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Time-resolved interaction of seawater with gabbro: An experimental study of rare-earth element behavior up to 475 °C, 100 MPa

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Abstract

Very high metal and rare-earth element (REE) concentrations with unusual (‘*atypical*’) normalized REE patterns are documented in fluids from active hydrothermal vent fields on the Mid-Atlantic Ridge 5°S and the East Scotia Ridge. Those fluids show relative enrichment of middle heavy REEs and almost no Eu anomalies in chondrite-normalized patterns. To understand the processes that produce such *atypical* REE patterns we ran a series of experiments, in which natural bottom seawater or aqueous solutions (NaCl, NaCl–$MgCl_2$, or NaCl–$CaCl_2$) were reacted with gabbro and gabbro mineral assemblages from 300 to 475 °C and 40 and 100 MPa. These P–T conditions are representative for water–rock interactions in hydrothermal root and discharge zones. Fluid flux variability and kinetics were addressed in the experiments by varying the water-to-rock mass ratios (w/r) from 0.5 to 10 and using different run durations from 3 to 720 h.

Only seawater and synthetic $MgCl_2$-bearing fluid mobilized significant amounts of REEs, Si, Ca, Fe, and Mn from gabbro, from clinopyroxene, and from plagioclase. At 425 °C and 40 MPa, fluids were initially acidic with pH (25 °C) of ~2 increasing to values between ~4 and 7 upon progressing reactions. Rare earth element and Fe concentrations peaked within 3–6 h after interaction with gabbroic mineral grains (125–500 μm) at w/r of 5 (REEs) and 2–5 (Fe) but decreased with continuing reaction without strong REE fractionation. Most of the REEs that were leached from primary minerals and dissolved in the fluids early became redeposited into solid reaction products after 720 h.

Contents of dissolved SiO_2 were shown to be pressure-dependent, being about twofold higher at 100 MPa than at 40 MPa (425 °C) and were below quartz saturation with gabbro and clinopyroxene as solid starting material and close to quartz saturation with plagioclase reactant. However, Si in fluids from the rock-dominated experiments at 100 MPa with gabbro (w/r 0.5–1) dropped to very low concentrations. A concomitant decrease in chlorinity suggests that these changes may be due to the formation of hydroxy chlorides.

Regardless of the starting solid reactants, fluid REE patterns were dominantly controlled by w/r. *Atypical* fluid REE patterns and very high fluid REE contents were obtained at high w/r ($\geqslant 5$). Whereas *typical* REE patterns known from many mid-ocean ridge vent fluids, showing relative enrichments of light REEs and a positive Eu anomaly, were obtained at low w/r of 0.5–1. Our results hence clearly show that REE contents and patterns of vent fluids are sensitive to variations in the w/r.

Keywords: Water–rock-interaction; Marine hydrothermal system; Mid-ocean ridge; Gabbro; Rare earth elements; Ca; Fe; Mn; Si; Cl; Hydrothermal experiments

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1. INTRODUCTION

High-temperature hydrothermal activity along mid-ocean ridges (MOR) creates elemental fluxes both into and out of oceanic lithosphere that significantly affect ocean chemistry (e.g., Elderfield and Schultz, 1996; German and Von Damm, 2003; German et al., 2010). Black smoker hydrothermal fluids are typically characterized by high concentrations of dissolved metals (e.g., Campbell et al., 1988; Butterfield et al., 1990; Charlou et al., 2000; Douville et al., 2002; Schmidt et al., 2010, 2011), leading to the formation of metal-rich sulfide mineralization (chimneys, mounds, subseafloor stockwork ores) and sediments (e.g., Boström et al., 1969). In contrast, the rare-earth element (REE) contents of black smoker fluids are typically low (e.g., Mitra et al., 1994; Douville et al., 1999), presumably because REEs are fairly immobile when rocks from the oceanic crust are undergoing hydrothermal alteration. However, significant leaching of REEs and transition metals from rocks of the oceanic crust are observed for sheeted dike complexes (SDC) (Zuleger et al., 1995; Bach et al., 1996) or in basalt breccias from hydrothermal upflow zones (Humphris et al., 1998). This apparently contrasting behaviors of REEs in seafloor hydrothermal processes can be reconciled if most of the REEs were re-deposited in the subseafloor.

Most hydrothermal MOR vent fluids sampled worldwide have a *typical* REE signature, which is characterized by an enrichment of light REEs (LREE, La-Sm) relative to heavy REEs (HREE, Gd-Lu) and a pronounced positive Eu anomaly in chondrite-normalized plots (e.g., Mitra et al., 1994; Douville et al., 1999) ('*typical*' pattern, Fig. 1). This *typical* fluid REE pattern appears to be largely independent of host rock lithology, which led to view that REE speciation in high temperature low density fluids exerts strong controls on fluid-rock partitioning of REEs (Michard, 1989; Bau, 1991). Due to the similarity of these *typical* REE patterns to those of plagioclase, some authors suggested that vent fluid REE chemistry results from plagioclase-fluid interactions in the reaction zone (Klinkhammer et al., 1994; Douville et al., 1999). However, Allen and Seyfried (2005) demonstrated that plagioclase is not needed to produce these *typical* fluid REE patterns by reacting plagioclase-free harzburgite with a $MgCl_2$–NaCl solution (at 400 °C, 500 bar, and a water-to-rock mass ratio, w/r, of 1) and producing fluids with *typical* fluid REE patterns.

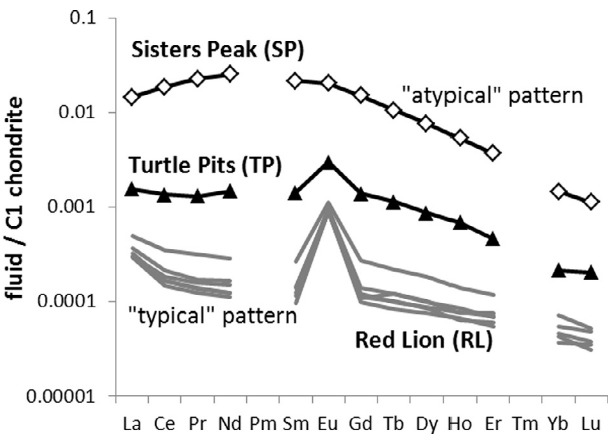

Fig. 1. Chondrite (C1) normalized (McDonough and Sun, 1995) REE patterns of vent fluids emanating at MAR 5°S. Red Lion vents have '*typical*' REE pattern that are characteristic for MOR vent fluids worldwide (e.g., Mitra et al., 1994; Douville et al., 1999). These exhibit an enrichment of light REEs (LREE, La-Sm) relative to heavy REEs (HREE, Gd-Lu) and a pronounced positive Eu anomaly. Neighboring Sisters Peak fluids have high REE contents and display an '*atypical*' REE signature with depletions of the LREEs (La-Pr) and HREEs (Gd-Lu) relative to the MREEs (Nd-Eu) and no Eu anomaly. Fluids venting at Turtle Pits have intermediate REE pattern and elevated REE contents.

In recent years, fluids venting at oceanic spreading centers have been reported that have high contents of REEs (Schmidt et al., 2010; Cole et al., 2014) and transition metals (Koschinsky et al., 2008; James et al., 2014). The REE patterns of these fluids (in the following denoted as *atypical* REE pattern) are completely different from the *typical* REE signature and exhibit relative enrichment of middle REEs (MREE, Nd-Dy) and slightly negative or no Eu anomaly ('*atypical*' pattern, Fig. 1). These occurrences relate to high-temperature vent fluids at 5°S on the slow-spreading Mid-Atlantic ridge (MAR) (Schmidt et al., 2010) and the East Scotia back arc spreading centre (ESR, segment E9) (Cole et al., 2014) which is intermediate-spreading (Livermore et al., 1997; Larter et al., 2003) but with a ridge morphology characteristic for slow-spreading ridges (German et al., 2000; Leat et al., 2000; Klinkhammer et al., 2001; Rogers et al., 2012). For example, REE patterns of the 5°S MAR vent fluids show strong variability and correlations with fluid temperature and variations of fluid flux intensity (Schmidt et al., 2010) involving most probably mixing of different fluid types (Coumou et al., 2009, 2008). Interestingly, at both ridges (5°S MAR and the ESR), fluids with *typical* REE patterns vent in areas very close to those *atypical* fluids described above (e.g., from the presumably older Red Lion – RL vent field at 5°S MAR, (Schmidt et al., 2010). At 5°S MAR, recent volcanic activity may have provided magmatic heating and new fluid pathways, which facilitated the development of vigorous high temperature venting (Haase et al., 2007). One hypothesis is that the related *atypical* REE patterns result from dissolution of anhydrite during up-flow (Schmidt et al., 2010; Cole et al., 2014). Another one is that it is characteristic for less evolved fluids created by early-stage fluid-rock interaction at peak *P*–*T* conditions (Bach and Irber, 1998; Schmidt et al., 2010). We hypothesize that the fluid flux, duration of water–rock interaction, and resulting effective w/r have a major control on the dissolution of REEs and other metals from host rocks. Moreover, we postulate that fluid fluxes related to the above-mentioned hydrothermal systems with *atypical* fluid REE patterns were high and that these conditions caused increased REE mobility.

Water-to-rock ratios were found to exert strong controls on leaching of transition metals from the oceanic crust (Seyfried and Bischoff, 1977; Hajash and Archer, 1980; Hajash and Chandler, 1981). In contrast, leaching of REEs