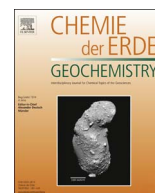




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Multi-isotope (Ba, C, O) partitioning during experimental carbonatization of a hyper-alkaline solution

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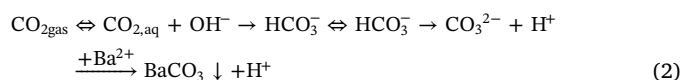
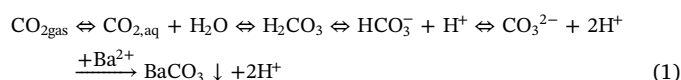
ABSTRACT

Carbonates formed from hyperalkaline aqueous solutions at the Earth's surface are known to bear the most extreme disequilibrium isotope signatures reported so far in nature. We present here the results for stable carbon (C), oxygen (O), and barium (Ba) isotope fractionation during the precipitation of witherite (BaCO₃) induced by the chemical absorption of atmospheric carbon dioxide (CO₂) into an aqueous hyper-alkaline solution (at 4° and 21 °C; 1 atm total pressure). Independent from temperature, the barium carbonate formation was associated with a substantial enrichment of the lighter C and O isotopes in the solid compared to the atmosphere (C, O), close to previous results found in experiments and nature. A new approach is introduced to explain oxygen isotope fractionation upon hydroxylation of CO₂. With Ba isotope enrichment factors between −0.45 and −0.53‰ (^{138/134}ε) or −0.34 and −0.40‰ (^{137/134}ε), respectively, the synthesized BaCO₃ displays the highest kinetic enrichment of the light Ba isotope in the carbonate solid reported so far.

1. Introduction

Carbonates formed from hyperalkaline solutions at the Earth's surface bear the most extreme kinetically impacted stable isotope signatures found so far on Earth, with carbon (C) signatures and oxygen (O) isotope signatures mimicking a pseudo-biogenic C origin and unrealistically high deposition temperatures, respectively (e.g., O'Neil and Barnes 1971; Macleod et al., 1991; Clark et al., 1992). The stable isotope composition of carbonate solids is controlled by the composition of the dissolved carbonate species and the physico-chemical boundary conditions (e.g., temperature, pH, precipitation rate) during the precipitation process (e.g., Kim and O'Neil, 1997; Beck et al., 2005; Hoefs, 2015; Zheng and Böttcher, 2016). Strong depletion of ¹³C and ¹⁸O have been observed in the dissolved carbonate species during intense photosynthesis in seawater accompanied by drastic pH-increase (Lazar and Erez, 1992), in calcite precipitating from natural solutions that are highly alkaline due to subterranean serpentinization of ultramafic rocks (O'Neil and Barnes 1971; Clark et al., 1992), and aquatic systems under anthropogenic impact of concrete and mortar degradation by meteoric

waters as found in recent drainage systems (Van Strydonck et al., 1989; Létolle et al., 1990a,b,1992; Macleod et al., 1990,1991; Dietzel et al., 1992, 2010; Rinder et al., 2013). In all these reported systems the alkaline solution was in contact to the quasi infinite atmospheric carbon dioxide (CO₂) reservoir. It has been shown that the developing overall stable C and O isotope effects upon transfer of CO₂ across the gas-liquid interface depend on the relative importance of (de)hydration versus hydroxylation reactions of carbon dioxide CO₂ (e.g., Baertschi, 1952; Craig, 1953, 1954; Usdowski and Hoefs, 1986; Fritz et al., 1985; Clark et al., 1992; Létolle et al., 1990a,b,1992; Dietzel et al., 1992; Zeebe and Wolf-Gladrow, 2001; Sade and Halevy, 2017; Devriendt et al., 2017), according to (written for the process involving the subsequent precipitation of BaCO₃):



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Under alkaline conditions, the hydroxylation reaction (2) dominates (Mills and Urey, 1940; Usdowski, 1982; Zeebe and Wolf-Gladrow, 2001) and the so-called ‘Baertschi-effect’ occurs, causing a kinetic enrichment of ^{12}C and ^{16}O in the produced bicarbonate compared to atmospheric CO_2 (Baertschi, 1952; Craig, 1953, 1954; Usdowski and Hoefs, 1986). The kinetic aspects and selected parts of the related previous experimental work have recently gained attraction and have been reviewed by Devriendt et al. (2017) and Sade and Halevy (2017).

Under (semi-) closed system conditions the fast and essentially quantitative precipitation of dissolved carbonate species (DIC) as BaCO_3 or SrCO_3 at high pH values is used in field methods for the fixation of soil CO_2 for later C isotope determinations (e.g., Michaelis et al., 1984; Fritz et al., 1985) and the chemical separation of DIC for stable carbon and oxygen isotope analysis (e.g., Beck et al., 2005; Uchikawa and Zeebe, 2013).

In this study we report on experimental results for the combined barium (Ba), C and O isotope effects during the chemical absorption of CO_2 by an aqueous hyperalkaline $\text{Ba}(\text{OH})_2$ solution. The BaCO_3 precipitation at this high pH takes place at very high rate and is essentially instantaneous. Therefore, strong kinetic isotope effects are not only expected to develop for C and O, but also for the metal isotopes. These new results add to the fundamental knowledge in one of the currently fastest growing metal isotope research areas (Hoefs, 2015; Johnson et al., 2004; Teng et al., 2017). Despite work on the stable isotopes of Ba since more than 80 years (Nier, 1938; Eugster et al., 1969), it is known only since 2010 that substantial isotope discrimination takes place in the global biogeochemical cycle of Ba (von Allmen et al., 2010). Since then, there is increasing experimental, field and modeling evidence for the magnitudes of different isotope effects (e.g., von Allmen et al., 2010; Böttcher et al., 2012,2018; Bullen and Chadwick, 2016; Horner et al., 2015, 2017; van Zuilen et al., 2016; Cao et al., 2016; Mavromatis et al., 2016; Bates et al., 2017; Hofmann et al., 2012; Pretet et al., 2016). Barium incorporated into CaCO_3 has the potential to serve as a (paleo)proxy for the seawater composition (Pretet et al., 2016; Hemsing et al., 2017; Hsieh and Henderson, 2017), and pure BaCO_3 may serve as a model system to understand the abiotic factors controlling the overall isotope fractionation processes upon mineralization of orthorhombic aragonite. Various results point to a substantial control of the isotope enrichment factor by kinetic effects (von Allmen et al., 2010; Mavromatis et al., 2016; Böttcher et al., 2018). We present here experimental evidence for the highest Ba isotope fractionation observed during BaCO_3 , in particular, and solid phase formation, in general, so far (Tables 1 and 2). Interestingly, these findings partly contrast with previous reports for witherite formed during precipitation at lower pH values (von Allmen et al., 2010; Mavromatis et al., 2016; Böttcher et al., 2018), indicating that factors other than precipitation rate, as for instance steric factors, the aqueous speciation of Ba or surface entrapment at the solid-solution interface (Watson, 2004; De Paolo, 2011; Schott et al., 2014) may also impact the fractionation degree in the barium carbonate system.

Table 1

Compilation of experimental results for the absorption of atmospheric carbon dioxide by an alkaline Ba hydroxide solution at 4 °C (FE1_4, FE2_4) and 21 °C (FE1_21, FE2_21). *f* is the fraction of remaining dissolved Ba at the end of the experimental run, calculated based on the initial conditions and the amount of precipitated BaCO_3 . $^{138}/^{134}\epsilon$ values were calculated from measurements assuming mass-dependent isotope discrimination (see text). Experiments FE1_4 and FE2_21 were carried out at run temperatures of 4° and 21 °C, respectively. $^{13}/^{12}\epsilon$ is related to an assumed $\delta^{13}\text{C}$ in air of -8‰ vs VPDB.

Experiment	Duration (h)	BaCO_3 (mg)	<i>f</i>	$\delta^{137/134}\text{Ba}$ (‰)	2 s ext. Std.dev.	$^{137}/^{134}\epsilon$ (‰)	$^{138}/^{134}\epsilon$ (‰)	$\delta^{13}\text{C}$ (‰)	$^{13}/^{12}\epsilon$ (‰)	$\delta^{18}\text{O}$ (‰)
FE1_4	12	68.3	0.90	-0.36	0.05	-0.40	-0.53	-21.4	-12.9	8.3
FE2_4	21	76.8	0.89	-0.32	0.05	-0.36	-0.48	-19.9	-11.4	8.4
FE1_21	12	72.0	0.90	-0.30	0.09	-0.34	-0.45	-25.3	-16.8	10.0
FE2_21	21	104.4	0.85	-0.35	0.09	-0.40	-0.53	-23.7	-15.2	9.8
$\text{Ba}(\text{OH})_2$				0.02	0.08	-	-	-	-	-
H_2O				-	-	-	-	-	-	-7

2. Materials and methods

2.1. Experimental methods

For the experiments (Fig. 1), an aqueous 1% $\text{Ba}(\text{OH})_2$ solution (initial pH of about 12.4 at room temperature) was prepared from synthetic $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (pro analysis (p.a.) grade quality, Merck). The experiments were carried out at 4 °C and 21 °C. For the experiments at 4 °C two 500 ccm glass beakers were filled with 200 ml of the hyperalkaline solution. In experiment FE1_4 the solution was constantly stirred with a magnetic stirrer for 12 h and experiment FE2_4, the solution was kept without stirring for 12 h plus further 9 h of continuous stirring. Experiments FE1_21 and FE2_21 at 21 °C were kept for 12 and 21 h, respectively, with constant stirring. Experiment FE_4 was initially kept unstirred, since a potential effect of hydrodynamic boundary conditions on C isotope fractionation was previously mentioned (Usdowski and Hoefs, 1986). Stirring in the final phase was initiated again, until obtaining sufficient witherite precipitate during experimental duration without enhancing the evaporation capacity that may lead to changes in the O isotope composition of the solution (e.g., Gat, 1996). No substantial impact of these boundary conditions, however, is observed in the present study, except for the overall CO_2 absorption rate (see below).

At the end of the experiment, the solid was quantitatively separated from the solution by membrane filtration (0.45 μm), washed with distilled water and ethanol, dried at 70 °C in a drying oven, weighed, and finally stored in closed glass vials until analysis.

2.2. Analytical methods

The C and O isotope composition of the precipitated BaCO_3 was analyzed on CO_2 that was liberated from Ba carbonate after dissolution in phosphoric acid (McCrea, 1950), accounting for the necessary isobaric interferences. Isotope measurements were carried out by means of irmMS using a Thermo Finnigan MAT 253 gas mass spectrometer coupled to a Gasbench II (72 °C). Scaling of measured carbon and oxygen isotope results took place via a comparison with carbonate reference materials (NBS19 and LVSEC), considering the compositional effect on the O isotope fractionation factor during the reaction with phosphoric acid (Böttcher, 1996). The C and O isotope data are given with respect to the VPDB and VSMOW standards, respectively, with a reproducibility based on replicates for standards of better than $\pm 0.15\text{‰}$. The O isotope composition of deionized water was measured by means of CRDS (Picarro L2140-i).

An aliquot of the BaCO_3 solid as well as the $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ used to prepare the initial solutions were dissolved in HNO_3 and analyzed for the Ba isotope composition by a Nu instruments Multi collector (MC-ICP-MS) system, as described previously in detail (von Allmen et al., 2010; Böttcher et al., 2012; Pretet et al., 2016). Results are given in the conventional δ -notation versus the NIST SRM 3104a standard (Pretet

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