



## Direct observations of the role of solution composition in magnesite dissolution

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Magnesite,  $\text{MgCO}_3$ , occurs in association with the alteration of ultramafic rocks and serpentine during metamorphic and metasomatic events. Its formation from the carbonation of olivine is an indication of natural  $\text{CO}_2$  sequestration. Both magnesite dissolution and precipitation are controlled by the strongly hydrated nature of the  $\text{Mg}^{2+}$  ion in solution. Flow-through experiments have shown that increased dissolution results from an increase in ionic strength of the solution (Pokrovsky and Schott, 1999). To test whether this observation is related to changes in Mg hydration, we have compared the dissolution of the  $\{10\bar{1}4\}$  magnesite surface in solutions of different electrolytes ( $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ ) using atomic force microscopy (AFM). As the dissolution of magnesite is slow at ambient conditions, experimental solutions (water, 10, 100 and 500 mM) were acidified (pH 2). In all electrolyte solutions, dissolution of the magnesite surface began by the nucleation of randomly spaced etch pits followed by the sudden nucleation of many pits across the entire surface. Coalescence of etch pits produced islands of remnant surface which then dissolved until a single layer was removed and a new flat surface generated. The process was then repeated via the further nucleation of random etch pits one unit cell deep ( $\sim 0.3$  nm). Dissolution rates were obtained from the frequency of this dissolution cycle using measurements of surface roughness and etch pit spreading rates. The reactivity of magnesite in the presence of added ions varied in the order  $\text{Na}_2\text{SO}_4 < \text{NaCl} < \text{NaNO}_3$ . Increased dissolution rates in the presence of  $\text{NO}_3^-$  compared to  $\text{Cl}^-$  is consistent with changes in Mg hydration (Ruiz-Agudo et al., 2010). However, although the ionic strength of the equivalent  $\text{Na}_2\text{SO}_4$  concentrations was higher than that of  $\text{NaCl}$  (expected to increase magnesite dissolution), we observed a decrease in dissolution. The effect of sulfate is most likely dependent on the formation of  $\text{Mg-SO}_4$  contact ion pairs (Rudolph et al., 2003) that are not expected to form in  $\text{Cl}^-$  or  $\text{NO}_3^-$  solutions. In all experiments, despite the undersaturation of original solutions with respect to Mg-carbonate phases, a precipitate formed on the surface indicating the formation of a fluid boundary layer supersaturated with respect to a new phase (probably hydrated magnesite). This is also consistent with Mg concentrations in experimental outflow solutions. At high ionic strength, despite the direct observations of an increase in dissolution, the Mg concentrations decreased. The precipitated phase was effectively passivating the mineral surface.

### References

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