

## Kinetics of Pyrrhotite Oxidation in Seawater: Implications for Mining Seafloor Hotspots

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A rapid increase in the price of transition metals in recent years has piqued interest in deep sea in situ mining of seafloor massive sulfide (SMS) deposits. There are unique incentives to seafloor mining that make it more attractive than traditional land mining of sulfides, but these are accompanied by important unanswered questions about the potential environmental effects, including localized sulfuric acid generation. Currently there is a paucity of data on the oxidation kinetics of sulfide minerals in seawater. Pyrrhotite specifically is of interest because it is a major non-economic component of SMS deposits that will be disposed of on or above the seafloor during mining. Pyrrhotite oxidizes rapidly via an irreversible, acid-producing reaction. Knowledge of sulfide mineral oxidation rates will also provide constraints on metal and sulfur cycling in oceans by quantifying the natural, abiotic weathering rates of SMS deposits.

Laboratory experiments have been performed to evaluate the effects of pH, temperature, oxidant concentration, and mineral surface area on the rate of oxidation of pyrrhotite in seawater. Temperature controlled circulation baths, Teflon reaction vessels, synthetic seawater, and pure, hand sorted natural pyrrhotite crystals are used in experiments. Both batch and flow-through reactor methods are employed. Reaction products are analyzed using ICP-MS. The rate law is expressed as follows:

$$R = -k (M_{O_2, aq})^a (M_{H^+})^b$$

where R is the specific oxidation rate of pyrrhotite, k is the rate constant (a function of temperature and surface area), and a and b are reaction orders for reactant concentrations (M) that need to be determined experimentally. The initial rate method is used to isolate the reaction order of each reactant.

Current data from batch experiments indicate positive influences of oxidant concentration, surface area, temperature, and  $[H^+]$  on the initial rate. Pyrrhotite oxidizes significantly faster than chalcopyrite, providing an upper limit to the anthropogenic and natural weathering rates of SMS deposits, but acid production rates do not appear to exceed the buffering capacity of seawater. There will be potential for microbial studies in the future to quantify the effects of bacterial oxidation of pyrrhotite using this study as a baseline.

## Evaluation of non-conventional geothermal potential in a Volcanic Island

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Madeira, is an intraplate volcanic island, located at the eastern North Atlantic Ocean, with an emerged area of 737 km<sup>2</sup> and maximum altitude of 1861 m. Although there are no historical eruptions, the existence of recent volcanism (6 my) with well preserved volcanic cones and thermal evidences, such as the occurrence of hot water rich in CO<sub>2</sub>, suggest a heat source at subsurface and the existence of rocks/water with significant temperatures at depths likely to be exploitable for economic generation of electricity.

In a volcanic geothermal system the heat source comes from magma emplacement at relatively shallow levels, thus knowledge of magma chamber(s) depth is one of the keys to geothermal reservoir assessment. In the evaluation of Madeira island geothermal potential, geophysical methods are being applied but, these are most useful for locating chambers beneath active volcanoes. Petrological and geochemical methods supported on whole rock analysis and mineral chemistry can be a helpful tool to constraint the crystallization temperatures and pressures/depths of magmas and to unveil the physical-chemical crystallization history of selected phenocrystals, hence the depth of magma chambers. Volcanic rocks (effusive and explosive) in Madeira are predominantly alkaline basalts. Generally they are holocrystalline presenting porphyritic texture with phenocrystals of olivine and clinopyroxene and, sometimes, calcic plagioclase in a groundmass composed by plagioclase microlites, clinopyroxene, oxides and occasionally interstitial glass. Petrographic and chemical criteria show that phenocrystals had a polybaric crystallization, suggesting that they paused in crustal magma chambers prior to eruption, and that the first minerals to crystallize were olivines and clinopyroxenes. One of the methods to determine the pressure of crystallization is the Ol-Cpx-Plag cotectic method that requires glass composition, or an assumption of it. We applied selected geothermobarometers, based on olivine-liquid and clinopyroxene-liquid equilibrium, to core-mantle analysis of olivine and clinopyroxene phenocrysts to estimate P, which is related to the depth at which magma resides in a chamber, and T of equilibrium crystallization. When required, oxygen fugacity ( $f_{O_2}$ ) was calculated from oxides and whole rock composition. The first results seem to point out a concentration of core crystallization occurring between 2 to 4 kb/6 to 12 km, which is a good indication of a single and wide magma chamber beneath the island.