

Barium isotope fractionation in the global barium cycle: First evidence from barium minerals and precipitation experiments

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In this study, we present first results from an ongoing investigation on the stable barium (Ba) isotope fractionation in the natural barium cycle. Stable Ba isotope signatures of international IAEA reference materials (synthetic barium sulfate, IAEA-SO-5, -6, and barium carbonate, IAEA-CO-9), natural Ba minerals and experimental Ba precipitates have been analyzed as a first approach to evaluate potential discriminating processes in the global geochemical barium cycle. Measurements were carried out on a multi-collector ICP-MS applying a $^{130}\text{Ba}/^{135}\text{Ba}$ double spike. Data are expressed as per mil deviation from a laboratory Ba nitrate standard solution in the $\delta^{137/134}\text{Ba}$ notation (external 2σ stdev $<0.1\%$). Whereas the various synthetic solid standards and a synthetic barium chloride show very similar isotope results close to the nitrate standard solution, the terrestrial barium gangue minerals (four barites, one norsethite $[\text{BaMg}(\text{CO}_3)_2]$) were close to, or depleted in the heavy isotope ($\delta^{137/134}\text{Ba}$ values down to -0.2%), compared to the standard solution.

A natural barite from China derived from a mineral collection gave an isotope value of -0.4% . High $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ ratios in this sample point to a formation under influence of microbial sulfate reduction, probably in a marine environment of sedimentary exhalative or diagenetic origin. A value of $\delta^{137/134}\text{Ba} = -0.5\%$ was found in a diagenetic barite sample from ODP Leg 207. The observed natural discriminations are clearly larger than the analytical uncertainty of the stable isotope measurements, indicating significant isotope discrimination in the natural barium cycle. Precipitation experiments from aqueous barium chloride solutions at temperatures of $\sim 21^\circ\text{C}$ and 80°C indicate that the light Ba isotope is enriched in pure barium carbonate and barium sulfate compared to the aqueous solution. A maximum isotope fractionation of -0.3% is observed for both barium carbonate and sulfate, that – in the case of BaCO_3 – seems to be influenced by precipitation rate and/or the aqueous speciation, but less by temperature.

1. Introduction

On the continents, barium (Ba) is liberated upon weathering from feldspars or locally enriched barium minerals, effectively sorbed to clay minerals, and transported in both sorbed or dissolved form to the oceans. Barium gangue minerals are formed from hydrothermal residual solutions or from solutions that leached Ba from silicate rocks (Puchelt, 1967). Detrital sources of Ba from continental runoff, hydrothermal alteration, and diagenetic Ba mobility are hard to constrain with Ba concentrations alone. The riverine and hydrothermal Ba input into to ocean, however, may be heterogeneous in isotopic

composition. Continental detrital contributions of Ba to marine sediments are not easily corrected for due to uncertainties in the estimates of the terrigenous Ba/Al ratio (Klump et al., 2000; Reitz et al., 2004). In the modern ocean, dissolved Ba shows a variable concentration and a nutrient-type behavior (Chan et al., 1976). As a non-conservative element, it has a relatively short residence time of 11 kyr (Edmond et al., 1979). Barium concentrations are reduced in the upper waters of the open ocean and enriched in deep waters and areas of nutrient upwelling (e.g., Church, 1979). Therefore, variations in the accumulation rate of barium bound to carbonate and sulfate in marine sediments are thought to be indicative of variations in marine biological productivity through time (e.g., Church, 1979; Paytan and Griffith, 2007). In this context, Ganeshram et al. (2003) studied barite formation in seawater with respect to plankton decay. Ba/Ca ratios of marine carbonates are applied based on the assumption that Ba is metabolically inert upon incorporation into carbonates, which goes conform with a recent study that showed that the Ba/Ca ratio of coccoliths varies linearly with the seawater Ba/Ca ratio (Langer et al., 2009). While Sr and Mg are known to get preferably mobilized during

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diagenetic alteration, Ba is considered to be a more stable element in sulfate-bearing sediment pore waters being at, or close to, saturation with respect to barite. Diagenetic anoxic mobilization in the zone of sulfate depletion and hydrothermal activity are known to produce relatively high levels of authigenic barium unrelated to biological surface water productivity (Torres et al., 1996). Furthermore, McManus et al. (1998) presented strong evidence that solid-phase Ba preservation may be compromised in the presence of suboxic diagenetic pore fluids.

In the present study, we introduce the fractionation of stable Ba isotopes as a new tool to constrain Ba behavior in the global element cycle. The isotopic composition of Ba was measured as early as 1938 (Nier, 1938). Eugster et al. (1969) improved the precision significantly (sub per mil range). These values were further refined by McCulloch and Wasserburg (1978). Ba isotope fractionation studies of terrestrial samples, however, are still scarce. Eugster et al. (1969) were the first to apply the double spike technique to Ba isotope fractionation measurements. They analyzed six stone meteorites, silicate inclusions of two iron meteorites, terrestrial diabase standard (W-1) and reagent barium. The average meteoritic Ba isotopic composition agreed with the terrestrial samples within less than 1%. Subsequently a large number of studies on Ba isotope anomalies in extraterrestrial material were published (e.g., McCulloch and Wasserburg, 1978; Hidaka et al., 2003; Ranen and Jacobsen, 2006; Andreassen and Sharma, 2007). In addition, Ba from the unique 2 Ga-old natural fission reactor of Oklo and Bangombé was analyzed for fissiogenic Ba isotope anomalies (e.g., Hidaka et al., 1993; Hidaka and Gauthier-Lafaye, 2008). The decay of Ba isotopes was investigated in barites (Pujol et al., 2009). However, the path of mass dependent fractionation of stable Ba isotopes was not further followed in terrestrial samples. Besides possible biological interactions, inorganic processes like mineral precipitation, complexation, diffusion and/or sorption-desorption, are processes that potentially may induce mass dependent variations in the Ba isotope composition of aqueous and solid phases. Therefore, besides analyzing different natural Ba minerals, we conducted a first set of experiments to study isotope discrimination occurring during precipitation of pure barium carbonate and sulfate at different temperatures, in order to give a first estimate for isotope fractionation upon diagenetic mineral precipitation. Ba isotopic compositions of various international IAEA standards (both carbonate and sulfate) are also reported for further use in interlaboratory comparison studies.

2. Material

2.1. Standard material

A barium nitrate ($\text{Ba}(\text{NO}_3)_2$) ICP-OES standard solution from Fluka Aldrich was used for internal isotope standardization in this study. Three international reference materials from IAEA (Vienna), namely IAEA-SO-5 (batch # 34) barium sulfate, IAEA-SO-6 (batch # 34) barium sulfate, and barium carbonate (batch # 56) IAEA-CO-9 were analyzed in this study. Due to the observed Ba stable isotope homogeneity, which is likely caused by the used Ba salt mother solution upon synthesis, we suggest to use both IAEA barium sulfate and barium carbonates as international Ba isotope standards.

2.2. Natural samples

The norsethite sample (NOR 847, $\text{BaMg}(\text{CO}_3)_2$; Böttcher et al., 1997) is a mineral from the zinc-lead-copper deposit in Rosh Pinah, Namibia (Steyn and Watson, 1967). The terrestrial barite samples were provided by Deutsche Baryt-Industrie, Bad Lauterberg, via M. Steinkamm except LB GH which is a barite gangue mineral from the valley of Lauterbrunnen, Switzerland. G-SE is a barite gangue mineral from Schlottwitz, Erzgebirge, Germany. G-GH and G-WH are barite gangue minerals from the localities Glücksrad and Wolkenhügel in the Harz

Mountains, Germany, respectively. Chin-1 is a massive white barite from an undisclosed locality in China that was provided by Deutsche Baryt-Industrie, Bad Lauterberg (Steinkamm, M., pers. communication, 2009). Sample DEM-1 is a well-defined clear diagenetic barite (BaSO_4), recovered from lower part of the core of the Demerara Rise, ODP Leg 207 (Hole 1258A, Core34R, Section 4W). This barite is precipitated from pore waters that are influenced by diffusional transport of the reacting species, induced by the anaerobic oxidation of methane (Arndt et al., 2009; Böttcher and Dietzel, 2010).

3. Methods

3.1. Chemical sample preparation

$\text{BaCl}_2 \cdot \text{H}_2\text{O}$ was dissolved in deionized water whereas BaCO_3 and $\text{BaMg}(\text{CO}_3)_2$ were dissolved in distilled 2.5 M HCl. To dissolve BaSO_4 samples and standards a method similar to that of Breit et al. (1985) was employed. However, to avoid Ba contamination, no paper filters were used. The grains of the natural barite samples were ground in an agate mortar. About 5 mg of barite powder, 50 mg of Na_2CO_3 (anhydrous suprapur, 99.999% sodium carbonate) and 1 ml of distilled water were added into a Savilex beaker. The mixture was heated for 4 h on 95 °C. Deionized water was intermittently added to keep the liquid content at approximately 1 ml. The newly formed liquid Na_2SO_4 (strongly alkaline) was separated from the solid residue (BaCO_3) using a pipette to decant. However, about 25 μl of Na_2SO_4 was left behind with the solid residue. Another 50 mg of Na_2CO_3 , along with 1 ml of deionized water, were added to the residue and the heating procedure was repeated. After decantation, the solid residue was repeatedly diluted with distilled water, which was subsequently decanted by pipette. Finally, the solid residue, along with about 25 μl of distilled water, was dissolved with distilled 2.5 M HCl. Based on semi-quantitative optical estimation sample DEM-1 had a solid residue of roughly 5% from the original 5 mg BaSO_4 . A second powder aliquot of DEM-1 was processed through chemistry as described above. However, the Na_2CO_3 -heating step was performed only once. The resulting main solution had a solid residue of roughly 10%. The solid residue of the sample was analyzed by SEM (FEI XL30 Sirion FEG, University of Fribourg). EDS (a lithium doped silicon detector with an S-UTW polymer window) semi-quantitative stoichiometrical analysis revealed the presence of BaSO_4 and a C-F phase. Hence, the sample was not completely dissolved. The C-F phase most likely is due to traces of Teflon. The unfractionated results are discussed in Section 4. Residues based on visual estimation were also detected in G-SE (~8%), G-GH (~8%) and LB GH (~10%). Further residues in other BaSO_4 samples/standards are possible but were not discernable due to the small fraction or the milky color of the beaker.

3.2. Precipitation experiments

An initial aqueous 5% BaCl_2 solution was prepared from synthetic $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (pro analysi (p.a.) grade quality, Merck). Precipitation experiments of synthetic BaCO_3 were carried out at room temperature (20 to 23 °C, hereafter termed 21°) and 80 °C. 13 ml of a 1% NaHCO_3 solution were slowly added to 100 ml of an aqueous 5% BaCl_2 solution (experiments Ba-BIK, slow precipitation rate). In the Ba-CAR experiments (fast precipitation rate), 10 ml of a 1% Na_2CO_3 solution were slowly added to 100 ml of an aqueous 5% BaCl_2 solution. The solutions were continuously agitated by a magnet stirrer that was also used to heat the experimental solution to 80 °C in the respective experiments. The pH in the 21 °C-experiments was measured in a parallel run with an ion-selective electrode (Mettler Toledo InLab Basics electrode with a Schott handylab pH11 pH meter) at the beginning of the experiment and after successive precipitation steps. It was found that the pH increased from initially 5.5 via 6.9 to a value of 6.2 after one hour (Ba-BIK). In experiment Ba-CAR, the pH increased from an initial value of

5.6 to 8.0 (immediately after the addition of the sodium carbonate solution) staying constant at 7.5 between 30 and 60 min. Barium sulfate was precipitated from 5% BaCl₂ solutions at 21° and 80 °C by the dropwise slow addition of 10 ml of a 1% Na₂SO₄ solution. In these experiments, the initial BaCl₂ solution was acidified with HCl to a pH below 4 to avoid co-precipitation of BaCO₃. The relatively small fractions of precipitated barium carbonate and barium sulfate were chosen to avoid changes in the barium isotopic composition of the mother metal solution due to Rayleigh-type closed system effects (e.g., Hartmann and Nielsen, 1969). 15 h after the precipitation experiment, the solution was filtered through 0.45 μm and the precipitate carefully washed with deionized water and dried at 60 °C in a drying oven. All chemicals used were of p.a. quality. The calculated total amount of barium precipitated in both experiments was below 5%.

3.3. Analytical considerations and techniques of Ba isotopes

Barium has 7 stable isotopes, which are 130, 132, 134, 135, 136, 137 and 138. Their abundance is 0.1058, 0.1012, 2.417, 6.592, 7.853, 11.232 and 71.699%, respectively (Eugster et al., 1969, Table 1). Ba masses 137 and 134 were selected as natural sample masses and the 130–135 pair was chosen as double spike masses. The four isotopes were selected to suit MC-ICP-MS and also possible TIMS analyses at a later stage. ¹³⁸Ba was considered not suitable for analysis as it is very abundant (71.7%) and, hence, the difference in monitored voltage between the various analyzed isotopes would be inconveniently large. Moreover, there are isobaric interferences of La and Ce on ¹³⁸Ba; Ce further interferes on ¹³⁶Ba (Table 1). ¹³⁷Ba was chosen as reference because it is the second most abundant in nature and the most abundant Ba isotope monitored. Generally, ¹³²Ba and ¹³⁶Ba are not reported due to larger contributions from the spike and isobaric interferences (¹³²Xe and ¹³⁶Ce); however, ¹³²Ba data are given for pure standard measurements (Table 2) (see below). A spike mixture was prepared that would allow 90%/10% spike versus analyte enrichment on the selected 130–135 spike masses.

Interfering elements on the measured Ba isotopes are Xe and Te (Table 1). Isobaric Xe interferences on MC-ICP-MS are possible from impurities of the Ar plasma. There is no interfering mass on ¹²⁹Xe and ¹³¹Xe; therefore these masses were selected to monitor xenon interferences on barium. In the case of ¹³¹Xe exceeding 0.2 mV the program calculations were set such that a Xe correction was applied to the barium masses 130, 132 and 134. Generally, relative ¹³⁰Xe interferences on ¹³⁰Ba were smaller than 0.06%. For unspiked measurements ¹³⁰Xe interferences occasionally reached up to 0.3%. Even for these samples the reproducibility of the ¹³⁰Ba/¹³⁵Ba ratio was 0.01%, indicating that the Xe correction is sufficiently precise (Table 2). Tellurium can cause isobaric interferences on ¹³⁰Ba. The very low concentrations of Te in deep seawater (0.02–0.05 ppt; Li, 1991) and continental crust (5 ppb; Wedepohl, 1995) in comparison to the much higher Ba concentrations of 15 000 ppt for deep seawater (Li, 1991) and 250–576 ppm for continental crust (Rudnick and Fountain, 1995; Rudnick and Gao, 2004) do not suggest significant

Table 1

Barium isotopes and interfering elements. Detected relative ¹³⁰Xe interferences on ¹³⁰Ba were smaller than 0.06%. ¹Rounded after Parrington et al. (1996). ²Percent of respective element. ³Eugster et al. (1969).

Ba mass	128	129	130	131	132	134	135	136	137	138
Atomic mass ¹	–	–	129.906	–	131.905	133.905	134.906	135.905	136.906	137.905
Abundance (%) ^{2,3}	–	–	0.1058	–	0.1012	2.417	6.592	7.853	11.232	71.699
Selected spike masses:			X				X			
Monitored masses:						X			X	
Interfering elements (%) ^{2,1}										
Xe	1.92	26.4	4.1	21.2	26.9	10.4		8.9		
Ce								0.19		0.25
La										0.09
Te	31.8		34.5							

Table 2

Isotopic composition of Ba (isotopes applied in this study). Average Ba isotope ratios from multiple unspiked measurements, compared to the respective data from Eugster et al. (1969). Note that ¹³⁰Ba/¹³⁵Ba and ¹³²Ba/¹³⁵Ba of this study have larger uncertainties than ¹³⁴Ba/¹³⁵Ba due to low abundance and Xe interference. For ¹³⁰Ba/¹³⁵Ba these influences are significantly reduced in spiked measurements due to the addition of ¹³⁰Ba from the spike. ¹³²Ba/¹³⁵Ba is not used for geological interpretations. ¹n = 5. ²All data were (re)normalized to ¹³⁷Ba/¹³⁵Ba = 1.73083.

	Eugster et al.	2σ std.err. (%)	This study	2σ std.err. (%) ¹
¹³⁷ Ba/ ¹³⁵ Ba ²	1.70383		1.70383	
¹³⁴ Ba/ ¹³⁵ Ba	0.36665	0.06	0.366678	0.002
¹³² Ba/ ¹³⁵ Ba	0.01536	0.09	0.015362	0.022
¹³⁰ Ba/ ¹³⁵ Ba	0.01605	0.09	0.016048	0.011

isobaric interferences from Te on ¹³⁰Ba for the samples analyzed here. The Ba/Te ratio of deep seawater is about 300 000 to 750 000 and for continental crust approximately 50 000 to 115 000. Furthermore, Te is mainly present as Te⁴⁺ and Te⁶⁺ in seawater. The small ionic radius of Te⁴⁺ and Te⁶⁺ does not make it a suitable candidate to substitute for Ba in the barite crystal lattice. To the extent that tellurate substitutes for sulfate in BaSO₄, it will also be discriminated against Ba together with sulfate in the dissolution process via BaCO₃ formation. To validate these considerations mass 128 (Te and Xe) was monitored by ion counting. After the Xe interference correction no detectable signal remained.

3.4. Standard and double spike calibration

Theoretical spike–sample mixtures were simulated in a lower hemisphere Excel calculation spreadsheet. These calculations allow simulating the angles between the pure standard fractionation trendline, the pure 130–135 spike fractionation trendline, and the spike–standard mixing line. Different spike compositions and sample–spike mixtures can be tested in the spreadsheet. Highest measurement precisions can be achieved at 130–135 spike mixtures and spike–sample mixtures where all three above-mentioned trendlines cross with high angles. If the trendlines cross at low angles the intersection is not well-defined which leads to a low precision.

The double spike was prepared from ¹³⁰Ba (from carbonate) and ¹³⁵Ba (from nitrate), (Oak Ridge National Laboratory; enrichment 37.6 and 93.4%, respectively). As a first approach pure standard and pure spike composition were determined from multiple measurements. Normalized standard ratios were then compared with data from Eugster et al. (1969) (Table 2) to ensure that no anomalies, apart from instrumental fractionation, are present within analytical error. In a next step pure standard and pure spike solutions were doped with a pure Nd standard of known isotopic composition. The instrumental fractionation correction was determined on the basis of the measured ¹⁴²Nd/¹⁴⁴Nd ratio of the Nd standard and then applied to correct the ¹³⁷Ba/¹³⁵Ba ratio of the pure standard and pure spike. The latter ratio was chosen to fit the collector spacing and mass range in combination with the Nd masses, and to avoid interferences. Subsequently, the calibration was verified by measuring different spike/standard

mixtures. Finally, the range of accurately measured spike/standard $^{130}\text{Ba}/^{137}\text{Ba}$ ratio was empirically defined to be between 0.1 and 0.43. Barium isotopes are given as $\delta^{137/134}\text{Ba} = ((^{137}\text{Ba}/^{134}\text{Ba})_{\text{sample}} / (^{137}\text{Ba}/^{134}\text{Ba})_{\text{standard}} - 1) * 1000$ relative to the $\text{Ba}(\text{NO}_3)_2$ -standard solution.

Table 3

Barium standard long-term record. The 2σ standard deviation of the long-term standard evolution over 10 months is $\pm 0.15\%$. The spike–standard mixture ratio was monitored as 130/137-ratio (only corrected for instrumental mass bias).

Date	Run number	$\delta^{137/134}\text{Ba}$	2σ sd	130/137	Cycles
05/04/2009	15123	0.00	0.02	0.17	35/40
05/04/2009	15126	0.00	0.03	0.17	36/40
05/04/2009	15130	0.02	0.02	0.17	39/40
05/04/2009	15134	0.01	0.02	0.17	37/40
05/04/2009	Average	0.01			
05/04/2009	2σ sd	0.02			
07/20/2009	15441	0.00	0.03	0.16	37/40
07/20/2009	15442	-0.07	0.02	0.16	36/40
07/20/2009	15443	0.01	0.03	0.16	38/40
07/20/2009	15445	0.00	0.02	0.16	37/40
07/20/2009	15449	0.00	0.03	0.16	37/40
07/20/2009	15453	-0.09	0.02	0.16	35/40
07/20/2009	Average	-0.02			
07/20/2009	2σ sd	0.09			
07/21/2009	15455	-0.03	0.03	0.18	38/40
07/21/2009	15456	-0.04	0.02	0.18	38/40
07/21/2009	15460	-0.07	0.02	0.18	36/40
07/21/2009	15464	-0.13	0.02	0.18	34/40
07/21/2009	15465	-0.02	0.02	0.18	36/40
07/21/2009	15466	-0.05	0.02	0.18	36/40
07/21/2009	15467	-0.05	0.02	0.18	34/40
07/21/2009	15470	-0.07	0.02	0.18	37/40
07/21/2009	Average	-0.06			
07/21/2009	2σ sd	0.07			
07/22/2009	15471	-0.05	0.02	0.18	35/40
07/22/2009	15472	-0.04	0.04	0.18	36/40
07/22/2009	15477	-0.04	0.03	0.18	39/40
07/22/2009	15478	-0.10	0.03	0.18	39/40
07/22/2009	15479	-0.17	0.02	0.18	36/40
07/22/2009	15480	-0.19	0.02	0.18	39/40
07/22/2009	15485	-0.04	0.03	0.18	35/40
07/22/2009	15488	-0.20	0.03	0.18	
07/22/2009	Average	-0.10			
07/22/2009	2σ sd	0.14			
10/29/2009	15947	0.10	0.02	0.18	38/40
10/29/2009	15952	0.12	0.03	0.18	37/40
10/29/2009	Average	0.11			
10/29/2009	2σ sd	0.03			
10/30/2009	15955	0.12	0.03	0.18	36/40
10/30/2009	15956	0.11	0.02	0.18	38/40
10/30/2009	15957	0.09	0.02	0.18	36/40
10/30/2009	15958	0.10	0.02	0.18	39/40
10/30/2009	15967	0.09	0.03	0.18	35/40
10/30/2009	15972	0.10	0.03	0.18	38/40
10/30/2009	15977	0.06	0.02	0.18	38/40
10/30/2009	Average	0.09			
10/30/2009	2σ sd	0.04			
11/05/2009	15997	0.03	0.02	0.18	36/40
11/05/2009	15998	0.00	0.03	0.18	35/40
11/05/2009	15999	0.06	0.03	0.18	37/40
11/05/2009	16000	0.09	0.03	0.18	39/40
11/05/2009	16001	0.02	0.03	0.18	36/40
11/05/2009	16005	-0.01	0.03	0.18	39/40
11/05/2009	16009	0.08	0.03	0.18	33/40
11/05/2009	16013	0.07	0.03	0.18	38/40
11/05/2009	16018	0.00	0.02	0.18	36/40
11/05/2009	Average	0.04			
11/05/2009	2σ sd	0.08			
11/06/2009	16019	0.06	0.03	0.18	38/40
11/06/2009	16020	0.08	0.03	0.18	36/40
11/06/2009	16021	0.02	0.04	0.18	35/40
11/06/2009	16025	0.04	0.02	0.18	35/40
11/06/2009	16029	0.02	0.03	0.18	34/40
11/06/2009	16034	0.05	0.02	0.18	38/40
11/06/2009	Average	0.05			
11/06/2009	2σ sd	0.05			

Table 3 (continued)

Date	Run number	$\delta^{137/134}\text{Ba}$	2σ sd	130/137	Cycles
02/24/2010	16378	-0.07	0.02	0.18	36/40
02/24/2010	16379	0.03	0.03	0.16	38/40
02/24/2010	16380	-0.09	0.03	0.16	37/40
02/24/2010	16384	-0.02	0.03	0.16	39/40
02/24/2010	16388	-0.03	0.02	0.16	37/40
02/24/2010	Average	-0.03			
02/24/2010	2σ sd	0.09			
	Average all data	0.00			
	2σ sd all data	0.15			

3.5. Data acquisition and reduction

Measurements were performed on a double focusing Nu instruments® multi-collector ICP-MS equipped with 12 fixed Faraday cups (and 3 ion counters) in static mode. Before analyses the plasma was run for at least 2 h to achieve stable measurement conditions. ^{131}Ba was set to be collected in the axial cup. Data acquisition generally comprised 4 blocks of 10 cycles per measurement. Peak centering was performed after each block.

Standard and sample solutions were mixed with the spike and diluted with 0.5 M HNO_3 to achieve a final natural ^{137}Ba concentration between approximately 0.025 and 0.030 ppm. Measurements consume about 1 ml of the solution, thus the ^{137}Ba amount needed is about 25 ng, or 230 ng of total Ba. Samples were ingested with a Teflon PFA micromist® ESI nebulizer and transferred into the ICP-MS through an ESI®Apex-Q desolvating high sensitivity Inlet system. After each measurement the system was cleaned by running 0.5 M HNO_3 for about 10 min. The background was acquired by deflection of the electrostatic analyzer (ESA). Generally, the internal standard was measured after three to four sample analyses. The barium blank was constantly <0.04 ng. The intensities of the spike/standard and spike/sample mixtures yielded on average around 1, 8, 0.24 and 0.2 V for barium masses 137, 135, 134 and 130, respectively. Intensities approaching 0.1 V were avoided as this leads to a magnification of the internal error. The spike–standard mixture ratio was monitored as $^{130}\text{Ba}/^{137}\text{Ba}$ -ratio.

The three-dimensional data reduction procedure of Siebert et al. (2001) was applied. It is very similar to procedures of Hofmann (1971) and Johnson and Beard (1999). Thereby, the exponential fractionation law is applied for instrumental and natural mass dependent fractionation.

3.6. Sulfur and oxygen isotope measurements

Sulfur and oxygen isotope measurements of sample Chin-1 were carried out using a Thermo Electron Finnigan MAT 253 gas mass spectrometer connected to a Thermo Finnigan Flash elemental analyzer or a Finnigan TC/EA via a Thermo Electron ConFlo-IV interface at IOW. Stable isotope ratios of DEM-1 were measured on a Thermo Finnigan Delta+ connected to a Eurovector elemental analyzer (EA) via a Thermo Finnigan ConFlo-III interface (at MPI-MM, Bremen). For sulfur isotope measurements international standards (IAEA-S-1, -3, SO-5, SO-6, NBS-127), and for oxygen isotope measurements, IAEA-SO-5 and -SO-6, as well as further IAEA standards and internal reference materials were used for calibration. Stable sulfur and oxygen isotope ratios are given in the conventional δ -notation via the V-CDT and V-SMOW standards, respectively.

4. Results and discussion

The long-term 2σ standard reproducibility of the Ba isotopes over a period of about 10 months was $\pm 0.15\%$ ($n = 55$, Table 3, Fig. 1). Samples were corrected relative to daily averages. Daily 2σ standard deviation values range from ± 0.02 to $\pm 0.14\%$. The $^{130}\text{Ba}/^{137}\text{Ba}$ spike/

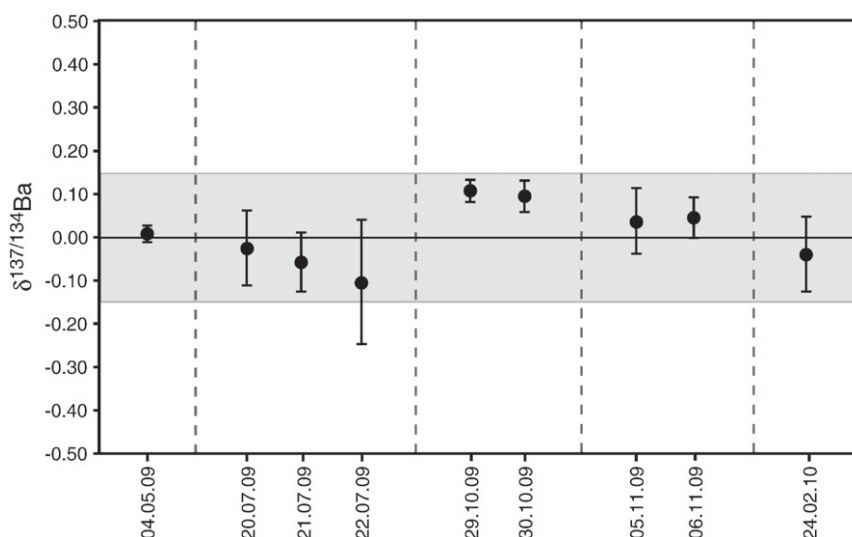


Fig. 1. Daily 2σ standard deviation values range from ± 0.02 to $\pm 0.14\%$ (see also Table 3). The long-term 2σ standard deviation of the internal standard over a period of 10 months is $\pm 0.15\%$ (grey shaded area, $n = 55$). Samples are corrected for the long time drift based on the daily mean. The x-axis is not to scale.

standard-ratio based on intensity is given as 130/137 in Tables 3 and 4. The DEM-1 aliquot that underwent the Na_2CO_3 treatment only once has a $^{130}\text{Ba}/^{137}\text{Ba}$ ratio of 0.32 opposed to 0.24 of the aliquot that was subject to this chemical step twice, even though the prepared spike to dissolved sample ratio was similar. However, weighing sample amounts of a few mg into Teflon beakers is prone to significant electrostatic problems. The observed $^{130}\text{Ba}/^{137}\text{Ba}$ ratios indicate that roughly 30% less BaSO_4 was dissolved from the aliquot that went only once through the Na_2CO_3 treatment. The two aliquots produced average $\delta^{137/134}\text{Ba}$ values of -0.51 and -0.49% , respectively. Consequently, the difference in dissolution does not affect the isotopic ratios (Table 4). Possible effects of partial sample dissolution on $\delta^{137/134}\text{Ba}$ were further investigated on powdered aliquots from the BaSO_4 IAEA-SO-5 standard by using lower amounts of Na_2CO_3 during chemical procedures. The partial dissolution of BaSO_4 of approximately 30, 15, 10% yielded a $\delta^{137/134}\text{Ba}$ of 0.03 ± 0.02 , 0.06 ± 0.02 and $0.05\% \pm 0.04$ (2σ sd). These results compare well with the average of $0.02\% \pm 0.02$ (2SEM) of the IAEA-SO-5 standard aliquot (Table 4) that underwent regular chemistry procedures. Thus, these experiments demonstrate, that potential partial dissolution during chemistry does not significantly affect the barium isotopic composition if at least 10% of the total aliquot was dissolved. There is further no resolvable offset between sample aliquots that underwent a chemical $\text{H}_2\text{O}_2/\text{HNO}_3$ treatment to remove possible interfering organic matter and aliquots that were not subject to this treatment (Hippler et al., 2004) (Table 4). All standard materials, i.e., all three IAEA standards (BaSO_4 and BaCO_3) and the in-house $\text{Ba}(\text{NO}_3)_2$ standard solution, and the synthetic $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ used in the precipitation experiments gave results within a very close range of 0.06% (Fig. 2, Table 4). This may indicate a similar isotopic composition of the barium source used in the industrial synthesis of the Ba salt and Ba nitrate solution as well as the IAEA Ba sulfate and carbonate preparation.

The different terrestrial Ba sulfate and BaMg carbonate gangue samples range from -0.02 to -0.17% (Fig. 2, Table 4). A natural barite, from an undisclosed Chinese locality, gave an isotope value of -0.4% . Considering the heavy values of $\delta^{34}\text{S}$ ($+36.4\%$ vs. V-CDT) and $\delta^{18}\text{O}$ ($+17.4\%$ vs. V-SMOW) in this sample the barite has been formed in a marine environment from sulfate that was modified by microbial sulfate reduction, probably under sedimentary exhalative or diagenetic conditions (Böttcher et al., 1998; Wortmann et al., 2007; Johnson et al., 2009). This relationship is further supported by the measurement of the diagenetic barite sample (DEM-1; $\delta^{34}\text{S} = +54.4\%$, $\delta^{18}\text{O} = +23.4\%$) from ODP Leg 207, with a $\delta^{137/134}\text{Ba}$ of

-0.5% (Fig. 2, Table 4). Not considering the Chinese sample, the terrestrial minerals, tentatively used here as a substitute for continental input into seawater, appear to be more or less homogeneous with respect to barium isotope composition, with a maximum range of 0.15% (Fig. 2, Table 4). This includes barium sulfates as well as the norsethite sample. The Ba isotopic composition of the investigated diagenetic barite sample is isotopically lighter than the gangue minerals. The diagenetic barite is precipitated from marine interstitial waters in counter-diffusional gradients of dissolved barium and sulfate (Torres et al., 1996). Therefore, Ba isotope discrimination could result from processes such as ion diffusion, sorption/desorption processes, and/or incomplete precipitation of the sulfate from the aqueous solution.

We investigated in a first approach Ba isotope discrimination upon precipitation of pure BaCO_3 and BaSO_4 from aqueous solutions at 21° and 80°C (1 atm total pressure). It was found that the heavy Ba isotope is generally depleted in the carbonate and sulfate solids down to -0.3% (Fig. 2, Table 4). No reservoir effect is expected in the performed experiments, since only a few % of the total dissolved barium concentration was precipitated. The magnitude of isotope discrimination seems independent of temperature (Fig. 2), but differences are observed between BaCO_3 that is formed upon addition of aqueous solutions of NaHCO_3 or Na_2CO_3 . Addition of the latter led to higher pH values (see above) and a spontaneous (“fast”) precipitation of the solid (Ba-CAR). This experiment (Ba-CAR) showed a maximum fractionation of -0.13% compared to the BaCl_2 -solution.

The addition of sodium bicarbonate (NaHCO_3) led to smaller pH shift, corresponding lower thermodynamic supersaturation, and resulting lower precipitation rate upon barium carbonate formation. This resulted in enhanced isotope discrimination, independent of temperature in the Ba-BIC experiments (Fig. 2). Thus, in the Ba-BIC experiments the metal isotopes are more fractionated between solution and solid than in the Ba-CAR experiments with a maximum of -0.31% (Fig. 2, Table 4). A similar value was found in the barite synthesis experiments (Fig. 2, Table 4), which took place at high precipitation rate. Hence, an even higher fractionation at lower precipitation rate can be expected. This clearly shows that Ba isotopes are fractionated during solid precipitation and that the magnitude is not constant. Besides precipitation rate, also the aqueous speciation of barium may influence isotope discrimination. The divalent Ba cation is hydrated and may also form ion pairs with the bicarbonate and carbonate ion. Therefore, the difference in pH, as observed in experiments Ba-CAR and Ba-BIC, may have been influenced by the

Table 4

Results were normalized to the daily average standard value. The $^{130}\text{Ba}/^{137}\text{Ba}$ column reflects the spike/sample mixture as measured, only corrected for instrumental mass bias. *Marks aliquots that underwent a $\text{H}_2\text{O}_2/\text{HNO}_3$ cleaning step to remove organics (Hippler et al., 2004). The 2 SEM is based on repeated measurements.

Mineralogy	Sample description	Provenance	Sample name	$\delta^{137/134}\text{Ba}$	2 σ int. error	2SEM	2 σ ext. sd	130/137	Cycles
BaSO ₄	Standard	IAEA	IAEA-SO-5	-0.01	0.03		0.09	0.21	38/40
			IAEA-SO-5	0.00	0.03		0.07	0.21	38/40
			IAEA-SO-5	0.03	0.03		0.14	0.21	35/40
			IAEA-SO-5	0.02	0.02		0.05	0.22	39/40
			IAEA-SO-5	0.05	0.03		0.05	0.22	35/40
			Average IAEA-SO-5	0.02		0.02			
			IAEA-SO-6	-0.03	0.03		0.07	0.22	35/40
			IAEA-SO-6	-0.07	0.03		0.07	0.22	35/40
			IAEA-SO-6	-0.02	0.03		0.04	0.23	38/40
			IAEA-SO-6	-0.01	0.03		0.04	0.23	38/40
BaSO ₄	Standard	IAEA	Average IAEA-SO-6	-0.04		0.03			
			IAEA-CO-9	-0.06	0.03		0.07	0.19	35/40
			IAEA-CO-9	0.00	0.03		0.07	0.19	35/40
			IAEA-CO-9	0.00	0.03		0.14	0.19	39/40
			IAEA-CO-9	-0.04	0.03		0.03	0.17	37/40
BaCO ₃	Standard, witherite	IAEA	Average IAEA-CO-9	-0.03		0.03			
			BaCl ₂	-0.01	0.03		0.03	0.16	
BaCl ₂	Educt salt	Experimental	BaCl ₂	-0.01	0.02		0.04	0.16	39/40
			Average BaCl ₂	-0.01		0.01			
			BaCO ₃ -20-CAR	-0.05	0.02		0.03	0.15	36/40
			BaCO ₃ -20-CAR	-0.10	0.02		0.04	0.15	39/40
			BaCO ₃ -20-CAR	-0.02	0.02		0.05	0.14	39/40
BaCO ₃	"Fast" at 21 °C	Experimental precipitate	BaCO ₃ -20-CAR	-0.07	0.03		0.05	0.14	36/40
			Average BaCO ₃ -20-CAR	-0.06		0.04			
			BaCO ₃ -80-CAR	-0.17	0.04		0.04	0.13	36/40
			BaCO ₃ -80-CAR	-0.11	0.02		0.05	0.12	36/40
BaCO ₃	"Fast" at 80 °C	Experimental precipitate	Average BaCO ₃ -80-CAR	-0.14		0.07			
			BaCO ₃ -20-BIK	-0.30	0.03		0.09	0.20	35/40
			BaCO ₃ -20-BIK	-0.44	0.04		0.04	0.22	35/40
			BaCO ₃ -20-BIK	-0.25	0.02		0.05	0.20	37/40
			BaCO ₃ -20-BIK	-0.28	0.03		0.05	0.20	38/40
BaCO ₃	"Slow" at 21 °C	Experimental precipitate	Average BaCO ₃ -20-BIK	-0.32		0.07			
			BaCO ₃ -80-BIK	-0.28	0.03		0.03	0.28	38/40
			BaCO ₃ -80-BIK	-0.28	0.02		0.04	0.18	37/40
			BaCO ₃ -80-BIK	-0.27	0.02		0.05	0.16	37/40
BaCO ₃	"Slow" at 80 °C	Experimental precipitate	Average BaCO ₃ -80-BIK	-0.28		0.01			
			BaSO ₄ -20	-0.25	0.04		0.04	0.29	37/40
			BaSO ₄ -20	-0.24	0.04		0.05	0.26	36/40
BaSO ₄	At 21 °C	Experimental precipitate	Average BaSO ₄ -20	-0.24		0.02			
			BaSO ₄ -80	-0.27	0.05		0.03	0.26	38/40
			BaSO ₄ -80	-0.33	0.04		0.03	0.26	34/40
			BaSO ₄ -80	-0.21	0.04		0.05	0.26	47/50
			Average BaSO ₄ -80	-0.27		0.07			
BaSO ₄	At 80 °C Terrestrial gangue	Experimental precipitate CH-Lauterbrunnen (Gnadensonne Hauriberg) China	BaSO ₄ -20	-0.02	0.02		0.07	0.23	36/40
			Chin-1	-0.39	0.03		0.07	0.24	37/40
			G-GH	-0.13	0.03		0.09	0.26	36/40
			G-GH	-0.20	0.05		0.14	0.26	37/40
			G-GH	-0.20*	0.03		0.08	0.23	39/40
			Average G-GH	-0.17		0.05			
			G-WH	-0.08	0.03		0.09	0.22	39/40
			G-WH	-0.05	0.03		0.14	0.22	38/40
			Average G-WH	-0.06		0.03			
			G-SE	-0.03	0.04		0.09	0.28	38/40
G-SE	-0.07*	0.03		0.14	0.27	37/40			
BaSO ₄	Terrestrial gangue	Schlottwitz, Erzgebirge, Germany	Average G-SE	-0.05		0.04			
			NOR 847	-0.15*	0.04		0.07	0.41	39/40
			NOR 847	-0.07*	0.03		0.14	0.23	38/40
			Average NOR 847	-0.11		0.09			
			DEM1	-0.58	0.07		0.02	0.32	37/40
BaMg(CO ₃) ₂	Terrestrial gangue	Rosh Pinah, Namibia	DEM1	-0.45	0.03		0.02	0.24	39/40
			DEM1	-0.53	0.03		0.02	0.24	38/40
			DEM1	-0.45	0.04		0.02	0.32	34/40
			DEM1	-0.53*	0.04		0.09	0.25	39/40
			Average DEM-1	-0.51		0.05			
BaSO ₄	Diagenetic barite	Demerara Rise ODP Leg 207	Average DEM-1	-0.51		0.05			

concentrations of available ligands in the solution, but also at the solution–solid interface. Further experiments regarding this issue as well as the role of foreign element concentrations are under way. In general, the preservation of isotope fractionation in a solid requires the presence of a dissolved reservoir and non-complete precipitation (no reservoir effect).

Stable metal isotope effects have previously been described upon calcite (Ca and Mg isotopes) or barite (Ca isotopes) formation (e.g., Griffith et al., 2008; Tang et al., 2008; Immenhauser et al., 2010). As in the case of Ba, it was generally observed, that the lighter isotopes of Mg and Ca are enriched in the solid compared to the dissolved cations, and a rate dependence of isotope discrimination was found. This

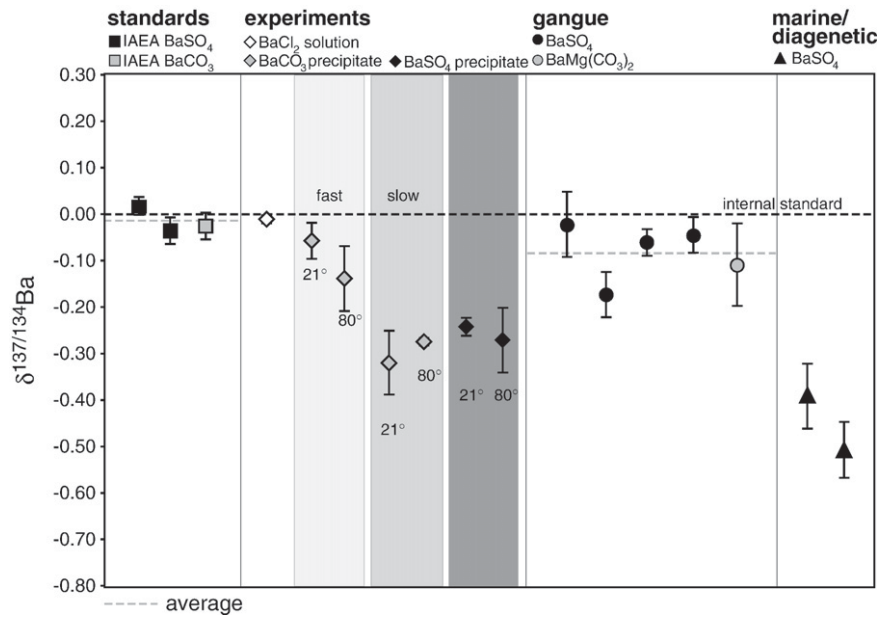


Fig. 2. The experiments were carried out in two different solutions. The precipitates marked with “fast” were precipitated from a BaCl₂ solution with 1% Na₂CO₃ solution added slowly. 1% NaHCO₃ solution was slowly added to the BaCl₂ solution in the experiments marked with “slow”. The BaSO₄ precipitates were precipitated from a BaCl₂ solution with 1% Na₂SO₄ solution slowly added. Each experiment was carried out at room temperature (~21 °C) and at 80 °C. Error bars are given as 2SEM of repeated measurement. For LB GH and Chin-1 (single measurement) the error bar reflects the 2σ external sd reproducibility (Table 4).

preferential uptake has been interpreted as results of dehydration of the cation, reaction kinetics, and a surface entrapment of the lighter isotope (Immenhauser et al., 2010). Ba isotope discrimination upon dissolution of isotopically homogeneous Ba carbonate and sulfate, in contrast, is not expected due to the ionic bonds of these salts. The latter hypothesis is supported by the here demonstrated dissolution experiments of BaSO₄ that did not reveal any fractionation due to partial dissolution. BaCO₃ dissolution was always complete. Experimental and field investigations to further understand the mechanisms behind the observed isotope discriminations in nature are currently under way.

5. Conclusion

Static MC-ICP-MS measurements applying double spike technique result in reproducible barium isotopic analyses and reveal differences between terrestrial gangue archives and diagenetic barites. Xe and possible Te interferences can be corrected for. The very low concentration of Te in seawater and continental crust, along with the small ionic radius, do not suggest any significant interference.

Whereas most of the terrestrial gangue samples of different mineralogy result in a δ^{137/134}Ba value close to the investigated in-house and international synthetic reference materials, the marine and the diagenetic barite were depleted in the heavy isotope down to -0.5% compared to a Ba nitrate standard solution. The observed Ba isotope fractionation in experiments and the presumed influence of precipitation rate on the magnitude of isotope discrimination opens routes in understanding the mechanistic base. It is also to be considered, that vital effects may occur upon Ba incorporation into biogenic solid phases such as carbonates or sulfates. Ongoing work focuses on the processes responsible for low temperature isotope discrimination and the effects of physicochemical boundary conditions.

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