

# Surface complexation modelling of the dissolution kinetics of Mg-bearing carbonate minerals

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Knowledge of carbonate mineral dissolution/precipitation kinetics is of crucial importance in modelling surficial aquatic environments and the biogeochemical cycles of carbon, phosphorus, calcium, magnesium and trace elements. Although magnesium-bearing carbonates (dolomite and magnesite) are ubiquitous in many sedimentary environments, few studies have been aimed at characterizing their interfacial chemistry and dissolution/precipitation kinetics. In this study, the surface complexation model of carbonate-aqueous solution interfaces of Pokrovsky *et al.* (1998) is used to interpret new data on the dissolution kinetics of magnesite and dolomite at 25°C.

## Experimental

Pure highly crystalline magnesite and dolomite 50–100 µm (specific surface area of 1270 and 900 cm<sup>2</sup>/g as determined by krypton absorption using the B.E.T. method) were used in this study. Steady-state dissolution rates were determined at 25.0 ± 0.2°C as a function of solution composition (ionic strength of 0.002 to 0.5 M, pH of 0.2 to 12, and ΣCO<sub>2</sub> of 0 to 0.1 M) and chemical affinity (*A*) using a mixed-flow reactor. Between 2 and 3 g of magnesite or dolomite was dissolved in fluids of prescribed input composition. Steady-state dissolution rates, as indicated by constant Mg concentration in outlet solutions, were obtained after 8 h to 5 days depending on the flow rate.

## Results and discussion

Magnesite dissolution rate data define four distinct regions as a function of pH. In strongly acidic solutions (pH ≤ 2.5), dissolution rates (*R*) are independent of pH and ionic strength:  $R = (2.43 \pm 0.46) \cdot 10^{-12}$  mol/cm<sup>2</sup>/s. In mildly acid solutions (3 ≤ pH ≤ 5), the dissolution rate is proportional to H<sup>+</sup> activity and depends strongly on ionic strength. At 5 ≤ pH ≤ 8, the dissolution rate is again of both pH and ionic strength independent:  $R =$

$(4.57 \pm 0.30) \cdot 10^{-14}$  mol/cm<sup>2</sup>/s. In alkaline solutions (pH > 8) rates decrease again with pH, and HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> concentration.

According to our speciation model (Pokrovsky *et al.*, 1998) the main carbonate species present at the magnesite surface are >CO<sub>3</sub><sup>-</sup> at pH > 5 and >CO<sub>3</sub>H<sup>0</sup> at pH < 3. The metal site is dominated by >MgOH<sub>2</sub><sup>+</sup> at 0 < pH < 8. At pH > 8, >MgOH<sub>2</sub><sup>+</sup> is successively replaced by >MgHCO<sub>3</sub><sup>0</sup>, >MgCO<sub>3</sub><sup>-</sup>, >MgOH<sup>0</sup>, and >MgO<sup>-</sup> with increasing pH. The proton promoted dissolution rate at 3 < pH < 5 is associated with the >CO<sub>3</sub><sup>-</sup> protonation. At pH < 3, MgCO<sub>3</sub> dissolution rate becomes pH independent as all >CO<sub>3</sub><sup>-</sup> sites are fully protonated. A plot of the proton-promoted dissolution rate (*R<sub>H</sub>*, mol/cm<sup>2</sup>/s) of magnesite as a function of >CO<sub>3</sub>H<sup>0</sup> concentration (Fig. 1) shows a fourth order dependence of dissolution rate on [>CO<sub>3</sub>H<sup>0</sup>], consistent with

$$R_H = 10^{7.20} \cdot [ >CO_3H^0 ]^{3.97} \quad (1)$$

This suggests the four surface carbonates

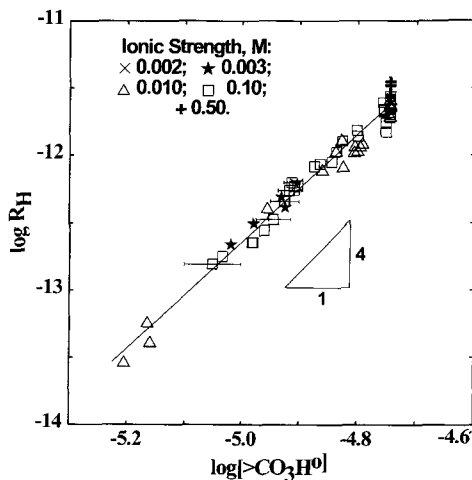


FIG. 1. Proton-promoted magnesite dissolution rate at 25°C and pH < 5 as a function of [>CO<sub>3</sub>H<sup>0</sup>] in solutions of various ionic strength.

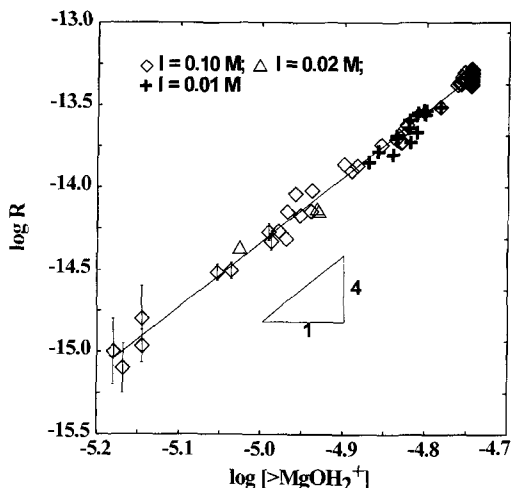


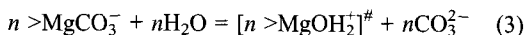
Fig. 2. Magnesite dissolution rate at 25°C and pH>8 as a function of [ $>MgOH_2^+$ ].

surrounding a hydrated surface Mg must be protonated to detach this metal from the surface. Dissolution at neutral and alkaline conditions is controlled by surface metal site hydration as demonstrated by the fourth order dependence of magnesite dissolution rate on [ $>MgOH_2^+$ ] (see Fig. 2):

$$R_{H_2O} = 10^{5.38} \cdot [ >MgOH_2^+ ]^{3.94} \quad (2)$$

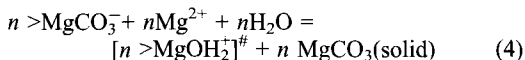
This suggests that magnesite dissolution requires the hydration of the four surface magnesium surrounding a surface carbonate site. This fourth reaction order with respect to both  $>CO_3H^0$  and  $>MgOH_2^+$  concentrations is not fortuitous. This result strongly suggests that the limiting step for magnesite dissolution is the breaking of oxygen bridges binding Mg ions to carbonate groups which is promoted by the full protonation/hydration of adjoining surface carbonates and/or hydration of surface Mg ions.

At close to equilibrium conditions, an overall rate equation can be generated within the framework of Transition State Theory (Oelkers *et al.*, 1994). Hydration of  $n$  magnesium sites to form the precursor complex ( $[>MgOH_2^+]^n$ ) can occur according to:



Assuming that close to the equilibrium ( $-2 \leq \Delta \leq 2$  kJ/mol) the surface precursor complex is the same for magnesite dissolution and precipitation, the rate limiting step for magnesite precipitation should

be:



Combining Eqns 1 and 2 with the equilibrium constants of reactions (3) and (4) yields the following expression for magnesite overall reaction rate:

$$R_T = K_{CO_3}^+ \cdot \{ >CO_3H^0 \}^m + K_{Mg}^+ \cdot \{ >MgOH_2^+ \}^n \cdot [1 - (Q/K_{sp}^0)^n]$$

where  $K_{CO_3}^0 = 10^{7.20}$ ,  $m = 3.97$ ,  $K_{Mg}^0 = 10^{5.415}$ ,  $n = 3.95$ , and the units of  $R_T$  and  $\{ > \}$  are mol/cm<sup>2</sup>/s and mol/m<sup>2</sup>, respectively;  $Q$  stands for ion activity quotient, and  $K_{sp}^0$  stands for magnesite solubility product.

It is proposed that similar reactions occurring independently on metal and carbonate sites, control the dissolution/precipitation of other carbonates. In particular, analysis of dolomite dissolution rates (Busenberg and Plummer, 1982; this work) leads to  $m \sim 2$  and  $n \sim 4$  assuming that the precursor complex in alkaline solution,  $>MgOH_2^+$ , does not contain calcium. For calcite, the values of  $m$  and  $n$  are equal to 2 (Van Cappelen *et al.*, 1991) and 1 (Chou *et al.*, 1989; this work), respectively. The different order of magnesite, dolomite, and calcite dissolution rates with respect to [ $>CO_3H^0$ ] and [ $>MgOH_2^+$ ] reflects the different reactivity of these minerals, having very close  $pK_{sp}^0$  values. As it was shown for orthosilicates (Westrich *et al.*, 1993) this difference is due to the different hydrolysis affinity of the metal cation and correlates with the rates of water exchange from the solvent into the hydration sphere of the corresponding dissolved cation.

## References

- Busenberg, E. and Plummer, L.N. (1982) *Amer. J. Sci.*, **282**, 45–78.
- Chou, L., Garrels, R.M. and Wollast, R. (1989) *Chem. Geol.*, **78**, 269–82.
- Oelkers, E.H., Schott, J. and Devidal, J.L. (1994) *Geochim. Cosmochim. Acta*, **58**, 2011–24.
- Pokrovsky, O.S., Schott, J., Thomas, F. and Mielczarski, J. (1998) *Mineral. Mag.*, this issue.
- Van Cappelen, P., Charlet, L., Stumm, W. and Wersin, P. (1993) *Geochim. Cosmochim. Acta*, **57**, 3505–18.
- Westrich, H.R., Cygan, R.T., Casey W.H., *et al.* (1993) *Amer. J. Sci.*, **293**, 869–93.