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# Sedimentary pyrite oxidation in the bioturbated zone: effects of redox scaling in space and time.

**ROBERT C. ALLER**, GERRIT TRAPP-MÜLLER, CHRISTINA HEILBRUN, JOSEPHINE Y. ALLER AND QINGZHI ZHU

Stony Brook University

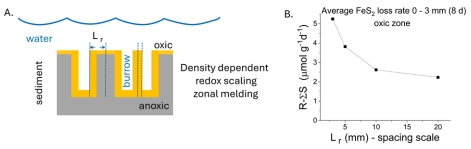


Figure 1.

Pyrite is a product of organoclastic sulfate reduction (OSR) during early diagenesis. Often ≳ 50% of buried pyrite is formed near the sediment–water interface (~1–5 cm). It has been known for >50 years that in bioturbated deposits, ~90 – 98% of the sulfide initially produced and precipitated, is reoxidized, often consuming ≳50% of the total $O_2$ flux to the seafloor. Bioturbation enhances pyrite formation by promoting $SO_4^{2-}$ supply and open-system behavior but also introduces $O_2$, which can inhibit OSR and oxidize pyrite. The impacts of bioirrigation are a strong function of burrow scaling in space and time and thus are faunal composition and size - density dependent. Oxic zones surrounding burrows contract as faunal densities decrease (spacing increases), and initial rates of pyrite oxidation within oxic zones decrease as competition for $O_2$ with anaerobic metabolites from surrounding sediment increases (Figure 1). The fate of generated $H_2SO_4$ is also a function of scaling: a greater proportion of acid is neutralized by overlying water versus carbonate dissolution when burrows are closely packed.

Initially high pyrite oxidation rates are attenuated as surfaces become passivated by Fe-oxyhydroxide coatings; leaving ~ 50% of pyrite stabilized for months [1]. When passivated pyrite is subject to anoxic conditions, coatings can be altered or removed. The reconstituted surfaces can be characterized by enhanced oxidation rates when re-exposed to $O_2$. Thus, net oxidation rates vary with the dynamics of burrow formation, maximizing rates during initial unsteady stages of irrigation but slowing if burrows remain stable. Biogenic mixing of particles plays a crucial role in enhancing oxidation rates and the extent of oxidation by exchanging sediment between oxic- anoxic zones. In bioturbated sediments, pyrite oxidation rates and preservation must vary widely. The time-dependent geometries of oxidation and residence times of pyrite within oxic – anoxic zones (redox oscillations) are functions of benthic community compositions and transport – reaction structure. These effects are not incorporated into typical diagenetic model parameterizations such as diffusive particle mixing or nonlocal solute transport.

[1] Trapp-Müller, G. , Aller, R.C., Karacic, S. ,Heilbrun, C. ,& Zhu Q. (submitted) Passivation governs pyrite oxidation kinetics in marine sediments.