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Iron-monosulfide oxidation and associated S transformations in a natural sediment were examined by combining selective extractions, electron microscopy and S K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The sediment examined in this study was collected from a waterway receiving acid–sulfate soil drainage. It contained a high acid-volatile sulfide content (1031 pmol g−1), reflecting an abundance of iron-monosulfide. The iron-monosulfide speciation in the initial sediment sample was dominated by nanocrystalline mackinawite (tetragonal FeS). At near-neutral pH and an O2 partial pressure of ~0.2 atm, the mackinawite was found to oxidize rapidly, with a half-time of 29 ± 2 min. This oxidation rate did not differ significantly (P < 0.05) between abiotic versus biotic conditions, demonstrating that oxidation of nanocrystalline mackinawite was not microbially mediated. The extraction results suggested that elemental S (S0) was a key intermediate S oxidation product. Transmission electron microscopy showed the S0 to be amorphous nanoglobules, 100–200 nm in diameter. The quantitative importance of S0 was confirmed by linear combination XANES spectroscopy, after accounting for the inherent effect of the nanoscale S0 particle-size on the corresponding XANES spectrum. Both the selective extraction and XANES data showed that oxidation of S0 to SO42− was mediated by microbial activity. In addition to directly revealing important S transformations, the XANES results support the accuracy of the selective extraction scheme employed here.

Introduction

Iron-monosulfides, such as amorphous FeS, mackinawite (tetragonal FeS), pyrrhotite (hexagonal FeS), and greigite (Fe3S4), occur in a range of anoxic systems (1–3). These include natural settings such as estuarine and marine sediments, wetland soils, and potential acid-sulfate soils, as well as engineered settings such as permeable reactive barriers for treatment of contaminated groundwater (4–8). In both natural and engineered systems, the formation and fate of iron-monosulfides strongly influences S, Fe, and C cycling, and often exerts a controlling effect on trace element mobility (5–12). As a consequence, the biogeochemical behavior of iron-monosulfide minerals is of widespread interest.

Iron-monosulfides may undergo significant oxidation-induced transformations when exposed to oxic conditions (13–16). This may occur when anoxic sediments are dredged and subsequently allowed to drain or when such sediments experience natural resuspension events (9, 13, 16–18). The oxidation of iron-sulfides ultimately results in the production of Fe(III)-oxyhydroxides, acidity, and sulfate (15–19). For iron-disulfides, such as pyrite and marcasite, it is well-known that oxidation proceeds via a series of abiotic and microbially mediated reaction steps (20). In contrast, there is relatively little known about the role of microbially mediated reactions in the oxidation of sedimentary iron-monosulfides (19).

Previous research on the geochemical behavior of iron-monosulfides has relied heavily on operationally defined extractions (4–13, 15–19). For example, acid-volatile sulfide (AVS) has been widely applied as a measure of iron-monosulfide abundance in natural sediments (2). Likewise, sequential extractions involving AVS, hot or cold chromium-reducible S and various solvent extractions have been used for quantification of solid-phase S speciation (7–12, 15–19). Although such extraction procedures provide valuable insights, they are inherently limited by not yielding direct speciation data (2).

In the past decade, synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy has emerged as a powerful tool for S speciation in natural materials (21). A major advantage of XANES spectroscopy is the capacity for direct S speciation in redox-sensitive samples under an inert atmosphere. Linear combination fitting of XANES data has been used for quantitative S speciation in several studies (22, 23). However, the technique has not yet been applied to follow S speciation pathways associated with sedimentary iron-monosulfide oxidation.

The objective of this study was to examine microbially mediated S transformations associated with iron-monosulfide oxidation in a natural sediment. Quantitative S speciation data was obtained by combining operationally defined selective extractions with S K-edge XANES spectroscopy and analytical transmission electron microscopy. The results provide new insights into (i) the role of microbially mediated S oxidation processes and (ii) the accuracy of selective extractions for S speciation in sediments.

Materials and Methods

General Methods. All laboratory glass- and plastic-ware was cleaned by soaking in 5% (v/v) HNO3 for at least 24 h, followed by repeated rinsing with deionized water. All chemicals were...
analytical reagent grade and all reagent solutions were prepared with deionized water (Milli-Q). Results for solid-phase analyses are presented on a dry weight basis, unless noted otherwise.

**Sediment Collection and Handling.** Benthic sediment was collected from a waterway (on the Clarence River floodplain in eastern Australia; 29°30′S, 153°15′E) known to receive Fe- and SO₄-rich drainage from acid–sulfate soils. The environmental setting and general characteristics of this acid–sulfate soil landscape, as well as background information on the in situ sedimentary Fe and S geochemistry, are presented in Burton et al. (7, 24, 25). Triplicate sediment cores (internal diameter of 10 cm) were collected with the use of a push-tube coring device. The cores were extruded under a stream of high purity N₂. The core samples were cut into 5-cm-long sections, and each section was subjected to the S extraction procedure. The suspension pH and Eh were determined at regular intervals through the oxidation experiment. Sediment moisture content was determined by drying at 105 °C. Sediment from the 5 cores (internal diameter of 10 cm) were collected with the use of a push-tube coring device. The cores were extruded under a stream of high purity N₂. The core samples were cut into 5-cm-long sections, and each section was subjected to the S extraction procedure.

**Oxidation Experiment.** The oxidation experiments involved the oxic resuspension of 0.5 L of sediment in 4.5 L of 0.1 M NaCl. The role of microbially mediated oxidation processes was examined by employing, in duplicate, both biotic and abiotic treatments. The abiotic treatment involved the use of sodium azide (at a final concentration of 50 mM) as a bacterial inhibitor (26). During the oxidation experiments, the sediment suspensions were magnetically stirred at ∼100 rpm using Teflon-coated stir-bars. Oxic conditions, with an O₂ partial pressure of ∼0.2 atm, were maintained by bubbling air into the suspension at a rate of 200 mL h⁻¹. Magnetic stirring and vigorous aeration ensured a homogeneous suspension.

The suspension pH and Eh were determined at regular time intervals (ranging from 15 min to 72 h) over 21 days. Aliquots of the sediment suspension were also retrieved via sampling ports using a 25 mL polypropylene syringe. The aqueous phase was separated by centrifugation and was filtered (0.45 µm) prior to pore-water analysis. The solid material was subjected to the S extraction procedure described below. Sediment was also retrieved at 1, 3, and 21 days and was stored frozen in gas-tight N₂-purged glass vials at room temperature (20 ± 2 °C) for 4 weeks. This may have affected the sediment properties (e.g., through formation of some iron-monosulfide during storage), but storage-associated effects were probably very minor as the fundamental properties of the stored sediment were consistent with previously reported in situ sediment properties for the study site (7, 24, 25).

**Analyses.** Sediment moisture content was determined by weight loss due to drying at 105 °C. Sediment pH and Eh were determined using calibrated probes and a TPS WD90 meter. Total C and S was determined on oven-dry (105 °C, 24 h) sediment samples using an Elementar combustion analyzer. Near-total Fe was determined by aqua-regia digestion (1:3 HNO₃:HCl, 20 min, 1000 W microwave at 10% power) of oven-dry sediment followed by inductively coupled plasma–atomic emission spectrometry (ICP–AES) using a Perkin-Elmer DV4300. Triplicate analysis of total C and total S and near-total Fe revealed that the analytical precision for these methods was within 4%. The abundance of Fe- and S-oxidizing microorganisms was determined using the most-probable number (MPN) approach described by Benner et al. (5) with triplicate vials per 10-fold dilution.

Samples for powder X-ray diffraction (XRD) were dried at room temperature under a stream of high purity N₂. The dried samples were exposed to air for <2 min prior to commencement of XRD in order to minimize potential oxidation-induced changes in mineralogy. X-ray diffractograms were obtained for randomly oriented powders using a Phillips PW 1050/70 diffractometer with a Cu X-ray tube. Samples were step scanned from 10° to 20° using a 0.05° step and a 3 s count time. Samples for transmission electron microscopy (TEM) were placed onto Cu or Ni grids and allowed to dry under vacuum. Previous TEM studies of synthetic iron-monosulfides show negligible oxidation-induced artifacts during TEM examination (27). The TEM observations reported here were obtained with a JEOL JEM-2010F operated at 200 kV and fitted with a Gatan Imaging Filter and a Noran System 6 energy dispersion X-ray microanalysis system.

The initial sediment pore-water was extracted by centrifugation (7, 11) at the time of commencement of the oxidation experiment. This pore-water, as well as aqueous-phase samples collected during the oxidation experiment, was transferred through an enclosed 0.45 µm syringe-driven filter. Porewater sulfide was immediately preserved using ZnOAc prior to determination by the methylene blue method (28). It should be noted that porewater sulfide determined via this method may include HS⁻ (aq), H₂S(aq), and Fe₂S₃(aq) cluster complexes, as well as some iron-monosulfide nanoparticles that may pass through a 0.45 µm filter. Aqueous Fe²⁺ and Fe³⁺ was determined using the 1,10-phenanthroline method (28). Aqueous Fe³⁺ was undetectable (i.e., < 3% of total aqueous Fe) and is not discussed further. Aqueous SO₄²⁻ was determined by turbidimetric analysis and total aqueous S was determined by ICP-AES (28). For all quantified porewater Fe and S analytes, triplicate analysis on approximately 15% of samples revealed that analytical precision was within 6%.

Operationally defined speciation of reduced inorganic S was determined by selective, sequential extraction of iron-monosulfides, elemental S and pyrite (10). Iron-monosulfides, defined operationally as acid-volatile sulfide (AVS), were extracted by shaking (150 rpm) 0.5 g of sediment with 10 mL of 6 M HCl/0.1 M ascorbic acid in gas-tight 55 cm³ polypropylene reactors for 16 h (10). The evolved H₂S was trapped in 7 mL of 3% Zn acetate in 2 M NaOH, and subsequently quantified via iodometric titration (28). Elemental S (S₀) was then extracted from the AVS-extracted sample by shaking the sediment with 10 mL of chloride for 16 h (29). An aliquot of the chloroform phase was analyzed for S₀ using cold cyanalysis in acetone (30). Residual S₀ was then removed from the sediment sample by three rinses with 25 mL of acetone, and a final rinse with 20 mL ethanol. Each rinse involved 10 min of shaking, with the sediment and acetone/ethanol phases separated between rinses by centrifugation at 4000 rpm for 10 min. Pyrite-S in the residual AVS- and S₀-extracted sediment was then quantified as Cr(II)- reducible S using the method of Burton et al. (31). On the basis of our previous studies, the precision of AVS, S₀, and pyrite-S analyses using the methods described here are generally within ±7% (7, 8, 10–12, 16, 24, 25, 31).

Solid-phase S speciation was examined by S K-edge XANES spectroscopy. The XANES data were collected on bending magnet beamline 16A at the National Synchrotron Radiation Research Centre (NSRRC) in Hsinchu, Taiwan (32). Mineral standards and sediment samples for XANES were transported from Australia to Taiwan frozen under N₂ (i.e., standards and samples were stored during the ~20 h transit period within N₂-purged glass vials, which were sealed with gastight Teflon-lined screw caps and kept frozen with the use of dry ice). Sediment samples and air-sensitive mineral standards were stored in this way until being mounted (in their natural water-saturated paste state) into 6 µm S-free Mylar film pouches (to minimize atmospheric exposure) prior to subsequent XANES analysis under an inert (He) atmosphere at ambient temperature. The XANES results for a synthetic nanoparticulate mackinawite reference standard (which was prepared in Australia by mixing equal volumes of 0.3 M
solutions of Na$_2$S and FeCl$_2$, and was also stored, transported to Taiwan and mounted as described above) confirmed the absence of any detectable oxidation-induced artifacts as a result of storage during transit or from the brief air-exposure during specimen mounting (see Supporting Information). Standards that were not sensitive to atmospheric exposure were spread thinly as dry powders on S-free Kapton tape. These standards were diluted 10–100-fold with graphite to overcome any self-absorption effects associated with high S loadings. The X-ray energy resolution was maintained by a fully tuned Si(111) double crystal monochromator, with the energy calibrated to the maximum of the first feature of Na$_2$S$_2$O$_3$·0.5H$_2$O at 2472.02 eV. X-ray fluorescence data were collected using a Lytle detector at ambient temperature under a He atmosphere.

Prior to XANES spectral analysis, the pre-edge background was subtracted and the edge jump was normalized to unity with the PySpline software package (33). Quantitative S speciation was determined by linear combination fitting of a sample spectrum with contributions from selected S reference standards. The choice of standards for linear combination fitting was based on mineralogical examination via XRD and TEM, and included an array of S-containing phases (see Supporting Information for a further description of the XANES standards). Linear combination fitting was performed with the WinXAS software package (34), with no energy shifts allowed during fitting. Previous sediment S speciation studies, which have employed XANES, report that the quantification error associated with linear combination fitting is approximately ±5% for each individual S species (22, 23).

Results and Discussion
Initial Sediment Properties. The initial sediment was near-neutral (pH 7.3), moderately reducing (Eh = +62 mV), with a water content of 88% (w/w). It contained total S at 1453 μmol g$^{-1}$, near-total Fe at 3950 μmol g$^{-1}$, and a total C content of 8.14%. The initial AVS content was 1031 μmol g$^{-1}$, with the selective extraction results also suggesting the presence of pyrite at 109 μmol g$^{-1}$ and $S_0$ at 60 μmol g$^{-1}$. This initial AVS content is high in comparison to normal marine and estuarine sediments, which typically contain AVS at <100 μmol g$^{-1}$ (4, 6, 33). However, the high AVS content and the other fundamental sediment properties described above are consistent with the in situ sediment geochemistry in waterways receiving drainage from acid-sulfate soil landscapes (7, 36–38).

Despite containing abundant AVS, the initial sediment contained undetectable (<0.002 mmol L$^{-1}$) pore-water sulfide. This can be attributed to low iron-monosulfide solubility under Fe-rich conditions, which is reflected in a relatively high concentration of pore-water Fe$^{2+}$ (0.55 mmol L$^{-1}$) in the initial sediment sample. This Fe-rich nature is evident from XRD, which showed major amounts of goethite (α-FeOOH) and siderite (FeCO$_3$) (see Supporting Information). The in situ co-occurrence of goethite and siderite, with large concentrations of AVS, is a common feature of Fe-rich benthic sediments present in waterways associated with acid-sulfate soil landscapes (8, 24). As discussed by Burton et al. (7), an abundance of porewater Fe$^{2+}$ in such sediments can lead to iron-monosulfide accumulation due to rapid sequestration of bacterially produced H$_2$S.

X-ray diffraction analysis of the initial sediment revealed a broad peak at ~17 °29 Cu Kα that is consistent with the (001) plane in mackinawite (14) (see Supporting Information). The occurrence of mackinawite was confirmed by TEM using selected area electron diffraction and energy-dispersive X-ray analysis (Figure 1a, 1b and 1c). High-resolution TEM revealed that the mackinawite was nanocrystalline, comprising only about 10–15 atomic layers perpendicular to the (001) plane (Figure 1d and 1e). The identification of nanocrystalline mackinawite is significant because the fundamental iron-monosulfide mineralogy and crystallite size has not been documented in previous sediments oxidation studies (9, 13, 15–18, 38).

Linear combination fitting of the XANES data presented in Figure 2 suggests that nanocrystalline mackinawite comprised ~84% of total S in the initial sediment sample. This is comparable with the AVS extraction data which suggests an iron-monosulfide content of 72 ± 6% of total S. The selective extraction data for the initial sediment also suggest that pyrite and $S_0$ were both minor constituents (7.7% and 4.2% of total S, respectively). This is consistent with the corresponding XANES spectrum, which was well...
described by a combination of mackinawite and SO₄, with negligible (<5% of total S) pyrite and S₈ (Figure 2).

The initial sediment contained Fe-oxidizers at 2 × 10⁶ MPN mL⁻¹ and S-oxidizers at 3 × 10⁷ MPN mL⁻¹. As expected, Fe- and S-oxidizing microorganisms were undetectable (according to the MPN procedure) following azide addition to the initial sediment. It is therefore reasonable to conclude that the addition of azide effectively inhibited the activity of both groups of microorganisms. As such, comparison between azide-treated and untreated sediment resuspension experiments facilitates evaluation of the role of microbially mediated oxidation processes.

**The Fast Oxidation of Iron-Monosulfide.** During the initial 3 h in both the abiotic and biotic systems, the suspension pH remained at ~7.3, while Eh increased from +62 mV to approximately +300 mV (Figure 3). During this period, the AVS concentration decreased from 1031 µmol g⁻¹ to <1 µmol g⁻¹ (Figure 3). The disappearance of AVS can be attributed to the relatively rapid oxidation of nanocrystalline mackinawite. The rate of nanocrystalline mackinawite oxidation (based on the decrease in AVS) was well described (R² > 0.95) by pseudo first-order kinetics. Importantly, the oxidation half-time (29 ± 2 min) did not differ significantly (P<0.05) between the biotic versus abiotic treatments (Figure 3). This demonstrates that the oxidation of nanocrystalline mackinawite was not microbially mediated.

An AVS oxidation half-time of 29 min is comparable to Di Toro et al. (13) and Burton et al. (16) who found half-times of approximately 40 – 50 and 60 min, respectively. The variation in oxidation half-times between the present study and previous studies may represent fundamental differences in the sediment properties, particularly the initial iron-monosulfide mineralogy and/or crystallite size. For example, Di Toro et al. (13) speculated that their sediment samples may have contained some oxidation-resistant greigite, in addition to mackinawite and amorphous iron-monosulfide. Unfortunately Di Toro et al. (13), like other sediment oxidation studies (e.g., refs 9, 15, 16, 38), provide little direct information on iron-monosulfide mineralogy or crystallite size.

**The Formation of S₈ as an Oxidation Product.** The disappearance of AVS during the initial 3 h was not associated with significant increases in either SO₄²⁻ or total aqueous S (Figure 3). In contrast, the selective extraction results show that the loss of AVS coincided quantitatively with accumulation of S₈ (Figure 3). This is consistent with Burton et al. (16) who found that AVS oxidized to an acetone-extractable S species, which was assumed to be S₈. The oxidation of AVS to S₈ can be explained according to

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FeS₄(a) + 3/4 O₂ + 1/2 H₂O → 1/8 S₈ + FeOOH(a)
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The importance of S₈ formation is supported by the absence of significant increases in the aqueous S concentration or changes in pH during AVS oxidation (Figure 3). The XANES data corroborate the selective extraction results by showing directly the loss of nanocrystalline mackinawite and formation of S₈ during the initial 24 h (Figure 2).

The reaction represented in eq 1 cannot occur via a single-step transformation of the S(-II) moiety in mackinawite to S₈. According to Schippers and Sand (20), the oxidation of acid-soluble monosulfide minerals occurs via intermediate aqueous polysulfide species. These species are highly reactive and rapidly dissociate to form aqueous sulfide and elemental S, with the latter precipitating as S₈ (20). Aqueous sulfide produced via this polysulfide dissociation process would have reacted very rapidly with the abundant Fe in the sediment examined here, either forming iron-monosulfide or additional aqueous polysulfide species. These species would then have cycled back into the overall fast oxidation process. The absence of detectable changes in the total aqueous S concentration during AVS oxidation (Figure 3) is consistent with very rapid decomposition of polysulfides to S₈ and with the very fast turnover rates of sulfide produced by polysulfide decomposition.

The XRD data for sediment sampled at 24 h revealed the disappearance of the broad nanocrystalline mackinawite (001) peak, yet did not identify the presence of oxidation products (see Supporting Information). The lack of XRD-detectable products suggests that the S₈ produced via mackinawite oxidation may have been amorphous. Transmission electron microscopy confirmed the formation of amorphous S₈, which occurred as ~100–200 nm globules (Figure 4). To our knowledge, this is the first direct evidence on the nanoglobular nature of S₈ formed by iron-monosulfide oxidation in natural sediments. Such small amorphous S₈...
globules contrast greatly with the 3–5 \( \mu \)m orthorhombic \( \text{S}_0^8 \) crystals that form during oxidation of synthetic mackinawite (16).

**Using XANES to Quantify \( \text{S}_0^8 \) Abundance.** Linear combination fitting of XANES data allows for quantitative S speciation in natural sediments (22, 23). However, using XANES for \( \text{S}_0^8 \) quantification requires caution because of a strong negative correlation between the peak XANES absorbance and the corresponding \( \text{S}_0^8 \) particle size (Figure 5). This relationship was first recognized by Pickering et al. (39) in a study of bacterially produced \( \text{S}_0^8 \) globules. These researchers attributed the particle-size effect to attenuation of the XANES absorbance by self-absorption (“thickness effects”) when using X-ray fluorescence. In agreement with Pickering et al. (39), we found that the maximum XANES absorbance for \( \text{S}_0^8 \) was strongly dependent on the corresponding \( \text{S}_0^8 \) particle size (Figure 5d).

Figure 5 shows that, due to self-absorption, the peak XANES absorbance of \( \text{S}_0^8 \) decreases as the \( \text{S}_0^8 \) particle size increases. This has important implications for using XANES for S speciation in sediments. In particular, it suggests that attempting to quantify \( \text{S}_0^8 \) abundance in natural sediments using common \( \text{S}_0^8 \) reference materials, such as finely ground \( \alpha \text{S}_0^8 \), may yield inaccurate results. Significantly, previous studies of sedimentary S speciation have used finely ground \( \alpha \text{S}_0^8 \) as their single \( \text{S}_0^8 \) reference phase for linear combination XANES spectroscopy (22, 23).

Based on TEM observations, the \( \text{S}_0^8 \) produced during the oxidation experiment had a particle size of \( \sim 100–200 \) nm (Figure 4). This particle-size is intermediate between \( \text{S}_0^8 \) dissolved in toluene and finely ground \( \alpha \text{S}_0^8 \) (i.e., with a particle size of \( \sim 5–50 \) \( \mu \)m, based on scanning electron microscopy; see Supporting Information). As such, the \( \text{S}_0^8 \) spectral component in the sediment examined here could be represented as a least-squares optimized combination of the XANES spectra for dissolved \( \text{S}_0^8 \) and finely ground \( \alpha \text{S}_0^8 \). This relatively simple solution provided a good fit to the experimental XANES spectra and allowed for quantification of \( \text{S}_0^8 \) abundance (Figure 2).

Linear combination fitting of the XANES data showed that the \( \text{S}(-II) \) initially contained within nanocrystalline mackinawite had oxidized quantitatively to \( \text{S}_0^8 \) within 24 h.
that S08 decreased under biotic conditions after a lag-period demonstrates that this process was not microbially mediated.

In contrast to oxidation under biotic conditions, the observed decrease in operationally defined S08 under abiotic conditions (Figure 2). This decrease exhibited pseudo first-order behavior with a half-time of 64 h (Figure 3). This decrease was associated with a substantial decrease in pH from ~7 to ~2.5 (Figure 3). The simultaneous release of SO42− and H+ can be attributed to S08 oxidation with O2 or Fe3+ as electron acceptors according to (16, 25):

\[
\frac{1}{8}S_8 + \frac{3}{2}O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (2)
\]

\[
\frac{1}{8}S_8 + 6Fe^{3+} + 4H_2O \rightarrow SO_4^{2-} + 6Fe^{2+} + 8H^+ \quad (3)
\]

The XANES data conclusively confirm the oxidation of S08 to SO42− in the biotic system (Figure 2). In particular, these data reveal quantitative replacement of S08 by SO42− between 1 and 21 days. Therefore, the XANES spectroscopic results corroborate the results obtained from selective extraction of S08 and the analysis of SO42−.

In contrast to oxidation under biotic conditions, the selective extraction data indicate that S08 remained relatively constant from 3 to 500 h under abiotic conditions (Figure 3). The XANES results also showed the persistence of S08 under biotic conditions (Figure 2). This distinct contrast with the biotic system indicates that oxidation of S08 was mediated by microbial activity.

Figure 3 shows a lag period of ~2 days between complete AVS oxidation and commencement of substantial S08 oxidation in the biotic system. This is consistent with a typical microbial growth pattern, which starts with a lag phase of low metabolic activity prior to an exponential phase of rapid growth in cell numbers (40). In the case of S08 oxidation, the lag phase may involve microbial colonization of the S08 surface and the production of enzymes which enhance S08 reactivity (41). While our results demonstrate the importance of microbial-mediation for S08 oxidation, further research is needed to resolve the microbial assemblage involved as well as the microbial oxidation mechanism.

Burton et al. (16) found that oxidation of S08 (formed via sedimentary iron-monosulfide oxidation) was associated with the mobilization of large concentrations of Al, Mn, Ni, and Zn. The pH-dependent release of these metals was attributed to severe acidification, which was caused directly by S08 oxidation (16). The present findings suggest that manipulating the activity of oxidizing bacteria (e.g., ref 41) may provide management options to minimize acidification and metal mobilization during controlled sediment oxidation (e.g., following dredging or dewatering operations). Furthermore, the microbial lag period suggests that if the supply of O2 can be halted within 2 days then S08 oxidation and the associated acidification and metal mobilization may be prevented.

Future Research. This study has demonstrated that the oxidation of nanocrystalline mackinawite to elemental sulfur in near-neutral sediments is rapid at an O2 partial pressure of ~0.2 atm. Under these conditions, the selective extraction and XANES data both conclusively show that oxidation of mackinawite to elemental sulfur was not microbially mediated. This implies that any potential microbial energy-gain associated with catalyzing mackinawite oxidation at near-neutral pH and an O2 partial pressure of 0.2 atm is negligible due to competition from the very rapid abiotic oxidation rate. A corollary of this point is that microbially mediated oxidation of mackinawite to elemental sulfur may become energetically feasible (i.e., for microbial metabolism) at lower O2 partial pressures due to a slower abiotic oxidation rate. Resolving the possibility of microbially mediated mackinawite oxidation at low O2 partial pressures may be a fruitful area for future research.

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Supporting Information Available

Tables showing the initial sediment properties and the quantitative speciation of solid-phase S; figures showing XRD results, XANES spectra for reference standards and electron micrographs for finely ground aS8. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


