Mg isotope fractionation during nucleation, growth and aging of nesquehonite

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Although carbonates from inorganic precipitation experiments and marine organisms show temperature dependent Mg isotope fractionations, strong kinetic and biological controls have also been identified in previous studies. A better understanding of factors that control Mg isotope fractionations in carbonates could help interpret the natural variations of Mg isotopes in oceans and sediments.

We conducted a set of experiments precipitating nesquehonite at 25ºC under controlled saturation state and aqueous $[Mg^{2+}]/[CO_3^{2-}]$ ratios. In each experiment, a certain amount of $NaHCO_3$, NaOH and $MgCl_2$ solution were rapidly mixed, to achieve oversaturation of nesquehonite in a closed stirring cell. Solution and solid samples were collected and separated continuously. Induction time was detected when the solution started to lose its transparency. The Mg concentration of the solution was measured by ICP-MS (Element) and the Mg isotope composition of the solution and solids were measured by MC-ICP-MS (Neptune) after being purified using cation exchange resin at Yale University.

Our results show that solutions with higher $[Mg^{2+}]/[CO_3^{2-}]$ activity ratio have longer induction time given the same saturation state. Moreover, solution with $[Mg^{2+}]/[CO_3^{2-}]$ ratio close to 1 tends to have shorter induction time, which is consistent with previously-published $CaCO_3$ growth data, indicating similar nucleation and growth mechanism between calcite and nesquehonite. The Mg isotope fractionation shows interesting behaviors over the course of nesquehonite precipitation. During the crystal growth stage, the Mg isotope fractionation between nesquehonite and solution ($\Delta_{nesquehonite-solution}$), and Mg concentration in the solution can be understood by the Rayleigh fractional crystallization model, and the $\Delta_{nesquehonite-solution}$ for experiments with slower growth rate is about -1.5 per mil and with faster growth is -1.2 per mil at 25ºC. During the crystal aging stage, the fractionation factor turns smaller, which could be explained by a dissolution and reprecipitation mechanism. A model is developed to explain the induction time, crystal growth and Mg isotope fractionation during the nucleation, crystal growth and aging process.