

Distinct barium isotope fractionation during barite nucleation and growth

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“Non-traditional” stable isotopes have been widely used to trace various biogeochemical crystallization processes. However, a complete understanding of isotope fractionation mechanisms during mineral nucleation and growth, as the basis of applying the isotopic tools, is still lacking, especially during nucleation process. Here using barite as a model mineral, distinct Ba isotope fractionation behaviors and mechanisms were discovered during barite formation via heterogeneous nucleation-dominate process ($\Delta^{138/134}\text{Ba}_{\text{barite-soln}} = -0.09 \pm 0.04\text{‰}$) on the surface of organic film and growth-dominate ($\Delta^{138/134}\text{Ba}_{\text{barite-soln}} = -0.55 \pm 0.08\text{‰}$) processes in bulk solution. Furthermore, by conducting homogenous precipitation experiments at various barite supersaturation conditions, we obtained increasing $\Delta^{138/134}\text{Ba}_{\text{barite-soln}}$ values (from $\sim -0.70\text{‰}$ to $\sim -0.20\text{‰}$) with increasing barite saturation index, while the barite crystal size decreased, which further confirmed the different isotope fractionation behavior between nucleation and growth. During nucleation, Ba isotope fractionation was mainly controlled by differences in barite solubility and Ba^{2+} ion diffusion rate for different Ba isotopes, and thus was much smaller than that during growth process controlled by Ba^{2+} ion desolvation and attachment/detachment rates onto/from barite. With the compiled models to integrate Ba isotope fractionation during nucleation and growth processes, we were able to calculate Ba isotope fractionation during barite formation under varied supersaturation conditions. Our findings also explained well the distinct Ba isotope fractionation behaviors during homogeneous barite formation in solution through growth and heterogeneous barite nucleation on organics which concentrated local Ba concentrations and thus increased local supersaturation promoting heterogeneous barite nucleation. The new findings could help explain barite formation in paleo-oceanic environments, and the new isotope fractionation mechanisms identified during crystal nucleation could be broadly adopted to understand isotope fractionation of other crystal formation.