

Deciphering rates and mechanisms of pyrite oxidation based on soil profiles and river chemistries - *IAGC*

Vernadsky Medal Lecture

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Signatures of mineral weathering can often be deciphered in the environment. For example, oxidative weathering of pyrite can be deciphered from weathering profiles of soils. When considered for a slow-eroding shale at grain or clast scales in Pennsylvania (USA), such analysis reveals oxidation at meters depth limited by diffusion of oxygen through pores and fractures that are too small for microbiota. Based on this, it is likely that the oxidation is mostly abiotic. This argument is consistent with the observation that the sulfate content of the shale-draining Pennsylvania stream never shows pyrite-derived sulfate concentrations higher than expected based on dissolved oxygen (DO) concentrations equilibrated with the atmosphere. In other words, as water infiltrates the shale, pyrite oxidation is a closed system such that once atmospheric DO is removed, reaction stops. However, when we analyze sulfate released to larger streams in similarly slow-eroding watersheds on sedimentary strata in the larger encompassing watershed, we observe sulfate concentrations above the value expected based on equilibrated DO. We infer that oxidation of the pyrite in the larger watersheds is no longer a closed system with respect to the oxidant. High sulfate concentrations point to open-system behavior where pyrite is exposed to oxygen at the land surface or to microbial catalysis of pyrite oxidation and recycling of Fe³⁺ as the oxidant. Either condition likely reflects that the larger watersheds were mined for coal, exposing pyrite. But fast-eroding watersheds elsewhere in the world also show higher sulfate concentrations than that expected based on closed-system DO. If the fracture density tends to increase with erosion rate, then open-system conditions for oxygen could describe pyrite weathering in the fast-eroding shales. Higher fracture densities in fast-eroding shales have also been invoked to explain the dependence of sulfate release rates on erosion rate. We infer that the near-surface increase in coal mining- or erosional fracture-exposed surface area of pyrite in some watersheds allow open-system conditions for pyrite oxidation. This in turn explains high sulfate concentrations in those watersheds. We conclude that both weathering profiles and stream chemistries can be used to interpret the rates and mechanisms of pyrite oxidation.