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Barium isotope fractionation during formation of anhydrous barium carbonate (witherite): Influence of experimental conditions

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In this study, we present new experimental results from an ongoing investigation on the stable barium (Ba) isotope fractionation in the natural barium cycle (Ref. 1). Ba isotope fractionation during formation of BaCO3 (W; witherite) was followed by six different experimental approaches:

#1: Slow degassing of CO2 from initially CO2- and witherite-saturated aqueous solution
#2: Absorption of CO2 by agitated alkaline Ba hydroxide solution
#3: Titration of Na bicarbonate solution into aqueous Ba chloride solution
#4: Titration of Na carbonate solution into aqueous Ba chloride solution
#5: Titration of Na bicarbonate solution into aqueous Ba chloride solution containing 5% methanol
#6: Slow transformation of CaCO3 (aragonite) to W in aqueous Ba chloride solution

Conditions were chosen to produce low (#1, #6), intermediate (#3, #5), and high (#2, #4) witherite precipitation rates. The aqueous solutions of experiments #1 and #2 contained no further foreign elements. The comparison between experiments #3 and #5 was designed to investigate the influence of cation and solid surface desolvation (Ref. 2).

Concentrations of dissolved metals were analyzed by ICP-OES (iCAP 6300 Duo, Thermo Fisher). Stable Ba isotope measurements were carried out on a multi-collector ICP-MS applying a 130Ba/135Ba double spike as described previously (Ref. 1). Data are given as per mil deviations from a laboratory Ba nitrate standard solution in the d137/134Ba notation (external 2s stdev < 0.1 per mil).

The light Ba isotope was generally enriched in the solid compared to the aqueous solution, with enrichment factors at 21°C between -0.06 and -0.69 per mil. The observed discriminations are larger than the analytical uncertainty of the isotope measurements, demonstrating general barium isotope discrimination upon formation of barium carbonate compared to the aqueous solution. Isotope fractionation into barium carbonate was found to be essentially independent from temperature (4 to 60°C in #1, #2, #6; 21° and 80°C in #3 and #4), but to vary with experimental boundary conditions. Highest fractionation was observed into barium carbonate that was precipitated due to CO2 degassing from initially CO2 and W-saturated solution, with no further foreign elements in aqueous solution. The addition of methanol (#5) was accompanied by a slight decrease in Ba isotope fractionation which is likely due to an enhanced precipitation rate (Ref. 2).

The formation of the anhydrous double carbonate BaMn(CO3)2 (Ref. 3) from aqueous metal chloride-bearing solution, yields a fractionation factor of -0.12 per mil at 21°C.

Therefore, our experimental results indicate a significant influence of both precipitation rate and aqueous speciation, but not temperature, on the magnitude of Ba isotope discrimination into anhydrous barium carbonate. The impact of aqueous speciation on Ba isotope discrimination has further to be investigated.

References:

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