Surface speciation of Ca and Mg carbonate minerals in aqueous solutions: a combined potentiometric, electrokinetic, and DRIFT surface spectroscopy approach

O. S. Pokrovsky
J. Schott
Laboratoire de Géochimie, UPS-CNRS (UMR 5563), 38, Rue des Trente-Six Ponts, 31400, Toulouse, France

F. Thomas
J. Mielczarski
Laboratoire Environnement et Mineralurgie (INPL-CNRS, UMR 7569), BP 40-54501 Vandoevre les Nancy, Cedex France

Although calcium and magnesium-bearing carbonates (calcite, dolomite and magnesite) are important constituents of the Earth's crust and regulate many chemical reactions at their surfaces, their surface chemistry has not been investigated in detail until recently. This work proposes a surface speciation model for magnesite and dolomite based on potentiometric titrations, electrokinetic measurements and a diffuse reflectance infrared spectroscopy.

Experimental

Pure and highly crystalline magnesite and dolomite were grounded to the surface area of 3.7 and 2.8 m^2/g, respectively, as determined by the B.E.T. method. The surface charge of these two minerals was determined via potentiometric titration at 25 ± 0.2°C in a limited residence time (1–2 min) reactor analogous to that used by Charlet *et al.* (1990). Typically, carbonate suspensions with a surface area from 30 to 80 m^2/l were used for titration. Zeta-potentials of magnesite and dolomite were determined as a function of pH and ionic strength in NaCl solutions containing different amount of Me^{2+} and HCO_3^- using streaming potential and electrophoresis techniques. Diffuse Reflectance Infrared Fourrier-Transformed (DRIFT) spectroscopy was used to investigate the surface hydroxyl and carbonate groups on dolomite and calcite powders before and after contact with solutions of different pH (5 to 12) and carbonate concentration (0.001 to 0.1 M) at 25°C. To minimize mineral surfaces alteration, the reflection spectra were recorded immediately after sample filtration. Nitrogen was used to dry the samples in the spectrometer at 25–30°C; spectra recorded in vacuum show no major difference from those collected at atmospheric pressure.

Results and discussion

The titration curves of magnesite and dolomite are divided into two distinct regions: a region of positive surface charge at $pH < pH_{p.z.c.}$ (where $pH_{p.z.c.}$ stands for the pH of zero charge point) and a region of great negative charge at $pH > pH_{p.z.c.}$ The pHs of p.z.c. of magnesite and dolomite were found to depend on

TABLE 1. Carbonates surface complexation reactions and their intrinsic stability constants (25°C, I = 0) obtained in this study

Surface reaction	log K°_{int}			
	Calcite	Magnesite	Dolomite	
	(Ca)	(Mg)	(Ca)	(Mg)
$>CO_3H^\circ = >CO_3^- + H^+$	−5.1	−4.65 ± 0.15	−4.8 ± 0.2	−4.8 ± 0.2
$>CO_3H^0 + Me^{2+} = >CO_3Me^+ + H^+$	−1.7	−2.2 ± 0.2	−1.8 ± 0.2	−2.0 ± 0.2
$>MeOH^\circ{-}H^+ = >MeO^-$	−12	−12 ± 2	−12 ± 0.2	−12 ± 0.2
$>MeOH^\circ + H^+ = >MeOH_2^+$	11.5	10.6 ± 0.15	11.5 ± 0.2	10.6 ± 0.2
$>MeOH^\circ + CO_3^{2-} + 2H^+ = >MeHCO_3^\circ + H_2O$	23.5	22.4 ± 0.5	24.0 ± 0.5	23.5 ± 0.5
$>MeOH^\circ + CO_3^{2-} + H^+ = >MeCO_3^- + H_2O$	17.1	14.4 ± 0.2	16.6 ± 0.2	15.4 ± 0.2

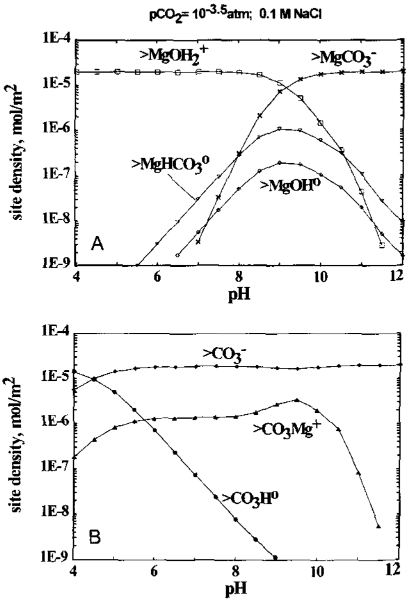

Fig. 1. Speciation diagram at the magnesite–solution interface at 25°C, $pCO_2 = 10^{-3.5}$, $[Mg^{2+}] = 0.001$ M in 0.1 M NaCl: (A) speciation at the $>MgOH^0$ sites; (B) speciation at the $>CO_3H^\circ$ sites.

$[Me^{2+}]_t$ and ΣCO_2 in solutions (e.g. for $MgCO_3$ it changes from = 6.5 at $\Sigma CO_2 = 0.02$–0.03 M to 8.7 at $\Sigma CO_2 = 0.001$ M). Magnesite and dolomite isoelectric points (i.e.p.) derived from electrokinetic measurements of ζ-potentials were found to be very close to their p.z.c. for similar solution composition. Based on these data and following the correlation between stability constants of surface and solute complexes (Stumm, 1992; Van Cappelen *et al.*, 1993), a surface speciation model was developed that postulates formation of $>MeOH_2^+$, $>MeO$, $>MeHCO_3^\circ$, $>MeCO_3^-$, $>CO_3Me^+$, and $>CO_3^-$ surface species from the two primary hydration sites, $>MeOH^\circ$ and $>CO_3H^\circ$, where Me = Ca, Mg. To reproduce the observed high surface charge at conditions far from p.z.c. and its weak dependence on ionic strength, it was necessary to assign high values to the electric double layer capacitance (10–100 F/m^2). The surface complexation reactions and the intrinsic stability constants obtained in this study are listed in Table 1. This model describes accurately both the surface charge and the sign and magnitude of |-potential of magnesite and dolomite suspensions in aqueous solutions of various composition. An example of calculation made with this model is shown in Fig. 1, where magnesite surface speciation in a solution with $pCO_2 = 10^{-3.5}$ atm is depicted as a function of pH. According to the model, the main carbonate surface species are $>CO_3^-$ (at pH > 5) and $>CO_3H^\circ$ (at pH <3). Metal site distribution is dominated by $>MgOH_2^+$ at $0 < pH < 8$. At pH> 8, $>MgOH_2^+$ is being successively replaced by $>MgHCO_3^\circ$, and $>MgCO_3^-$, as pH increases.

There is no available surface titration data for calcite. Thus, the surface stability constants of this mineral were derived from the numerous determinations of its |−potential and $pH_{i.e.p.}$ (7.5–11.4) in solutions of various compositions (Cicerone *et al.*, 1992). Intrinsic surface stability constants for calcite proposed in this study are close to those derived by Van Cappelen *et al.* (1993) on the basis of a single $pH_{i.e.p;}$ (8.2 at $pCO_2 = 10^{-3.5}$ atm). Unfortunately, in the absence of calcite surface charge data, the K°_{int} for this mineral in Table 1 should be considered preliminary, amenable to further refinement.

The DRIFT surface spectroscopy study provides an independent evidence of the correctness of the surface speciation model proposed in this study. In particular, both calcite and dolomite have a single IR-band at 3400–3420 cm^{-1} observed at a pH below 7 that is attributed to hydroxyl groups present at the mineral surface as $>MeOH_2^+$. At higher pH in carbonate-bearing solutions, this peak decreases significantly and tends to disappear. This correlates well with the predicted transformation of $>MeOH_2^+$ to $>MeHCO_3^0$ and $>MeCO_3^-$ in these solutions. In addition, the intensity of the double carbonate peak at 1400–1440 cm^{-1} increases with increasing pH and carbonate concentration reflecting CO_3^{2-} adsorption on the solid surface with formation of the $>MeCO_3^-$ species as predicted by the model.

The surface complexation model presented in this study provides a rigorous description of chemical speciation at the carbonate–solution interface. It should lead to an improved description of the dissolution/precipitation kinetics of minerals in the system Ca-Mg-CO_2-H_2O (Pokrovsky and Schott, 1998).

References

Charlet, L., Wersin, P. and Stumm, W. (1990) *Geochim. Cosmochim. Acta,* **54,** 2329–36.

Cicerone, D.S., Regazzoni, A.E. and Blesa, M.A. (1992) *J. Colloid Interf. Sci.,* **154,** 423–33.

Pokrovsky, O.S. and Schott, J. (1998) *Mineral. Magazine,* this volume.

Stumm, W. (1992) *Chemistry of the Solid-Water Interface.* Wiley.

Van Cappelen, P., Charlet, L., Stumm, W. and Wersin, P. (1993) *Geochim. Cosmochim. Acta,* **57,** 3505–18.