Chemical Geology 400 (2015) 44–55

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Pyrite formation and mineral transformation pathways upon sulfidation of ferric hydroxides depend on mineral type and sulfide concentration

Stefan Peiffer [a,*], Thilo Behrends [b], Katrin Hellige [a,1], Philip Larese-Casanova [c], Moli Wan [a,1], Kilian Pollok [d,e]

[a] Department of Hydrology, Universität Bayreuth, Universitätsstraße 30, D-95445 Bayreuth, Germany
[b] Department of Earth Sciences, Geochemistry, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands
[c] Department of Civil and Environmental Engineering, Northeastern University, 469 Snell Engineering, 360 Huntington Ave, Boston, MA 02115, USA
[d] Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstraße 30, D-95445 Bayreuth, Germany
[e] Institute of Geosciences, Mineralogy, Friedrich-Schiller-Universität Jena, Carl-Zeiss-Promenade 10, D-07745 Jena, Germany

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form 29 January 2015
Accepted 31 January 2015
Available online 9 February 2015

Editor: Michael E. Böttcher

Keywords:
Ferric hydroxides
Dissolved sulfide
Ferrous iron
Pyrite formation
Electron transfer
Bulk mineral electrons

ABSTRACT

The reaction of ferric (hydr)oxides with dissolved sulfide does not lead to the instantaneous production of thermodynamically stable products but can induce a variety of mineral transformations including the formation of metastable intermediates. The importance of the various transformation pathways depends, among other factors, on the characteristics of the ferric (hydr)oxides but a mechanistic model which relates the mineralogy of the ferric (hydr)oxides to the type of reaction products and their evolution over time is still missing. Here, we investigate the kinetics of the reaction between dissolved sulfide (6.7–7.5 mmol L^{-1}) with ferrihydrite (Fh, 12 mmol L^{-1}), lepidocrocite (Lp, 26.6 mmol L^{-1}), and goethite (Gt, 22 mmol L^{-1}) in batch experiments at pH 7 and room temperature. The time evolution of solution and solid phase composition was monitored over 2 weeks while TEM, and Mössbauer spectroscopy were used to characterize the transformations of the solid phases.

Dissolved sulfide was consumed within 2 (Fh, Lp) to 8 h (Gt) with methanol extractable sulfur and HCl extractable Fe(II) ($Fe(II)_{HCl}$) being the main products after this time. The mass balances of Fe and S indicated that a large fraction of the $Fe(II)_{HCl}$ in the reactions with Fh (46% of $Fe(II)_{HCl}$) and Lp (36% of $Fe(II)_{HCl}$) was solid-phase bound but not associated with sulfur. This excess Fe(II) exceeded the adsorption capacity of the solids and remained associated with the oxides. Over the time scale of days, the concentrations of MES and $Fe(II)_{HCl}$ decreased and this process was accompanied by the formation of secondary iron oxides and pyrite in all experiments. The pyrite yield after two weeks showed the same trend as the amounts of intermediately produced excess Fe(II): Fh (84% of initial S(−II)) > Lp (50%) > Gt (13%). Besides the formation of pyrite, Fh transformed completely into thermodynamically more stable iron oxides such as hematite or magnetite. In contrast, formation of other iron oxides was only minor when Lp or Gt reacted with sulfide.

We propose that the extent of pyrite and secondary iron mineral precipitation is controlled by the ratio between the competing formation rates of excess Fe(II) and surface bound FeS (FeS_s) in the early stage of the reaction. Formation of excess Fe(II) is a prerequisite for rapid pyrite formation and induces secondary formation of iron oxides. The competition between excess Fe(II) and FeS_s formation, in turn, is ruled by two factors: 1) the ratio between added sulfide and available surface area, and 2) the capability of the iron(hydr)oxide to conduct electrons from surface bound Fe(II) to bulk Fe(III) and to accommodate structural Fe(II). This capability is largest for Fh and explains the most pronounced excess Fe(II) production and, by this, the greatest pyrite yield in experiments with Fh. During the reaction with Gt, in contrast, formation of FeS_s outcompetes the accumulation of excess Fe(II) and consequently the precipitation of pyrite is only minor.

This conceptual model constrains conditions at which relatively fast pyrite formation within the time scale of days or weeks might be relevant in natural environments. Suitable conditions are expected in environments with low sulfide levels in which formation of reactive iron (hydr)oxides is stimulated by redox oscillations (e.g., wetlands, riparian soils, tidal flats).

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Reduction of ferric (hydr)oxides is a prominent pathway contributing to electron fluxes in subsurface environments (Raiswell and

---

[*] Corresponding author. Tel.: +49 921 552253; fax: +49 921 552366.
E-mail address: s.peiffer@uni-bayreuth.de (S. Peiffer).

[1] Tel.: +49 921 552251; fax: +49 921 552366.

http://dx.doi.org/10.1016/j.chemgeo.2015.01.023
0009-2541/© 2015 Elsevier B.V. All rights reserved.

Canfield, 2011) and is directly connected to the bioavailability and mobility of nutrients (Einsele, 1936) and contaminants (Haderlein and Pecher, 1998). Reductive dissolution occurs either enzymatically (e.g., /INS; Thamdrup, 2000) or chemically (Cornell and Schwertmann, 2003) with dissolved sulfide being a powerful and ubiquitous reductant in anoxic environments (e.g., Canfield et al, 1992). Ferric (hydr)oxides display a wide spectrum of reactivity (Postma, 1993) as being controlled by surface area (Roden, 2003) but also by thermodynamic properties such as E_h (Fischer, 1987) or solubility product (Bonneville et al, 2009). Interaction with sulfide is regarded to be a surface controlled process (Dos Santos Afonso and Stumm, 1992; Peiffer et al., 1992). Under acidic conditions Fe(II) becomes completely dissolved (Peiffer and Gade, 2007) whereas solid FeS is a common initial product at circumneutral pH (Rickard, 1974; Pyzik and Sommer, 1981).

It has been early recognized that sulfidation of ferric (hydr)oxides also triggers the formation of pyrite (Rickard, 1975). The accepted model for pyrite formation is the reaction between an aqueous FeS species and dissolved polysulfides, which requires solid FeS as a precursor species (cf. review in Rickard, 2012 and references therein), irrespective of the origin of the reactants. In a recent study, it was demonstrated that sulfidation of lepidocrocite at millimolar S(−II) concentration and at pH 7 is a highly dynamic process (Hellige et al, 2012). High resolution transmission electron microscopy (HRTEM) revealed that lepidocrocite crystals were covered with FeS after 2 h when dissolved S(−II) was completely consumed. FeS started to disappear after 72 h along with the formation of amorphous Fe and S phases. Nanopyrite particles formed after only one week. Cryogenic X-ray photoelectron spectroscopy measurements demonstrate that a substantial fraction (>50%) of the S species consisted of surface-bound polysulfides (Wan et al., 2014) with only small amounts (<1%) of the initial sulfide being recovered as aqueous polysulfides.

Poulton et al. (2004) investigated the reaction of various ferric (hydr)oxides with dissolved sulfide at pH 7.5 and observed the accumulation of acid extractable Fe(II) which is neither Fe(II) extractable as acid volatile sulfur (AVS) nor is it exchangeable with other cations. They considered this fraction to be associated with the surface, but the amount of Fe(II) in this pool exceeded in lepidocrocite the number of sites at the oxide surface by a factor of 10. The nature of this Fe(II) containing phase remained unclear. Similarly, a significant fraction of solid-phase Fe(II) in excess to surface Fe(II) associated with sulfur species was observed during sulfidation of lepidocrocite (Hellige et al, 2012). The excess Fe(II) was interpreted as uptake of electrons into the bulk mineral (Gorski and Scherer, 2012). The amount of produced pyrite was higher in experiments in which high concentrations of excess Fe(II) were intermediately formed. It was therefore proposed that the pool of excess Fe(II) triggered the sequence of mineral transformations and promoted the formation of pyrite.

The relative importance of excess Fe(II) formation during the reaction may also depend on the type of ferric iron (hydr)oxide. Poulton et al (2004) observed a range in reactivity towards sulfide covering two orders of magnitude when normalized to surface area. According to our proposed model, channeling of electrons into the bulk structure can therefore be expected to be less significant at low reactivity, i.e. higher crystallinity.

We therefore hypothesize that the extent of excess Fe(II) production and hence the extent of pyrite formation upon sulfidation is different for various ferric (hydr)oxides and depends on their electron transfer properties, but also on their ability to accommodate Fe(II) within the structure. Adsorption of Mössbauer-insensitive ^{56}Fe(II) to various ferric (hydr)oxides revealed dramatic variations in magnetic response of ferrihydrite (Williams and Scherer, 2004), hematite (Larese-Casanova and Scherer, 2007), magnetite (Gorski and Scherer, 2009) and goethite (Gorski and Scherer, 2012) that is being attributed to a varying degree of electron delocalization in the bulk minerals (Gorski and Scherer, 2012). As a consequence, type and concentrations of secondary Fe minerals such as pyrite forming upon the reaction with S(−II) are expected to differ between different ferric iron (hydr)oxides in relation to the relative production of excess Fe(II).

Here, we compare the reductive dissolution of lepidocrocite with those of ferrihydrite and goethite, representing a less stable and a more stable iron oxide phase, respectively. We conducted batch experiments with the same set-up and analytical methods as described in Hellige et al. (2012) with a focus on the reactivity of these hydr(oxides) in sulfide-rich systems at pH 7 in regard to the reaction rates, intermediate phases, and final products.

2. Materials and methods

2.1. Ferric (hydr)oxides

Synthetic 6-line ferrihydrite was prepared after Schwertmann and Cornell (2000). Under rapid stirring, 20 g of $Fe(NO_3)_3 \cdot 9H_2O$ was added to 2 L 75 °C hot distilled water. After 12 min of stirring, the solution was cooled and dialyzed for three days. The final product was freeze dried.

Synthetic lepidocrocite and goethite were purchased from Lanxess (Leverkusen, Germany). The trade names are Bayferrox 920 Z for goethite and Bayferrox 943 for lepidocrocite. To remove sulfate from the iron oxide surface (which commercial ferric (hydr)oxides typically contain), 1 mol L^{-1} of each hydroxide was suspended in 0.01 mol L^{-1} $NaNO_3$ and the pH was adjusted to 10 with NaOH. After 4 days of shaking the suspension was washed and freeze-dried.

The ferric (hydr)oxides were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Lepidocrocite contained 5–10 wt.% goethite and had a particle size of 0.2–0.4 μm as determined by SEM. Goethite had a particle size of 0.2–0.9 μm. Ferrihydrite particles were <10 nm as revealed by TEM (cf. Fig. 6). Surface area was measured by multipoint BET-N_2 (Brunauer, Emmett and Teller) method (Gemini 2375 Surface Area Analyzer). Surface areas were determined to be 140 $m^2\ g^{-1}$ for ferrihydrite, 17.34 $m^2\ g^{-1}$ for lepidocrocite and 9.12 $m^2\ g^{-1}$ for goethite.

2.2. Experimental set-up

Kinetic batch experiments were conducted in an anoxic glove box at pH 7 at a constant ionic strength of $I = 0.1$ mol L^{-1} NaCl and at room temperature. In this publication data are presented from those three experiments only where we have a complete data set in regard to wet chemical analysis, TEM and Mössbauer spectroscopy. Additional results from lepidocrocite experiments have been published in Hellige et al (2012). Ferric (hydr)oxide concentrations in these three experiments ranged between 12 and 26.6 mmol L^{-1} and the initial dissolved sulfide concentration between 6.7 and 7.5 mmol L^{-1} (cf. Table 1). Initial sulfide concentrations were in large excess relative to initial surface site concentrations of the three mineral phases (Table 1). All reactions were conducted in a 500-mL glass vessel with ports for sampling, addition of reactants and for a pH electrode. The solution was stirred with a Teflon-coated stirring bar at constant rate. With an automatic pH-stat device the pH value was kept constant by adding HCl (0.5 mol L^{-1}) in the glove box. The reaction suspension was prepared by mixing 50 mL of 0.1 mol L^{-1} NaCl solution containing approx. 1 g ferric (hydr)oxide with 450 ml of 0.1 mol L^{-1} NaCl to which appropriate amounts of NaHS (as a 1:1. mixture between $Na_2S \cdot 9H_2O$ (0.5 mol L^{-1}) and HCl (0.5 mol L^{-1})) were added. In order to convert the mass of the ferric (hydr)oxides into molar concentrations, the molar mass of ferrihydrite was determined to be 92.3 g/mol after dissolution in 6 N HCl and determination of Fe. Molar masses of 89 g/mol were used for lepidocrocite and goethite. The sulfide concentration was determined before each run.

During the reaction, aliquots were taken to monitor the time evolution of dissolved Fe(II) and S(−II), Fe(II) extractable with 0.5 N HCl,

Download English Version:

https://daneshyari.com/en/article/4698563

Download Persian Version:

https://daneshyari.com/article/4698563

Daneshyari.com