

## Scale, Carbonate Weathering, and the Laboratory/Field Dichotomy

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Dissolution within porous media is a critical process in many environmental and geological settings. The formation and evolution of soils, rocks, and landscapes, efficiency of carbon capture in geological reservoirs, and weathering of man-made structures depend on mineral and rock dissolution rates. Limestone, in particular, is an important inorganic carbon sink, and understanding its weathering provides insights into the global carbon cycle and development of geological repositories for CO<sub>2</sub> sequestration. While porosity is a critical factor in limestone weathering, evidence suggests weathering rates are a function of both microstructures and larger-scale structures, the latter of which are not usually captured in laboratory experiments. Emmanuel and Levenson (2014) found that erosion rates in fine-grained limestone are as much as two orders of magnitude higher than those in coarse-grained limestones due to rapid dissolution along micron-scale grain boundaries, followed by mechanical detachment, but the larger-scale structures such as bedding, stylolites, fractures and other fast-transport pathways also play a critical role that may explain the observed differences between laboratory experiments and rates measured in the field.

In this work experiments were conducted on the weathering of four limestones with different starting microstructures as a function of time and solution pH and compared to natural weathering patterns and structures of those same materials. Cores 5/8" long by 5/8" in diameter of the four limestones (Netzer, Shivta, Carthage Marble, Texas Cream) were exposed to flowing water at 30°C and several pH values to mimic the weathering process. Annular Cd masks of stepped sizes, and small beam stepped locations analyses, were used to analyze the weathering structure by small and ultra-small angle neutron and X-ray scattering analysis of thin sections of the reacted limestone as a function of distance from the edge. The pore structure and surface weathering was also examined via SEM. The results, both in terms of core/rim variations and pore size dependence, were found to be strongly dependent on initial permeability and rock structure, as well as time and pH, and not to, necessarily, scale directly with initial porosity or grain size.

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