

Microbial sulfur cycling in the modern Black Sea

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The evolution of Earth's oceans on geologic timescales has included episodes when basinal waters were anoxic and sulfidic (euxinic). The expansion of sulfidic bottom waters has the potential to drive significant chemical and biological changes in benthic environments. Considerable interest exists to develop tools that can be used to identify these conditions. Sulfur isotope analyses ($^{33}\text{S}/^{32}\text{S}$, $^{34}\text{S}/^{32}\text{S}$ and $^{36}/^{32}\text{S}$) in combination with other geochemical indicators show promise in studies of dynamic bottom-water conditions in low oxygen settings. Here, we present multiple sulfur isotope analyses of sulfate, dissolved sulfide, and sedimentary sulfides (AVS and pyrite) from diverse settings in the modern Black Sea to address basin-wide sulfur cycling. Within this well constrained depositional and environmental context, we describe variations in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ that, along with other geochemical proxies such as iron geochemistry, track the historical shoaling of sulfidic deep waters. Multiple sulfur isotope approaches are especially sensitive to oxidative and reductive pathways of microbial S metabolisms that vary in phase with changes in bottom-water redox. The processes that control the sulfur isotopic signatures are ultimately related to the interplay of rates of pyrite formation, sulfide oxidation, and diffusion of sulfide and dissolved iron in the sediments. By extrapolation, we argue that the sulfur isotope signatures may provide a tool for identifying chemocline shoaling events and ecological changes in the biologic S cycle in the geologic past.

Kinetic of H_2O_2 generation and decay during pyrite-water reactions

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The oxidative dissolution of pyrite is driven by a complex mechanism that involves the transient formation of H_2O_2 and other reactive oxygen species [1], however, a kinetic analysis dealing with the time evolution of these species is presently lacking. In this work, we measured the real-time generation and decomposition of H_2O_2 on pyrite surfaces under different boundary conditions with amperometric biosensors. In addition, simultaneous measurement of the O_2 , Fe(II), together with Fe(III) generated as a byproduct of Fenton reaction, were done with Clark sensors, and UV-VIS spectroscopy. The observed general pathway for H_2O_2 time evolution consisted of an S-shaped stretched exponential profile, with a first stage marked by an increasing generation of H_2O_2 until a critical concentration value of peroxide was reached. From this moment on, the measured amount of H_2O_2 in solution decreased towards a nearly stationary value. Further, experiments were performed to assess the reversibility of the process and to evaluate the possible role of pyrite-generated H_2O_2 and other ROS in the long-term redox evolution in natural environments. A new kinetic model based the coupling between H_2O_2 and Fenton reaction in aqueous solution was performed to fit the experimental data. Results showed that the observed amount of peroxide at each instant can be closely related to the supply rate of Fe^{+2} resulting from pyrite dissolution, which progressively degrades H_2O_2 inducing the continuous generation of secondary ROS in solution. Thus, it can be speculated that the mineral pyrite may act as a Fenton-like reagent, able to induce long-term oxidation through the geological realm.

[1] Schoonen *et al.* (2010) *Geochim. et Cosmochim. Acta* **74** (17), 4971-4987.