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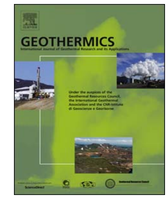

Induced rare earth element fractionation in brines by hydraulic fracturing of their aquifer rocks

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ABSTRACT

Stimulation of rocks deteriorates the equilibrium distribution of rare earth elements and yttrium (REY) between solids and brines. By stimulation of the Permian, Lower Rotliegend formations in the well Groß Schönebeck 3/90 the volcanites are less affected by stimulation than the overlying conglomerate and sandstones. Brines from different lithological sections differ in REY patterns and gain anomalies of Eu, Gd, and Y during processes of recrystallization. The initially small anomalies increase during stimulation but decrease with both ongoing pumping and recrystallization. The REY patterns and their Eu, Gd, Y anomalies of brines from the conglomerate and volcanites distinctively differ from those of the sandstones. The Gd and Y anomalies are strongly correlated and both increase in sandstones with distance from the underlying conglomerate and volcanite. The correlation plot of Gd and Y anomalies does not describe a mixing line between brines from the volcanite and conglomerate but it reveals the extent of recrystallization of rapid precipitations and growth of minerals immediately after the stimulation and the slow re-equilibration of REY between solids and brines in each section of rocks. Extreme recrystallization occurred within the conglomerates, the least ones in the volcanite. REY patterns with their characteristic Eu, Gd, and Y anomalies are reliable indicators of the source of brines after stimulation. The time-dependence of changes of Eu, Gd and Y anomalies reflect the process of recrystallization.

1. Introduction

The series of stable rare earth elements REE are a unique tool in hydrological studies because of their coherent chemical properties of their trivalent ions. Because of the same radii and charges Y is implemented either before or after Ho in the suite of REE and this series is henceforth termed REY patterns (Bau, 1996). Non-linear changes of properties are observed for Gd in liquid–liquid extraction (Peppard et al., 1969), ion hydration (Mioduski and Siekierski, 1976), and both Gd and Y in complex formation by OH^-, HCO_3^-, CO_3^{2-} (Klungnes and Byrne, 2000; Luo and Byrne, 2004) and partial molar volumes (Spedding et al., 1966). Redox sensitive Eu and Ce also occur as Eu(II) and Ce(IV) species under reducing and oxidizing conditions, respectively.

Y, Gd and Eu are fractionated with respect to the general trend of the REE pattern. Gd and Y show an enhanced affinity for the aqueous phase (Möller and Dulski, 2000). Eu behaves anomalous because it can also be present as Eu(II) in minerals formed at temperatures $> 200\,^{\circ}C$ (Möller and Holzbecher, 1998) such as igneous feldspars from which Eu (II) is released during alteration reactions (Möller and Mücke, 1984).

REY patterns and their anomalies were already used to decipher the lithological sources of hot fluids in geothermal fields such as Larderello-Travale and Monte Amiata, Italy (Möller et al., 2003,2009), and Kizildere, Turkey (Möller et al., 2008).

The aim of this study is to report changes of REY abundance and Eu, Gd and Y anomalies induced by stimulation of the Permian Rotliegend aquifer of the North German Basin as observed in the well 3/90 of Groß Schönebeck, Germany. The results of this case study yield insight into chemical processes such as recrystallization associated with hydraulic fracturing and the source of the brine.

2. Geologic setting

The North German Basin is part of the Southern Permian Basin and extends between Poland and the south-eastern North Sea (Fig. 1). This basin formed during the Variscan orogeny between the Cadomian to Variscan crystalline basement blocks in the south and the Precambrian Baltic Shield in the north (Brink et al., 1992). During the Permo-Carboniferous rifting Mg-andesites, dacites and rhyolites covered the basin floor with thicknesses of 200–500 m in the area of Groß Schönebeck (Beneck et al., 1996; Geißler et al., 2008). With ongoing subsidence of the basin the developing sub-basins between the volcanoes were the

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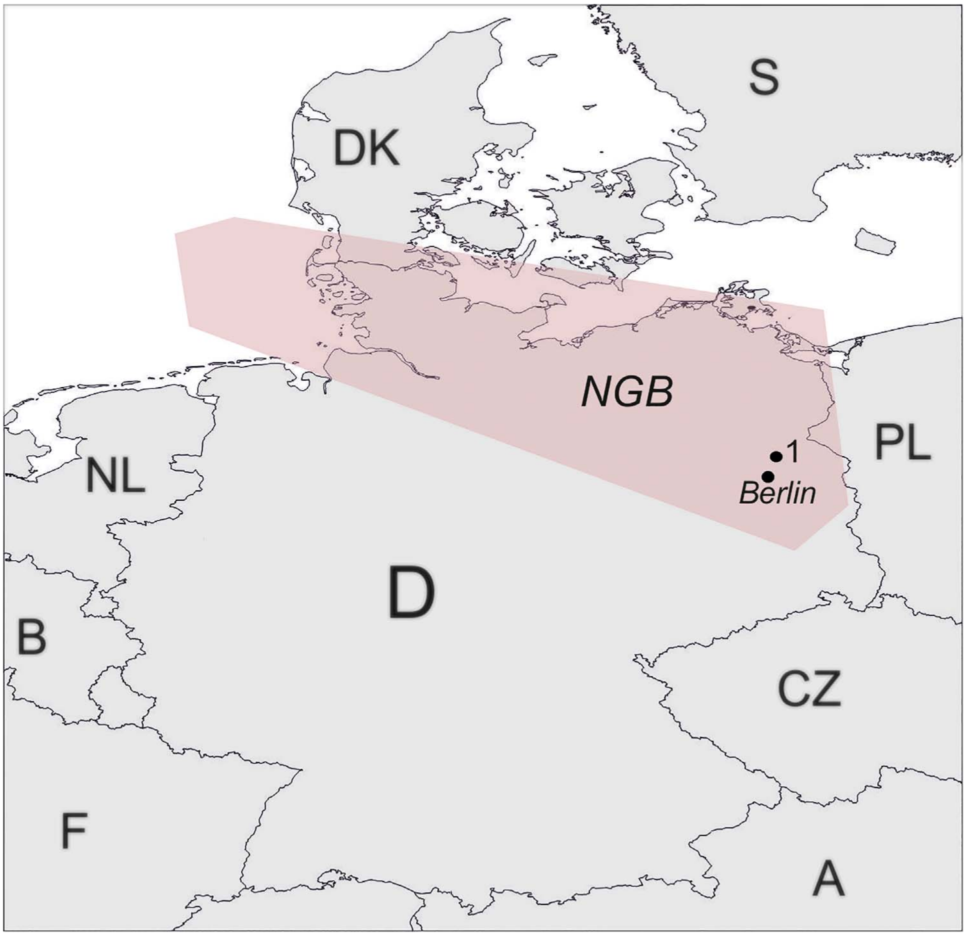

Fig. 1. Location map. 1 = location of well Groß Schönebeck 3/90: NGB schematic outline of the North German Basin after Ziegler (1999).

Table 1
Sampling of brines from the well Groß Schönebeck 3/90.

Date	Action	ID	Depth of sampling
27.01.2002–28.01.2002	Stimulation with HTU-Gel and proppants		
03.02.2002	Lift test (N_2)	#1	3900–4294 m; open hole
28.02.2002	Lift test (N_2)	#2	3900–4294 m; open hole
10.06.2002–25.06. 2002	Moderate pumping test; 94.7 m^3		
20.06.2002	Pumping	#3	3900–4294 m; open hole
13.08.2002	Lift test (N_2)	#4	3900–4294 m; open hole
03.09.2002	Lift test (N_2)	#5	3900–4294 m; open hole
12.09.2002	Lift test (N_2)	#6	3900–4294 m; open hole
05.08.2002–16.09.2002	Long-time pumping test; 580 m^3		
14.10.2002	Sampling of packer intervals	#7	4100 m; sandstone
	Sampling of packer intervals	#8	4135 m; sandstone
15.10.2002	Sampling of packer intervals	#9	4190 m; sandstone
	Sampling of packer intervals	#10	4215 m; conglomerate
	Sampling of packer intervals	#11	4235 m; volcanite
	Sampling of packer intervals		
17.1.2003	Lift test (N_2)	#12	3900–4294 m; open hole

sinks of erosion products such as volcanic debris, tuffs and sands (McCann, 1998; Geißler et al., 2008). At the beginning of the Lower Rotliegend sedimentation the climate changed from humid to arid (Gast, 1991; Gebhardt, 1994; Gaupp et al., 2000). Alluvial and lacustrine sediments deposited and a playa-like environment with salty swamps and evaporites developed. At the drilling site of Groß Schönebeck, north of Berlin, Germany (Fig. 1), the volcanites are overlain by about 50 m of conglomerate and about 300 m of sandstones and siltstones. The sandstones (quartz-arenites) contain up to 25% of cements containing calcite, albite, anhydrite, hematite, illite, and chlorite (Holl, 2002; Wolfgramm et al., 2004). The sequence of sandstones is covered by the Zechstein Group consisting of mudstones and a huge stack of evaporites.

3. Well conditions and sampling

The well Groß Schönebeck 3/90 was originally drilled to depth of 4240 m for gas exploration in 1990/91. Because of insufficient gas it was sealed but re-opened in the year 2000 for geothermal research activities. The well was deepened into the volcanite zone (4294 m) to enlarge the anticipated productivity of geothermal brine. The well is cased to the base of the Zechstein Formation (Lenz and Hoffmann,