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Tracing of Ba isotope exchange shows rapid recrystallization rates of barite

DR. KIRSTEN VAN ZUILEN[1,2], ANNA HARRISON[3,4], JESSICA A. STAMMEIER[5], THOMAS NAGLER[3] AND VASILEIOS MAVROMATIS[3,4]

[1]Shell International Bv
[2]Vrije Universiteit Amsterdam
[3]University of Bern
[4]Geosciences Environnement Toulouse
[5]GFZ German Research Centre for Geosciences

Presenting Author: kirsten.vanzuilen@shell.com

Barite is an important archive of paleo-productivity, and Ba isotopes have proven a robust tool for tracing sources and sinks of Ba in the ocean. Previous studies have shown that rapid Ba isotope exchange may occur between barite and aqueous fluids under chemical equilibrium (Curti et al., 2010). Here, we experimentally investigated isotope exchange rates and equilibrium isotope fractionation between barite and aqueous fluids. Natural barite powder was allowed to equilibrate in 17 reactors with a barium-sodium-chloride solution, enriched in ^{135}Ba. The reactors were sampled at increasing time intervals covering 25 months.

Equilibrium Ba isotope fractionation between barite and Ba^{2+} (aq) was estimated by the three-isotope method and yielded a $\Delta^{137/134}Ba_{barite\text{-}Ba2+}$ value of -0.07 ± 0.08 ‰. Barite crystals recovered after 25 month of reaction reveal smoothing of solid surfaces but also typical dissolution features such as development of pits and cracks. Thus, dissolution/re-precipitation is likely the mechanism controlling the observed isotope exchange.

Additionally, isotope exchange was traced by $^{135}Ba/^{134}Ba$ and was found to fit a second-order law yielding a surface normalized isotope exchange rate of 2.8×10^{-10} (mol/m^2/s). Depending on the applied model, the extent of exchange varies, but was deeper than a few surface layers in all models. The calculated exchange rate could result in complete isotope exchange between pelagic barite with a 1 μm edge size and a fluid within ~1.7 years at 25 °C. Although there is considerable uncertainty in extrapolating experimental results to longer time scales, the rapid rates of exchange observed experimentally over short timescales suggest that isotope exchange in pelagic barite should be considered during interpretation of the isotope composition as a paleoarchive.

Curti, E. et al. (2010), *GCA* 74, 3553-3570.