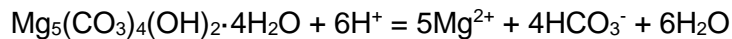


ON THE REACTIVITY OF MG-CARBONATES

A systematic study of Mg-carbonate reactivity, specifically dissolution and precipitation kinetics, in natural environments is presented within this thesis.

Experiments characterizing the dissolution and precipitation behavior of the most abundant natural hydrous Mg-carbonate phase, hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), were performed in closed-system reactors as a function of temperature (22.5 to 75 °C) and pH (8.6 to 10.7). The equilibrium constant for the reaction

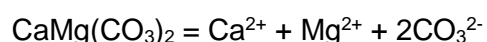


was determined by bracketing the final fluid compositions obtained from the dissolution and precipitation experiments. The resulting hydromagnesite precipitation rates normalized on BET surface area increase by a factor of ~ 2 with the pH decreasing from 10.7 to 8.6. Measured rates are approximately two orders of magnitude faster than corresponding forsterite dissolution rates. This suggests that the overall rates of the low temperature carbonation of olivine are controlled by the relatively sluggish dissolution of the magnesium silicate mineral.

The mechanisms of hydromagnesite dissolution and precipitation were characterized using the temporal evolution of magnesium isotope compositions during fluid-mineral interaction. All experiments were performed in batch reactors in aqueous sodium carbonate buffer solutions having a pH from 8 to 9. During hydromagnesite dissolution and precipitation the magnesium isotope composition of the fluid became heavier after the fluid attained chemical equilibrium with the mineral; at the end of the experiments the $\delta^{26}\text{Mg}$ composition of the fluid was up to ~ 0.25 ‰ heavier than the dissolving hydromagnesite. These observations are consistent with the theoretical hypothesis that fluid-mineral equilibrium is dynamic (*i.e.*, dissolution and precipitation occur at equal, non-zero rates at equilibrium). Moreover the results presented in this study confirm that the isotopic compositions of carbonate minerals continue to equilibrate even when the mineral is in bulk chemical equilibrium with its coexisting fluid. This observation suggests that the preservation of isotopic signatures of carbonate minerals in the geological record requires some sort of combination of the isolation of fluid-mineral system from external chemical input and/or the existence of a yet to be defined dissolution/precipitation inhibition mechanism.

The effect of aqueous calcium on magnesite (MgCO_3) growth kinetics at 100 °C and pH ~ 7.7 was determined. Through a series of hydrothermal atomic force microscopy (HAFM) experiments obtuse step velocities on (104) surfaces during magnesite growth were measured to be 4 ± 3 nm/s at fluid saturation states of 86 to 117. These rates do not vary systematically with aqueous calcium concentration. Similarly, magnesite growth rates determined by hydrothermal mixed-flow reactor (HMFR) experiments are found to be negligibly affected by the presence of aqueous calcium. All measured HAFM and HMFR rates can be accurately described taking into account the combined effects of both mechanisms spiral growth and two dimensional nucleation/growth. Despite the lack of a clear effect of aqueous calcium on magnesite growth rates, Raman spectroscopy confirmed the incorporation of up to 8 mole percent of Ca^{2+} into the growing magnesite structure.

The solubility of natural dolomite ($\text{CaMg}(\text{CO}_3)_2$) was investigated from 50 to 175 °C in 0.1 molal NaCl solutions by using a hydrogen electrode concentration cell (HECC). Attempts were made to attain fluid-dolomite equilibrium from both undersaturated and supersaturated conditions. Although dissolution readily led to a fluid-dolomite equilibrium state at all temperatures, an apparent equilibrium was obtained via precipitation only at temperatures at 150 and 175 °C. The solubility product for the reaction



obtained in this study is nearly equal to that predicted by SUPCRT92 at 200 °C, but about one order of magnitude higher at 50 °C, suggesting that dolomite is somewhat less stable than previously assumed.

The precipitation of dolomite on its (104) surface was investigated using HAFM at temperatures up to 100 °C, pH ranging from 4 to 8, and pressures up to 5 bars. Most of the growth experiments, however, led to growth of one or two layers of a carbonate (layer height ~ 3 Å), which morphologically reproduced the initial surface features, resembling a template effect. Growth on top of these layers was strongly inhibited and did not show any crystallographically orientated growth morphologies. As such, this study shows that, while dissolution can readily release material from the dolomite surface to great depths, growth becomes sparingly slow after the first monolayer has been precipitated on the surface.