



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



Amy L. Wolfe<sup>a</sup>, Brian W. Stewart<sup>a,\*</sup>, Rosemary C. Capo<sup>a</sup>, Ran Liu<sup>b,c</sup>, David A. Dzombak<sup>b</sup>, Gwyneth W. Gordon<sup>d</sup>, Ariel D. Anbar<sup>d,e</sup>

<sup>a</sup> Department of Geology & Environmental Science, University of Pittsburgh, Pittsburgh, PA 15260, USA

<sup>b</sup> Department of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

<sup>c</sup> Pennsylvania American Water, 852 Wesley Drive, Mechanicsburg, PA 17055, USA

<sup>d</sup> School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287, USA

<sup>e</sup> School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA

## ARTICLE INFO

### Article history:

Received 26 August 2015

Received in revised form 12 February 2016

Accepted 14 February 2016

Available online 16 February 2016

### Keywords:

Fe isotope

Pyrite

Rare earth element

REE

Mass fractionation

Coal

## ABSTRACT

Oxidative dissolution experiments were carried out on pyrite from multiple petrogenetic environments (hydrothermal, sedimentary, 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  $+1.3\text{‰}$ , 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 interpretation is consistent with pyrite rare earth element (REE) patterns. 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.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Iron sulfides constitute a diverse group of solid and dissolved species in aqueous geochemical systems, and play an essential role in regulating and controlling the global geochemical Fe and S cycles. Pyrite ( $\text{FeS}_2$ ), 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 ( $<100\text{ °C}$ ) 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

\* Corresponding author.

E-mail address: [bstewart@pitt.edu](mailto:bstewart@pitt.edu) (B.W. Stewart).

soils (Fantle and DePaolo, 2004; Emmanuel et al., 2005; Ingrid 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–pO<sub>2</sub> 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 min.

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 min and stored in a desiccator. Samples were used within 2 h 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 ± 0.01 °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 °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 ml of sample was collected periodically over a 24 h time period, and then filtered through a 0.45 μm disposable filter into a 20 ml polyethylene scintillation vial containing 5 ml 10% nitric acid (HNO<sub>3</sub>) for Fe and S elemental analyses. A three-way stopcock was used for sampling to ensure that 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 μg/L and graphite furnace AA was used for samples with lower concentrations of iron (detection limit = 1.0 μg/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 ±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.

**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 <sup>a</sup> (M)	Specific surface area <sup>b</sup> (m <sup>2</sup> /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

<sup>a</sup> S/Fe determined by ICP-AES on total sample digestion.

<sup>b</sup> Specific surface area measured by nitrogen adsorption multipoint BET method (ISO, 2010).

Download English Version:

<https://daneshyari.com/en/article/6436141>

Download Persian Version:

<https://daneshyari.com/article/6436141>

[Daneshyari.com](https://daneshyari.com)