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Sulfide-driven arsenic mobilization from arsenopyrite and black shale pyrite

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Abstract

We examined the hypothesis that sulfide drives arsenic mobilization from pyritic black shale by a sulfide–arsenide exchange and oxidation reaction in which sulfide replaces arsenic in arsenopyrite forming pyrite, and arsenide (As−1) is concurrently oxidized to soluble arsenite (As+3). This hypothesis was tested in a series of sulfide–arsenide exchange experiments with arsenopyrite (FeAsS), homogenized black shale from the Newark Basin (Lockatong formation), and pyrite isolated from Newark Basin black shale incubated under oxic (21% O_2), hypoxic (2% O_2, 98% N_2), and anoxic (5% H_2, 95% N_2) conditions. The oxidation state of arsenic in Newark Basin black shale pyrite was determined using X-ray absorption-near edge structure spectroscopy (XANES). Incubation results show that sulfide (1 mM initial concentration) increases arsenic mobilization to the dissolved phase from all three solids under oxic and hypoxic, but not anoxic conditions. Indeed under oxic and hypoxic conditions, the presence of sulfide resulted in the mobilization in 48 h of 13–16 times more arsenic from arsenopyrite and 6–11 times more arsenic from isolated black shale pyrite than in sulfide-free controls. XANES results show that arsenic in Newark Basin black shale pyrite has the same oxidation state as that in FeAsS (−1) and thus extend the sulfide–arsenide exchange mechanism of arsenic mobilization to sedimentary rock, black shale pyrite. Biologically active incubations of whole black shale and its resident microorganisms under sulfate reducing conditions resulted in sevenfold higher mobilization of soluble arsenic than sterile controls. Taken together, our results indicate that sulfide-driven arsenic mobilization would be most important under conditions of redox disequilibrium, such as when sulfate-reducing bacteria release sulfide into oxic groundwater, and that microbial sulfide production is expected to enhance arsenic mobilization in sedimentary rock aquifers with major pyrite-bearing, black shale formations.

1. INTRODUCTION

Arsenic has long been recognized as a toxic metalloid (National Research Council: Subcommittee to Update the 1999 Arsenic in Drinking Water Report, 2001). The U.S. EPA lowered the arsenic standard for drinking water to 10 μg L^{-1} in 2001 (EPA, 2001), yet more than ten million people in the U.S. are exposed to potentially harmful levels (>10 μg L^{-1}) of arsenic in their drinking water (Welch et al., 2000; Ryker, 2003).

The release of arsenic into the environment can occur as a result of human activities related to agriculture (Reedy et al., 2007; Signes-Pastor et al., 2007) and mining (Carrillo and Drever, 1998; Bayard et al., 2006; Kwong et al., 2007; Lazareva and Pichler, 2007). However, arsenic is also a component of subsurface rocks in many aquifers and is released through natural weathering processes (Dowling

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et al., 2002; Ahmed et al., 2004; Polizzotto et al., 2005; Lowers et al., 2007). Natural sources of arsenic include sulfide minerals (e.g., pyrite, mackinawite, arsenopyrite, realgar, orpiment) and arsenic adsorbed onto mineral oxides (Smedley and Kinniburgh, 2002). Arsenopyrite (FeAsS) and arsenic-rich pyrites ($FeAs_xS_{2-x}$) are commonly found in hydrothermal sulfide deposits and diagenetic sediments with high sulfur and organic matter contents such as black shale (Brown et al., 1999; Wilkin, 2001; Farquhar et al., 2002; Kober et al., 2005; Paikaray et al., 2005; Blanchard et al., 2007; Lowers et al., 2007). Under anoxic conditions and with high (mM) concentrations of arsenic, arsenite partitioned onto pyrite appears to form a surface solid phase of arsenopyrite by substitution for sulfur (Bostick and Fendorf, 2003). Therefore, arsenopyrite may provide a model mineral for the study of arsenic mobilization from pyrite.

During pyrite weathering, associated trace metals and metalloids including As, Cd, and Pb are released to the dissolved phase (Bednar et al., 2002) and such trace elements may accelerate pyrite weathering compared to the pure mineral (Savage et al., 2000; Lehner et al., 2007; Lehner and Savage, 2008). The release of arsenic from arsenopyrite and arsenic-rich pyrite has been examined under oxidizing conditions (Komnitsas et al., 1995; Nesbitt et al., 1995; Nesbitt and Muir, 1998; Craw et al., 2003; Yu et al., 2004) and at the extremely low pH of acid mine drainage (Komnitsas et al., 1995; Yu et al., 2004), but not at neutral pH and under hypoxic or redox disequilibrium conditions where sulfide and oxygen or other oxidants may coexist due to biological activity and groundwater flow.

Sulfide is produced by sulfate reducing anaerobes in groundwater only under anoxic conditions where sulfate is present at concentrations high enough to support its use as a terminal electron acceptor (Singleton, 1993; Saunders et al., 2005; Roesler et al., 2007). Under such conditions, dissolved arsenite and arsenate may react with sulfide to form solid phases (Das et al., 1996; O'Day et al., 2004) or aqueous complexes (Stauder et al., 2005). In addition, soluble arsenite may adsorb onto iron sulfide minerals such as troilite, mackinawite, and pyrite (Farquhar et al., 2002; Bostick and Fendorf, 2003; Wolthers et al., 2005; Lowers et al., 2007). The interactions between sulfide and solid phase iron arsenides, however, have not been systematically examined.

Arsenic may be mobilized from arsenopyrite by reaction with sulfide in the presence of oxygen (or another oxidant) through sulfide–arsenide exchange:

$$\begin{aligned} &FeAsS + HS^- + H^+ + 5/4O_{2(aq)} + 1/2H_2O \\ &\quad \rightarrow FeS_2 + As(OH)_{3(aq)} \end{aligned} \tag{1}$$

This reaction is thermodynamically very favorable ($\Delta G^{\circ\prime}_{298} = -510\ kJ\ mol^{-1}$ at pH 8; see Table EA1 in the Electronic Annex for species free energies and in situ concentrations) as are other analogous reactions in which Fe(III) serves as the oxidant in the conversion of arsenide to arsenite. Sulfide–arsenide exchange in arsenopyrite is thought to be important in geothermal systems (Heinrich and Eadington, 1986; Ballantyne and Moore, 1988), but has not been examined at ambient groundwater conditions of low temperature and neutral pH. The oxidation of arsenopyrite by oxygen ($FeAsS + 3/4O_{2(aq)} + 1.5H_2O \rightarrow FeS + As(OH)_{3(aq)}$) occurs in the absence of dissolved sulfide, but it is thermodynamically less favorable ($\Delta G^{\circ\prime}_{298} = -271\ kJ\ mol^{-1}$) than sulfide–arsenide exchange, particularly under hypoxic conditions. The mobilization of arsenic and sulfur from arsenopyrite was recently shown to be enhanced by an autotrophic arsenite oxidizing microorganism (Rhine et al., 2008), but whether this mobilization involves direct oxidation of mineral arsenide or results from a shift in the redox poise of dissolved arsenic remains to be determined.

Since arsenic has been shown to substitute for sulfur in pyrite (Savage et al., 2000) and form an arsenopyrite-like solid (Simon et al., 1999; Bostick and Fendorf, 2003; Blanchard et al., 2007), we hypothesized that sulfide may drive the release of arsenic from black shale pyrites. To examine this hypothesis, we measured the sulfide-driven mobilization of arsenic from arsenopyrite, whole black shale, and isolated black shale pyrite under various redox conditions (hypoxic, oxic, and anoxic) and determined the oxidation state of arsenic in Newark Basin (Lockatong formation) black shale pyrite.

2. MATERIALS AND METHODS

2.1. Materials

Sulfide–arsenide exchange was examined in arsenopyrite, homogenized black shale, and isolated black shale pyrites. Arsenopyrite (FeAsS) was obtained from a commercial supplier and verified as to element content and mineral structure by XRF and X-ray diffraction analyses. Partially weathered black shale (fractured, water-saturated) was collected from an outcrop of the Newark Basin's Lockatong formation near Trenton, New Jersey (As concentration = 6–26 mg kg^{-1}). Black shale pyrites (1–5 mm prior to pulverization, As concentration = 0.2–0.6% by micro-XRF) were chiseled from Newark Basin (Lockatong formation) rock cores. All reagents were analytical grade and solutions were prepared with ultrapure water.

2.2. Abiotic arsenic mobilization experiments

Arsenic mobilization from arsenopyrite, homogenized black shale, and isolated black shale pyrites was examined in batch incubation experiments conducted in the presence or absence of sulfide, under oxic, hypoxic, or anoxic (arsenopyrite and homogenized black shale only) conditions. Rock samples were pulverized to a fine powder, over 95% of which passed through an 80-mesh screen. Visual inspection indicated that clay material accounted for less than 10% of the pulverized black shale pyrite samples. A constant mass of each material (arsenopyrite 0.02 g, black shale 0.2 g, pyrite 0.09 g) was added to 40 ml of 10 mM HEPES–KOH (pH 8) buffer solutions in 50 ml polypropylene tubes and incubated in duplicate. A solution of sodium bisulfide (NaHS, Aldrich) was prepared in deoxygenated (N_2 purged) ultrapure water and added to an initial concentration of 1 mM. Sulfide-free control experiments were also performed for each material. Solids were sterilized by autoclaving at 121 °C for 25 min or immersion in ethanol overnight. The HEPES buffer was sterilized by autoclaving. After sterilization, solids were rinsed with sterile buffer solution three times in order to remove loosely bound arsenic including iron arsenate or iron arsenite surface coatings on arsenopyrite or pyrite (Nesbitt et al., 1995). Oxic experiments were performed using air-equilibrated buffer. Hypoxic conditions were established in a glove bag flushed with high purity N_2 for 10 min. For hypoxic and anoxic experiments, buffer solutions were purged with high purity N_2 for at least 30 min. During hypoxic incubations, oxygen concentrations increased from 30 to 70 μM over 3 days. Anoxic conditions were established in an anaerobic chamber (N_2:H_2 = 95:5) where oxygen is strictly excluded. Subsamples were removed from anoxic incubation tubes within the chamber to avoid oxygen exposure. All batch experiments were conducted at room temperature (20 °C).

Batch reactors were sampled for soluble arsenic at 0.5 h after initiation and once or twice a day up to 4 days thereafter. Prior to sampling, tubes were centrifuged at 3200 rpm for 5 min and 1–10 ml of particle-free supernatant was taken and preserved with EDTA (final concentrations of 1.25 mM for arsenopyrite samples, 0.125 mM for black shale and pyrite samples) in 15 ml polypropylene tubes. Samples were stored in the dark at 4 °C until analysis. The addition of EDTA was necessary to preserve arsenic oxidation states (Bednar et al., 2002). Arsenic concentrations and speciation were determined within 48 h of collection.

2.3. Biological arsenic mobilization from black shale under sulfate reducing conditions

Biological mobilization of arsenic from homogenized black shale under sulfate reducing conditions was examined in 84 day batch incubation experiments. Slurries of unsterilized, pulverized Newark Basin black shale (10% w/v) were prepared in triplicate in acid-washed, 160 ml serum bottles with sterilized, deoxygenated (N_2 purged) BT culture media (41 mM phosphate, pH 7) containing 0.4 mM sulfate and 10 mM acetate. For biologically active treatments, unsterilized black shale was used as the microbiological inoculum. For abiotic controls, dry pulverized shale was autoclaved under argon gas for 30 min, three times over 3 days prior to preparation of slurries. Biologically active and sterile slurries were incubated at 30 °C in the dark and thoroughly mixed each day. Samples for arsenic analysis were collected periodically from the overlying water of settled slurries (prior to mixing).

2.4. Analytical techniques

Soluble arsenic in the abiotic mobilization experiments was measured by anodic stripping voltammetry (ASV) using a gold-plated, nano-array carbon electrode (Trace-Detect Nano-Band^{TM}) with a platinum wire auxiliary electrode and a Ag/AgCl/KCl reference electrode (Huang and Dasgupta, 1999). Reagent grade concentrated hydrochloric acid and nitric acid were used to acidify samples to pH less than 2 before analysis. Arsenite was reductively plated as elemental arsenic on the electrode at a potential of −400 mV for 20–60 s. Arsenic was stripped from the electrode by anodic scanning from −400 to +800 mV with a step voltage of 17 mV and a frequency of 1250 s^{-1}. Since ASV only detects As(III), total dissolved As was detected after reduction of As(V) to As(III) with sodium thiosulfate (0.5 N) for at least four minutes (Anezaki et al., 1999). Sodium arsenite ($NaAsO_2$) was dissolved in 1% (v/v) HCl to make a 1000 ppm As(III) stock solution. Working solutions of As(III) were prepared daily from the stock solution. Calibration was performed before each group of analyses. The detection limit of As(III) analysis by ASV was 4 nM based on three times the standard deviation of the blank. The pH in each solution was measured using an Accumet Basic (Fisher scientific) pH electrode and dissolved oxygen was measured using a DO electrode (model 850, Thermo Orion). Total soluble arsenic in the biological mobilization experiment was measured by ICP-MS at Rutgers Environmental and Occupational Health Sciences Institute (Xie et al., 2006).

The oxidation state of arsenic in Newark Basin pyrite was determined by X-ray absorption-near edge structure (XANES) spectroscopy. Arsenic K-edge absorption spectra were collected at the National Synchrotron Light Source at Brookhaven National Laboratory on beamline X-11A. Experiments were conducted using isolated black shale pyrites (As concentration = 0.2–0.6%) chiseled from Newark Basin (Lockatong formation) rock cores and pulverized to a fine powder. K-edge data were calibrated by defining the inflection point of the gold L_3-edge. The energy value assigned to the Au L_3-edge was 11.919 keV. Gold foil spectra were also measured between sample runs. XANES measurements were collected from 11.800 to 12.200 keV in fluorescence mode. For data analysis, the background was subtracted and the jump height was normalized to unity using the software WinXAS (Ressler, 1997). Experimental spectra of the pulverized black shale pyrite were compared to powder arsenic reference standards including the As(III) oxide, sodium arsenite ($NaAsO_2$), the As(II) sulfide, realgar (AsS), and the As(-I) iron sulfide, arsenopyrite (FeAsS).

3. RESULTS

3.1. Sulfide-driven arsenic mobilization from arsenopyrite

Arsenic mobilization from arsenopyrite was enhanced by sulfide under oxic and hypoxic, but not anoxic conditions. In the absence of sulfide, 2–5 μM of soluble arsenic was released from arsenopyrite in 24 h under all redox conditions (Fig. 1). The release of soluble arsenic from arsenopyrite (as well as from whole black shale and black shale pyrite, see below) in the absence of sulfide was likely due to the dissolution of small amounts of arsenate or arsenite solids left on the mineral surfaces after rinsing with buffer. With the addition of 1 mM sulfide, however, more than 20 μM of soluble arsenic was released from arsenopyrite in 24 h under oxic and hypoxic conditions (Fig. 1). In

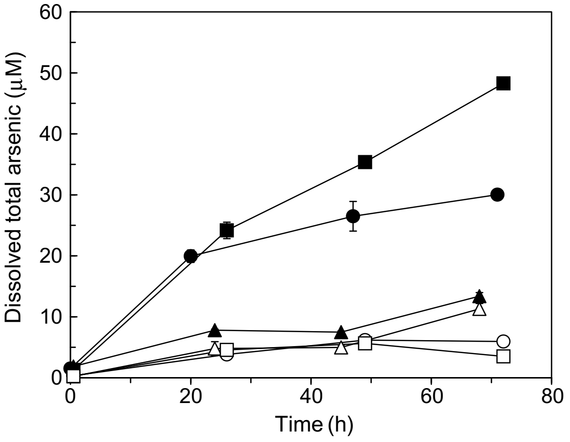

Fig. 1. Mobilization kinetics of total arsenic from arsenopyrite incubated at pH 8 under oxic (20% O_2; circles), hypoxic (≈2% O_2; squares), and anoxic (5% H_2, 95% N_2; triangles) conditions with (filled) or without (open) 1 mM sulfide. Means of duplicate incubations are plotted; error bars show upper and lower values.

addition, the release of soluble arsenic from arsenopyrite continued in the oxic and hypoxic incubations for up to 72 h in the sulfide treatments, but ceased after 24 h in those without sulfide (Fig. 1). Sulfide did not enhance arsenic mobilization from arsenopyrite in the anoxic treatment. Among all incubations, the highest total soluble arsenic concentrations after 72 h were found in the hypoxic-sulfide treatment, followed by the oxic-sulfide treatment (Fig. 1). Note that only 20–25% of the initial added sulfide was consumed by reaction with oxygen in oxic and hypoxic treatments without minerals or shale over 72 h.

Both arsenite and arsenate were generated by decomposition of arsenic mobilized from arsenopyrite in oxic and hypoxic incubations (Fig. 2). The temporal patterns of total arsenic mobilization from arsenopyrite was similar to that of arsenite indicating that arsenate (difference between total arsenic and arsenite) was produced from the oxidation of mobilized arsenite.

3.2. Sulfide-driven arsenic mobilization from homogenized black shale and isolated black shale pyrite

The general patterns of arsenic mobilization from homogenized whole black shale and isolated black shale pyrite were similar to those observed with arsenopyrite; arsenic mobilization was higher in the presence than absence of sulfide and the rates and extents of arsenic mobilization were higher under hypoxic than oxic conditions (Figs. 3 and 4). In contrast to the arsenopyrite experiments, however, soluble arsenic concentrations declined after 50 h in oxic and hypoxic incubations of whole black shale and black shale pyrite in the presence of sulfide (Fig. 3) and all arsenic mobilized from whole black shale and black shale pyrite was present as arsenate. Soluble arsenic was below detection (4 nM) in anoxic incubations of whole black shale in both sulfide and sulfide-free treatments.

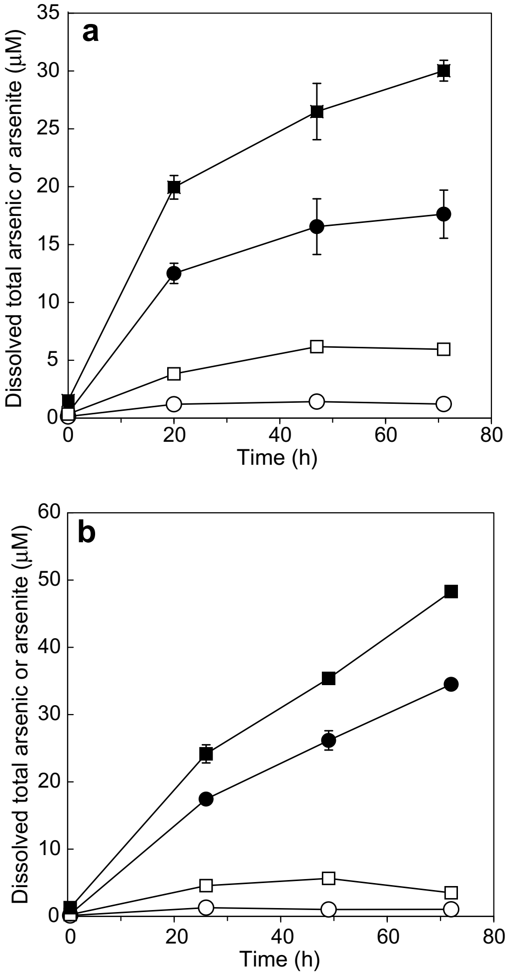

Fig. 2. Mobilization kinetics of total arsenic (squares) and arsenite (circles) from arsenopyrite under oxic (a), and hypoxic (b) conditions with (filled) or without (open) 1 mM sulfide. Arsenite was measured by ASV in acidified samples and total arsenic was measured after reduction with thiosulfate. Means of duplicate incubations are plotted; error bars show upper and lower values.

3.3. XANES spectroscopy of arsenic in black shale pyrite

The energy positions of the XANES edge for arsenic in sodium arsenite, realgar, and arsenopyrite were 11.870, 11.868, and 11.867 keV, respectively (Fig. 5). The XANES data indicate that the position of the As K-edge shifts to lower energies with decreasing oxidation states. The peak position of the edge measured for arsenic in black shale pyrite was 11.867 keV. A comparison of inflection points of the XANES spectra indicates that the arsenic hosted in the Newark Basin black shale pyrite has the same oxidation state (−1) as arsenic in the arsenopyrite standard.

3.4. Biological arsenic mobilization from homogenized black shale under sulfate reducing conditions

Immediately following the addition of unsterilized and autoclaved black shale to deoxygenated culture media (within 10 min), 1.0 and 1.5 μM, respectively, of soluble

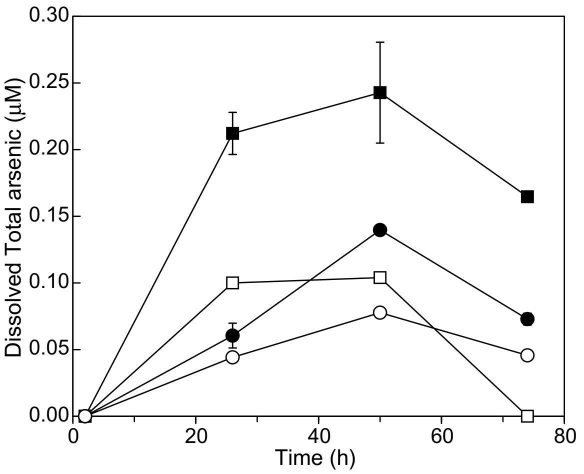

Fig. 3. Mobilization kinetics of total arsenic from homogenized Newark Basin black shale under oxic (circles) and hypoxic (squares) conditions with (filled) or without (open) 1 mM sulfide. Means of duplicate incubations are plotted; error bars show upper and lower values.

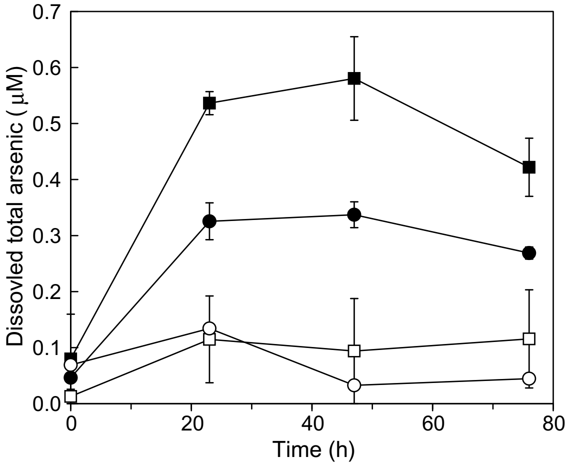

Fig. 4. Mobilization kinetics of total arsenic from isolated Newark Basin black shale pyrite under oxic (circles) and hypoxic (squares) conditions with (filled) or without (open) 1 mM sulfide. Means of duplicate incubations are plotted; error bars show upper and lower values.

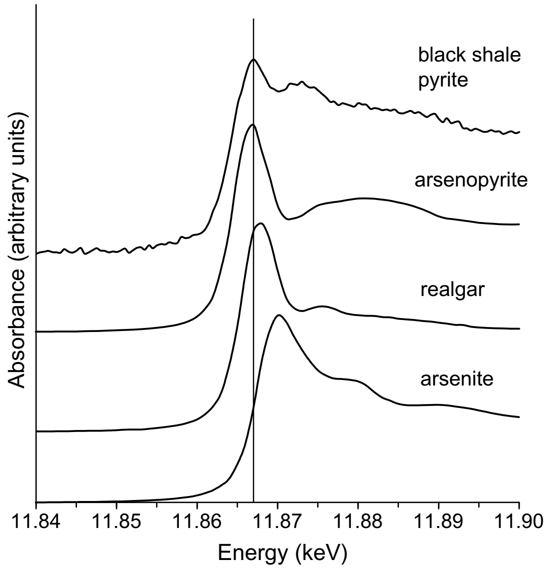

Fig. 5. Arsenic K-edge X-ray absorption-near edge structure (XANES) for the As(III) oxide, sodium arsenite ($NaAsO_2$), the As(II) sulfide, realgar (AsS), the As(-I) iron sulfide, arsenopyrite (FeAsS), and arsenian pyrite isolated from Newark Basin (Lockatong formation) black shale. Vertical line shows peak arsenic absorbances for arsenopyrite and Newark Basin arsenian pyrite (11.867 keV).

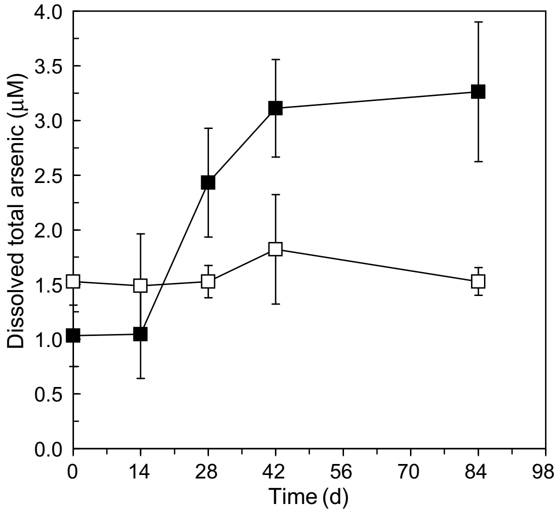

Fig. 6. Arsenic mobilization from homogenized Newark Basin black shale incubated under biologically active, sulfate reducing (filled squares) and sterile (open squares) conditions. Values are means of triplicate incubations ±1 standard deviation.

arsenic was released (0 day in Fig. 6). These initial concentrations of soluble arsenic were likely due to the desorption of loosely bound arsenate or arsenite associated with the unrinsed black shale. (Note that the concentration of shale was 20 times higher in these mobilization experiments than in the sulfide–arsenide exchange experiments described in Section 3.2.) After the initial release of adsorbed arsenic, little or no arsenic was mobilized from the black shale during the first 14 days of the incubations under biologically active or sterile conditions (Fig. 6). However, from 14 to 42 days, more than 2 μM arsenic was mobilized from the black shale in the biologically active treatment, while only 0.3 μM arsenic was mobilized in the sterile control (Fig. 6). The time lag of arsenic mobilization in the biologically active treatment during the first 14 days may reflect the acclimation of the microbial community to the experimental media. After 42 days, the concentration of soluble arsenic remained constant in the biologically active treatment, but decreased in the sterile control.

4. DISCUSSION

4.1. Sulfide-driven arsenic mobilization from arsenopyrite and pyritic black shale

The results presented here show that sulfide increases the mobilization of arsenic from arsenopyrite, whole black shale, and isolated black shale pyrite under hypoxic and oxic conditions compared with sulfide-free controls. We propose that this mobilization occurs via sulfide–arsenide exchange as in reaction (1). Other processes that could have driven arsenic release in our experiments include the oxidation of arsenopyrite or arsenian pyrite and sulfide complexation of dissolved arsenic. Sulfide-free controls showed little arsenic mobilization (Figs. 1–4) confirming that purely oxidative arsenic mobilization did not occur to a major extent. Sulfide complexation of dissolved arsenic (i.e., formation of thioarsenites or thioarsenates) should have driven arsenic mobilization under anoxic as well as oxic and hypoxic conditions, but arsenic mobilization was lowest in the anoxic treatments.

For arsenopyrite, sulfide–arsenide exchange is thought to be important in low pH, geothermal systems (Heinrich and Eadington, 1986; Ballantyne and Moore, 1988), but our results demonstrate its potential importance in low temperature circum-neutral pH settings as well. We can extend this mechanism to black shale arsenian pyrite using arsenopyrite as a model mineral for sulfide-driven arsenic mobilization and by comparing the chemical forms of arsenic in black shale pyrites and arsenopyrite. It was previously shown by X-ray photoelectron spectroscopy that 85% of the arsenic in arsenopyrite is present as arsenide (-1 oxidation state) with the remaining 15% present as elemental arsenic (Nesbitt et al., 1995). Furthermore, previous XANES measurements have shown that arsenic is present as As(-1) in arsenian pyrite (Simon et al., 1999; Savage et al., 2000). Our XANES results (Fig. 5) are consistent with these studies and show that arsenic in Newark Basin black shale pyrite is most likely present as arsenide (-1 oxidation state). Black shale arsenian pyrite may therefore be susceptible to the same sulfide-driven arsenic mobilization process as occurs in arsenopyrite.

The lack of an effect of sulfide on arsenic mobilization from arsenopyrite and whole black shale under anoxic conditions indicates that sulfide-driven arsenic mobilization from both materials requires an oxidant as in reaction (1).

All three materials released more arsenic under hypoxic (30–70 μM O_2) than oxic conditions. This may have resulted from the formation of iron oxide crusts on pyrite surfaces in the oxic treatments that slowed or prevented reactions of solid phase arsenic with sulfide (Komnitsas et al., 1995; Nesbitt et al., 1995; Schaufuss et al., 2000; Yu et al., 2004; Walker et al., 2006). In addition, the oxidation of sulfide was more rapid under oxic than hypoxic conditions decreasing sulfide's reactive lifetime.

In the proposed sulfide–arsenide exchange reaction, arsenic is mobilized as arsenite, but soluble arsenate represented 30–70% of dissolved arsenic in the oxic and hypoxic incubations of arsenopyrite and was the only soluble form of arsenic detected in the whole black shale and black shale pyrite experiments. Soluble arsenate in these experiments was likely produced by the oxidation of mobilized arsenite in solution. Since the concentrations of dissolved arsenic were 100 times higher in the arsenopyrite incubations than in the black shale and black shale pyrite incubations, only partial oxidation of mobilized arsenite occurred with arsenopyrite, while with the black shale and black shale pyrite, arsenite oxidation was nearly complete. Desorption of arsenate from arsenopyrite and pyrite surfaces can occur (Yu et al., 2004), but much if not all adsorbed arsenate should have been removed by rinsing with incubation buffer prior to the start of these experiments (Nesbitt et al., 1995). Another possible source of arsenate is the production of thioarsenate ($H_2AsO_3S^-$) by the reaction of arsenite and sulfide or elemental sulfur (Stauder et al., 2005), however, this would only be possible in the sulfide treatments.

The precipitation of orpiment could not have removed soluble arsenite in the whole black shale and black shale pyrite experiments since it was undersaturated in these incubations. However, arsenite could have been selectively removed from solution by adsorption since at pH 8, arsenite shows greater adsorption on iron sulfide minerals than arsenate (Bostick and Fendorf, 2003).

Although the mechanistic details of sulfide–arsenide exchange will require further study, it is likely that this reaction proceeds by the initial binding of sulfide to iron on arsenopyrite or arsenian pyrite surfaces destabilizing solid phase arsenide. Destabilized arsenide on the surface of these minerals would be susceptible to oxidation by aqueous or solid phase oxidants. The oxidation and subsequent hydrolysis of arsenic would lead to the release of soluble arsenite and allow bound sulfide to form pyrite.

4.2. Implications for the environment

Groundwater arsenic concentrations in sedimentary rock aquifers often exceed the U.S. Maximum Contaminant Level of 10 $\mu g\ L^{-1}$ (0.13 μM) (Welch et al., 2000; Ryker, 2003). Although the weathering of pyritic black shale appears to be the ultimate source of arsenic to groundwater in sedimentary rock aquifers (Peters and Burkert, 2008), the mechanism of arsenic mobilization is unclear. Our results indicate that a sulfide–arsenide exchange and oxidation reaction may drive arsenic mobilization from sedimentary rock pyrites. This mechanism will be most important at the boundary of oxidizing and reducing environments that support sulfate reducing bacteria. Such conditions of redox disequilibrium occur in confined aquifers where oxygenation rates are slow and hypoxic and anoxic groundwaters mix (Massmann et al., 2003; Yamanaka et al., 2007).

The redox stoichiometry of sulfide–arsenide exchange indicates that if sulfide is present, arsenic may be mobilized from arsenopyrite and arsenic-rich pyrite only when an oxidant is available. In natural groundwater, Fe(III), Mn(IV), or nitrate could serve as oxidants in the absence of oxygen. Indeed the energetics of sulfide-driven arsenic mobilization from arsenopyrite (at pH 8) are favorable for reactions with $Fe(OH)_3$ ($\Delta G^{o\prime}_{298} = -143\ kJ\ mol^{-1}$), MnO_2 ($\Delta G^{o\prime}_{298} = -405\ kJ\ mol^{-1}$), or nitrate ($\Delta G^{o\prime}_{298} = -360\ kJ\ mol^{-1}$).

Analogous thermodynamic calculations are not possible for arsenian pyrite which is a heterogeneous solid of variable composition. However, we can predict that arsenic-enriched pyrite surfaces of arsenian pyrite are less stable than pure arsenopyrite. In this case, sulfide–arsenide exchange with arsenian pyrite will be even more favorable than that for arsenopyrite. Arsenic mobility in fractured rock aquifers containing pyritic black shale will therefore be determined in part by the concentrations of sulfide and available oxidant. Sulfide-driven arsenic mobilization reactions will proceed until the surfaces of the exposed arsenopyrite or arsenian pyrite are depleted of arsenic and enriched in pure pyrite. Once new arsenic-rich surfaces become exposed through the oxidation of surface pyrite and/or the formation of new fractures in the shale, the process will begin again.

The mobilization of arsenic in biologically active incubations under sulfate reducing conditions (N_2 atmosphere, sulfate, organic carbon) was seven times higher than in sterile controls (Fig. 6). One explanation for this result is that sulfide generated by sulfate reducing bacteria in the biologically active incubations drove arsenic mobilization from the solid phase as in our abiotic experiments, although other direct or indirect, microbially catalyzed processes resulting in the dissolution of the solid phase are also possible. The continuous mobilization of arsenic over a period of four weeks in the biologically active treatments (Fig. 6), compared with a time scale of arsenic release of only 2 days in the abiotic sulfide exchange experiments (Fig. 3), reflects the continuous production of sulfide by sulfate reducing bacteria during their growth and provides a more realistic model of how this process may occur in an aquifer. Sulfate reduction has been shown to lower dissolved arsenic levels in unconsolidated glacial aquifers, presumably through the precipitation of arsenic sulfides and/or iron sulfides (Kirk et al., 2004). In sedimentary rock aquifers with major formations of pyritic black shale, however, our results suggest that microbial sulfide production will enhance arsenic mobilization to groundwater.

The importance of sulfide–arsenide exchange to arsenic mobilization in a given black shale aquifer will depend on the relative rates of this and competing processes. Our results show that the abiotic mobilization of arsenic from arsenopyrite and black shale arsenian pyrite by reaction with oxygen is much slower than that of sulfide–arsenide exchange (Figs. 1–4). Moreover, the maximum specific rate of arsenic mobilization from arsenopyrite by sulfide exchange observed here ($5.4 \times 10^{-3}\ d^{-1}$) is comparable to that for biological mobilization of arsenic from arsenopyrite catalyzed by a dense, lab-grown culture of an arsenic oxidizing aerobe ($9.3 \times 10^{-3}\ d^{-1}$) (Rhine et al., 2008). This indicates that, if conditions are favorable (sulfide and an oxidant are present), sulfide–arsenide exchange has the potential to compete with biologically driven mobilization of arsenic from arsenian pyrite.

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APPENDIX A. SUPPLEMENTARY DATA

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