

## Mg isotope fractionation during the formation of Mg-calcite via an amorphous precursor phase

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Magnesium isotope fractionation between Mg-bearing CaCO<sub>3</sub> solids and aqueous fluid has been studied at 25°C and pH 8.3 during the precipitation of amorphous calcium carbonate (Mg-ACC) and its transformation into Mg-calcite, under near equilibrium conditions. The obtained results indicate that the apparent Mg isotope fractionation between Mg-ACC and the fluid,  $\Delta^{26}\text{Mg}(\text{app}) = \delta^{26}\text{Mg}_{\text{solid}} - \delta^{26}\text{Mg}_{\text{fluid}}$ , is  $-1 \pm 0.1\%$  whereas that between Mg-calcite and the fluid reaches  $-3.6 \pm 0.25\%$ . Taking account of Mg speciation in the reacting fluid and the isotope fractionation among aqueous Mg species, it is calculated that the Mg isotope fractionation between Mg-ACC and Mg<sup>2+</sup>(aq) is ranging between +2.0 and 0.0‰. In contrast the calculated Mg isotope fractionation between Mg-calcite and Mg<sup>2+</sup>(aq) is negative and its extent increases with the calcite Mg content, reaching values as low as -3‰ in Mg<sub>19</sub>Ca<sub>81</sub>CO<sub>3</sub>. This increase cannot be attributed to calcite growth kinetics as the overall enrichment of calcite with Mg occurs at near zero growth rates, but is likely controlled by the increase of the Mg-O bond length in the crystal lattice at elevated Mg concentration in Mg-calcite. The obtained results are of great importance for the interpretation of Mg isotope signatures in biogenic and sedimentary calcites as they indicate that: i) the isotopic signatures of Mg-ACC reveal a precipitation mechanism which involves the entrapment in the solids of MgHCO<sub>3</sub><sup>+</sup> and MgCO<sub>3</sub><sup>°</sup> as well as the Mg aquo ion, ii) the isotopic composition of high Mg-calcite is not only controlled by its growth rate but also by its Mg content, iii) the isotopic signatures of Mg-rich calcite formed via an amorphous precursor record the chemical parameters of the confined fluid, where transformation occurs, by dissolution and re-precipitation mechanisms and not those of the open ocean.