

# Computational insights into $Mg^{2+}$ dehydration in the presence of carbonate

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The kinetics and thermodynamics of water exchange around solvated ions in solution play a fundamental role in understanding their reactivity in the aqueous phase. Unlike other divalent cations, water exchange around magnesium is very slow (~ms). The kinetic constraints resulting from these strong hydration effects are often cited as the reason why magnesite ( $MgCO_3$ ) and dolomite ( $CaMg(CO_3)_2$ ) cannot be synthesized abiotically from solution at low temperatures ( $T < 60C$ ) [1]. In the case of dolomite, the paradoxical lack of modern dolomites despite the mineral's major occurrence in past sedimentary rocks even gave rise to the so-called *dolomite problem* that geochemists have been trying to resolve for years [2]. Therefore, gaining a detailed description of magnesium dehydration mechanisms is an essential step toward a better understanding of the nucleation and growth of magnesium-bearing carbonate minerals.

While the timescale of water exchange around  $Mg^{2+}$  is inaccessible to unbiased *ab initio* molecular dynamics and classical simulations, enhanced sampling methods, such as metadynamics, can reliably describe and overcome the barrier height for water exchange. In this contribution, we investigate the dehydration of free  $Mg^{2+}$  in solution and that of  $Mg^{2+}$  paired with carbonate, using classical molecular dynamics and free energy methods [3]. Two force fields, either based on a rigid-ion or on a polarizable model, and fitted to reproduce the hydration structures of magnesium and carbonate, are examined. Both models are found to give a good agreement with the experimental pairing free energy of magnesium carbonate. We show that the formation of a magnesium carbonate contact ion pair significantly decreases the barrier height for water exchange around magnesium relative to the free ion in solution.

[1] Lippmann (1973) *Springer, Berlin Heidelberg* pp 229.

[2] Van Tuyl (1916) *Iowa Geol. Surv. Annu. Rep. 25*, 251–422.

[3] Aufort, Raiteri & Gale (2022), *ACS Earth Space Chem.* 6, 733-745.