Rare earth elements in Permian salts and brines, Thuringia, Germany

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ABSTRACT

Salts and brines have very low rare earth element (REE, La-Lu) concentrations. Thus, there is less knowledge of possible transfer of REE patterns during salt dissolution in water-rock interaction. REE levels in both media are close to or rather below limit of detection of commonly used methods. By dissolving salt samples in water followed by REE pre-concentration, REE contents of about 6.2 to 322 ng g^{-1} were measured for four samples from the Merkers salt mine, Germany. These salts previously were identified to consist mainly of carnallite, halite and/or sylvite. Assuming congruent dissolution, REE patterns of brines and salts differ. Thus, a more complex interaction with (secondary) phases and complexation of REE should be taken into account to explain REE patterns in brines.

1. Introduction

To use rare earth elements (REE, La-Lu) as process indicators in water-rock interaction requires REE concentrations in water, rock and released contents from the respective rock or mineral above limit of detection. For water from Cl$^-$ brines or even sea water, heavy REE (HREE; Ho-Lu) and middle REE (MREE, Sm-Dy) enrichment compared to light REE (LREE; La-Nd) was reported based on shale and PAAS (Post Archean Australian Shale)-normalised patterns (Elderfield and Greaves, 1982; Kulaksız and Bau, 2007; Tesmer et al., 2007). Total REE concentrations from brine/ salinar in Saxony-Anhalt, which borders Thuringia, reached values up to 0.194 µg L^{-1} (Tesmer et al., 2007; ΣREE without Tm). Cl$^-$ brines usually are the result of interactions with salt minerals such as halite (NaCl), sylvite (KCl) or carnallite (KMgCl$_3$·6(H$_2$O)). Unfortunately, REE contents in salts from various environments are very low. Analyses by common geochemical methods result in values below limit of detection (LOD). Thus, in water rock-interactions salts are expected to affect REE pattern in solution only to minor extent (e.g. Möller et al., 2008). As far as known the only complete REE dataset for salts was provided by Steinmann and Stille (1998), who dissolved carnallite in water prior to pre-concentration with exchange resin. In the recent work, we used a similar method for four samples from the salt mine Merkers, where Permian salts of the Werra-formation were mined. Our dataset will give a deeper insight into REE contents and REE patterns of salinar rocks. For comparison to REE patterns of Cl$^-$-brine, a well in Bad Salzungen and a spring in Artern, both Thuringia, Germany, were sampled.

2. Materials and methods

Four salt samples were collected at Merkers salt mine in Western Thuringia, Germany, in the west of the city Bad Salzungen. They were crushed and dried for 10 days at 35 °C in an oven until constant weight. In between processing, the samples were stored in a desiccator. For mineralogical and REE determination, salts firstly were ground in an agate mortar. To obtain information on the mineralogy, X-ray diffractometry (XRD) was carried out with a Bruker D8 Advance Da Vinci diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu Kα radiation, 40 kV, 40 mA within an interval of 5−80°2θ in 0.02°2θ steps. Data evaluation was done with the DIFFRAC.Evaluation software (release 2012, Bruker AXS 2010–2013, V. 3.0.0.8) based on the PDF-2 database (release 2011). To achieve REE concentrations above LOD, each salt sample was dissolved and REE were pre-concentrated. A similar procedure was described by Steinmann and Stille (1998) for a salt profile next to a basaltic intrusion. In our procedure, firstly 2 L pure water (Purelab, USF Seral, 0.055 µS cm^{-1}) were adjusted to pH 3.5 with HCl (35%, suprapur, Roth) to avoid that REE sorb to vessel walls in the following. Even lower pH might have negative effects on the membrane of the filters used later. Then, 25 g of each ground salt sample were dissolved in a 500 mL calibrated glass flask filled with the prepared acidic solution and equipped with a magnetic stirrer. All flasks were rinsed with few mL HCl (35%, suprapur, Roth) and twice with pure water before use. Since salts always also contain small particles (e.g. clay particles), samples were filtrated to 0.2 µm (Minisart syringe filters, Sartorius, cellulose-acetate membrane) after dissolution. Filters were weighed before use, dried after use and weighed again. The

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weight difference together with the dried residues in the respective calibrated flask was subtracted from the initial sample weight to achieve the correct amount of salt which got dissolved. The filtered solution was adjusted to pH 2.00 with HCl (35%, suprapur, Roth) and REE were pre-concentrated following a slightly modified scheme of Shabani et al. (1992) as described in Grawunder et al. (2017). Changes included a modification of the pump rate during preconcentration (13–14 mL min^{-1} instead of 20 mL min^{-1}), the amount of 0.01 M HCl for washing the cartridge to remove matrix elements (80 mL instead of 5 mL) and the amount of acid which was used after evaporation of the final eluates (2 mL 65% HNO_3 + 1 mL 5 M HNO_3, instead of 1 mL 65% HNO_3).

To evaluate possible effects of high concentrations of competing elements such as Al, Ca, Fe and Mg on the pre-concentration procedure (Shabani et al., 1992; Möller et al., 2005; Grawunder et al., 2017), a smaller amount of salt (2.5 g) was dissolved and filtered as described above. Then, element concentrations (Al, Ca, Fe, and Mg) were measured in solution.

For comparison, brine originating from about 128 m depth (Hecht, 2008) was sampled from a well in Bad Salzungen (=BS, 50°48′55.891″N, 10°14′3.510″E; drilling No. Sol Sa 4/1869-Bohrung IV) in March and October 2011 and April 2013. Furthermore, a karst spring was sampled in Artern, which is located in North Thuringia (=Art, 51°22′21.489″N, 11°17′238″E), in November 2012 and 2015. Both brines originated from Permian Zechstein. REE from water samples were pre-concentrated from about 5 L brine filtered to 0.2 μm (Sartobran® 150, Sartorius Stedim Biotech) following the modified scheme of Shabani et al. (1992) as described above. Since the exact sample volume was determined by weight, data were density-corrected. The water density was determined by means of a pycnometer (Duran) in triplicate. The complete hydrochemical dataset of the water samples is given in supplementary material 1.

REE isotopes measured by inductively coupled plasma-mass spectrometry (ICP-MS, X-series, ThermoFisher Scientific, Bremen, Germany) were: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{160}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu. Interferences of $BaO(H)^+$ on Eu and of light $REEO^+$ on heavier REE were corrected as described in Merten and Büchel (2004). Al, Ca, Fe and Mg concentrations were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian 725 ES). To obtain REE patterns, which can be used in interpretation of water-rock interaction, REE concentrations were normalised to PAAS standard (McLennan, 1989) as representative of the upper continental crust. Ratios of representatives of the subgroups LREE (Pr), MREE (Tb) and HREE (Lu) were calculated from normalised values, the Ce anomaly after Lawrence et al. (2006, there Eq. 7).

3. Results and discussion

The salts were identified by XRD as halite, sylvite + halite, carnallite and carnallite + minor proportions of halite (Table 1, supplementary material 2). An effect of competing elements (supplementary material 3) on pre-concentration is only expected for the carnallite samples because of their high content of Mg. In a previous study (Grawunder et al., 2017) a concentration of 490 mg L^{-1} mg in 2.5 L (in total 1225 mg Mg) caused a loss of about 10–15% of La recovery. Here in total 1724 and 2173 mg Mg, respectively, passed the cartridge during pre-concentration. This might affect especially La and, to lower extent, the other LREE. Nevertheless, the REE contents were highest in the carnallite sample (at least 322 ng g^{-1}) and lowest in the carnallite-halite and sylvite-halite polymineral samples (6–7 ng g^{-1}), respectively. The latter ones were in a comparable range with literature data for carnallite (7.5 and 20.8 ng g^{-1}; Steinmann und Stille, 1998; Steinmann et al., 2001, there R4253 and R4254). The REE patterns did not follow a similar trend; rather the patterns differed from each other. Only the samples "sylvite + halite" and "carnallite + halite" were similar. Both showed MREE enrichment with [Lu/Tb]$_{PAAS}$ ratios of 0.3

and [Tb/Pr]$_{PAAS}$ ratios of 3.1 and 6.0, respectively (Table 1, Fig. 1a). The halite sample was more flat with a weak MREE enrichment ([Lu/Tb]$_{PAAS}$ = 0.5; [Tb/Pr]$_{PAAS}$ = 2.0). The carnallite sample was different and enriched in LREE and MREE compared to HREE ([Lu/Pr]$_{PAAS}$ = 0.2; [Tb/Pr]$_{PAAS}$ = 1.0). The both carnallite samples from literature were also rather enriched in MREE (Steinmann and Stille, 1998). All Ce/Ce* values were within the 1.0 ± 0.1 interval, which is not interpreted as anomaly. However, alteration of REE contents in salts can, of course, lead to a change in the REE patterns as found by Steinmann and Stille (1998) for a salt profile next to a basaltic intrusion. Also release from any particle contaminations (e.g. clay minerals, organic matter) for instance during the dissolution step can affect the REE contents and patterns. For our samples after dissolution of approx. 25 g salt several milligrams of residues (probably mainly silicates) were left (29.3–148.9 mg) and considered in calculation of the final REE contents.

The ΣREE (excluding LREE) concentrations in the Na-Cl$^-$-waters were with 6.09–7.05 ng L^{-1} for Bad Salzungen and 3.84 and 3.97 ng L^{-1} for Artern in a low range (Table 1). LREE values were not considered because the high concentrations of Ca (Bad Salzungen 1.3–1.4 g L^{-1}; Artern 1.1 g L^{-1}) might negatively affect the recovery during pre-concentration (Shabani et al., 1992; Möller et al., 2005; Grawunder et al., 2017). ΣREE values for Permian brine/ saline from Saxony-Anhalt/Germany were reported in a range up to 194 ng L^{-1} (Tesmer et al., 2007; ΣREE without Tm).

In general, salts are easily soluble what causes salt karst in numerous regions in the world. Based on molar Na:Cl ratios of 0.98 ± 0.01 (N = 5; includes all water samples from Bad Salzungen and Artern) dissolution of halite very close to congruent state could be expected. Hence, it seems all the more surprising that especially the brine sampled in Bad Salzungen was rather enriched in HREE (and likely MREE) compared to LREE ([Lu/Tb]$_{PAAS}$ = 3.4-3.7) (Fig. 1b, Table 1). The shape of the Artern samples was at least for MREE and HREE very comparable to those from Bad Dürrenberg (Tesmer et al., 2007). In direct comparison, REE patterns of salts and brines hint on more complex water-rock interactions than just salt dissolution. None of the salts was enriched in HREE like the brines, rather they showed MREE enrichment. Complexation of REE by Cl$^-$ was discussed to be very weak (Luo and Byrne, 2001) and associations to other mineral phases (sorption, (co)precipitation) might play a more important role. Something similar already was suggested by Möller et al. (2008), who stated that due to the low REE contents in halite and other salts, the REE pattern in the brines were expected to be more strongly affected by dissolution of other minerals than salts in the aquifer. Further, Steinmann et al. (2001) found especially LREE underlying preferential scavenging by accessory phases. This would result in HREE enrichment in solution. Another source for HREE might be desorption and exchange processes, respectively, from clay minerals. As mentioned above, several milligrams of residues were found after dissolution of our four samples which likely also contain clay minerals. In general, clay minerals were found to enrich especially HREE (Aagaard, 1974; Coppin et al., 2002). To separate different components of such a "mixed-sources" REE pattern might be a focus of future projects employing different techniques and larger datasets. However, also a minor influence of surface-near water has to be considered for the brines of Bad Salzungen, but therefore detailed isotopic studies should be carried out.

4. Conclusion

This dataset showed different REE patterns for different chloride minerals, whereas all had an at least weak MREE enrichment. Alteration by fluids affecting the REE contents and REE patterns cannot be excluded. A direct transfer of the REE patterns from salt minerals to solution during water-rock-interaction is not expected since in comparison to the salt minerals brines were enriched in HREE. Instead, formation of secondary phases or dissolution of associated non-salt