



# Experimental determination of barium isotope fractionation during diffusion and adsorption processes at low temperatures

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## Abstract

Variations in barium (Ba) stable isotope abundances measured in low and high temperature environments have recently received increasing attention. The actual processes controlling Ba isotope fractionation, however, remain mostly elusive. In this study, we present the first experimental approach to quantify the contribution of diffusion and adsorption on mass-dependent Ba isotope fractionation during transport of aqueous  $\text{Ba}^{2+}$  ions through a porous medium. Experiments have been carried out in which a  $\text{BaCl}_2$  solution of known isotopic composition diffused through u-shaped glass tubes filled with silica hydrogel at 10 °C and 25 °C for up to 201 days. The diffused Ba was highly fractionated by up to  $-2.15\text{‰}$  in  $\delta^{137/134}\text{Ba}$ , despite the low relative difference in atomic mass. The time-dependent isotope fractionation can be successfully reproduced by a diffusive transport model accounting for mass-dependent differences in the effective diffusivities of the Ba isotope species ( $D_{137\text{Ba}}/D_{134\text{Ba}} = (m_{134}/m_{137})^\beta$ ). Values of  $\beta$  extracted from the transport model were in the range of 0.010–0.011. Independently conducted batch experiments revealed that adsorption of Ba onto the surface of silica hydrogel favoured the heavier Ba isotopes ( $\alpha = 1.00015 \pm 0.00008$ ). The contribution of adsorption on the overall isotope fractionation in the diffusion experiments, however, was found to be small. Our results contribute to the understanding of Ba isotope fractionation processes, which is crucial for interpreting natural isotope variations and the assessment of Ba isotope ratios as geochemical proxies.

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## 1. INTRODUCTION

Barium (Ba) has received attention in the past as geochemical proxy in both low and high temperature

environments. In the oceans, precipitation of barite ( $\text{BaSO}_4$ ), being the main carrier of particulate Ba in the water column, is associated with the decay of planktonic organic matter (Goldberg and Arrhenius, 1958; Dehairs et al., 1980; Bishop, 1988; Ganeshram et al., 2003). Consequently, export fluxes of  $\text{C}_{\text{org}}$  and Ba from the water column are positively correlated (Dymond et al., 1992; Dymond and Collier, 1996). Based on this correlation, Ba accumulation rates in marine sediments have been widely

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used to reconstruct paleo-productivities (e.g., Dymond et al., 1992; François et al., 1995; Paytan and Kastner, 1996; Paytan et al., 2007; Paytan and Griffith, 2007; Hull and Norris, 2011). The validity of this proxy, however, must be questioned for samples derived from sediments, where microbial sulphate reduction has taken place, as barite remains no longer stable (McManus et al., 1998; Paytan and Griffith, 2007).

Due to the flux of particulate Ba to the seafloor and hydrothermal activity (e.g., Dymond et al., 1992; Cronan and Hodkinson, 1997), Ba is strongly enriched in marine sediments relative to mid-ocean ridge basalt (MORB) (Plank and Langmuir, 1998). Subduction of these sediments, followed by extraction of Ba from the subduction slab into magmatic fluids, leads to Ba enrichment in the mantle wedge (Morris and Ryan, 2003). Thus, Ba has been used to trace subduction components in arc lavas (Elliott et al., 1997; Pearce and Stern, 2006; Plank and Langmuir, 1993, 1998) or recycled sediments in the mantle (Rapp et al., 2008; Kuritani et al., 2011).

The interest in mass-dependent Ba isotope fractionation in terrestrial (Miyazaki et al., 2014; Horner et al., 2015; Hsieh and Henderson, 2015; Kinsley et al., 2015; Nan et al., 2015; Bullen and Chadwick, 2016; Cao et al., 2016; Pretet et al., 2016) and extraterrestrial material (Moynier et al., 2015) has increased since the first Ba isotope study using multi-collector inductively-coupled mass spectrometry (MC-ICP-MS) (von Allmen et al., 2010). For instance, Ba isotope fractionation might take place during magmatic processes, as indicated by variable Ba isotopic compositions of igneous rocks (Miyazaki et al., 2014; Nan et al., 2015). However, the observed isotopic variability in those rocks is relatively small ( $<0.3\%$  in  $\delta^{137/134}\text{Ba}$ ; Nan et al., 2015). Larger Ba isotope fractionation is documented in low temperature environments (von Allmen et al., 2010; Bullen and Chadwick, 2016; Pretet et al., 2016). It was found that Ba in the ocean is isotopically heterogeneous (Horner et al., 2015; Hsieh and Henderson, 2015; Cao et al., 2016; Pretet et al., 2016), and Ba isotopes may, thus, prove to be a useful indicator for different water masses with distinct isotopic compositions (Horner et al., 2015). In addition, Ba isotopes may complement the existing Ba proxies, e.g., by validating the pelagic origin of barites found in marine sediments. Yet, the fractionation mechanisms causing the observed variations in Ba isotopic composition remain largely unknown. To date, it is only established that precipitating sulphates and carbonates preferentially incorporate the lighter Ba isotopes (von Allmen et al., 2010; Böttcher et al., 2012b). From other alkali and alkaline earth metals, however, we know additional processes and reaction mechanisms that can cause isotope fractionation, such as adsorption (Bolou-Bi et al., 2010; Huang et al., 2012; Hindshaw et al., 2013), complexation (Gussone et al., 2003; Rustad et al., 2010) or diffusion (Richter et al., 1999, 2006; Watkins et al., 2009; Bourg et al., 2010; Chopra et al., 2012).

Our study aims to quantify the fractionation of Ba isotopes by diffusive transport through a porous, surface-reactive medium at low temperatures. In nature, such transport of Ba ions takes place for instance in soils, sediments

and sedimentary rocks. Classical natural micro-environments comprise of amorphous and jellylike inorganic structures, interrelated solid particles from micro- to nanoscale in aqueous media, e.g., clays and (hydr)oxides, and organic tissues and matrices, such as extracellular polymeric substances. We have designed a simplified experimental setup that will allow for diffusive transport through a silica hydrogel uniquely driven by a concentration gradient. The transport process is accompanied by sorption processes of  $\text{Ba}^{2+}$  onto reactive surface sites of the gel. Ba isotope fractionation factors related to mass-dependent differences in the isotopes' diffusivities and the impact of Ba adsorption on the overall fractionation are evaluated using transport diffusion models. The experimentally determined Ba isotope fractionation will provide crucial information to correctly interpret Ba isotope variations in nature.

## 2. MATERIALS AND METHODS

### 2.1. Experimental setup

Diffusion experiments were conducted in glass tubes with an inner diameter of 0.9 cm. The u-shaped glass tubes were equipped with two reservoirs for source and sink, separated by a central part containing the silica hydrogel as porous medium at a centre distance of 10 cm (Fig. 1a). Silica hydrogel was freshly prepared from sodium silicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) and hydrochloric acid (HCl). 13.6 g of sodium silicate were dissolved in 50 ml of de-ionized water, yielding a pH of 12.7. About 48.7 ml of the sodium silicate solution were then stepwise admixed in increasingly smaller portions with a total of 40 ml of 2 M HCl to reach a pH of 5.13. A volume of 9 ml of the still liquid medium was immediately transferred into the glass tubes where it solidified overnight. The next day, the source and sink reservoirs of the glass tubes were filled with 5 ml of  $\text{BaCl}_2$  solution (pH  $\sim 7$ ) and de-ionized water (pH  $\sim 6$ ), respectively, and tightly closed.  $\text{Na}^+$  and  $\text{Cl}^-$  ions were liberated during hydrolysis of the sodium silicate. Concentrations of both ions in the pore fluids of the solidified gel were estimated to be about 0.86 M for all experiments.  $\text{Ba}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  were present as free ions throughout the experiment, based on speciation calculations using PHREEQC (Parkhurst and Appelo, 2013).

A total of 40 single experiments were set up, divided into two separate series (G and G2), which were started within 10 months of each other. The experimental series were designed with two defined initial Ba concentrations in the source (0.1 and 1.0 M  $\text{BaCl}_2$ , respectively) at two different temperatures ( $10 \pm 0.1$  °C and  $25 \pm 0.1$  °C, respectively), which were kept constant using water baths. The duration of the experiments were 2, 6, 12, 20 and 27 days, respectively, for series G and 20, 40, 61, 79 and 201 days, respectively, for series G2. After the defined run duration of each experiment, source and sink solutions were sampled completely by decanting the liquids in acid-cleaned sample tubes in order to ensure homogeneity of the reservoirs. It is assumed that no significant amounts of pore fluid from the gel compartment were admixed during sampling. The

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