Role of Arsenic in Pyrite Oxidation

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Introduction

The oxidation of pyrite and other sulfide minerals impacts the environment, acidifying surface and ground water and releasing associated heavy metals into the environment. The rate of pyrite oxidation determines the rate of toxic element and acid release; consequently, it has been studied in great detail. Pyrite oxidation rates vary depending on surface characteristics, including the presence of defects [1], crystallographic orientation [2], and surface coverage [3]. Ion substitution in the bulk lattice also may influence pyrite oxidation.

Materials and Methods

This research chronicles the effect of arsenic, an element commonly associated with pyrite [4], on pyrite oxidation. Sorption of arsenite, $As(OH)_3$, and arsenate, H_3AsO_4, was examined using synchrotron-based X-ray photoelectron spectroscopy (XPS). Arsenic-exposed surfaces were then exposed to oxygen, and the products compared to As-free surfaces. The effect of structural As on pyrite oxidation was also examined by microcapillary X-ray absorption spectroscopy (µ-XAS). The rate of pyrite oxidation was measured by comparing the relative As concentration and pyrite oxidation rate throughout a pyrite (100) thin section.

Results and Conclusions

The sorption of both arsenite and arsenate caused oxidation of the pyrite surface. Surface Fe(II) was partially converted to an Fe(III) oxide by As sorption; however, surface sulfur groups exhibited only limited oxidation and only small fractions of sulfate were detected. The limited sulfur oxidation may be due to the dissolution of oxidized sulfur species from the surface during oxidation. Arsenic sorption also impacted further oxidation by molecular oxygen. The µ-XAS experiments also suggest that structural arsenic influences the rate of pyrite oxidation.

References

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Microbial sulfate reduction in deep sediments of ODP Leg 181: Evidence from stable sulfur isotope fractionation and pore water modeling

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Interstitial water samples from seven ODP sites (Leg 181; Sites 1119 to 1125) of the southwestern Pacific Ocean have been analyzed for the stable sulfur isotopic composition of dissolved sulfate along with major and minor ions (Böttcher et al. 2002, in press). Sulfate from the interstitial fluids ($\delta^{34}S$ values between +20.7 and +60‰ versus the SO_2-based Vienna-Canyon Diablo troilite standard (V-CDT)) was enriched in ^{34}S with respect to modern sea water ($\delta^{34}S \approx +20.6$‰) indicating that microbial sulfate reduction takes place to different extents at all investigated sites. Microbial sulfate reduction (MSR) was found at all sites, the intensity depending on the availability of organic matter which is controlled by paleo-sedimentation conditions (sedimentation rate, presence of turbidites) and productivity. Microbial net sulfate reduction was additionally confirmed by modeling interstitial water sulfate profiles. Areal net sulfate reduction rates up to 14 mmol m^{-2} yr^{-1} have been calculated which were positively related to sedimentation rates. Total reduced inorganic sulfur (TRIS; essentially pyrite) as a product of microbial sulfate reduction was isotopically characterized in squeeze cake samples and gave $\delta^{34}S$ values between -51 and +9‰ indicating pyrite formation both close to the sediment-water interface and later diagenetic contributions.

References

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