2.2.12

Surface coordination theory and the dissolution/precipitation rates of carbonate minerals in a wide range of T, pCO$_2$ and solution composition

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Available rate data on the dissolution/crystallization of divalent metal carbonates as a function of temperature (25 to 150°C), pH (0 to 13), various ligands concentration, ionic strength and pCO$_2$ (0 to 60 bars) have been analyzed within the framework of the surface coordination theory. It is shown that these data can be described using a surface complexation model (SCM) of the solution-carbonate interface that postulates the formation of the following species: $>CO_3H^0$, $>CO_3^-$, $>CO_3Me^+$, $>MeOH^0$, $>MeO^-$, $>MeOH^{2+}$, $>MeHCO_3^0$, and $>MeCO_3^-$. Within this scheme, the following general rate equation that takes into account the protonation of carbonate groups in acidic region, metal centers hydrolysis in neutral/alkaline region and the effect of chemical affinity at close to equilibrium conditions is proposed:

$$R_T = [k_{CO3}\{>CO_3H^0\}^m + k_{Me}\{>MeOH_2^+\}^n] \times [1 - (Q/K^0_{sp})^n]$$

where m and n are the reaction orders with respect to surface protonated carbonate and hydrated metal centers, respectively, Q is the activity product, K^0_{sp} is the solubility product of the metal carbonate, and k_{CO3} and k_{Me} are kinetic constants for proton- and hydration-promoted dissolution, respectively.
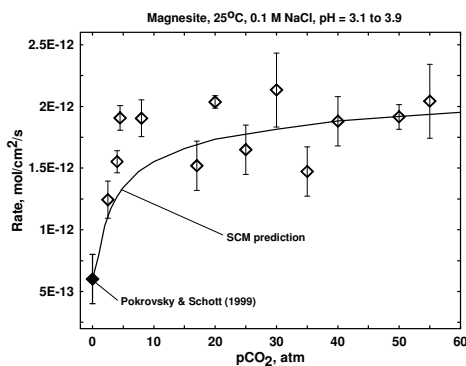

Figure- Kinetics of magnesite dissolution as a function of pCO$_2$: experimetal data and predictions of the SCM model.

It follows from the results of this study that no explicit term (surface species) for CO_2(aq)- or (H_2CO_3*)-affected dissolution is necessary and that this SCM model should allow to predict carbonate minerals reactive transport in various environments and to assess the feasibility of CO_2 mineralogical and geological sequestrations.

2.2.13

Calcite dissolution rates: The effects of naturally incorporated trace metals in "Iceland spar"

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Understanding processes at the fluid-mineral interface has significance for environmental questions concerning groundwater quality and chemical weathering. It has long been known that pH, saturation state and the presence of other cations in the solution strongly affect calcite dissolution rates. The effect of these parameters can also be observed at micrometer scale, in-situ, using Atomic Force Microscopy (AFM). Monitoring etch-pit development on the (10$\underline{1}$4) cleavage surface of calcite during in-situ fluid cell AFM allows determination of calcite dissolution rates. Most published studies use commercially available optically transparent calcite, frequently referred to as "Iceland spar". This common and high-purity calcite is believed to provide scientists with the necessary reference material required for experimental reproducibility. However, this assumption is seldom accompanied and supported by geochemical analysis. To test the neutrality of the calcite substrate during dissolution of the (10$\underline{1}$4) surface, in-situ fluid cell AFM dissolution experiments on "Iceland spar" quality calcite from a number localities were made. Bulk geochemical analysis for each calcite was collected using Atomic Absorption Spectroscopy (AAS). These analyses revealed distinct differences in the trace element concentrations of Mg^{2+}, Mn^{2+} and Sr^{2+} between the various "Iceland spar" materials. Samples were prepared by cleaving fresh, flat pieces along the (10$\underline{1}$4) plane in calcite immediately before the experiments. For each dissolution run, a single droplet of *MQ*-water was added to the fresh surface. By measuring the relative growth of etch-pits on the (10$\underline{1}$4) surface as a function of time, dissolution rates were determined for the obtuse (v_{obtuse}) and acute (v_{acute}) sides of the rhomb-shaped etch-pits. In spite of apparent visual similarity in quality of the "Iceland spar" samples and identical experimental conditions, significant differences in dissolution rates were observed. The observed scatter in dissolution rates correlates with the trace composition of the "Iceland spar" samples. Our observations clearly illustrate the role of naturally incorporated trace metals as an important parameter affecting the dissolution rate of calcite. This shows that in addition to the already known effects of varying solution properties, naturally incorporated trace components must also be taken into account when considering processes at the fluid-mineral interface.