

Nickel isotope fractionation during Ni coprecipitation with calcite at 25 °C

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Nickel speciation in seawater-type solutions is dominated by NiCO_3° , NiHCO_3^+ , NiSO_4° along with $\text{Ni}^{2+}_{(\text{aq})}$ whereas Ni substitutes for Ca in calcite as octahedral Ni^{2+} . As a result, the Ni isotopic composition of sedimentary calcite can provide precious information on the chemical composition, pH and pCO_2 of past oceans. In an attempt to calibrate this new proxy, we have investigated Ni isotope fractionation at 25°C during i) Ni adsorption on calcite in a closed system and ii) Ni coprecipitation with calcite using a mixed-flow reactor. The experiments have been performed as a function of solution pH, pCO_2 and calcite growth rate (from $\log r_p = -8.2$ to $-7.3 \text{ mol m}^{-2} \text{ s}^{-1}$).

Nickel has then been separated from the matrix elements using a 4-step anion-exchange procedure, and Ni isotopes were measured by MC-ICPMS.

Our results are in good agreement with previous work where Ni incorporation in calcite does not seem to be affected by growth rate [1]. Our preliminary data shows a preferential incorporation of light Ni isotopes in calcite. Owing to its strong hydration in the aqueous phase, it is expected that Ni isotope fractionation decreases as precipitation rate increases, as is the case for Mg. All experimental data are further compared with the results of ab initio calculations of Ni isotope equilibrium fractionation [2] and available kinetic models.

[1] Lakshatanov and Stipp (2007), GCA 71, 3686-3697.

[2] Fujii et al. (2010) GCA 75, 469–482.