

Weathering of shales in outcrops: The importance of carbonate for preserving inorganic geochemical proxies

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The oxidation of pyrite (FeS_2), is key to the chemical weathering behaviour of shales. Pyrite oxidation provides protons for the hydrolysis of aluminosilicates and dissolution of carbonates and consumes oxygen, inhibiting organic matter oxidation. On the other hand, the oxidation of pyrite in shales can negatively impact the preservation of geochemical proxies, both directly (changing the primary Fe speciation for distributing between euxinic and ferruginous bottom water conditions) and indirectly (changing the contents of pyrite-bound redox-sensitive trace metals).

Understanding the mechanism of pyrite oxidation is, therefore, vital for understanding the mechanisms of shale weathering and its effect on geochemical proxies.

Here we present the results of an artificial shale weathering experiment. Key findings are the apparent passivation of pyrite grains at circum-neutral pH by Fe (oxyhydr)oxide rims (seen in SEM-BSE) and the conservation of original trace metal contents, probably due to co-precipitation with/sorption to Fe(oxyhydr)oxides. Circum-neutral pH, in turn, is only maintained during weathering of shale samples containing carbonate. In these samples, trace metal and Fe speciation proxies ($\text{Fe}^{\text{HR}}/\text{Fe}^{\text{T}}$) are reliable when samples are taken at quickly eroding locations usually chosen for geochemical studies. In our case study (Cretaceous shales from Colombia), we use this information to infer that low trace metal contents encountered in the samples are a surprising yet genuine depositional signature.