

Rates of low-pH biological Fe(II) oxidation in the Appalachian Coal Basin and the Iberian Pyrite Belt

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Low-pH Fe(II) oxidation can be exploited for the treatment of acid mine drainage (AMD). However, natural or engineered terraced iron formations (TIFs) are underutilized for AMD treatment because of uncertainties with respect to treatment performance. To address this problem we measured the rates of Fe(II) oxidation multiple times at seven sites in the Appalachian Bituminous Coal Basin and three sites in the Iberian Pyrite Belt (IPB). Longitudinal geochemical transects were measured downstream of emergent anoxic AMD sources. Water velocities were measured at each sampling location and used to transform concentration versus distance profiles into concentration versus travel time for kinetic analysis of field data. Both zero-order rates and first-order rate constants were used to compare Fe(II) oxidation kinetics. Zero-order Fe(II) oxidation rates ranged from $8.60 - 97.0 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ at the Appalachian sites and $13.1 - 67.9 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ at the IPB sites. In contrast, first-order Fe(II) oxidation rate constants ranged from $0.035 - 0.810 \text{ min}^{-1}$ at the Appalachian sites and $0.003 - 0.010 \text{ min}^{-1}$ at the IPB sites. The fastest zero-order rates of Fe(II) oxidation were measured at two sites (one in Appalachia and one in IPB) where little to no oxidative precipitation of Fe(III) occurred. Laboratory-based rates of Fe(II) oxidation were measured with TIF sediments and emergent AMD collected from the seven Appalachian sites. A zero-order laboratory-based removal rate for Fe(T) was used to calculate performance criteria of $2.6 - 8.7 \text{ g Fe day}^{-1} \text{ m}^{-2}$ (GDM) for both natural and engineered TIFs. These GDM values could be used to size TIFs for AMD treatment.

Alteration and fluid flow in large continental hydrothermal systems

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Large volumes of hydrothermally altered rocks are found in calderas and around shallow plutons in the continental crust. The alteration is the product of water/rock interaction in hydrothermal systems that are convectively driven by cooling plutons, and record mass and heat flux through the shallow crust. They often host hydrothermal mineralization. O and H isotope ratios have been used to map large hydrothermal systems at the 23 Ma Lake City caldera and the 3-4 Ma Rico hydrothermal systems, CO, in Eocene hydrothermal systems, Idaho Batholith, ID, and in the active Yellowstone system, WY, all in the USA. These studies define a general architecture for continental hydrothermal systems.

Gradual variations of O isotope ratios in the altered rocks are observed both laterally and vertically, with lower values in central hydrothermal upflow zones with higher temperatures and enhanced fluid flux, and deeper where temperatures are higher. Fluids in deeper (more than 4km) portions of the systems can include a significant magmatic component near intrusions, where they are related to the formation of porphyry deposits. Fluids in shallower portions are dominated by meteoric ground waters. Thermal profiles in the shallowest (less than about 300 meters) epithermal near-surface environments are controlled by the hydrostatic boiling curve. In all cases, fractures and other permeable zones control the most important fluid flow paths.

Argillization and acid-sulfate alteration are widespread within a kilometer or so of the paleosurface, where boiling in rising fluids can be important. Propylitization is dominant in deeper parts of the systems, and potassic and quartz-sericite-pyrite porphyry-style alteration is prevalent near some deeper intrusions. The most important mass chemical effect of propylitic alteration is hydration. Although mineral reactions are pervasive in those altered rocks, major element concentrations suggest that their flux is minimal in the propylitic environment. Ba and Sr are generally added. Leaching of nearly all components, sometimes extreme, is characteristic of shallow alteration. Diffusion models of O isotope ratio profiles in altered feldspar phenocrysts at Rico suggest a hydrothermal duration on the order of about 100,000 years, whereas the Yellowstone system has been active for at least 400,000 years, although we do not know if its activity has been continuous or intermittent.