

## Effect of organic ligands on Mg partitioning and Mg isotope fractionation during low-temperature precipitation of calcite

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Calcite growth experiments have been performed at 25 °C and 1 bar pCO<sub>2</sub> in the presence of aqueous Mg and six organic ligands in the concentration range from 10<sup>-5</sup> to 10<sup>-3</sup> M. These experiments were performed in order to quantify the effect of distinct organic ligands on the Mg partitioning and Mg stable isotope fractionation during its incorporation in calcite at similar growth rates normalized to total surface area. The organic ligands used in this study comprise of (i) acetate acid, (ii) citrate, (iii) glutamate, (iv) salicylate, (v) glycine and (vi) ethylenediaminetetraacetic acid (EDTA), containing carboxyl- and amino-groups. These functional groups are required for bacterial activity and growth as well as related to biotic and abiotic mineralization processes occurring in sedimentary and earliest diagenetic aquatic environments (e.g. soil, cave, lacustrine, marine). The results obtained in this study indicate that the presence of organic ligands promotes an increase in the partition coefficient of Mg in calcite ( $D_{Mg} = \frac{(Mg/Ca)_{calcite}}{(Mg/Ca)_{fluid}}$ ). This behaviour can be explained by the temporal formation of aqueous Mg-ligand complexes that are subsequently adsorbed on the calcite surfaces and thereby reducing the active growth sites of calcite. The increase of  $D_{Mg}$  values as a function of the supersaturation degree of calcite in the fluid phase can be described by the linear equation

$$\text{Log}D_{Mg} = 0.3694 (\pm 0.0329) \times \text{SI}_{calcite} - 1.9066 (\pm 0.0147); R^2 = 0.92$$

In contrast, the presence of organic ligands, with exception of citrate, does not significantly affect the Mg isotope fractionation factor between calcite and reactive fluid ( $\Delta^{26}\text{Mg}_{calcite-fluid} = -2.5 \pm 0.1 \%$ ). Citrate likely exhibits larger fractionation between the Mg-ligand complexes and free aqueous Mg<sup>2+</sup>, compared to the other organic ligands studied in this work, as evidenced by the smaller  $\Delta^{26}\text{Mg}_{calcite-fluid}$  values. These results indicate that in Earth's surface calcite precipitating environments that are characterized by low dissolved organic carbon levels, the presence of organic ligands is rather unlikely to significantly affect the Mg isotope composition of precipitated calcite.