

MODELING THE DEEP ABIOTIC WEATHERING OF PYRITE

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Oxidative weathering of pyrite (OWP) was studied in shale fragments collected at depths 15--16m under a ridge of the Shale Hills critical zone observatory (Pennsylvania, USA) [1]. The low porosity of those fragments and the presence of pore throats with 10--20nm indicate that bacteria are not likely to play a role in this process. Thus, chemical analysis and transmission electron microscopy images showing ferrihydrite layers around partially weathered grains were used to determine the main reaction of the mineral. However, the estimated time of full OWP is several orders of magnitude longer than the time predicted by the laboratory rates of oxidation and by the oxygen concentration in water flowing at the observed depths, implying an effectively very small field rate.

The focus of this presentation is the solution of that apparent contradiction by a model in which OWP is limited by oxygen diffusion in rock fragments [1]. It leads to diffusion coefficient $\sim 10^{-12} \text{m}^2/\text{s}$, consistently with laboratory estimates on shale with porosity 4.5%, and leads to a reaction front thickness of a few millimeters, consistently with the width of the zone of partial OWP in a rock fragment. The extension of the model to shales from two other watersheds explains the OWP at depth. However, when the estimate of atmospheric oxygen concentration before the great oxidation event (GOE) is used, the model predicts that pyrite was exposed at the land surface in the three sites, which quantitatively confirms the proposal of previous works that pyrite oxidation at the land surface before the GOE was responsible for events of enhanced sulfate delivery to the oceans and their acidification.

[1] Gu, Heaney, Reis & Brantley (2020), *Science* 370, eabb8092.