Effects of organic ligands on magnesite precipitation rates

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Accurate knowledge of magnesium carbonates (magnesite and dolomite) crystallisation rates is of primary importance to assess, model and optimize both natural and industrial CO_2 mineral sequestration. Recent measurements of magnesite precipitation rates and their activation energy at 100 to 200°C [1] show that rates for magnesite are much lower than those of calcite (by ~6 orders of magnitude at 25°C), due to the strong hydration of Mg^{2+} in solution.

Although organic ligands are extensively present in deep sedimentary basins as well as continental waters, their effect on magnesite precipitation has not yet been investigated. Published results on calcite suggest that organic ligands commonly encountered in nature have little influence on calcite precipitation [2]. However, this may not be the case for Mg-carbonates as carboxylic ligands could significantly accelerate the rates of exchange of water molecules in Mg^{2+} coordination sphere, thus facilitating its dehydration. Such an increase of water molecules exchange rates has indeed been observed for Al^{3+} in presence of oxalate ligands [3].

This study therefore aims at investigating the influence of various natural and synthetic organic ligands (oxalate, acetate, EDTA) on magnesite precipitation kinetics, as a function of pH and solution saturation index at conditions relevant to CO_2 geological storage (100°C, variable CO_2 partial pressure). Experiments are performed in mixed-flow titanium reactors at a constant ionic strength, using synthetic magnesite powder as seed for precipitation.

The results are interpreted in terms of solution speciation, surface chemistry, and ligand properties. They help to understand the role of different organic ligands in magnesite precipitation, and provide insights into mechanisms that may partially control magnesite formation at depth in association with organic compounds, possibly originating from bacterial activity.

[1] Saldi *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, A868 [2] Reddy & Hoch (2001) *Journal of Colloid and Interface Science* **235**, 365-370 [3] Phillips, Crawford & Casey (1997) *Geochim. Cosmochim. Acta* **61**, 4965-4973.

Mg isotope fractionation in the Ca-chloride Dead Sea brine system

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The Dead Sea (DS) evolved through seawater evaporation and mineral precipitation within the Sedom Lagon, and water rock interaction with the rocks exposed along the DS Rift Valley escarpment. Yet the Mg isotopic composition of the DS ($\delta^{26}Mg_{SRM-3}$ = -0.6‰) is slightly, but nevertheless significantly enriched compared to seawater (-0.8‰). Here we attempt to identify the processes that lead to this isotopic enrichment.

Sedimentary records indicate that extremely saline conditions prevailed in the Sedom Lagon, allowing for the precipitation carnallite ($KMgCl_3 \cdot 6H_2O$). Today carnallite precipitates from the DS industrial evaporation ponds and is harvested for the production of potash and metal Mg. The Mg isotopic composition of this carnallite, which precipitates at density > 1.30 gr/cc, is 0.0‰, testifying to the high isotopic fractionation that occurs during carnallite precipitation ($\alpha \geq 1.0006$; Δ=0.6‰). The 'End Brines', the concentrated reject brines after evaporation, are accordingly isotopically depleted (-0.9‰). Thus, precipitation of carnallite in the Sedom Lagon would have left the brine isotopically depleted relative to seawater, in contrast to the isotopic enrichment of the DS.

A major process in the evolution of the unique Ca-chloride composition of the DS, which can account for the DS Mg isotopic composition, is dolomitization by the Sedom Lagoon brines, of Upper Cretaceous limestones surrounding the DS Rift Valley. Comparison between rock sections near the DS and several kilometers away, indicate that this dolomitization involved huge volumes of rocks. These epigenetic (late Pliocene - Early Pleistocene) dolomites are isotopically depleted (-2.2‰) relative to seawater, and similar in composition to adjacent Upper Cretaceous dolomites (-2.0±0.2‰). It should be noted that these two types of dolomites are easily distinguished in the field. It follows therefore that 1) the relatively enriched isotopic composition of the DS evolved through dolomitization reaction. This enrichment was enough to compensate for the isotopic depletion that may have occurred due to carnallite precipitation. 2) On a global scale, the similar isotopic compositions of the two types of dolomites suggest that the Mg isotopic composition of seawater has not changed significantly since at least the Upper Cretaceous.