

Mechanism of wollastonite carbonation deduced from micro- to nanometer length scale observations

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ABSTRACT

The microstructural evolution of CaSiO₃ wollastonite subjected to carbonation reactions at $T = 90$ °C and $p\text{CO}_2 = 25$ MPa was studied at three different starting conditions: (1) pure water; (2) aqueous alkaline solution (0.44 M NaOH); and (3) supercritical CO₂. Scanning and transmission electron microscopy on reacted grains prepared in cross-section always revealed unaltered wollastonite cores surrounded by micrometer-thick pseudomorphic silica rims that were amorphous, highly porous, and fractured. The fractures were occasionally filled with nanometer-sized crystals of calcite and Ca-phyllsilicates. Nanoscale chemical profiles measured across the wollastonite-silica interfacial region always revealed sharp, step-like decreases in Ca concentration. Comparison of the Ca profiles with diffusion modeling suggests that the silica rims were not formed by preferential cation leaching (leached layer), but rather by interfacial dissolution-precipitation. Extents of carbonation as a function of time were determined by quantitative Rietveld refinement of X-ray diffractograms performed on the reacted powders. Comparing the measured extents of carbonation in water (condition 1) with kinetic modeling suggests that carbonation was rate-controlled by chemical reactions at the wollastonite interface, and not by transport limitations within the silica layers. However, at conditions 2 and 3, calcite crystals occurred as a uniform surface coating covering the silica layers, and also within pores and cracks, thereby blocking the connectivity of the originally open nanoscale porosity. These crystals ultimately may have been responsible for controlling transport of solutes through the silica layers. Therefore, this study suggests that pure silica layers were intrinsically non-passivating, whereas silica layers became partially passivating due to the presence of calcite crystallites.

Keywords: CO₂ sequestration, wollastonite, carbonation, dissolution-reprecipitation, diffusion modeling, leached layers, FIB-TEM, Rietveld refinement