

Surface oxidation of iron monosulphide: an X-ray photoelectron spectroscopic study

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In a number of recent investigations (e.g. Schoonen and Barnes, 1991; Rickard and Luther, 1997), iron monosulphide has been identified as a precursor phase to pyrite formation, where 'FeS' may range in crystallinity from amorphous iron sulphide to mackinawite (Fe_{1+x}S). Pyrite accumulation in diagenetic environments is often associated with the oxic-anoxic interface where, depending on the geochemical conditions, disulphide may be produced from monosulphide via the addition of polysulphide S (S_x^{2-}) (Schoonen and Barnes, 1991) or through the reduction of H^+ in hydrogen sulphide to $\text{H}_2(\text{g})$ (Rickard and Luther, 1997).

The surface chemistry of iron monosulphide at the oxic-anoxic interface is therefore a critical factor in the kinetics of the transformation reaction. Since an oxidizing agent (e.g. oxygen) is needed for the production of disulphide from monosulphide, it is likely that ferrous iron is also susceptible to oxidation by the same oxidant, and that the redox transformation may produce other S species besides disulphide. As there have only been a few previous studies on the surface chemistry of iron monosulphide (e.g. Herbert *et al.*, 1998), this study reports on the formation of oxidized surface species after a brief exposure to oxygen.

Methodology

The iron monosulphide sample was recovered from a permeable reactive barrier installed at the Nickel Rim Mine near Sudbury, Ontario, Canada, for the passive remediation of groundwater contaminated with acid mine drainage (Benner *et al.*, 1997). Within the reactive barrier, piezometer bundles constructed of polyethylene tubing were used for the collection of groundwater samples; iron sulphide discussed in this paper formed as black precipitates on this tubing. A 10 cm segment of piezometer tubing was cut from a

sampling tube and immediately placed in a GasPak[®] anaerobic jar containing an activated pouch for generating H_2/CO_2 gas, silica gel, and a Pd catalyst. The H_2 gas reacts with O_2 at the Pd surface, creating H_2O vapour that is removed by the silica gel.

The iron monosulphide precipitates are characterized using field emission scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX), X-ray diffractometry (XRD), and X-ray photoelectron spectroscopy (XPS). For SEM and XPS analysis, one cm samples were cut from the tube segments in an argon-filled glovebag, and transfer to the XP spectrometer proceeded in an Ar atmosphere. XPS spectra were obtained using apparatus and techniques described in Herbert *et al.* (1998).

Results and discussion

The XRD analysis of the black precipitates that formed on the polyethylene tubing indicates that the mineral is mackinawite (d-spacings at 5.03, 2.97, 2.31, 1.808, and 1.725 Å). However, the diffraction peaks are quite broad, with the (001) reflection exhibiting a full width at half maximum of about 3 Å, indicating that the poorly crystallized phase is disordered mackinawite (cf. Wilkin and Barnes, 1997). Employing field emission SEM analysis, the disordered mackinawite crystals appear as convoluted discs roughly 200 to 400 nm in diameter. The EDX analysis of the sulphide yields a Fe:S atomic ratio of 0.95 to 1.00.

Narrow region XPS spectra are reported here for O(1s), Fe(2p_{3/2}), and S(2p). Four peaks were fitted to the O(1s) spectrum corresponding to O bound in oxide, hydroxide, and water bonding environments. Oxide O was fit at 530.0 eV within the BE range reported for iron oxides and oxyhydroxides.

The spectra for Fe(2p_{3/2}) and S(2p) are shown in Fig. 1. The low energy shoulder of the Fe(2p_{3/2})

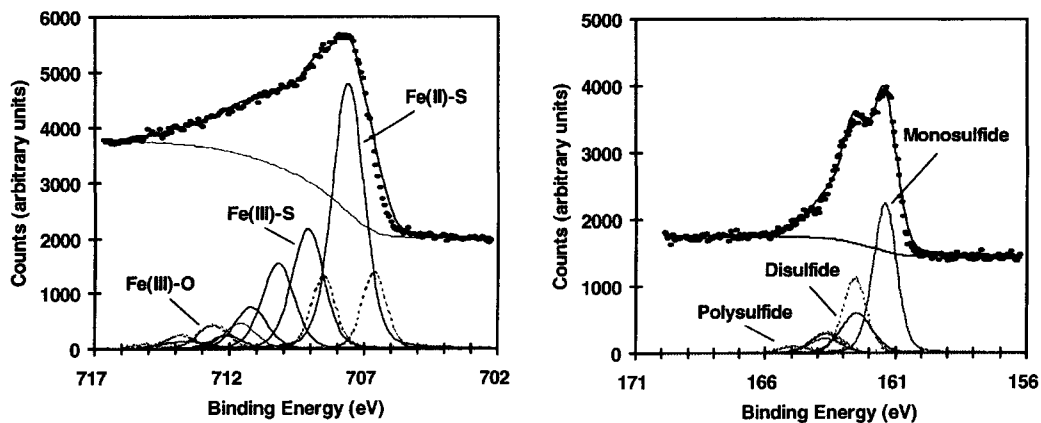


FIG. 1. Narrow region scans of Fe($2p_{3/2}$) and S($2p$) XPS spectra (left and right, respectively).

spectrum was fitted with a ferrous iron component (707.6 eV) with two multiplets in the BE range representative of Fe(II)-S bond types. The long, high energy tail on the Fe($2p_{3/2}$) spectrum could be adequately fitted with peak sequences for ferric iron bound with both S and O. The Fe(III)-S and Fe(III)-O bond types produce XP spectra with a main peak and three multiplets; the major peaks were fitted at 709.1 eV and 711.6 eV, respectively. The S($2p_{3/2}$) spectrum is fitted with a major peak at 161.4 eV and a multiplet at half its intensity, corresponding to S present as monosulphide (S^{2-}). The high energy tail was fitted with two minor peaks and their multiplets corresponding to disulphide and polysulphide species.

The Fe($2p_{3/2}$) and S($2p_{3/2}$) spectra therefore indicate that the mineral surface possesses primarily a ferrous monosulphide composition. However, during the brief exposure of mackinawite to atmospheric oxygen during sampling, Fe(III)-S, disulphide, and polysulphide bond types were formed at the precipitate surface.

Conclusions

The combination of the XRD, EDX, and XPS data suggest that the sample consists of an unoxidized core of disordered mackinawite overlain by an oxidized, iron-deficient surface layer with a composition similar to greigite (Fe_3S_4). The ratio of Fe(III)-S to Fe(II)-S species at the mackinawite surface in this study is 0.6, much less than 2.0 for stoichiometric greigite, such that there seems to be only partial coverage of the surface by oxidized iron. The XPS spectra and SEM images for the iron sulphide analysed in this study are quite similar those previously presented for iron sulphide precipitated

in media for the growth of sulphate-reducing bacteria (Herbert *et al.*, 1998).

The transformation of mackinawite to greigite can be expressed as follows (Wilkin and Barnes, 1997):



where ferrous iron may be transported by diffusion from the immediate site of FeS oxidation and precipitate elsewhere as goethite, leading to depletion in total Fe at that location. Equation 1 requires the loss of iron from the mackinawite structure for the formation of iron-deficient greigite, which is the energetically most efficient transformation between mackinawite and greigite (Wilkin and Barnes, 1997, and references therein). The results of this investigation support the claims of previous studies (e.g. Wilkin and Barnes, 1997) that low levels of dissolved oxygen at the oxic – anoxic interface may react with mackinawite to form greigite, which in turn can transform to pyrite by the loss of structural iron.

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