Iron isotope investigation of hydrothermal and sedimentary pyrite and their aqueous dissolution products

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1 ABSTRACT

Oxidative dissolution experiments were carried out on pyrite from multiple petrogenetic environments (hydrothermal, sedimentary fossil replacement, and coal-related nodules) to investigate possible variations in the iron isotopic composition of pyrite and the products of pyrite dissolution. The experimental materials were leached under carefully controlled abiotic conditions, and a subset of leachates and starting materials from these experiments was analyzed for $^{56}\text{Fe}/^{54}\text{Fe}$ by multicollector ICP-MS. Bulk pyrite $\delta^{56}\text{Fe}$ values (relative to IRMM-014) ranged from -0.1 to +1.3‰, with hydrothermal bulk pyrite values $< +0.5\text{‰}$ and those of coal and sedimentary nodular pyrite $\geq +0.5\text{‰}$, higher than most previously measured values for Phanerozoic sedimentary pyrite. We suggest that this reflects precipitation of coal pyrite from a high- $\delta^{56}\text{Fe}$ continental source, such as Fe derived from dissolution of Fe(III) oxides. This could allow differentiation of Fe contributed from coal- and shale-related pyrite at abandoned mine drainage sites. Leachates from oxidative dissolution of the pyrite at pH=3 yielded, with few exceptions, $\delta^{56}\text{Fe}$ values equal to or lower than those of the coexisting bulk pyrite, by up to about 1‰. These shifts are consistent in direction (but not magnitude) with equilibrium isotope fractionation predictions from theory, with possible second order effects from isotopic heterogeneity within individual natural pyrite samples.

1. Introduction

Iron sulfides constitute a diverse group of solid and dissolved complexes in aqueous geochemical systems, and play an essential role in regulating and controlling the global geochemical Fe and S cycles. Pyrite (FeS_2), the most common sulfide mineral on the Earth's surface (Vaughan, 2006), is found in a wide variety of geologic environments. It can form under high temperature conditions, including contact metamorphism and hydrothermal fluid circulation, and in low temperature ($<100^\circ\text{C}$) sedimentary environments. In the latter case, pyrite is considered a redox buffer in anoxic conditions, and its presence is a strong indicator of reducing conditions (Descostes et al., 2004). Metastable Fe sulfide phases have important roles in biogeochemical processes (Rickard and Luther, 2007). In addition, oxidative dissolution of Fe sulfide minerals is the cause of acid mine drainage (AMD), a serious water quality problem in coal and metal mining regions.

Experimental studies of pyrite dissolution, conducted primarily on hydrothermal pyrite, have shown that the rate of pyrite oxidation is dependent on factors such as pH, dissolved oxygen, ferric Fe concentrations and the presence of Fe- or S-oxidizing bacteria (e.g., Singer and Stumm, 1970; McKibben and Barnes, 1986; Moses et al., 1987; Moses and Herman, 1991; Williamson and Rimstidt, 1994; Holmes and Crundwell, 2000; Weber et al., 2004; Paschka and Dzombak, 2004). However, even when these variables are controlled, there can still be significant differences in experimental dissolution rates when pyrite samples from different environments are used as starting material (Liu et al., 2008b).

In this study, Fe isotopes were measured during oxidative dissolution experiments using different pyrite types (hydrothermal, fossil replacement, and sedimentary) as a new approach to track pyrite dissolution, especially under AMD conditions, as well as to identify possible isotope variations due to pyrite petrogenesis. Iron isotopes are fractionated during biological and abiotic

redox changes, organic complexation, bacterial interactions, and surface adsorption and mineral precipitation reactions (Beard and Johnson, 1999; Johnson and Beard, 1999; Anbar et al., 2000; Bullen et al., 2001a; Icopini et al., 2004; Borrok et al., 2009; Czaja et al., 2010; Morgan et al., 2010; Guilbaud et al., 2011). Iron isotopes have been used as a tool to examine sources and mechanisms controlling Fe cycling in freshwater environments and soils (Fantle and DePaolo, 2004; Emmanuel et al., 2005; Ingri et al., 2006; Bergquist and Boyle, 2006; Borrok et al., 2009), and during oxidative weathering of sulfide rich rocks and minerals (Herbert and Schippers, 2008; Borrok et al., 2009; Fernandez and Borrok, 2009). Theoretical estimates using Mössbauer and vibrational spectroscopy predict significant fractionation effects between pyrite and ferrous Fe (Polyakov and Mineev, 2000), but interpretations remain somewhat unclear given the lack of experimental determination of Fe fractionation factors associated with pyrite formation and dissolution (Severmann et al., 2006). This is an investigation of Fe isotope fractionation occurring during pyrite oxidation under highly controlled pH-pO₂ conditions.

2. Methods

2.1. Samples and characterization

The eight pyrite samples used in this study, three hydrothermal and five sedimentary, were the same as those used in the oxidative dissolution experiments reported by Liu et al. (2008b), and their morphology and geological origins are provided in **Table 1**. The hydrothermal pyrite samples are nodular single crystals, while the sedimentary pyrite samples include massive pyrite found within shale (pyrite sun; SED-1), a fossil replacement (SED-2), and nodular pyrite collected from coal seams (SED-COAL-1, SED-COAL-2, SED-COAL-3).

Pyrite samples were crushed, milled, and wet sieved using a procedure developed by Wolfe et al. (2007) to obtain 45-75 µm fractions for use in dissolution experiments. The specific

surface area of each sample was measured by the nitrogen adsorption multipoint BET method with a Quantosorb instrument (ISO, 2010); accuracy of the instrument was verified by measurements on alumina and black carbon standards of known surface area. Particle surfaces were examined pre- and post- cleaning using a Philips XL-30 FEG field emission scanning electron microscope. The crushed and sieved samples were split for geochemical/isotopic analysis and dissolution experiments. The geochemical splits were dissolved in warm nitric acid, and aliquots were taken for trace element and Fe isotope analyses. The remainder of the 45-75 μm material was used for abiotic oxidative dissolution experiments, as reported by Liu et al. (2008b). Three of the samples (HY-3, SED-2, and SED-COAL-1) were also used for electrochemical dissolution experiments (Liu et al., 2008a; 2009).

2.2. Dissolution experiment setup

For each pyrite sample, dissolution rates were determined under oxic conditions in a batch reactor with highly controlled pH and redox conditions (described in Liu et al., 2008b). Prior to the experiments, pyrite samples were treated to remove any surface Fe oxides or Fe sulfates that could have been produced when the samples were exposed to the atmosphere. This procedure, a modified version of a method used by Paschka and Dzombak (2004), involved boiling 7–8 g of pyrite in 50 ml concentrated hydrochloric acid (HCl) for approximately 10 minutes. The sample was rinsed with boiling concentrated HCl at least twice, then rinsed with 25 ml deionized water, followed by a boiling acetone rinse using a vacuum filter. The acetone rinse was repeated a minimum of three times. The sample was dried in an oven at 115°C for about 10 minutes and stored in a desiccator. Samples were used within two hours of preparation. Specific surface area measurements were conducted prior to the cleaning procedure.

A 5.355 ± 0.005 g aliquot of the cleaned pyrite was added to 1.5 L of deionized water in a stirred, jacketed glass vessel with a lid having sealed ports for insertion of reagents and withdrawal of samples from the reactor; the initial ionic strength was adjusted by addition of 0.01 M sodium chloride (NaCl). During the experiments, the reactor was covered with aluminum foil to exclude light, and the temperature was kept at $25 \pm 0.01^\circ\text{C}$. A constant pH of 3.00 ± 0.05 , to mimic the AMD environment and inhibit oxidation and precipitation of the released Fe, was maintained by the addition of HCl or sodium hydroxide (NaOH) via acid/base pumps and a pH-stat. The concentration of dissolved oxygen was maintained in the range of 9-12 ppm (corresponding to freshwater air saturation concentrations at temperatures $< 25^\circ\text{C}$; Colt, 2012) by controlling the oxygen partial pressure in the reactor headspace (Paschka and Dzombak, 2004; Liu et al., 2008b).

Concentrations of Fe and S were measured in the leachate to monitor pyrite dissolution. Five milliliters of sample were collected periodically over a 24 hour time period, and then filtered through a $0.45\ \mu\text{m}$ disposable filter into a 20 ml polyethylene scintillation vial containing 5 ml 10% nitric acid (HNO_3) for Fe and S elemental analyses. A three-way stopcock was used for sampling to ensure the headspace of the reactor would remain unaffected by the outside environment during the experiments. Additional details are provided by Liu et al. (2008b).

2.3. Elemental analyses

Total dissolved iron in the leachates was measured using atomic absorption spectroscopy (AA); flame AA was used for samples containing iron concentrations greater than the detection limit of $100\ \mu\text{g/L}$ and graphite furnace AA was used for samples with lower concentrations of iron (detection limit = $1.0\ \mu\text{g/L}$; Liu, 2007). Dissolved sulfur concentrations within the experimental leachates and S and Fe concentrations in the bulk pyrite digestions were measured

on a SpectroFlame End-On Plasma inductively coupled plasma atomic emission spectrometer (ICP-AES) using EPA Method 6010C (US EPA, 2007). Accuracy of measurements was within $\pm 5\%$ of true values. Instrument calibration was carried out using standard solutions (5% nitric acid matrix) containing different concentrations of Fe and S. All the aqueous samples were preserved in a 5% nitric acid matrix before ICP-AES and AA measurements. In the dissolved bulk pyrite solutions, abundances of more than 40 trace elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) by contract with Activation Laboratories Ltd., Ontario, Canada.

2.4. Isotopic analyses

Aliquots of leachate samples from each pyrite dissolution experiment were collected for Fe isotope analysis at 1, 8 and 24 hours from the start of the experiment, with the exception of sample HY-3, in which the first sample was collected at 6 hours. The isotopic composition of the leachate collected at each time interval (1, 8, and 24 hr) is cumulative (versus cyclic, e.g., Fernandez and Borrok, 2009) and reflects the average of all isotopic changes prior to each sampling interval. Aliquots of the bulk dissolved samples (HY-1, HY-2, SED-1, SED-COAL-1, SED-COAL-3) were quantitatively separated for Fe isotope analysis. Iron separations for all samples were conducted in a laminar flow clean hood based on a procedure modified after Bullen et al. (2001b). Aliquots containing at least 20 μg of Fe were evaporated to dryness in Teflon containers and redissolved in 5 mL of 6.0 N HCl for anion exchange chromatography. The solution was loaded onto an anion exchange column (BioRad AG1X8) previously cleaned with alternating 1.0 N HCl and ultrapure water. The resin was then conditioned using 6 ml of 6.0 N HCl. After the sample solution had been loaded on the resin, the matrix was removed in 11 ml of 6.0 N HCl and 1 ml of ultrapure water. The Fe was eluted with alternating 1 ml aliquots of 1.0

N HCl and ultrapure water, evaporated to dryness, and then the column separation procedure was repeated. After passing through the column a second time, the sample was evaporated to dryness and redissolved in 2% HNO₃ for MC-ICP-MS analysis. Columns were calibrated throughout the procedure using matrix-matched samples to ensure quantitative yields within error of Fe concentration measurements.

Isotopic ratios were measured at Arizona State University using a Thermo Neptune multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Solutions were analyzed at a concentration of 2-3 ppm Fe with a NIST Cu spike added to correct for instrumental mass bias (Maréchal et al., 1999; Arnold et al., 2004). Sample solution duplicates and one procedural blank were analyzed for each petrogenetic group of samples. All reported Fe isotopes values reflect the average of replicate measurements. The ratios ⁵⁶Fe/⁵⁴Fe and ⁵⁷Fe/⁵⁴Fe were measured simultaneously; as a quality control measure, analyses that did not demonstrate the expected mass-dependent relationship within 0.03‰ per amu between these ratios were rejected and rerun. Samples were run with an in-house ICP Fe solution as the bracketing standard and corrected to the international IRMM-014 Fe standard. IRMM-014 and TAG-01 (an in-house marine sediment digest) were run in parallel with the samples, and gave values accurate to within 0.05‰ from the long-term laboratory average. In addition, two standards (Grav-ICPB and GrvIRMM) had been created by addition of a calibrated ⁵⁴Fe isotope spike to a known 1.05‰ from their respective standards. Both of these “gravimetric” standards gave values within 0.05‰ from their independently known values. The measured δ⁵⁶Fe values were compared with and without normalization to a constant NIST Cu ratio, and there was always less than a 0.13‰ difference between the two methods of calculation, indicating that the samples had low residual matrix and that the instrumental mass bias was smoothly varying during the analyses. Isotopic ratios are expressed in standard delta notation (in units of per mil, ‰) relative to IRMM-014:

$$\delta^{56}\text{Fe} = \left[\left(\frac{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{sample}}}{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{IRMM}}} \right) - 1 \right] \times 1000$$

The measurement uncertainty (2σ) was less than $\pm 0.1\%$ of the reported $\delta^{56}\text{Fe}$ value.

3. Results

3.1. Bulk pyrite sample characterization

X-ray diffraction analyses (Philips XRD PW3710) indicated that all samples consisted primarily of pyrite, although SED-COAL-3 contained minor ($\leq 10\%$) quartz. Chemical analyses of Fe and S concentrations in the bulk pyrite samples confirmed stoichiometric FeS_2 in the starting material (i.e., S:Fe molar ratio = 2; **Table 1**). Chemical analyses of more than 40 trace elements, including the rare earth elements (REE), showed that hydrothermal pyrite samples generally contained more Co, Bi and Te, and less Tl, Ba, Rb and Sr than the sedimentary pyrite samples (**Table 2**). Sedimentary samples associated with coal (SED-COAL-1, -2, and -3) contained more Hg compared to the other sedimentary (SED-1 and -2) and hydrothermal pyrite samples.

REE concentrations can provide information about the source of solutes in solutions associated with pyrite formation. Because the REE do not readily substitute for major constituents in the pyrite structure, they are thought to be held in fluid inclusions or crystal defects (Zhao and Jiang, 2007), and the patterns reflect those of the mineralizing fluids (Mills and Elderfield, 1995; Song et al., 1997). The REE concentrations in most of the pyrite samples analyzed here fell below chondritic values (Anders and Grevasse, 1989), with the exceptions of SED-COAL-2 and HY-3 (**Table 2, Fig. 1**). The sedimentary pyrite samples generally showed an enrichment in light REE (i.e., La to Sm) similar to that of the North American Shale Composite

(NASC; Gromet et al., 1984), but at significantly lower concentrations. The patterns (but not concentrations) were also similar to those of Pennsylvanian coals analyzed by Schatzel and Stewart (2003). While the lower concentrations in the pyrite from this study were most likely due to exclusion of REE from the pyrite crystal structure, the marked light REE enrichment of the sedimentary pyrite samples suggests derivation of the REE from a shale-like source (i.e., the shale or coal host rock; McLennan, 1989). Two of the hydrothermal pyrite samples (HY-2 and HY-3) exhibited a distinctive middle-REE enrichment superimposed on an overall flat pattern (**Fig. 1**). This is consistent with precipitation from a hydrothermal fluid which may have interacted with multiple rock types before and during pyrite crystallization (Fralick et al., 1989; Mills and Elderfield, 1995; Chen et al., 1998; Zhao and Jiang, 2007).

3.2. Dissolution experiments: Aqueous chemistry vs. time

The dissolved iron and sulfur concentrations in leachate collected during each sampling interval (1, 8, and 24 hours) over the course of the pyrite dissolution experiments, and corresponding S:Fe ratios, are shown in **Table 3**. Experimental results showed that pyrites from different geologic environments exhibited distinctive dissolution behavior (Liu et al., 2008b). Based on the total dissolved Fe released over the experimental period (24 hr), the extent of dissolution was similar for the hydrothermal and the two sedimentary pyrite samples (SED-1, SED-2); however, coal pyrite samples dissolved much faster than the other pyrite samples, with SED-COAL-3 > SED-COAL-1 > SED-COAL-2 > HY-1 > SED-1 > SED-2 > HY-3 > HY-2. When normalized for surface area, these differences are reduced, but not completely eliminated (Liu et al., 2008b). The fraction of total iron released from each sample over the experimental period was <0.13% (range = 0.06 – 0.13%) for hydrothermal and sedimentary pyrite samples, and ranged between 0.5 - 1.1% for the coal pyrite samples. Dissolved S concentrations also

increased over time for all pyrite samples (**Table 3**) and the total fraction of sulfur released into solution from each sample was similar to the trends observed in total Fe calculations (<0.10% for hydrothermal and sedimentary pyrite and ranged between 0.5 – 0.9% for the coal pyrite samples).

Aqueous speciation for dissolved iron and sulfur, in contact with solid (i.e., undissolved) pyrite, was calculated using Visual MINTEQ (summarized in Table 4 and Figure2; Gustafsson, 2012), using measured pH, oxidation-redox potential, dissolved oxygen, sulfur, and iron concentrations, and the (calculated) amount of pyrite remaining in solution at each sampled time interval (i.e., 1, 8, and 24 hr; Liu, 2007). Results indicated that, over the duration of the experiment, iron existed predominantly as $\text{Fe}^{2+}(\text{aq})$, with minor (<0.5%) $\text{FeSO}_4(\text{aq})$, and FeCl^+ ; these results are consistent with previous experimental work with hydrothermal pyrite under the same conditions in which no ferric Fe was detected at any time during the experiment (Paschka and Dzombak, 2004; Liu et al., 2008b). Speciation calculations for sulfur indicated that SO_4^{-2} was the dominant species over the 24-hour experimental period, with minor (<10%) HSO_4^- , $\text{FeSO}_4(\text{aq})$ and NaSO_4^- also present. These calculations support ion chromatography measurements in which sulfate was the only oxidized S species detected (Paschka and Dzombak, 2004). Speciation calculations indicated that the solutions were saturated with respect to elemental sulfur for all samples, at each sampling interval, but decreased over the experimental period. No H_2S (or other sulfur gas, e.g., Descostes et al., 2004) was present.

A solution phase molar S:Fe ratio of 2:1 would be expected from stoichiometric dissolution of pyrite, from a reaction such as

(McKibben and Barnes, 1986). Ratios of S to Fe in the experimental solutions (**Table 3**) demonstrated that pyrite did not dissolve stoichiometrically, at least in the early stages of dissolution. The S/Fe ratio of all samples increased over the duration of the experiment (**Fig. 3**), with the exception of sample SED-COAL-3, where the S/Fe ratio remained approximately constant at ~1.7. Liu et al. (2008b) suggested that the low initial S/Fe ratios (i.e., sulfur deficit) could have resulted from a multistep reaction (after Descostes et al., 2004) involving intermediate thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and tetrathionate ($\text{S}_4\text{O}_6^{2-}$) ions and solid phase elemental sulfur, with the overall reaction:

Druschel and Borda (2006) also present possible reactions involving multiple sulfur species to describe different pathways for pyrite oxidation. Liu et al. (2008b) further suggested that thermodynamically allowable shifts in the stoichiometric coefficients for $\text{S}^0(\text{s})$ and SO_4^{2-} in Eq. (2) could be responsible for S/Fe ratios <1.6. They noted that the S:Fe ratio increased with time, but did not reach the 2:1 molar ratio expected for stoichiometric dissolution. When the amounts of S and Fe released during each time interval during the dissolution experiments (rather than the cumulative total) are calculated (i.e., $[\text{S}]_{8\text{hrs}} - [\text{S}]_{1\text{hr}}$ etc.), it becomes apparent that the *instantaneous* dissolution ratio approaches that of stoichiometric dissolution of pyrite (**Fig. 4**). These trends provide further support that oxidation of pyrite occurred via multiple pathways over the course of the experiment.

3.3. Iron isotope signatures of bulk pyrite material

Iron isotope data for bulk pyrite samples and for the aqueous leachates from the pyrite dissolution experiments are presented in **Table 5** and plotted in **Figure 5**. Bulk pyrite $\delta^{56}\text{Fe}$ values spanned a range from -0.1 to +1.3. In general, hydrothermal bulk pyrite samples exhibited a slightly lower $\delta^{56}\text{Fe}$ value (around 0.0) compared to the sedimentary pyrite samples (+0.5 to +1.3). The $\delta^{56}\text{Fe}$ values for bulk hydrothermal pyrite from this study were within the previously measured range for hydrothermal pyrite (Sharma et al., 2001; Rouxel et al., 2003; 2004; 2008; Graham et al., 2004; Wawryk and Foden, 2015).

3.4. Iron isotopes in leachates

The Fe isotope compositions of hydrothermal and sedimentary pyrite dissolution samples over the experimental reaction periods studied are presented in **Table 5** and plotted against sampling time in **Figure 6**. For those cases where data were obtained for both the bulk pyrite and leachate samples, the leachates were generally lower in $\delta^{56}\text{Fe}$ (i.e., lighter) than the bulk pyrite. The magnitude of offset was typically $<0.5\text{‰}$, but could be as large as 1‰ in some cases (**Figs. 5, 6**), and well outside the experimental uncertainty of $\pm 0.1\text{‰}$. In **Figure 7**, the $\delta^{56}\text{Fe}$ values for the leachates are normalized to the first leachate value and plotted against the sampling time for the oxidative dissolution experiments. In the majority of cases, the leachate values remained constant or decreased with increasing time of leaching. The major exception to this was sedimentary pyrite sample SED-2, which showed a significant increase (0.9‰) from 480 minutes (8 hours) to 1440 minutes (24 hours). $\delta^{56}\text{Fe}$ values from the 60 minute leachate and bulk pyrite were not obtained for this sample. In addition, the coal pyrite sample SED-COAL-3 showed an increase of $\sim 0.2\text{‰}$ from 1 to 8 hours, followed by a significant drop by the 24 hour sampling interval (**Fig. 7**).

4. Discussion

4.1. Iron isotope composition of bulk pyrite samples

The rate and extent to which pyrite forms and accumulates within the environment is principally controlled by the amount of organic matter, the availability of reactive Fe minerals (those that react with sulfide, primarily Fe oxides; Canfield, 1989; Canfield et al., 1992) within the sediment, and the availability of dissolved sulfate. These various reactions and the central role of Fe in them suggest that pyrite formed in different diagenetic environments could have different Fe isotope ratios.

Figure 8 summarizes the Fe isotopic compositions of marine pyrite samples that have been measured to date. Rouxel et al. (2005) analyzed the Fe isotope composition of diagenetic pyrite from marine shales and found systematic variations in the $\delta^{56}\text{Fe}$ range and values over geologic time, with highly negative values (some below -3.5‰) occurring mostly in the Archean (pre-2.3 Ga), positive values up to +1.2 in the Paleoproterozoic (2.3-1.8 Ga), and a fairly narrow range of values (-0.5 to +0.2) from ~1.5 Ga to the present. They interpreted the pyrite as largely recording the Fe isotope composition of seawater, which was controlled by precipitation of Fe oxides (with high $\delta^{56}\text{Fe}$) under varying redox conditions and seawater Fe concentrations. In contrast, Archer and Vance (2006) suggested that multiple cycles of dissimilatory Fe reduction (DIR) were responsible for a wide range of negative $\delta^{56}\text{Fe}$ values (-2.7 to -0.9; **Fig. 8**) that they measured within a small section of core from the Archean Belingwe sedimentary basin in Zimbabwe. Johnson et al. (2008) and Czaja et al. (2010; 2012) identified biological processes as responsible for the wide range of Precambrian $\delta^{56}\text{Fe}$ values, including a bacterial DIR-driven “shuttle” in which strongly ^{56}Fe -depleted iron is captured in a sulfidic trap in the euxinic portions of oceanic basins. Based on lake sediments that serve as an Archean ocean analogue, Busigny et

al. (2014) suggest that Archean pyrite Fe isotope variability reflects precipitation at a migrating redox boundary, probably related to photosynthesis. Meso- and Neoarchean pyrite grains interpreted to be detrital yielded $\delta^{56}\text{Fe}$ values ranging from -3.6 to +1.2 (Hofmann et al., 2009). Nishizawa et al. (2010) analyzed numerous Precambrian sedimentary pyrite grains by laser ablation, and found a wide range of $\delta^{56}\text{Fe}$ values for pre-2.2 Ga sediments (-2.9 to +2.2), while 0.70-0.63 Ga sediments yielded a smaller range of values (-0.2 to +0.6). Laser ablation analysis of 2.7-2.5 Ga marine sediments and 3.7-3.8 Ga metasediments (Yoshiya et al., 2012; 2015) yielded a wide range of values (-4.2 to +2.8). *In situ* secondary ion mass spectrometry (SIMS) analyses of two ~2.7 Ga pyrite nodules yielded $\delta^{56}\text{Fe}$ values ranging from -2.1 to +0.7 (Marin-Carbonne et al., 2014). $\delta^{56}\text{Fe}$ values of pyrite from Phanerozoic and modern sediments were mostly negative, in the range of -1.6 to +0.2 (Fehr et al., 2008; 2010; Duan et al., 2010). However, individual SIMS spots from diagenetic pyrite grains in Holocene Baltic Sea sediments yield $\delta^{56}\text{Fe}$ values ranging from -3.1 to +4.1 (Virtasalo et al., 2013). Iron isotope measurements of mid-ocean ridge hydrothermal sulfides, altered oceanic crust, and a continental Sb-W deposit yielded a range of values from -2.1 to 0.0 (Sharma et al., 2001; Rouxel et al., 2003; 2004), and $\delta^{56}\text{Fe}$ values from a laser ablation study of pyrite from a porphyry Cu-Au deposit ranged from -1.7 to +1.1 (Graham et al., 2004).

The sedimentary and coal nodule bulk pyrite samples analyzed here, all of Paleozoic age, yielded positive $\delta^{56}\text{Fe}$ values that fall outside of the range of most Phanerozoic or modern sedimentary pyrite samples measured to date, with the exception of the SIMS analyses of Holocene Baltic Sea sediments (Virtasalo et al., 2013). The sedimentary pyrite samples studied are likely to have formed in sediments of non-marine or marginal-marine origin (i.e., continental margin coal-forming mires), with the possible exception of SED-2 (**Table 1**). In these settings, the most reactive Fe fraction is fine-grained ferric oxides formed via continental weathering,

while less reactive fractions include clay-bound Fe and other Fe-containing minerals (Berner, 1984). Other sources of Fe may include ionic form in solution, Fe as organic complexes (e.g., Toner et al., 2009), and Fe released by decay of plant debris (Wiese and Fyfe, 1986). Canfield (1989) determined that early pyrite forms almost exclusively from Fe oxides, with little evidence for the involvement of silicate minerals. Precipitation of Fe(III) oxides enriches the oxides in heavy Fe, so Fe oxides likely provided a high- $\delta^{56}\text{Fe}$ pool of Fe from which the sedimentary pyrite precipitated. The high $\delta^{56}\text{Fe}$ of the coal-related sedimentary pyrite nodules argues against a strong biological role in their formation, or fractionation effects related to partial $\text{Fe(II)}_{\text{aq}}$ utilization during abiotic precipitation (Guilbaud et al., 2011), as both would result in relatively low $\delta^{56}\text{Fe}$. Instead, these values suggest a continentally-derived heavy $\delta^{56}\text{Fe}$ oxide source that was almost completely transformed to pyrite.

The positive $\delta^{56}\text{Fe}$ values measured here in coal pyrite contrast with the largely negative shale pyrite values measured in most Phanerozoic marine sediments. This suggests that Fe isotopes have the potential to serve as tracers to identify the source of Fe in acid mine drainage situations; that is, to distinguish between pyrite in coal and pyrite from adjacent marine shale units often associated with coal units. Pyrite from sample SED-2 formed as a fossil replacement during or after diagenesis. This sample, as well as SED-1, was selected for practical reasons in regard to the dissolution experiments, and would not necessarily represent the “typical” $\delta^{56}\text{Fe}$ of Phanerozoic shale pyrite.

4.2. Iron isotope composition of pyrite leachates

The Fe isotope data from the oxidative dissolution experiments indicate: (1) $\delta^{56}\text{Fe}$ values of the leachates were equal to or less than bulk pyrite values, where available (**Fig. 5**); and (2) with a few exceptions, as leaching time increased, the $\delta^{56}\text{Fe}$ values remained constant or decreased

(**Fig. 7**). Fernandez and Borrok (2009) carried out leaching experiments and Fe, Cu and Zn isotope analyses on sulfide-rich rocks associated with hydrothermal metal deposits. These samples, which were crushed and leached in bulk, included mine waste rock and altered volcaniclastic bedrock containing pyrite, chalcopyrite and sphalerite. These authors observed a similar trend of decreasing $\delta^{56}\text{Fe}$ over time, with a drop of $\sim 1\text{‰}$, for experiments conducted at pH=2 (buffered with HCl). A significant difference, however, was that the $\delta^{56}\text{Fe}$ value in their leachates started out higher than the bulk sample, and gradually approached the bulk sample value. In the experiments reported here, most of the leachate values initially were equal to or less than the bulk pyrite value (where available), and remained constant or decreased with time (**Figs. 6, 7**). Fernandez and Borrok (2009) attributed the trend they observed to dissolution of high- $\delta^{56}\text{Fe}$ Fe(III) oxides that formed in the elapsed time between when the rock was crushed and the experiment was started (up to 7 months). In the experiments carried out in this study, care was taken to remove or minimize any Fe oxides or sulfates from surfaces prior to dissolution (Paschka and Dzombak, 2004; Liu et al., 2008b); our Fe isotope results suggest that these surface coatings were successfully removed.

Iron isotope fractionation in solution and the solid phase during pyrite dissolution provides insights into the dissolution processes involved. Theoretical studies by Polyakov and Mineev (2000) and Schauble et al. (2001) suggest that Fe in pyrite should be isotopically heavier than coexisting aqueous Fe(III) at equilibrium. Butler et al. (2005) found measurable isotope fractionation between aqueous Fe(II) and solid FeS (mackinawite) in precipitation experiments; they calculated a kinetic fractionation factor, $\Delta_{\text{Fe(II)-FeS}}$ ($\delta^{56}\text{Fe}$ of Fe(II)[aq] - $\delta^{56}\text{Fe}$ of FeS[s]), of $0.85 \pm 0.30\text{‰}$, and an equilibrium fractionation factor of $\sim 0.3\text{‰}$. Thus, in their experiments, the solid FeS was isotopically lighter than the aqueous Fe(II). Equilibrium pyrite precipitation experiments at 300-350°C by Syverson et al. (2013) yielded a fractionation factor of 0.99‰ , in

good agreement with theoretical calculations. Further work by Guilbaud et al. (2011) demonstrated kinetic isotope fractionations, $\Delta_{\text{Fe(II)}-\text{FeS}_2} \approx \Delta_{\text{FeS}-\text{FeS}_2}$, of +1.7 to +3.0‰ during pyrite precipitation experiments, which they attribute to a change in coordination from $\text{Fe(II)}_{\text{aq}}$ to $\text{Fe(II)}_{\text{pyrite}}$. Czaja et al. (2012) argued that these large fractionations resulted from the rapid precipitation of pyrite during laboratory experiments, and that such fractionation would not be present in geologic environments where pyrite forms slowly. While isotope fractionation is expected and experimentally observed between pyrite and $\text{Fe(II)}_{\text{aq}}$, it is not clear to what extent these experiments can be translated to oxidative dissolution of pyrite. The data obtained in our study did not yield a consistent value for $\Delta_{\text{Fe(II)}-\text{FeS}_2}$, with possible values ranging from 0 to -1. While the direction of fractionation generally agrees with theoretical predictions (Polyakov and Mineev, 2000), there may be other processes controlling the $\delta^{56}\text{Fe}$ of the pyrite leachates. The dissolution of pyrite is an oxidation–reduction reaction and involves the movement of charge across the solid-solution phase boundary (Crundwell, 2013 and references therein). Kavner et al. (2005; 2009) and Black et al. (2010), for example, demonstrated a voltage-dependent Fe fractionation associated with the kinetic effects of electron transfer. The fraction of Fe released from the pyrite in our experiments was <2% of the total pyrite placed in the reactors, precluding a total mass balance calculation.

As discussed earlier and shown in **Figures 3 and 4**, the molar S/Fe ratio increased over the course of most dissolution experiments. This increase corresponded with the generally observed but less consistent decrease in $\delta^{56}\text{Fe}$ values during the dissolution experiments. A change in reaction pathway from, for example, the multistep process summarized in Equation (2) to stoichiometric pyrite dissolution (Eq. 1), as discussed in Section 3.2, could affect the Fe isotope composition of the reaction products. However, there is no clear correlation between the S/Fe ratio (cumulative or instantaneous) and shifts in $\delta^{56}\text{Fe}$ over the course of the experiments. While

kinetic isotope fractionation effects could also contribute to changes in the leachate $\delta^{56}\text{Fe}$, modeling by Visual MINTEQ indicates that pyrite is near equilibrium with the fluid during the dissolution reactions reported here.

Another possible explanation for the decreasing $\delta^{56}\text{Fe}$ values seen in most of the leachates is that some of the initial excess Fe (relative to S) in solution could have been resorbed on the pyrite surface as Fe(III), which would be expected to be enriched in heavy Fe. Thus, by mass balance, the $\delta^{56}\text{Fe}$ of the remaining solution would decrease. This is consistent with the observation that the sample with the greatest surface area (SED-COAL-3; Table 1), therefore possibly with the greatest capacity to resorb Fe, shows the largest decrease in $\delta^{56}\text{Fe}$ at the end of the experimental period (**Figs. 5, 6**). Both ferrous and traces of ferric iron (hydr)oxides have been detected on the pyrite surface, within the domain of acid pH ($\text{pH} \leq 4$), using various analytical techniques (Bonnissel-Gissinger et al., 1998; Rosso and Vaughan, 2006) and speciation modeling (Evangelou, 1995). Fernandez and Borrok (2009) saw evidence of Fe(III) in their pH=5 leaching studies of sulfide-rich rocks, although they did not present S concentrations from their leaching experiments to allow complete comparison of the experimental data. However, modeling with Visual MINTEQ indicates that hematite (Fe_2O_3), goethite ($\text{FeO}(\text{OH})$), and other Fe(III) species are undersaturated in all of the experiments reported here, arguing against an Fe(III) deposition mechanism.

Morimoto (1992) suggested that the molar ratio of $(\text{As}+\text{Sb})/(\text{Co}+\text{Ni})$ is an indicator of pyrite thermoelectric potential, and Liu et al. (2008b) found that this ratio correlated somewhat with the calculated dissolution rate, with much higher dissolution rates for samples in which the ratio was >1 . They suggested that this could be due to differences in corrosion by electron holes and conductivity (see Lehner et al., 2007). However, we did not find any significant correlations of

Fe isotope ratios or shifts in the ratio over time with (As+Sb)/(Co+Ni), or with any other trace element reported from the dissolution experiments by Liu (2007) and Liu et al. (2008b).

Some of the shifts in $\delta^{56}\text{Fe}$ of the leachates could also conceivably be caused by isotopic heterogeneity of the pyrite itself. Pyrite in the natural environment is likely to form over long time periods from fluids that could contain multiple sources and generations of Fe. This is likely to be especially true in sedimentary pyrite, which forms diagenetically in subsiding basins in which the Fe might be expected to evolve continuously over time (e.g., Severmann et al., 2006). While the leachates from both the hydrothermal and the sedimentary pyrite examined in this study exhibited significant variations in $\delta^{56}\text{Fe}$, the largest variations were observed in sedimentary coal sample SED-COAL-3 and fossil replacement SED-2. In particular, SED-2 had a change in $\delta^{56}\text{Fe}$ of almost 1‰ from 480 to 1440 minutes, and in the opposite direction of most other samples (**Figs. 5, 6**). This shift could represent a change in dissolution from low- to high- $\delta^{56}\text{Fe}$ pyrite within the sample, with possible isotopic shifts correlating with morphological changes that affect the ease of dissolution. *In situ* Fe isotope analyses of sedimentary pyrite by laser ablation (Nishizawa et al., 2010) and SIMS (Whitehouse and Fedo, 2007; Virtasalo et al., 2013; Marin-Carbonne et al., 2014) indicates significant shifts in $\delta^{56}\text{Fe}$ even within individual grains or nodules. Similar variations were seen in pyrite from massive sulfide deposits (Graham et al., 2004). Nonetheless, the observation that nearly all leachates in the experiments reported here shifted to lower $\delta^{56}\text{Fe}$ values over the course of the experiment (**Fig. 7**) argues that pyrite heterogeneity is a secondary effect in most cases. Resolution of this issue will require experiments on demonstrably isotopically uniform pyrite, perhaps prepared synthetically under carefully controlled conditions.

5. Conclusions

Oxidative dissolution experiments were carried out on pyrite from multiple petrogenetic environments to investigate possible variations in the Fe isotopic composition of pyrite and pyrite leachates. The experimental materials were separated into aliquots of uniform grain size (after Wolfe et al., 2007), and were dissolved under carefully controlled conditions (Liu et al., 2008b). A subset of samples from these experiments was analyzed for $^{56}\text{Fe}/^{54}\text{Fe}$ by multicollector ICP-MS.

Bulk pyrite $\delta^{56}\text{Fe}$ values ranged from -0.1 to +1.3, with hydrothermal bulk pyrite $\delta^{56}\text{Fe} < 0.5$ and coal and sedimentary pyrite nodule $\delta^{56}\text{Fe} \geq 0.5$. The hydrothermal bulk pyrite $\delta^{56}\text{Fe}$ value is within the range of previously analyzed hydrothermal pyrite, but the coal/sedimentary values are higher than those of previously analyzed pre-Holocene Phanerozoic sedimentary pyrite. We suggest that this reflects precipitation of pyrite from a high- $\delta^{56}\text{Fe}$ continental source, such as Fe derived from dissolution of Fe(III) oxides.

Leachates from oxidative dissolution of pyrite at pH=3 generally yielded $\delta^{56}\text{Fe}$ values equal to or below those of the coexisting bulk pyrite, by up to ~1‰, and in most cases, the $\delta^{56}\text{Fe}$ values of the pyrite leachates decreased with time of reaction. Although the observed shifts were not consistent in magnitude, the direction of fractionation was consistent with theoretical predictions (Polyakov and Mineev, 2000). Release of Fe from different portions of isotopically heterogeneous pyrite grains may be a secondary effect in some cases.

Results of this study demonstrate that Fe isotopes can yield important information about surface processes during oxidative dissolution of pyrite. $\delta^{56}\text{Fe}$ values can also be used to distinguish between waters that interacted with continentally-derived pyrite (e.g., from coal) and pyrite formed under marine or hydrothermal conditions. This suggests that Fe isotopes could be

468 a useful tool for tracking Fe sources and biogeochemical processes that operate in coal mine
469 drainage systems.
470

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Figure Captions

Fig. 1. Rare earth element (REE) patterns for sedimentary and hydrothermal bulk pyrite samples from this study. Also shown for comparison: the North American Shale Composite (NASC; Gromet et al., 1984), and the range of values for Pennsylvanian coal (shaded area) from Schatzel and Stewart (2003).

Fig. 2. Equilibrium speciation of dissolved iron in pyrite dissolution leachates, as a function of p_e at $pH = 3$ and $25^\circ C$. Dissolved sulfate ($a[SO_4^{2-}] = 10^{-3.3} M$) and chloride ($a[Cl^-] = 10^{-2} M$). Activity calculations were conducted using Visual MINTEQ (Gustafsson, 2012).

Fig. 3. Leachate solution molar S/Fe ratios for each sampling point during the eight pyrite dissolution experiments at $pH=3$. Note that the bulk solution composition does not reach the stoichiometric pyrite S:Fe ratio (2:1) after 24 hours.

Fig. 4. Calculated S/Fe ratio released at each leaching time interval for the $pH=3$ leaching experiments is plotted against the total amount of pyrite dissolved at the end of that interval. When calculated this way, it can be seen that the Fe and S being released approaches a ratio close to that of stoichiometric pyrite after $\sim 0.5\%$ dissolution (contrast with Fig. 3). The dashed exponential curve is shown for comparison only.

Fig. 5. Variation in bulk pyrite (closed square) and pyrite leachate (open symbol) $\delta^{56}Fe$ values. Bulk pyrite values are not available for HY-3, SED-2 and SED-COAL-2. Error bars represent external 2σ uncertainty.

Fig. 6. $\delta^{56}\text{Fe}$ of leachate solution sampled at different time intervals during pyrite oxidative dissolution experiments at pH=3. Where available, bulk pyrite values are plotted on the right. Complete dissolution of the samples would bring the solution to the bulk pyrite $\delta^{56}\text{Fe}$ value. Error bars represent external 2σ uncertainty.

Fig. 7. Leachate Fe isotopic evolution for pH=3 experiments is shown as the difference between a given leachate $\delta^{56}\text{Fe}$ and that of the first leachate (usually at 60 min) for that sample. For sample HY-3, the first leachate analyzed was at 6 hours, and for SED-2, the first analysis was at 8 hours. In most cases, the leachate $\delta^{56}\text{Fe}$ remained the same or decreased over time; SED-2 is the major exception.

Fig. 8. Summary of published Fe isotope data from pyrite of sedimentary and hydrothermal origin (open symbols), with a comparison to values from this study (closed symbols). Note that we report Phanerozoic sedimentary pyrite with significantly positive $\delta^{56}\text{Fe}$ values. Published data are from Sharma et al. (2001); Rouxel et al. (2003; 2004; 2005; 2008); Johnson et al. (2003); Graham et al. (2004); Matthews et al. (2004); Archer and Vance (2006); Severmann et al. (2006; 2008); Fehr et al.; (2008; 2010); Hofmann et al. (2009); Duan et al. (2010); Nishizawa et al. (2010); Fabre et al. (2011); Yoshiya et al. (2012; 2015); Marin-Carbonne et al. (2014); Scholz et al. (2014); and Wawryk and Foden (2015). Individual SIMS spot analyses of Holocene diagenetic pyrite from the Baltic Sea (not shown) range from -3.1 to +4.1 (Virtasalo et al., 2013).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1. Characteristics of pyrite samples used in this study. Mineralogy was confirmed using x-ray diffraction.

Sample ID	Source/Location	Morphology	Petrogenetic Environment	Mineralogy	S/Fe ^a (molar)	Specific Surface Area ^b (m ² /g)
HY-1	Hubbard Scientific	Nodular	Hydrothermal	Pyrite	2.01	0.22
HY-2	Peru	Nodular	Hydrothermal	Pyrite	2.02	0.10
HY-3	Spain	Nodular	Hydrothermal	Pyrite	2.03	0.07
SED-1	Illinois, USA	Nodular, pyrite sun	Sedimentary, within bedding planes of shale	Pyrite	2.02	0.35
SED-2	New Albany Shale; Indiana, USA	Nodular	Sedimentary; fossil replacement	Pyrite	2.04	0.21
SED-COAL-1	Pennsylvania, USA	Nodular	Sedimentary, within coal	Pyrite	2.02	2.82
SED-COAL-2	Texas, USA	Nodular	Sedimentary, within coal	Pyrite with minor quartz	1.97	0.42
SED-COAL-3	Texas, USA	Nodular	Sedimentary, within coal	Pyrite	1.97	5.37

^aS/Fe determined by ICP-AES on total sample digestion.

^bSpecific surface area measured by nitrogen adsorption multipoint BET method (ISO 2010).

Table 2. Trace element concentrations (µg/g) in bulk pyrite samples. Where indicated, minimum (>) and maximum (<) values fell outside the limits of quantification by ICP-MS.

trace element concentration, µg/g																				
Element	Ag	As	Al	Au	Ba	Bi	Br	Ca	Cd	Co	Cr	Cs	Cu	Ga	Ge	Hf	Hg	K	In	Li
Detection Limit	0.2	0.03	2	0.002	0.1	0.3	3	700	0.01	0.005	0.5	0.001	0.2	0.01	0.01	0.001	0.2	30	0.001	1
HY-1	0.6	> 25	23	0.003	0.0	17.7	3	602	0.03	> 25	0.9	0.041	> 25	0.13	0.16	0.003	< 0.2	6	0.128	< 1
HY-2	0.7	20.14	31	0.001	0.1	10.6	4	149	0.11	14.330	0.3	0.002	> 27	0.12	0.41	0.001	0.0	20	0.223	< 1
HY-3	0.2	4.43	> 313	0.007	0.5	19.4	4	1816	0.07	> 31	5.9	0.044	> 31	0.77	0.47	0.074	0.0	49	0.003	< 1
SED-1	2.0	> 64	259	0.001	4.2	< 0.3	8	289	0.38	7.924	5.8	0.076	> 64	0.54	0.69	0.042	0.3	199	0.001	< 1
SED-2	< 0.2	32.15	401	0.004	20.5	< 0.3	24	2569	0.08	13.375	2.3	0.202	> 177	0.67	1.27	0.019	< 0.2	434	0.001	< 1
SED-COAL-1	< 0.2	> 54	305	< 0.002	8.3	< 0.3	8	189	0.35	0.250	1.4	0.311	> 54	0.16	0.24	0.029	3.1	132	0.007	< 1
SED-COAL-2	0.1	> 53	531	0.001	23.9	< 0.3	6	398	0.08	12.633	10.8	0.441	> 53	1.79	0.60	0.176	3.3	870	0.019	7.17
SED-COAL-3	< 0.2	> 49	276	< 0.002	4.0	< 0.3	6	197	0.26	0.708	0.7	0.107	> 49	0.14	0.29	0.021	8.6	79	0.005	< 1
trace element concentration, µg/g (continued)																				
Element	Mg	Mn	Mo	Na	Nb	Ni	Pb	Rb	Re	Ru	Sb	Se	Si	Sn	Sr	Ta	Te	Th	Ti	Tl
Detection Limit	1	0.1	0.1	5	0.005	0.3	0.01	0.005	0.001	0.01	0.01	0.2	200	0.1	0.04	0.001	0.1	0.001	0.1	0.001
HY-1	134	103.6	0.7	12	0.009	69.6	4.10	0.028	0.021	0.11	0.36	> 31	< 25	0.6	0.37	0.001	18.9	0.073	0.7	0.006
HY-2	46	0.3	0.1	6	0.024	4.2	19.06	0.089	0.002	0.00	1.14	12.0	< 27	> 11	0.41	0.019	13.8	0.006	0.4	0.006
HY-3	576	27.6	0.1	13	0.118	> 157	17.07	0.246	0.000	0.05	0.44	22.5	251	0.5	0.92	0.013	1.3	2.693	39.9	0.011
SED-1	43	3.8	33.7	68	0.017	75.1	> 64	0.937	0.019	0.01	11.97	76.4	257	0.3	0.64	0.004	< 0.1	0.209	8.7	> 6.4
SED-2	284	132.9	13.2	201	0.032	179.8	12.49	1.754	0.003	0.03	0.25	13.1	354	0.2	6.09	0.011	0.1	0.098	3.5	1.41
SED-COAL-1	22	1.2	24.9	118	0.027	1.3	8.43	1.021	0.001	0.00	0.02	8.4	108	2.4	2.12	0.002	< 0.1	0.443	15.0	> 5.4
SED-COAL-2	2545	56.8	3.9	67	0.133	69.8	19.98	3.875	< 0.001	0.00	1.06	> 66	451	0.2	5.39	0.005	< 0.1	3.238	67.9	> 5.3
SED-COAL-3	14	3.1	14.5	89	0.014	1.8	15.47	0.518	< 0.001	0.01	0.41	8.0	99	1.2	2.12	0.003	< 0.1	0.104	4.4	> 4.9
trace element concentration, µg/g (continued)							rare earth element concentration, µg/g													
Element	U	V	W	Y	Zn	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Detection Limit	0.001	0.1	0.02	0.003	0.5	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
HY-1	0.317	0.5	> 2.5	0.399	12.1	0.10	0.198	0.658	0.111	0.449	0.068	0.028	0.074	0.010	0.054	0.011	0.034	0.005	0.036	0.005
HY-2	0.319	> 6.8	> 2.7	0.036	> 34	0.02	0.007	0.026	0.003	0.019	0.009	0.002	0.010	0.002	0.009	0.002	0.005	0.001	0.005	0.001
HY-3	0.366	2.7	> 3.1	1.185	26.1	2.43	0.302	0.709	0.095	0.437	0.236	0.105	0.344	0.054	0.276	0.048	0.132	0.019	0.140	0.018
SED-1	0.236	4.7	> 6.4	0.172	18.8	1.70	0.104	0.227	0.026	0.096	0.021	0.004	0.021	0.003	0.023	0.006	0.021	0.004	0.032	0.006
SED-2	0.044	2.0	> 18	0.315	64.7	0.71	0.187	0.407	0.055	0.221	0.057	0.014	0.059	0.009	0.049	0.009	0.023	0.004	0.022	0.004
SED-COAL-1	0.032	0.8	2.37	0.411	15.4	0.80	0.711	1.818	0.202	0.792	0.157	0.028	0.135	0.017	0.075	0.012	0.035	0.004	0.027	0.004
SED-COAL-2	0.525	11.4	> 5.3	2.471	38.0	5.49	6.263	13.057	1.505	5.547	1.075	0.255	1.016	0.128	0.581	0.096	0.268	0.033	0.225	0.031
SED-COAL-3	0.020	0.5	> 4.9	0.226	23.0	0.67	0.077	0.243	0.023	0.103	0.028	0.007	0.037	0.006	0.033	0.007	0.020	0.003	0.017	0.003

Table 3. Dissolved Fe and S concentrations in leachate collected during pyrite dissolution experiments at pH=3.

Sample ID	Sampling time (min.)	Fe (μM)	S (μM)	Molar S/Fe
HY-1	60	9.7	6.5	0.67
	480	23.0	27.8	1.21
	1440	54.5	78.2	1.43
HY-2	60	10.2	7.1	0.69
	480	15.8	16.4	1.04
	1440	35.7	48.2	1.35
HY-3	360	10.1	14.4	1.43
	480	11.5	14.3	1.24
	1440	28.1	42.9	1.53
SED-1	60	10.2	7.4	0.72
	480	24.3	25.6	1.05
	1440	59.8	79.9	1.34
SED-2	60	8.6	7.0	0.81
	480	20.2	29.0	1.44
	1440	52.1	84.8	1.63
SED-COAL-1	60	56.1	72.3	1.29
	480	157.0	259.0	1.65
	1440	427.0	828.0	1.94
SED-COAL-2	60	22.2	26.1	1.18
	480	71.4	108.0	1.51
	1440	220.0	400.0	1.82
SED-COAL-3	60	38.3	64.8	1.69
	480	161.0	287.0	1.78
	1440	477.0	807.0	1.69

Table 4. Speciation calculation results for S (top) and Fe (bottom) in the pyrite dissolution experiments using Visual MINTEQ.

	1 hour				8 hour				24 hour			
Sulfur												
Sample ID	SO ₄ ²⁻ %	HSO ₄ ⁻ %	FeSO _{4, aq}	NaSO ₄ ⁻ %	SO ₄ ²⁻ %	HSO ₄ ⁻ %	FeSO _{4, aq}	NaSO ₄ ⁻ %	SO ₄ ²⁻ %	HSO ₄ ⁻ %	FeSO _{4, aq}	NaSO ₄ ⁻ %
HY-1	90.2	6.41	0.091	3.26	90.0	6.50	0.211	3.32	89.8	6.24	0.477	3.52
HY-2	90.2	6.41	0.096	3.26	90.2	6.37	0.146	3.33	89.9	6.26	0.315	3.53
HY-3 ^a	90.2	6.41	0.095	3.26	90.3	6.24	0.106	3.33	90.0	6.26	0.248	3.54
SED-1	90.2	6.41	0.096	3.26	90.1	6.36	0.224	3.32	89.8	6.10	0.524	3.53
SED-2	90.2	6.41	0.081	3.26	90.1	6.36	0.186	3.32	89.9	6.11	0.457	3.53
SED-COAL-1	89.9	6.37	0.518	3.24	89.1	6.24	1.37	3.25	87.5	5.95	3.24	3.32
SED-COAL-2	90.0	6.54	0.207	3.25	89.7	6.32	0.644	3.30	88.9	5.84	1.81	3.44
SED-COAL-3	89.9	6.25	0.337	3.53	89.1	6.23	1.40	3.24	87.3	5.79	3.61	3.31
Iron												
Sample ID	Fe ²⁺ %	FeSO _{4, aq} %	FeCl ⁺ %		Fe ²⁺ %	FeSO _{4, aq} %	FeCl ⁺ %		Fe ²⁺ %	FeSO _{4, aq} %	FeCl ⁺ %	
HY-1	99.5	0.061	0.413		99.3	0.255	0.433		98.8	0.685	0.473	
HY-2	99.5	0.066	0.413		99.4	0.151	0.433		99.1	0.425	0.475	
HY-3*	99.5	0.135	0.413		99.4	0.132	0.434		99.1	0.379	0.475	
SED-1	99.5	0.070	0.413		99.3	0.236	0.433		98.8	0.700	0.473	
SED-2	99.5	0.066	0.413		99.3	0.268	0.433		98.8	0.744	0.473	
SED-COAL-1	98.9	0.668	0.409		97.3	2.26	0.419		93.3	6.28	0.433	
SED-COAL-2	99.3	0.244	0.412		98.6	0.971	0.428		96.3	3.29	0.455	
SED-COAL-3	99.0	0.570	0.474		97.1	2.49	0.418		93.5	6.11	0.434	

^aThe first leachate collected from Sample HY-3 was at 6 hours

Table 5. Iron isotope data for bulk pyrite samples and dissolved Fe sampled during pyrite oxidative dissolution experiments conducted at pH=3 (relative to standard IRRM-14).

Sample	$\delta^{56}\text{Fe}^a$				
	Bulk Pyrite	dissolution experiment leachates			
		1 hr.	6 hr.	8 hr.	24 hr.
HY-1	0.19	-0.05		-0.15	-0.09
HY-2	-0.10	-0.13		-0.36	-0.63
HY-3			0.73	0.61	0.60
SED-1	1.34	1.21		1.18	1.15
SED-2				-0.38	0.53
SED-COAL-1	0.51	0.57		0.50	0.56
SED-COAL-2		0.74		0.60	0.46
SED-COAL-3	0.57	0.33		0.54	-0.48

^aMeasurement uncertainty (2σ) for all reported values is $\pm 0.1\%$.