

Nickel isotope fractionation during sorption on calcite surface and coprecipitation with calcite

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Because Ni aqueous speciation strongly depends on fluid pH and $\Sigma\text{CO}_2(\text{aq})$ concentration, the isotopic composition of Ni sorbed on calcite surface and/or incorporated in calcite lattice could provide precious information on the chemical environment in which this mineral formed. To calibrate this tool, experiments were performed at 25°C to determine Ni isotope fractionation during 1) Ni adsorption on calcite surface as a function of solution pH (from 7.5 to 8.7) and 2) Ni coprecipitation with calcite at pH = 6.2, $p\text{CO}_2 = 1$ atm and calcite growth rates ranging from $10^{-8.2}$ to $10^{-7.3}$ mol m⁻² s⁻¹)

Nickel concentrations in the aqueous and solid samples were measured using Atomic Adsorption Spectroscopy. In order to perform the isotope analyses, Ni has been separated from the matrix elements using a 4-step anion-exchange procedure, and Ni isotopes were measured by MC-ICPMS.

Our data shows that the equilibrium fractionation factor $\Delta^{60}\text{Ni}_{\text{solid-solution}}$ for Ni adsorption on calcite is equal to $-0.48 \pm 0.08\%$, and is pH - independent. During coprecipitation with calcite, light Ni isotopes are also preferentially incorporated in the crystals with an extent of fractionation decreasing from 0.5 to 0.2‰ as the precipitation rate increases from $10^{-8.2}$ to $10^{-7.3}$ mol m⁻² s⁻¹. This specific behavior, due to the strong hydration of the Ni²⁺ aquo ion, may serve to approximate calcite precipitation rates and $p\text{CO}_2$ in past oceans.

