks were crushed and minerals were separated by hand-picking. About 10 mg of mineral sample was digested in a mixture of 40% hydrofluoric acid and 65% nitric acid. After acid evaporation the sample residue was dissolved in 6N hydrochloric acid and again evaporated. For isotopic analysis the sample residue was dissolved in 2.5N hydrochloric acid and separation of Sr from other ions was carried out on ion-chromatography columns using Biorad AG 50x8 (200-400 mesh) resin and 2.5 N hydrochloric acid following the procedure used for Sr isotopic analysis of the water samples.

4. RESULTS AND DISCUSSION

Based on major element compositions, mineral and thermal water of the URG and adjacent Black Forest area were divided into three main groups: Ca-HCO_3/SO_4, Na-HCO_3, and Na-Cl type water. In addition, Na-Ca and Ca-Na dominated HCO_3-SO_4-Cl type groundwater exists, potentially displaying mixtures of groundwater from various sources. The variability of water types is associated with different aquifers formed by limestone and siliciclastic sedimentary rocks as well as gneisses and granitic rocks. To elucidate sources of solutes, $^{87}Sr/^{86}Sr$ ratios of dissolved Sr in groundwater was compared to the isotopic composition of Sr in minerals from various host rocks in the study area. $^{87}Sr/^{86}Sr$ ratios of mineral and thermal water samples range between 0.708 and 0.722. $^{87}Sr/^{86}Sr$ ratios in mineral separates of silicate rocks range from 0.714 in feldspar to 3.65 in biotite. The average $^{87}Sr/^{86}Sr$ ratio for Triassic limestone of the Muschelkalk formation is ~0.708 (Korte et al. 2003), while for the Jurassic limestone of the Hauptrogenstein formation $^{87}Sr/^{86}Sr$ ratios between 0.707 and 0.708 are considered (Jones et al. 1994). Because of the small range of Sr isotopic ratios in marine limestone of the two formations and the high solubility of calcium carbonate, Sr in groundwater of the limestone aquifers is likely controlled by calcium carbonate dissolution and exhibit $^{87}Sr/^{86}Sr$ ratios similar to the aquifer rock.

For groundwater in contact with silicate mineral phases, a more radiogenic Sr isotope composition can be expected. This is due to the elevated $^{87}Sr/^{86}Sr$ ratio in dissolving mineral phases such as feldspars and mica. The range of Sr isotopic ratios in feldspars of granitic rocks in the Black Forest area is generally between 0.714 to 0.728, but higher values may exist. Feldspar in gneiss shows $^{87}Sr/^{86}Sr$ ratios of ~0.711 (Glodny et al. 2009). Preliminary $^{87}Sr/^{86}Sr$ data from feldspars of Permian and Triassic sandstone deposits range from 0.721 to 0.734.

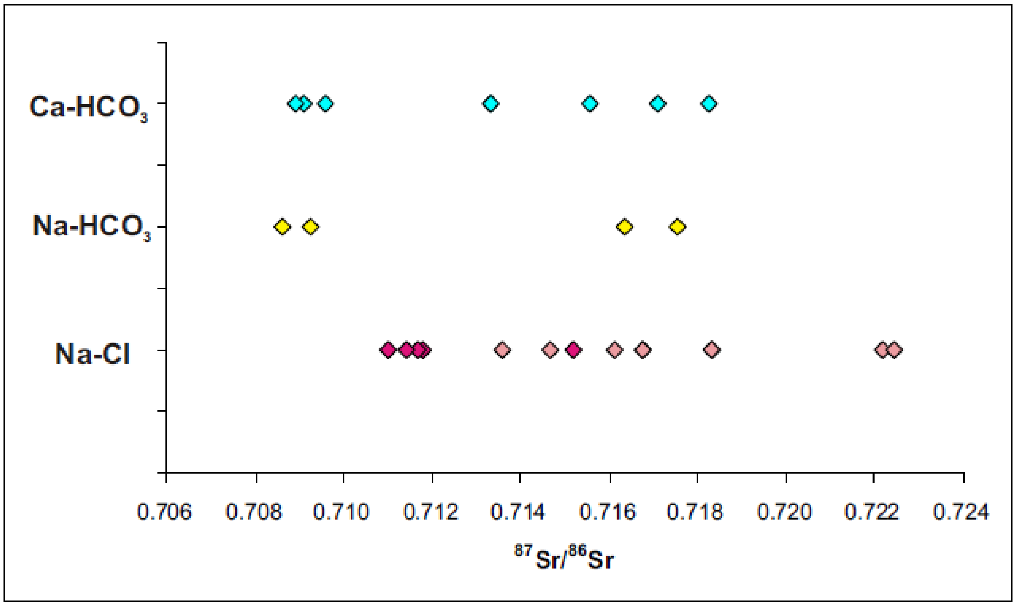

Figure 2: Distribution of $^{87}Sr/^{86}Sr$ ratios of mineral and thermal water samples by water type. Dark red diamonds indicate brine samples from deep geothermal wells.

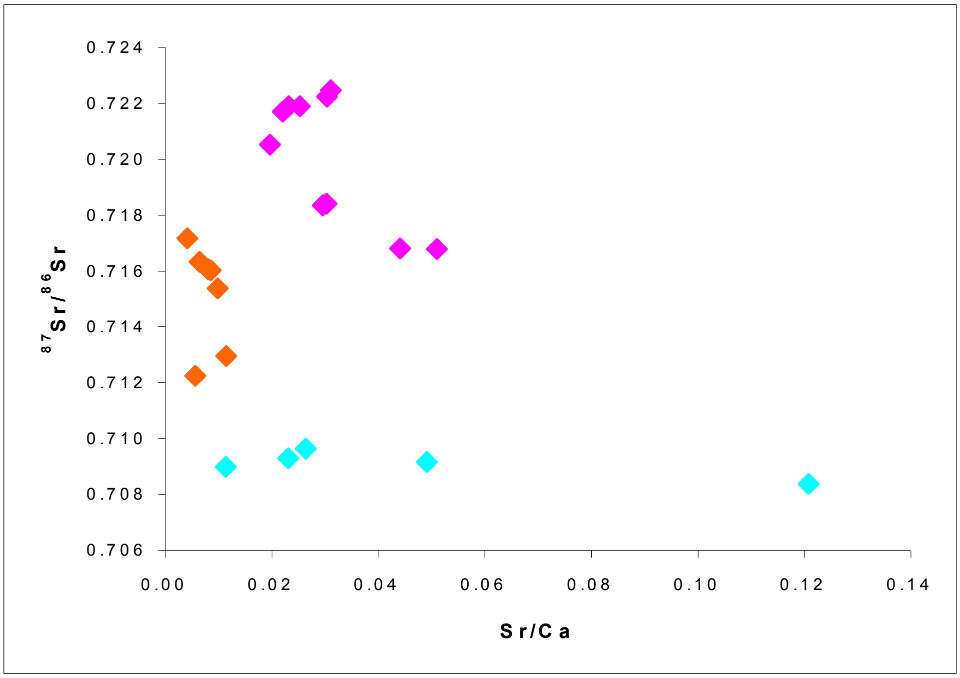

Figure 3: Variation of ^{87}Sr/^{86}Sr and Sr/Ca ratios in mineral and thermal water of the URG and Black Forest. Symbols: blue = groundwater from limestone aquifers; orange = groundwater from siliciclastic sediments and gneisses; pink = groundwater from granitic aquifers.

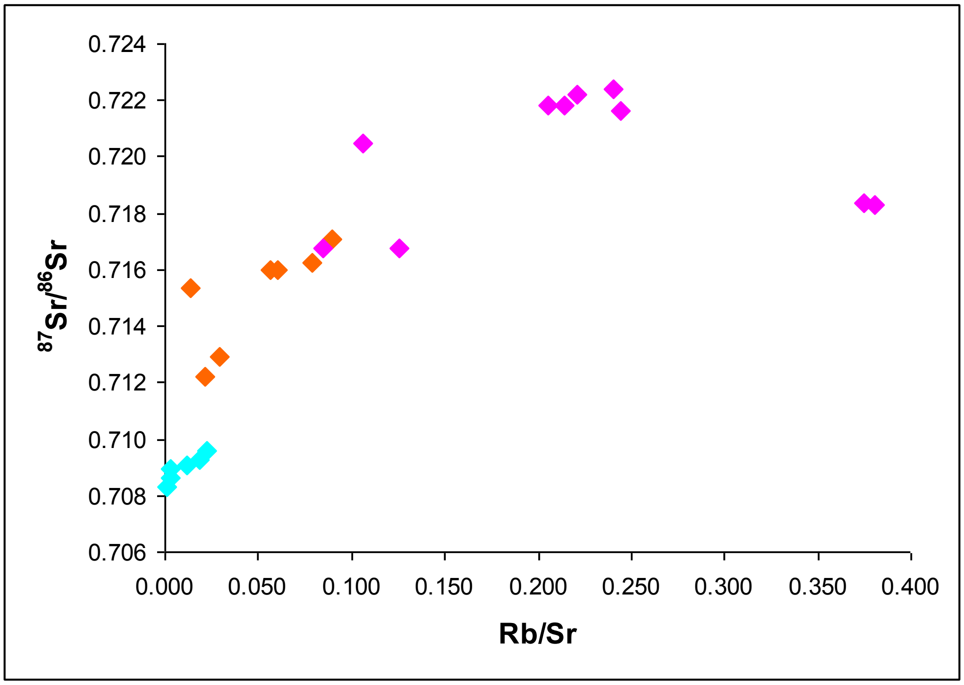

Figure 4: Distribution of ^{87}Sr/^{86}Sr and Rb/Sr ratios in mineral and thermal water of the URG and Black Forest. Symbols: blue = groundwater from limestone aquifers; orange = groundwater from siliciclastic sediments and gneisses; pink = groundwater from granitic aquifers.

Figure 2 displays the distribution of $^{87}Sr/^{86}Sr$ ratios for the main water types of mineral and thermal water collected from surface springs and from wells above 1000 m depths as well as brine samples collected from deep geothermal wells >2000 m depth. The large spread of Sr isotope ratios in addition to overlapping $^{87}Sr/^{86}Sr$ ratios for the various water types suggests common sources of dissolved Sr in the waters and may indicate complex mixing processes in the reservoir and producing aquifers of the URG and Black Forest area.

Generally, groundwater mixing includes components such as low-mineralized groundwater recharge close to the surface, potentially contributions of thermal water ascending from deeper aquifers along permeable fracture and fault zones, and Sr contributions from water-rock interaction along flow paths.

In regard of the mineralogical composition, limestone aquifers are associated with lowest Sr isotope ratios in the water, while sandstone and gneissic aquifers produce intermediate $^{87}Sr/^{86}Sr$ ratios, and granitic aquifers are associated with high Sr isotope ratios (Fig. 3). This suggests that $^{87}Sr/^{86}Sr$ ratios in limestone aquifers is dominated by dissolution of calcium carbonate, while release of Sr from feldspar in sandstone, gneiss, and granite dominates the Sr isotopic composition of the mineral and thermal water in aquifers dominated by silicate rocks. Na-Cl dominated groundwater is often associated with high Sr isotope ratios, suggesting a genetic relationship to intrusive rock complexes and major fault zones in the area.

Rb/Sr ratios display a positive trend with $^{87}Sr/^{86}Sr$ ratios (Fig. 4). This observation provides additional evidence for the dissolution of Rb-bearing mineral phases such as feldspar and biotite in controlling the isotopic composition of Sr in mineral and thermal water from aquifers composed of granitic rocks, siliciclastic sediments, and gneisses. Mineral and thermal water from limestone aquifers show typically low Rb/Sr ratios due to the generally low Rb relative to a high Sr content of carbonate minerals.

5. CONCLUSION

The comparison of $^{87}Sr/^{86}Sr$ ratios of mineral and thermal water with major rock forming silicate minerals such as feldspar and mica from granitic and siliciclastic sedimentary rocks in the URG and adjacent Black Forest area suggests that dissolution of feldspars and biotite govern the isotopic composition of Sr in mineral and thermal water of silicate-dominated aquifers. In contrast, low $^{87}Sr/^{86}Sr$ ratios in mineral and thermal water of limestone aquifers confirm dissolution of calcium carbonate as the main source of dissolved Sr. Considerable variation in major element composition and water types across a range of Sr isotope ratios likely accounts for complex mixing processes that should be further addressed.

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