Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.20306

# Precipitation During Hydrothermal Plume Formation; The Dominance of Pyrite.

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Rapid mineral precipitation is induced when high temperature (T) hydrothermal fluids egress into cold seawater at globally distributed seafloor venting sites. This precipitation, commonly referred to as black smoke, is composed of a large diversity of mineral phases that strongly influence elemental mass transfers from the solid Earth to the oceans. Larger precipitates sink and partition their mass to seafloor sediments, while nanoparticles can loft within buoyant plumes and disperse thousands of kilometers along isopycnals, seeding vast expanses of the pelagic ocean with limiting bionutrients like iron. Here we investigate the formation of various black smoker particulate phases—including their abundance, stoichiometry, and thermodynamic properties—emerging from mixing between globally distributed hydrothermal fluids and seawater. We also model out-of-equilibrium mixing across a large range of endmember hydrothermal fluid compositions to more comprehensively chart the energetic states of elements/species of interest as hydrothermal fluids (and precipitates) interact with seawater. We find that pyrite is nearly ubiquitous, while its diverse associates (other Fe, Cu, Ni, Pb, and Zn sulfides) occur more heterogeneously and in lower mass fractions.

We subsequently establish and quantify three thermodynamic hypotheses for the global homogeneity and mass-fraction dominance of pyrite relative to other hydrothermal plume precipitates. (1) The thermodynamic drive for pyrite formation increases as hydrothermal fluids mix with seawater due to its +dK/dT; (2) pyrite maintains a large stability field relative to all realistic variations in temperature, pressure, and hydrothermal fluid compositions; and (3), pyrite draws from the largest combined pool of reactants relative to other phases that might otherwise compete for Fe and S. This suggests that even when other phases form, they are likely to be limited by reactants that pyrite is not, which halts their depletion of Fe or S, allowing pyrite to maintain its beneficial energetic driving force. These findings are important for predicting particulate iron speciation in vent plumes and improving our knowledge of hydrothermal contributions to biogeochemical cycling on Earth and within extraterrestrial oceans.