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Dissolution rates and pit morphologies of rhombohedral carbonate minerals

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ABSTRACT

The dissolution and precipitation rates of rhombohedral carbonate minerals, such as $CaCO_3$, $ZnCO_3$, $MnCO_3$, $FeCO_3$, and $MgCO_3$, affect the alkalinity and redox state of natural waters. In the current study, the rates and mechanisms of carbonate dissolution are investigated utilizing an atomic force microscope/flow-through reactor. Based on time series changes of the microtopography, we classify the studied minerals as type I (Ca, Mn), type II (Fe, Mg), or type III (Zn) carbonates. Type I carbonates develop shallow rhombohedral pits, and the step-retreat velocities are pH-dependent for pH < 4. Type II carbonates form deep rhombohedral pits at circumneutral to alkaline pH. The rhombohedral shape alters for pH < 4, and the step retreat velocities are weakly pH-dependent. Type III carbonates develop shallow distorted pits at circumneutral to alkaline pH and triangular pits at acidic pH. Groups of point defects vs. line dislocations apparently give rise to type I vs. type II behavior, whereas the unique tetrahedral surface coordination of adsorbed Zn^{2+} may explain type III behavior. For type I at all pH values and type II carbonates for pH < 4, geometric models employing the microscopic step retreat velocities are accurate predictors of the absolute rates of macroscopic dissolution. Macroscopic circumneutral dissolution rates, which trend with both water exchange rates and lattice formation energies, vary from $10^{-5.5}$ to $10^{-9.1}$ mol/m^2·s at circumneutral pH and 25 °C.