Modeling the deep abiotic weathering of pyrite

Fabio Reis[1], Xin Gu[2], Peter Heaney[2], Susan Brantley[2]
[1]Universidade Federal Fluminense, Niteroi, Brazil, [2]The Pennsylvania State University, State College, United States

Pyrite (FeS) is the most abundant sulfide mineral in the Earth crust. It is oxidized in contact with water and the atmosphere, but this reaction is catalyzed by microorganisms, which may cause acidification of the landscape. This phenomenon is frequently observed in mined regions where pyrite is artificially exposed. In this work, oxidative weathering of pyrite (OWP) was studied in shale fragments collected at depths from 15m to 16m in a ridge of the Shale Hills critical zone observatory (Pennsylvania, USA). Considering the rates of topsoil erosion and regolith production, full OWP occurs is estimated to occur in a geological time of ~50kyr. 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 [Fe(OH)_3] layers around partially weathered grains were used to determine the main reaction of pyrite. 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. This apparent contradiction is solved with the proposal of a reaction-diffusion model in which the OWP is limited by oxygen diffusion in the rock fragments of sizes ~11.6cm. The solution of that model leads to a diffusion coefficient consistent with laboratory estimates on shale with the same porosity (~4.5%) and leads to a reaction front thickness ~0.5-1cm, which is consistent with the width of the zone of partial OWP in a rock fragment. When the model is extended to shales from other two watersheds, it also explains the OWP at depth. However, when the estimate of atmospheric oxygen concentration before the great oxidation event (GOE; 2-2.4 billions of years ago) is used, the model predicts that pyrite was exposed at the land surface in the three sites. This result 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 consequent acidification. [Science 370, eabb8092 (2020)]