



Barium isotope fractionation in the global barium cycle: 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 and barium carbonate), and terrestrial Ba gangue minerals 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 given as per mil deviations from a laboratory Ba nitrate standard solution in the $d_{137/134}\text{Ba}$ notation (external $2s$ stdev < 0.1 per mil).

Whereas the various synthetic solid standards and p.a. quality 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 depleted in the heavy isotope ($d_{137/134}\text{Ba}$ values between 0 and -0.2 per mil). A natural barite, from an unknown Chinese locality, gave an isotope value of -0.4 per mil. Also measured high $^{34}\text{S}/^{32}\text{S}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in this sample indicate that this barite has been formed under influence of microbial sulfate reduction, probably in a marine diagenetic environment. The observed natural discriminations are by far larger than the analytical uncertainty of the isotope measurements, indicating isotope discrimination in the natural barium cycle. Precipitation experiments from aqueous barium chloride solutions at temperatures of 20° and 80°C indicate that the light Ba isotope is enriched in pure barium carbonate or barium sulfate compared to the aqueous solution. A maximum isotope fractionation of -0.3 per mil is observed, for both barium carbonate and sulfate, that seems to be influenced by precipitation rate (BaCO_3) and/or the aqueous speciation, but less by temperature.