Oxidative transformation of natural monosulfidic ooze: New insights from estuarine sediments

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Iron monosulfides (FeS) are the initial Fe sulfide minerals that form in organic matter rich reducing benthic subsurface sediments. Due to their chemistry, monosulfidic black oozes (MBOs) are often an important sink for heavy metals, and nutrients and play a major role in regulating the mobility and bioavailability of these constituent in estuaries [1,2]. MBOs from three contrasting sites in Peel-Harvey Estuary were examined and the oxidative transformation of sulfur and iron speciation during the resuspension of MBOs over 14 days was investigated. Solid phase changes were quantified for key forms of iron and sulfur fractions during oxidation.

Solid bound Fe was most abundant as HCl-extractable Fe(II) (a proxy for iron monosulfides –FeS), then followed in descending abundance 'organic bound Fe' and 'oxide-Fe'. The majority of FeS was oxidised within 48 hours in aerobic conditions. The oxidation of FeS, ES and FeS₂ each contribute to the consumption of dissolved oxygen, yet the contributions to oxygen demand from dissolved organics and other properties of these sediments need also be considered.

The rapid oxidation of FeS within 24 hours was within expectations, for these mineral phases are highly unstable. Interestingly, significant amount of pyrite also oxidised within 7 days, exceeding expectations for near-neutral sediments and extending the magnitude of short-term mineral transformations of relevence for contaminant mobility.

[1] Burton *et al Environ. Sci. Technol.* **40**: 1217, 2006 [2] Kraal *et al Geochim. Cosmochim. Acta*, **122**: 75, 2013