Zinc isotope fractionation during adsorption and incorporation with calcite

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The mass balance of Zn in the oceanic environment has been studied recently, and the isotopic compositions of major sources and sinks have been presented[1]. While surface seawater, rivers, hydrothermal fluids, and eolian dust fall within a range of 0.0 to 0.5‰ (in $\delta^{66/64}$Zn), ferromanganese crusts and carbonates are enriched in heavier isotopes[1-4]. However, insights into the mechanisms driving isotope fractionations in the oceans are relatively limited. In this study, we seek to constrain the mechanism by which carbonates are enriched in heavier Zn isotopes.

Zinc adsorption and incorporation experiments were conducted at low and high ionic strength. A series of small batch reactions were used for adsorption experiments. Calcite suspensions were first equilibrated with air until a stable *p*H of 8.3 was reached, then doped with Zn for adsorption. (The system was undersaturated with respect to hydrozincite.) For incorporation experiments, a dual-syringe pump delivered 0.1M $CaCl_2$ and Na_2CO_3 solutions to a reaction bottle containing dissolved Zn and calcite seed crystals at *p*H of 8.2. This method was modified from a previous method[5]. Experimental duration varied from 0.5 to 120 hours. Solids and solutions were separated by filtration, purified by ion exchange chromatography, and analyzed by MC-ICP-MS. The Zn adsorbed on calcite was isotopically heavier than in the co-existing solutions, with $\Delta^{68/66}Zn_{calcite\text{-}solution}$ of 0.4‰ and 0.7‰ in low and high ionic strength solutions, respectively. Preliminary results indicate that Zn co-precipitation with calcite results in progressive depletion of the solution in heavier isotopes.

Previous work determined that Zn adsorbed on calcite surfaces is tetrahedrally coordinated, sharing three oxygens with the calcite surface[6], and density functional theory calculations predicted that tetrahedral Zn-O species should be heavier than octahedral Zn-O species[7]. These studies agree with the results of our experiments. Therefore, we infer that the isotope fractionation in our experiments at equilibrium is due to the different coordination numbers of dissolved Zn (octahedral) and adsorbed Zn (tetrahedral).

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