The use of a surface complexation model to describe the crystal growth of calcite

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Calcite crystal growth rates were studied at 25°C in a 0.1 M NaCl solution using the constant composition method. The experiments were performed in slightly supersaturated solutions, Ω 1.5–9.8, over a wide range of $(CO_3^{2-})/(Ca^{2+})$ ratios and at two different partial pressures of CO_2. In general the rate of crystal growth increases with supersaturation but variations in PCO_2 and the $(CO_3^{2-})/(Ca^{2+})$ ratio have a major effect on the rate. At fixed values of Ω, rates increase with increasing PCO_2 and with increasing $(CO_3^{2-})/(Ca^{2+})$ ratio, or pH. Based on a surface complexation model (van Cappellen *et al.*, 1993) we propose a mechanistic model for the crystal growth of calcite that strongly eliminates this effect. In the model we have explained the crystal growth of calcite with three reversible reactions where we combine the activity of $CaCO_3°$ and Ca^{2+} in solution and the concentration of specific surface complexes. In the proposed reaction mechanism we assume that free calcium has a slower water exchange rate than carbonate complex, although we have not found any data on the water exchange rate for this complex in the literature. In general, the replacement of water by a monodendate or bidendate ligand is a reaction that increases the exchange rate of the remaining water in the metal complex (Margerum *et al.*, 1978). From the rate constants in the model we have been able to estimate the enhanced exchange rate of water in this complex to ~20 times faster than that of free calcium.

Recently a model for rhodochrosite ($MnCO_3$) crystal growth was proposed (Sternbeck, 1997). Since these models are similar, as well as the experimental conditions, it is possible to compare the reaction mechanisms. Near equilibrium the crystal growth of rhodochrosite is about 3500 times slower than calcite crystal growth and the difference cannot solely be explained by solubility products. Therefore we discuss if the water exchange rates for manganese and calcium can explain the large difference in the crystal growth rate between these two isomorphos minerals.

References

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