Kinetics of sulfide mineral oxidation in seawater: Implications for acid generation during *in situ* mining of seafloor vents

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Growth in global metal demand has fostered a new age of unconventional mining. *in situ* pulverization and extraction of seafloor massive sulfide (SMS) deposits is economically attractive due to minimal overburden and high ore grades. However, important environmental questions remain on the significance of localized acid generation via irreversible sulfide oxidation during the mining process.

Laboratory experiments were performed to evaluate the effects of pH, T, dissolved O_2, and surface area on the oxidation rates of pyrrhotite (po) and chalcopyrite (cpy) in seawater; i.e., how quickly SMS mining will produce acid. These minerals provide an upper and lower bound since po oxidizes relatively quickly while cpy is kinetically slow.

The rate laws derived from these experimental data for the abiotic oxidation of po and cpy in seawater at 23°C are given in the form: $R_{sp} = k\,(m_{O2(aq)})^a(m_{H+})^b$, where R_{sp} is the specific rate (moles $m^{-2}\,sec^{-1}$), k is the rate constant, oxygen and proton concentrations are expressed in molalities (m), and their reaction orders are a and b, respectively. The specific rate laws for each sulfide studied are:

$$R_{sp(po)} = -10^{-7.27}(m_{O2(aq)})^{0.30\pm0.07}(m_{H+})^{0.08\pm0.03}$$
$$R_{sp(cpy)} = -10^{-9.38}(m_{O2(aq)})^{1.16\pm0.03}(m_{H+})^{0.36\pm0.09}$$

Further, we calculate the residence times of crushed sulfides in seawater with low P_{O2} and find that, depending on grain size, mining waste grains may persist near the seafloor for a period of years. The implications are positive in terms of slow acid production, but problematic considering the potential ecological effects of an unnatural influx of particulates (Table 1).

When used to quantitatively predict acid generation rates, these data indicate that acid production from *in situ* SMS mining is insufficient to exceed the buffer capacity of advecting seawater and will not introduce “acid mine drainage” impacts to the seafloor environment.

Table 1: Grain lifetime (*Δt*) at* P_{O2}*=0.10, pH=8, T=23°C.

Diameter:	1 μm	8 μm	100 μm
Δt_{po} (years):	0.02	0.16	2.04
Δt_{cpy} (years):	0.87	6.93	86.62