

Release of arsenic associated with the reduction and transformation of iron oxides

Hanne D. Pedersen *, Dieke Postma, Rasmus Jakobsen

Institute of Environment and Resources, Technical University of Denmark, Bygningstorvet, Building 115, DK-2800 Kgs. Lyngby, Denmark

Received 24 January 2006; accepted in revised form 13 June 2006

Abstract

The behaviour of trace amounts of arsenate coprecipitated with ferrihydrite, lepidocrocite and goethite was studied during reductive dissolution and phase transformation of the iron oxides using [⁵⁵Fe]- and [⁷⁵As]-labelled iron oxides. The As/Fe molar ratio ranged from 0 to 0.005 for ferrihydrite and lepidocrocite and from 0 to 0.001 for goethite. For ferrihydrite and lepidocrocite, all the arsenate remained associated with the surface, whereas for goethite only 30% of the arsenate was desorbable. The rate of reductive dissolution in 10 mM ascorbic acid was unaffected by the presence of arsenate for any of the iron oxides and the arsenate was not reduced to arsenite by ascorbic acid. During reductive dissolution of the iron oxides, arsenate was released incongruently with Fe²⁺ for all the iron oxides. For ferrihydrite and goethite, the arsenate remained adsorbed to the surface and was not released until the surface area became too small to adsorb all the arsenate. In contrast, arsenate preferentially desorbs from the surface of lepidocrocite. During Fe²⁺ catalysed transformation of ferrihydrite and lepidocrocite, arsenate became bound more strongly to the product phases. X-ray diffractograms showed that ferrihydrite was transformed into lepidocrocite, goethite and magnetite whereas lepidocrocite either remained untransformed or was transformed into magnetite. The rate of recrystallization of ferrihydrite was not affected by the presence of arsenate. The results presented here imply that during reductive dissolution of iron oxides in natural sediments there will be no simple correlation between the release of arsenate and Fe²⁺. Recrystallization of the more reactive iron oxides into more crystalline phases, induced by the appearance of Fe²⁺ in anoxic aquifers, may be an important trapping mechanism for arsenic.

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1. Introduction

Arsenic is a toxic metalloid and may occur either as inorganic compounds or as organic arsenic. Organic arsenic compounds are, however, rarely quantitatively important, and in natural waters arsenic is mostly found in inorganic forms as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)).

The WHO guideline value for arsenic in drinking water is 10 µg/L. However, groundwaters with an arsenic concentration exceeding 200 µg/L have been reported from places like Bangladesh, W. Bengal, Vietnam and Inner Mongolia (Berg et al., 2001; Anawar et al., 2002; Mandal and Suzuki,

2002; Ryu et al., 2002; Smedley and Kinniburgh, 2002; Smedley et al., 2003). The most serious occurrences in terms of population exposed is Bangladesh where up to 30–35 million people are adversely affected by arsenic contaminated drinking water (BGS and DPHE, 2001).

The situation in Bangladesh has led to an increased interest in arsenic geochemistry and several studies have been conducted to elucidate the mechanisms responsible for the enhanced arsenic concentrations. Though it is generally agreed that the arsenic in Bangladesh stems from natural sediment-water interaction, there is no consensus about the mechanisms releasing arsenic to the groundwater. Proposed mechanisms include the oxidation of pyrite containing arsenic (Das et al., 1996; Mandal et al., 1998); the reduction of adsorbed arsenate to arsenite (BGS and DPHE, 2001; Bose and Sharma, 2002), competitive anion exchange of adsorbed arsenic (Acharyya et al., 1999; 5

Corresponding author. Tel.: +45 25 21 72.

E-mail address: hdp@er.dtu.dk (H.D. Pedersen).

Appelo et al., 2002) and reductive dissolution of iron oxides containing arsenic (Nickson et al., 2000; McArthur et al., 2001; Tareq et al., 2003; Swartz et al., 2004).

The reported arsenic content of naturally occurring iron oxides shows great variation, ranging from an As/Fe molar ratio of 2.4×10^{-6} –0.09 (Bowell, 1994; Pichler et al., 1999; BGS and DPHE, 2001). Iron oxides are probably the most important adsorbents for arsenic in sandy aquifers because of their great abundance and strong binding affinity, and both arsenite and arsenate show a high affinity for the iron oxide surface (Manning et al., 1998; Raven et al., 1998; Dixit and Hering, 2003). While arsenate binds to iron oxides through an inner sphere surface complex (Manceau, 1995; Sun and Doner, 1996; Farquhar et al., 2002; Sherman and Randall, 2003), arsenite has been found to adsorb both through an inner sphere and an outer sphere surface complex (Goldberg and Johnston, 2001).

Iron oxides are present in the environment as a wide range of minerals, most commonly ferrihydrite, lepidocrocite, goethite and hematite, with different characteristics such as stability, specific surface area and reactivity (Larsen and Postma, 2001; Cornell and Schwertmann, 2003). The formation and persistence of the unstable oxides is due to slow kinetics in formatting the more stable phases. However, with time the more unstable oxides such as ferrihydrite and lepidocrocite are recrystallized into more stable phases such as goethite and hematite. This transformation is usually slow at ambient temperatures and neutral pH. Studies on the fate of arsenic during the transformation of iron oxides have therefore been conducted at elevated temperatures (40–70 °C) and high pH (11–12) to promote the transformation process (Paige et al., 1994, 1996; Sun et al., 1999; Ford, 2002). The discovery that aqueous Fe^{2+} catalyses the transformation of the least stable iron oxides (Pedersen et al., 2005) opens to a new experimental setup where the fate of adsorbed arsenate during the transformation of iron oxides can be studied at room temperature and near neutral pH values.

Under anoxic conditions iron oxides may become reduced either biotically or abiotically while releasing Fe^{2+} (dos Santos Afonso et al., 1990; Lovley, 1992; Thamdrup,

2000). It has been hypothesised that adsorbed arsenate is released to solution during the reductive dissolution of iron oxide but the actual processes have not yet been studied in detail. Furthermore, previous studies have found an inhibiting effect of the oxyanions arsenate and phosphate, on the dissolution of iron oxides (Bondietti et al., 1993; Biber et al., 1994; Paige et al., 1997a; Eick et al., 1999). These studies used relatively high oxyanion/Fe molar ratios and the effect of trace amounts of arsenate on the rate of reductive dissolution of iron oxides remains unknown.

The objectives of this study are therefore to elucidate the behaviour of arsenic associated with iron oxides during reductive dissolution, as well as during the transformation of ferrihydrite and lepidocrocite into more stable phases like goethite. Iron and arsenic radiotracers are used to obtain accurate measurements of even very small concentrations and they also allow direct measurements of the dynamics of the processes.

2. Methods

2.1. Synthesis of iron oxides

2-L ferrihydrite, lepidocrocite and goethite were synthesized in the presence of arsenic following the procedures in Schwertmann and Cornell (1991) with minor modifications. 2-L ferrihydrite was precipitated by addition of 1 M NaOH to a 0.2-M FeCl_3 solution containing trace amounts of ^{55}Fe and various amounts of arsenate labelled with ^{73}As . The molar ratio of As and Fe was 0, 0.001, 0.0025 and 0.005 (Table 1). Lepidocrocite was synthesized at 10 °C by oxidizing a 0.2-M ^{55}Fe -labelled FeCl_2 solution containing arsenate labelled with ^{73}As , with compressed air, purged free of CO_2 by bubbling it through a 2-M NaOH solution, at a rate of approximately 100 mL/min. The molar ratio of As and Fe was 0, 0.001 and 0.005 (Table 1). Poorly crystalline goethite was synthesized by oxidizing a 0.07 M ^{55}Fe -labelled FeCl_2 solution containing arsenate with an As/Fe molar ratio of 0 and 0.001 (Table 1) and labelled with ^{73}As in a 1 M NaHCO_3 buffer solution with air at a rate of 30–40 mL/min. The arsenic content in the iron

Table 1
Characteristics of the iron oxides

Name	Iron oxide	As/Fe	Surface area (m ² /g)	Reactivity		Initial surface flux g/m ² /s
				k' (s ⁻¹)	γ	
Ferri0	Ferrihydrite	0	241	5.1×10^{-4}	0.88	2.1×10^{-6}
Ferri0.001a	Ferrihydrite	0.001	219	4.9×10^{-4}	0.87	2.2×10^{-6}
Ferri0.001b	Ferrihydrite	0.001	237	4.6×10^{-4}	0.83	1.9×10^{-6}
Ferri0.0025	Ferrihydrite	0.0025	223	5.1×10^{-4}	0.88	2.3×10^{-6}
Ferri0.005	Ferrihydrite	0.005	240	4.2×10^{-4}	0.85	1.7×10^{-6}
Lepi0	Lepidocrocite	0	162	1.9×10^{-4}	1.19	1.1×10^{-6}
Lepi0.001a	Lepidocrocite	0.001	137	1.2×10^{-4}	0.96	8.8×10^{-7}
Lepi0.001b	Lepidocrocite	0.001	124	1.3×10^{-4}	3.57	1.1×10^{-6}
Lepi0.005	Lepidocrocite	0.005	139	1.7×10^{-4}	1.00	1.2×10^{-6}
Goet0	Goethite	0	37	1.1×10^{-6}	0.62	3.0×10^{-8}
Goet0.001	Goethite	0.001	27	3.8×10^{-6}	0.58	1.7×10^{-7}

oxides was measured after total dissolution of the iron oxides using a slightly modified hydride generation-AAS method (APHA, 1995).

The specific activity of the oxides was 0.7–0.9 kBq ^{55}Fe /mmol Fe and 0.4–0.6 kBq ^{73}As /mmol Fe. After their synthesis the iron oxides were centrifuged at 3000 rpm and washed repeatedly in milliQ[®] water and stored in suspension in the dark at 5 °C. Less than 1% of the ^{55}Fe and the ^{73}As were lost during the washing. Preliminary experiments showed no change in the reactivity of the iron oxides due to washing.

2.2. Characterization of iron oxides

Subsamples of the iron oxides were freeze dried and then characterized by powder X-ray diffraction (XRD) and surface area measurements. XRD was performed using $\text{CoK}\alpha$ radiation on a Siemens D5000 X-ray diffractometer and confirmed the mineralogy and the purity of the iron oxides. The specific surface area was determined by the BET gas adsorption method (Atkins and de Paula, 2002) using a Micromeritics Gemini III 2375 (Table 1).

2.3. Arsenic speciation

Aqueous arsenate and arsenite were separated by filtering the water sample through a 0.2- μm membrane filter to remove particulate iron followed directly by passing the water through a disposable cartridge at a flow rate of approximately 6 mL/min using a syringe (Meng and Wang, 1998). The cartridges contain 0.8 g aluminosilicate adsorbent that selectively adsorbs arsenate but not arsenite. Arsenite was determined as the arsenic concentration in the water filtered through a cartridge, and arsenate was calculated as the difference between the total arsenic concentration and the arsenite concentration. Preliminary tests showed no isotopic exchange between aqueous As(III) and aqueous ^{73}As (V).

When speciating adsorbed arsenic, the sorption capacity of the cartridges was exceeded due to the high arsenate concentration used to desorb the ^{73}As (see below) and therefore up to 40 times dilution of the samples was necessary. Total adsorbed arsenic and aqueous arsenic were determined on undiluted samples.

2.4. Measurement of ^{55}Fe and ^{73}As

The activities of ^{55}Fe and ^{73}As were measured by liquid scintillation counting, injecting the samples directly into the liquid scintillation cocktail (Ultima Gold[™] from Perkin-Elmer). The activities were counted on a Wallac WinSpectral 1414 liquid scintillation counter with a data accumulation of half an hour.

A method for the simultaneous measurements of the activities of ^{55}Fe and ^{73}As was developed. A prerequisite for measuring the activity of ^{55}Fe and ^{73}As simultaneously is that the counts from the two isotopes are distinct from

each other. Tests showed that the counts from ^{55}Fe have their maximum in the energy range 0.03–8.24 keV, whereas the counts from ^{73}As show two peaks: one in the energy range 0.03–8.24 keV and one in the energy range 8.37–28.12 keV, the counts in the first peak being equal to 89% of the counts in the second peak. The radioactivity of ^{55}Fe and ^{73}As was determined by counting in two windows: one with the energies 0.03–8.24 keV and another with the energies 8.37–28.12 keV. Total counts of ^{55}Fe and ^{73}As per minute (CPM) were subsequently calculated by the following equations:

$$^{73}\text{As}_{\text{activity}} = 0.89 \times \text{CPM}_{\text{window 2}} + \text{CPM}_{\text{window 1}}$$

$$^{55}\text{Fe}_{\text{activity}} = \text{CPM}_{\text{window 1}} - 0.89 \times \text{CPM}_{\text{window 2}}$$

Correction for quenching was subsequently done manually. Due to the short half life of ^{73}As (80.3 d) correction for decay was made for this isotope. No correction for decay was done for ^{55}Fe having a half life of 2.7 years.

2.5. Desorption of ^{73}As

Adsorbed ^{73}As was desorbed from the iron oxide surface by extraction in a 250- μM arsenate solution for 2 h. The extractable ^{73}As was measured by directly injecting a subsample of the suspension into a sealed 20 ml serum glass flask containing an anoxic 500 μM arsenate solution in the ratio 1:1, to give a final arsenate concentration of 250 μM . The addition of a high concentration of unlabeled arsenate causes almost all the arsenate to be present in solution. Since ^{73}As distributes between the pools of arsenate as the bulk of arsenate, adsorbed ^{73}As will desorb and can be measured as ^{73}As in solution. Adsorbed ^{73}As was calculated as the ^{73}As extracted by 250 μM arsenate for 2 h minus the aqueous ^{73}As .

During the analytical procedure for measurement of adsorbed ^{73}As in the transformation experiments, an arsenic containing phase precipitated owing to the high arsenate concentrations applied to desorb ^{73}As , resulting in too low measurements of desorbable ^{73}As . Tests showed that the phase is dissolved in ascorbic acid, and that approximately 24% of the arsenic remains in solutions. The total desorbable ^{73}As was subsequently calculated by assuming that the measured activity of ^{73}As constitutes 24% of the total desorbed arsenic.

2.6. Reductive dissolution of iron oxides

The reactivity of the iron oxides was determined by reductive dissolution in 10 mM ascorbic acid at pH 3 as described in Larsen and Postma (2001). Sampling syringes were flushed five times with purified N_2 . The release of Fe^{2+} was followed by filtering aliquots through a 0.2- μm membrane filter directly into the ferrozine reagent and the Fe^{2+} concentration was subsequently measured spectrophotometrically (Stookey, 1970). Aqueous ^{55}Fe

and total aqueous ^{73}As were determined by filtering aliquots through a 0.2- μm membrane filter directly into the liquid scintillation cocktail. The procedures for As(III)/As(V) separation and the determination of adsorbed ^{73}As are described above.

2.7. Transformation of iron oxides

Transformation experiments were carried out for ferrihydrite and lepidocrocite as described by Pedersen et al. (2005). One thousand millilitre infusion bottles was flushed in 6 M HCl before being washed in 10% HNO_3 overnight and rinsed five times in milliQ[®] water. To each bottle containing 600 mL oxygen free milliQ[®] water (boiled and purged with N_2 purified by bubbling through an Fe^{2+} -Na-acetate solution) variable amounts of an FeCl_2 stock solution were added by a syringe to give concentrations of approximately 0–1.0 mM. NaHCO_3 was added to buffer the pH at 6.5. As a check on the presence of O_2 , the bottles were left overnight since any intruding O_2 would react with Fe^{2+} to form Fe(III), changing the colour of the solutions from clear to yellowish. No colour change was observed in any of the bottles.

The initial Fe^{2+} concentration was measured and the experiment was initiated by addition of an amount of a stock suspension of the ^{55}Fe and ^{73}As labelled iron oxide to give a final concentration of approximately 0.5 mmol Fe(III)/L. During the experiments, the bottles were stored in a 25 °C water bath. Aliquots were taken over time, filtered through a 0.2- μm membrane filter and the activity of aqueous ^{55}Fe , total aqueous ^{73}As ,

aqueous $^{73}\text{As(III)}$, total adsorbed ^{73}As and adsorbed $^{73}\text{As(III)}$, and pH were measured. The Fe^{2+} concentration was measured as before. Total Fe was measured by addition of hydroxylamine-hydrochloride to a filtered aliquot, 30 min before the spectrophotometric measurement, and the Fe^{3+} content was calculated as the difference between total Fe and Fe^{2+} . At the end of the experiments the suspensions were filtered anaerobically and the filtrate conserved with a 1:1 mixture of glycerol and water (Hansen, 1989) and frozen until characterized by XRD analysis.

3. Results

3.1. Release of arsenic during reductive dissolution of iron oxides

The release of arsenic coprecipitated with iron oxides, during reductive dissolution, was investigated using 10 mM ascorbic acid at pH 3. Ferrihydrite and lepidocrocite had an As/Fe molar ratio ranging from 0 to 0.005 and goethite an As/Fe molar ratio of 0 and 0.001 (Table 1). The initial As/Fe molar ratio in the iron oxides was confirmed by measuring the aqueous arsenic and iron concentration after total dissolution of the iron oxides.

3.1.1. Reactivity of iron oxides

The reductive dissolution of the iron oxides can be monitored by following the aqueous Fe^{2+} concentration (Fig. 1) since Fe^{2+} will not adsorb onto the iron oxides at pH 3. While the reduction of all the ferrihydrites, lepidocrocite

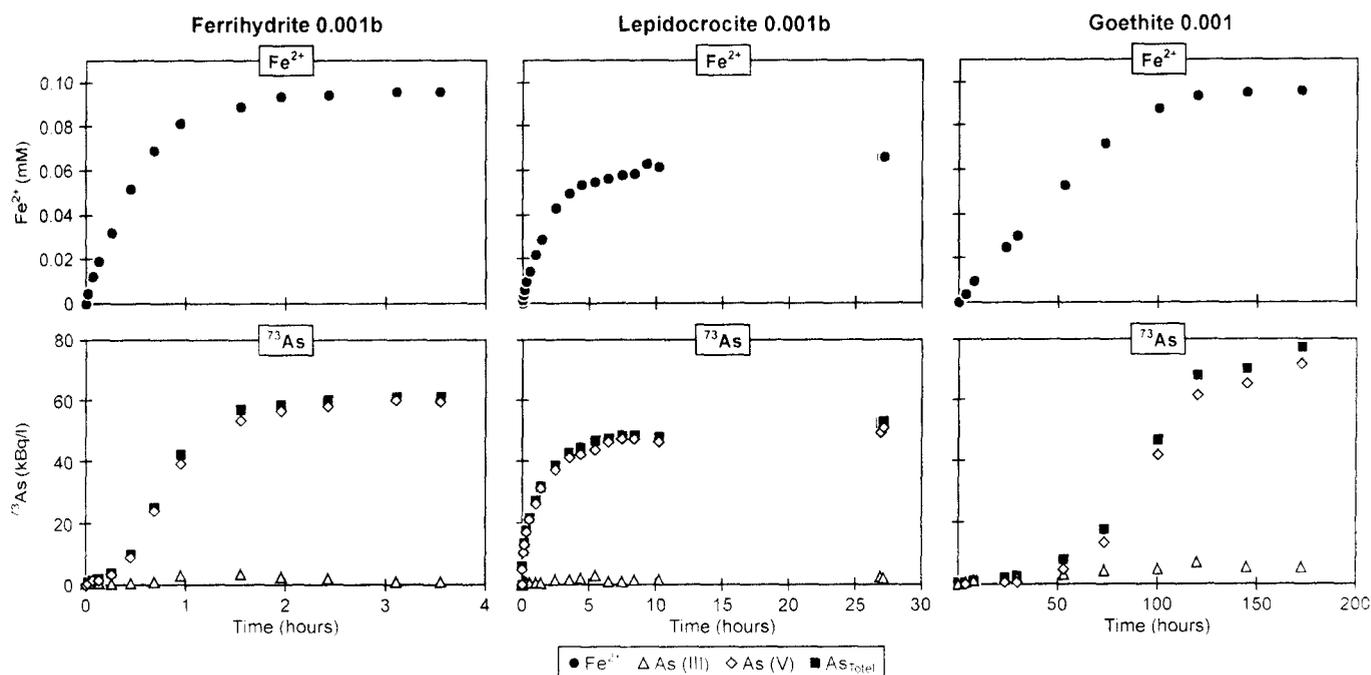


Fig. 1. Fe^{2+} concentration and the activity of total aqueous ^{73}As , aqueous $^{73}\text{As(V)}$ and $^{73}\text{As(III)}$ during reductive dissolution in 10 mM ascorbic acid of Ferri0.001b, Lepi0.001b and Goet0.001.

0, 0.001a and 0.005 and goethite shows the expected patterns (Larsen and Postma, 2001; Pedersen et al., 2005), the release of lepidocrocite 0.001b is much slower (40 days as compared to 10 h for the other lepidocrocite), and the initial fast release of Fe^{2+} was followed by a much slower release stage (only the first 30 h are shown in Fig. 1).

The reactivity of the iron oxides was estimated (Table 1) by fitting the data to the rate expression $J/m_0 = k'(m/m_0)^{-\gamma}$ (Postma, 1993), where J is the overall reduction rate (mol/s), m_0 the initial amount of iron oxides (moles) and m/m_0 the undissolved fraction. The reactivity is given by the parameters k' which is the initial reduction rate, and γ which is a measure of the decrease in the reduction rate due to changes in factors like crystal geometry, particle size distribution and reactive site density. Similar reactivities were found by Postma (1993), Larsen and Postma (2001) and Pedersen et al. (2005), but the lepidocrocites in this study appear to be more reactive than the ones synthesized by Larsen and Postma (2001). This may be attributed to a higher specific surface area of the lepidocrocites as the result of a lower synthesis temperature.

Fig. 2 compares the reactivity of the iron oxides, showing the rate expression of the iron oxides in terms of $-\log(J/m_0)$ versus $-\log(m/m_0)$. The rate expression results in a straight line where the value of $-\log(J/m_0)$ at $-\log(m/m_0) = 0$ equals the rate constant, k' , and the slope of the line corresponds to the exponent γ . Fig. 2 and Table 1 illustrate that for the various ferrihydrites and lepidocrocites, the rate expression and the surface flux i.e. the initial reduction rate normalized to the specific surface area, are unaffected by the arsenic content. For the goethites the initial reduction rate and the surface flux appear to change with the arsenic content. However, both the initial reduction rates and the surface fluxes remain within the range previously reported for goethite (Larsen and Postma, 2001), implying that the difference can be attributed to an unavoidable variation in the synthesis.

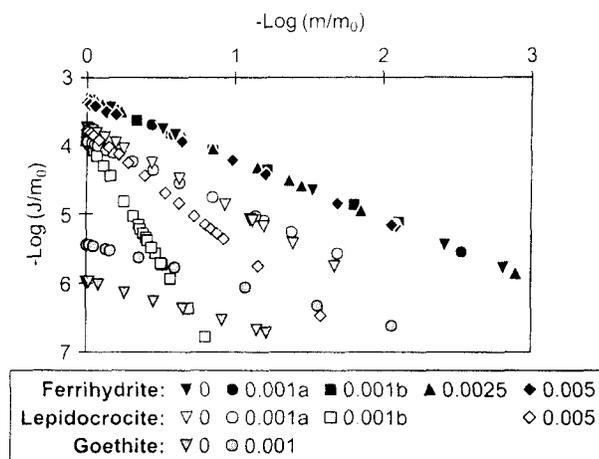


Fig. 2. Comparison of the reduction rates, normalized over initial mass (J/m_0) versus the fraction remaining in the solid phase (m/m_0) for ferrihydrite, lepidocrocite and goethite with various As/Fe molar ratios. The legend denotes the molar As/Fe ratio of the iron oxides.

3.1.2. Release of arsenic during reductive dissolution of iron oxides

The release of ^{73}As during reductive dissolution of Ferri0.001b, Lepi0.001b and Goet0.001 is also shown in Fig. 1. Since all isotopes of an element behave identically (except for very minor mass effects), the release of the bulk arsenic follows that of ^{73}As . The concentration of aqueous arsenite is insignificant compared to that of arsenate and so the arsenate associated with the iron oxides is not reduced by the ascorbic acid in the course of reductive dissolution. Equilibrium chemistry also predicts the reduction of arsenate to arsenite to occur after Fe(III) reduction which has also been found experimentally by Islam et al. (2004).

Fig. 3 shows the fraction of total aqueous ^{73}As as a function of the fraction of Fe^{2+} released. The straight line in the figures represents a stoichiometric release of arsenate and Fe^{2+} during reductive dissolution. For ferrihydrite and goethite, the release of arsenate is delayed considerably

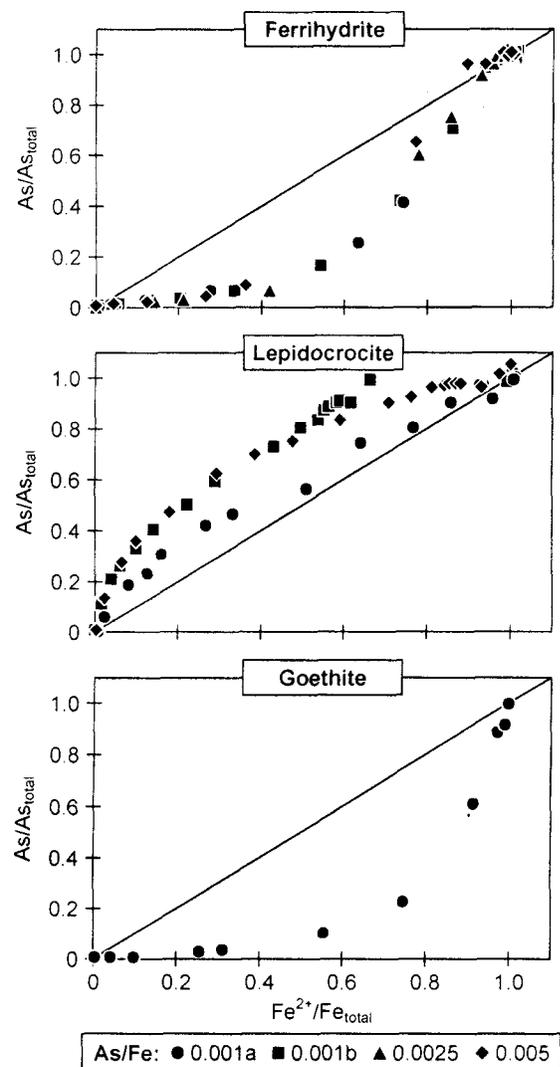


Fig. 3. Relative release of ^{73}As versus the relative release of Fe^{2+} during reductive dissolution of Ferri0.001b, Lepi0.001b and Goet0.001. The straight line indicates congruent release of ^{73}As and Fe^{2+} .

compared to the release of Fe^{2+} and a significant amount of arsenate does not accumulate in solution until 50% of the iron oxide has been reduced. In contrast, arsenate is rapidly released to solution during the reductive dissolution of lepidocrocite and relatively more arsenate accumulates in solution as compared to Fe^{2+} . The release of arsenate during reductive dissolution of Lepi0.001b is different from the others since all the arsenate is apparently released to solution during the reduction of the first 70% of the oxide (Fig. 3). Possibly, the Lepi0.001b consists of two phases: a more reactive phase with a high specific surface area to which arsenic is adsorbed and a more inert phase that does not adsorb much arsenate. We were unable to identify the presence of two different phases by XRD indicating that both are lepidocrocite.

3.1.3. Adsorbed ^{73}As

To further investigate the incongruent release of ^{73}As from the iron oxides, a method for determining adsorbed ^{73}As was developed. The method exploits that ^{73}As tracer partitioning between the pools of arsenic is the same as for the bulk of arsenic. Therefore, when a surplus of unlabelled arsenic is added to a suspension containing adsorbed ^{73}As , all adsorbed ^{73}As will desorb and can be measured as aqueous ^{73}As . The resulting increase in aqueous ^{73}As is a measure for adsorbed ^{73}As .

Fig. 4 shows the concentrations of aqueous and adsorbed arsenate, and the sum of the two, termed extractable arsenate, during the reductive dissolution of Ferri0.001b, Lepi0.001b and Goet0.001. For ferrihydrite and lepidocrocite, extractable (= aqueous + adsorbed) arsenate remains nearly constant and equal to total arsenic during the reductive dissolution of the iron oxide, indicating that all the non-aqueous arsenate is associated with the iron oxide surface. For ferrihydrite, the arsenate remains adsorbed until approximately 50% of the oxide has dissolved after which adsorbed arsenate decreases as aqueous arsenate increases. In contrast, for lepidocrocite adsorbed arsenate decreases as soon as dissolution is initiated with a concurrent increase in aqueous arsenate.

For goethite, extractable arsenate constitutes approximately 30% of total arsenate associated with the iron oxide until 30–40% of the oxide has dissolved after which extractable arsenate increases until the reductive dissolution is complete (Fig. 4). Since aqueous arsenate is initially absent, adsorbed arsenate is also constant at 30% of the total arsenate until 30–40% of the oxide has dissolved. Thereafter adsorbed arsenate increases until approximately 80% of the oxide has dissolved after which it decreases as the last 20% of the goethite is dissolved and aqueous arsenate increases.

3.2. Fate of arsenic during transformation of iron oxides

Aqueous Fe^{3+} catalyses the transformation of ferrihydrite and lepidocrocite (Pedersen et al., 2005). To investigate what happens to arsenic associated with ferrihydrite

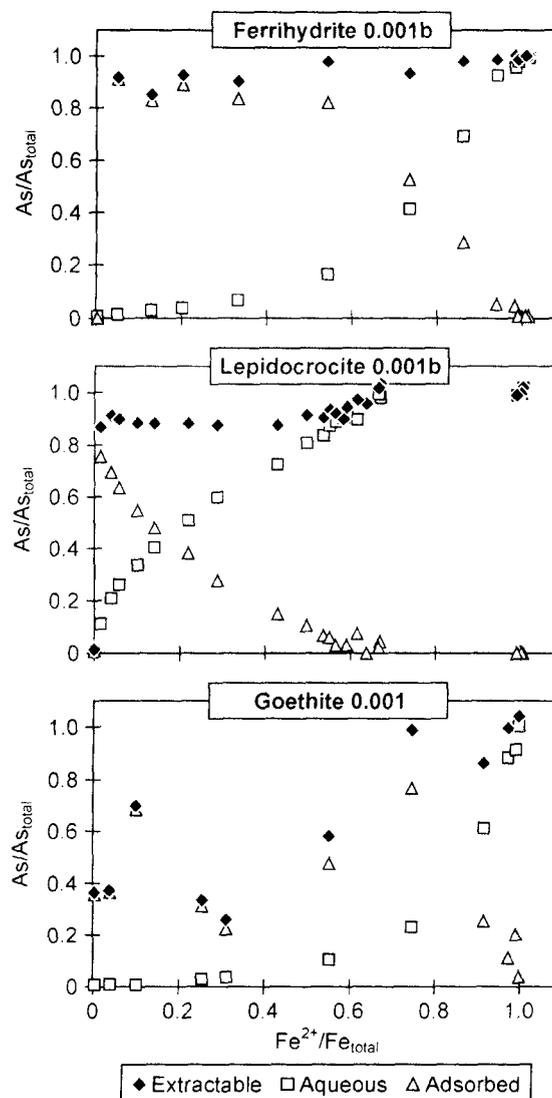


Fig. 4. The fraction of adsorbed and aqueous ^{73}As ($^{73}\text{As}/^{73}\text{As}_{\text{total}}$) versus the fraction of dissolved crystal ($\text{Fe}^{2+}/\text{Fe}^{2+}_{\text{total}}$) during reductive dissolution of Ferri0.001b, Lepi0.001b and Goet0.001. Extractable arsenic corresponds to the sum of adsorbed and aqueous arsenic.

and lepidocrocite during the transformation process, the iron oxides were submerged into solutions containing different Fe^{2+} concentrations at 25 °C and pH 6.5.

3.2.1. Transformation of iron oxides

XRD analysis of the solid phase at the end of the experiments show that within 5 days ferrihydrite was transformed completely into lepidocrocite and goethite at the lower Fe^{2+} concentrations and into goethite and magnetite at higher Fe^{2+} concentrations. Lepidocrocite remained lepidocrocite at lower Fe^{2+} concentrations and transformed partly or completely (1.0 mM) to magnetite at higher Fe^{2+} concentrations. To trace the transformation of the iron oxides, an ^{55}Fe radiotracer was incorporated homogeneously into the iron oxides and the iron oxides were thus radio labelled with both ^{55}Fe and ^{73}As . The homogeneous incorporation of ^{55}Fe in the iron oxides was documented

by the congruent release ($r^2 = 0.982\text{--}0.999$) during dissolution in ascorbic acid (Fig. 5).

The recrystallization of the iron oxides was monitored by the release of ^{55}Fe from the oxides to solution. Fig. 6 shows the activity of aqueous ^{55}Fe during the recrystallization of Ferri0.001b and Lepi0.001b in solutions containing variable Fe^{2+} concentrations. In the absence of aqueous Fe^{2+} there is no recrystallization and therefore no ^{55}Fe in solution, but when Fe^{2+} is present, the activity of aqueous ^{55}Fe increases rapidly in the experiments

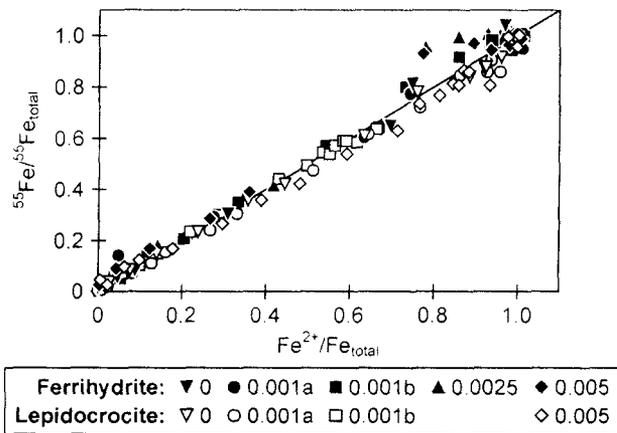


Fig. 5. The release of Fe^{2+} versus the release of ^{55}Fe during reductive dissolution in 10 mM ascorbic acid of ferrihydrite and lepidocrocite with various As/Fe molar ratios. Concentrations and activities are normalized to the added amount. The line represents congruent release.

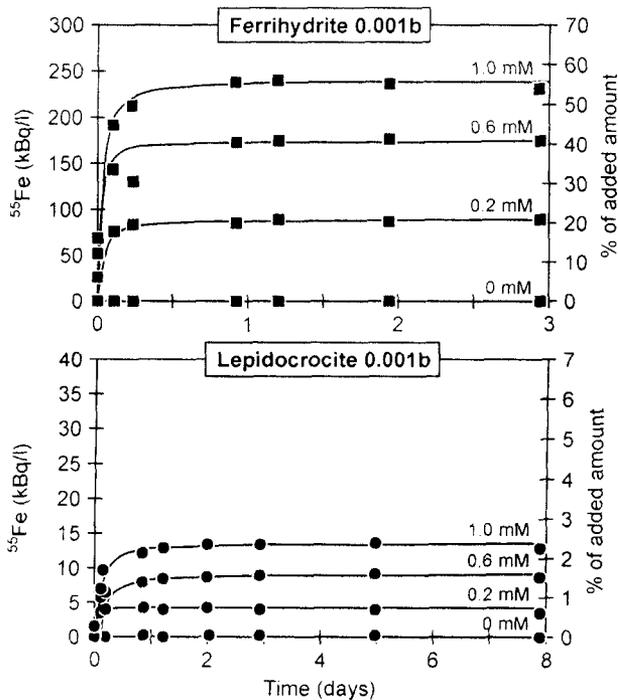


Fig. 6. The release of ^{55}Fe into solution during transformation of Ferri0.001b and Lepi0.001b dispersed in solutions containing 0, 0.2, 0.6 and 1.0 mM Fe^{2+} . Lines are provided for visual aid. Note the different scales.

with Ferri0.001b. Within 24 h the release of ^{55}Fe from ferrihydrite levels off and the activity becomes constant at a level that depends on the relative pool size of Fe^{2+} as compared to solid phase Fe. Similar results were found for the other ferrihydrites and for Lepi0 and Lepi0.001a and are in accordance with the results of Pedersen et al. (2005). However, Lepi0.001b and Lepi0.005 (not plotted) show a slightly different pattern since less than 3% of the ^{55}Fe associated with the oxide mineral is released to solution (Fig. 6).

The distribution of bulk Fe and ^{55}Fe between the aqueous and solid (including adsorbed) phase at the beginning and end of the experiments with Ferri0.001b and Lepi0.001b is shown in Fig. 7 for aqueous Fe^{2+} concentrations of 0.2 and 1.0 mM. Initially all the ^{55}Fe is contained in the solid phase. But at the end of the experiments with ferrihydrite ^{55}Fe has become distributed proportional to bulk Fe between the aqueous and solid phases, indicating a complete isotopic equilibration. The same results were found for all the ferrihydrites, Lepi0 and Lepi0.001a. However, Lepi0.001b and Lepi0.005 differ from this general pattern as there occurs almost no redistribution of ^{55}Fe during the recrystallization and the ^{55}Fe remains largely incorporated in the solid phase after the recrystallization (Fig. 7).

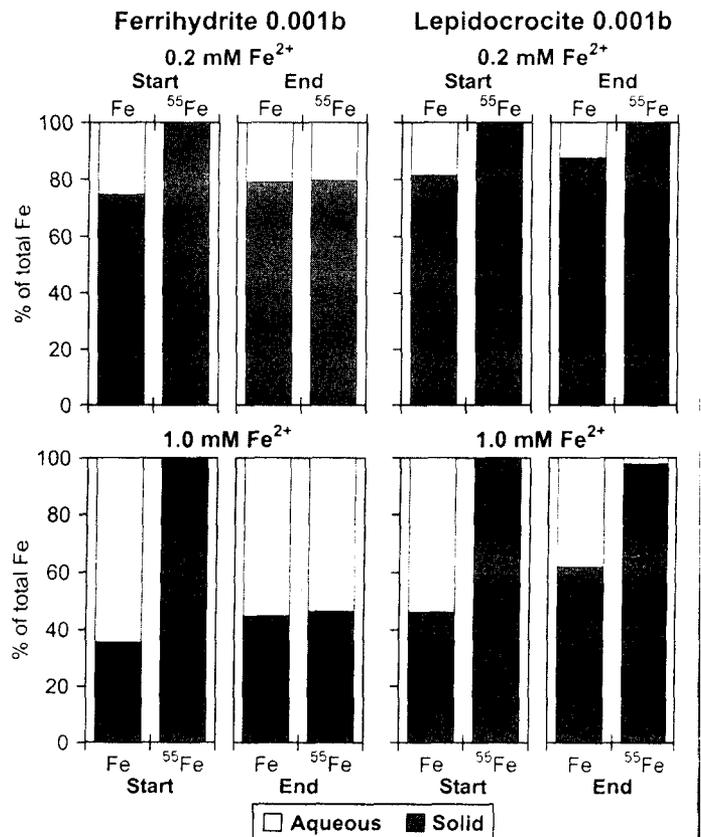


Fig. 7. Distribution of bulk Fe and ^{55}Fe over the aqueous and solid phases at the start and end of experiments with Ferri0.001b and Lepi0.001b suspended in a 0.2 and 1.0 mM Fe^{2+} solution.

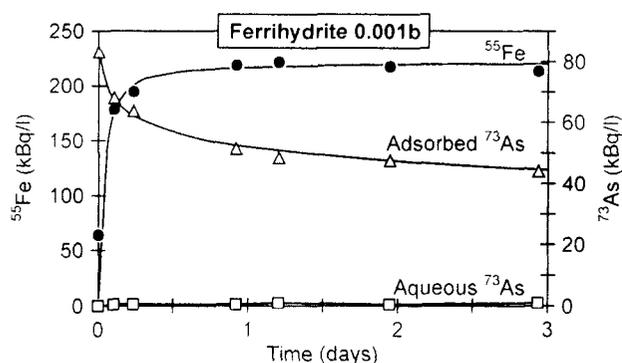


Fig. 8. Aqueous ^{55}Fe , adsorbed ^{73}As and aqueous ^{73}As during recrystallization in 1.0 mM Fe^{2+} of Ferri0.001b. Lines are added for visual aid.

3.2.2. Release of arsenic during transformation of iron oxides

As the activity of aqueous ^{55}Fe increases during the recrystallization of ferrihydrite, the activity of adsorbed arsenic decreases to 45% after 3 days (Fig. 8). Adsorbed arsenic is exclusively present as arsenate and the concentration of aqueous arsenic remains insignificant.

The activity of adsorbed and aqueous ^{73}As during the recrystallization of Ferri0.001b and Lepi0.001b at various Fe^{2+} concentrations is shown in Fig. 9. In the absence of Fe^{2+} , there is no recrystallization of ferrihydrite according to XRD and adsorbed arsenic remains constant. However, in the presence of Fe^{2+} adsorbed arsenic decreases over time as ferrihydrite transforms into lepidocrocite and goethite at lower Fe^{2+} concentrations and into goethite and

magnetite at the higher Fe^{2+} concentrations. For Lepi0.001b, adsorbed ^{73}As remains constant at Fe^{2+} concentrations up to 0.4 mM (Fig. 9), whereas adsorbed ^{73}As decreases at Fe^{2+} concentrations above 0.6 mM. XRD showed that lepidocrocite did not recrystallize at the lower Fe^{2+} concentrations, whereas magnetite was formed at an Fe^{2+} concentration above 0.6 mM. The decrease in adsorbed arsenic is clearly correlated with the transformation of ferrihydrite and lepidocrocite into new phases.

During recrystallization less than 1% of the total amount of arsenic is released and aqueous ^{73}As remains insignificant compared to the adsorbed ^{73}As (Fig. 9). The observed decrease in adsorbed arsenic therefore reflects that arsenic becomes bound more strongly to the recrystallized iron oxides. Interestingly the small amount of arsenic that is released to solution is present as arsenite, and some of the arsenate originally adsorbed onto the surface of the oxides must have been reduced to arsenite prior to its release.

4. Discussion

4.1. Association of arsenate with iron oxides

Previous studies of arsenate coprecipitation with ferrihydrite, using As/Fe molar ratios as high as 0.68, have shown no evidence for the formation of a ferric arsenate, a solid solution, or of an As-bearing surface precipitate as has been proposed for phosphate and ferrihydrite (Fox, 1989.

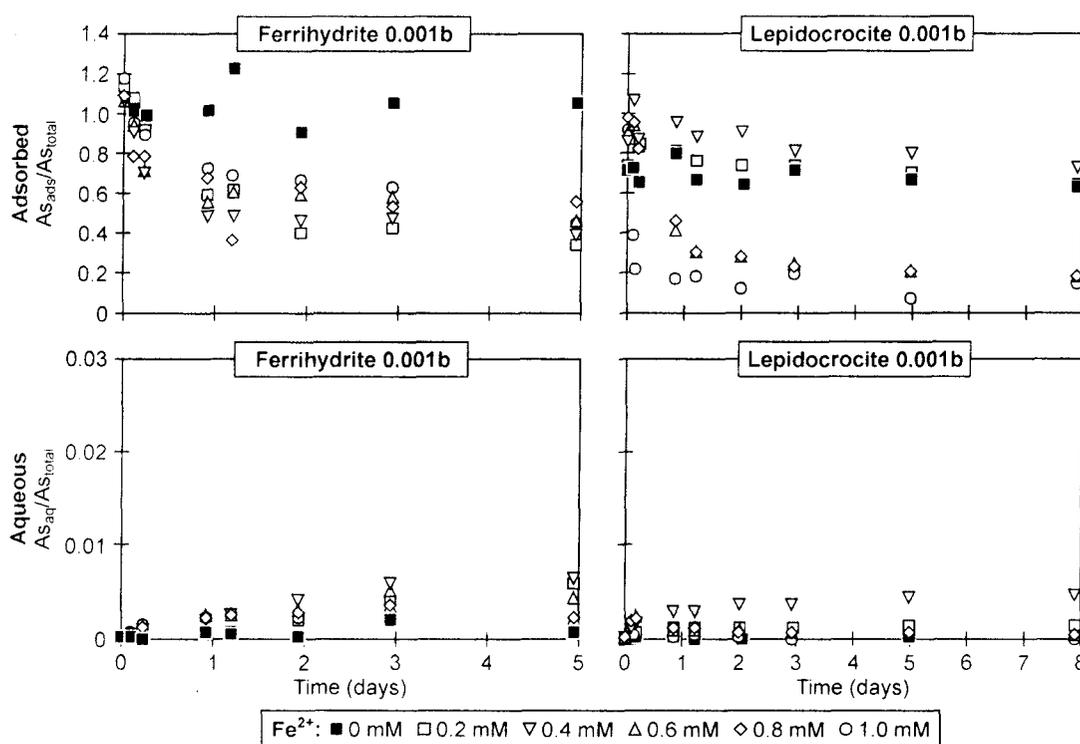


Fig. 9. Adsorbed (top) and aqueous (bottom) ^{73}As during recrystallization at various Fe^{2+} concentrations, indicated by the symbols, of Ferri0.001b (left) and Lepi0.001b (right).

1991). Instead, arsenate is believed to remain adsorbed onto the surface of ferrihydrite, even during ongoing precipitation (Fuller et al., 1993; Waychunas et al., 1993, 1996; Paige et al., 1997a; Rancourt et al., 2001; Richmond et al., 2004). This study further documents that arsenate remains adsorbed onto the surface of ferrihydrite as well as of lepidocrocite, and is not incorporated into the crystal structure (Fig. 4). Aging a Ferri0.001b suspension for up to 4 weeks gave no change in the concentration of adsorbed arsenate indicating that arsenate does not diffuse into the ferrihydrite particles over time, as has been described for Zn into ferrihydrite (Schultz et al., 1987) and Ni, Zn and Cd into goethite particles (Brümmer et al., 1988). The reactivity of the ferrihydrite did not change during the 4 weeks of storage, indicating that recrystallization of ferrihydrite did not occur in the absence of Fe^{2+} .

In contrast, about 70% of the arsenate is bound so strongly to goethite that it cannot be desorbed. Although the ionic radius of arsenate is optimal for incorporation into goethite (Cornell and Schwertmann, 2003), this process has not been demonstrated previously beyond doubt (Paige et al., 1994, 1996; Sun et al., 1999; Ford, 2002; Cornell and Schwertmann, 2003).

During the precipitation of ferrihydrite, lepidocrocite and schwertmannite the adsorption of arsenate onto the primary ferrihydrite crystallites retards crystal growth and coagulation by preventing further Fe–O–Fe-polymerization (Fuller et al., 1993; Waychunas et al., 1993, 1995, 1996; Randall et al., 2001; Richmond et al., 2004; Regenspurg and Peiffer, 2005). The inhibition of crystal growth during synthesis results in a decreased mean crystallite size and an enlarged surface area (Fuller et al., 1993; Dixit and Hering, 2003). In this study the surface area of both ferrihydrite and lepidocrocite remained unaffected by the arsenic content (Table 1) which may be due to the low arsenate content. However, the surface area of Goet0.001 was smaller than of Goet0 but the surface areas of both goethites remained within the range previously reported for goethite (Larsen and Postma, 2001).

4.2. Reductive dissolution of iron oxides

4.2.1. Arsenate and reduction rate

The effect of adsorbed oxyanions on the dissolution rate of iron oxides has been studied under varying conditions such as the type of iron oxide, the dissolution pathway, the oxyanion/Fe molar ratio and pH (Bondietti et al., 1993; Biber et al., 1994; Paige et al., 1997a; Eick et al., 1999). Both an inhibiting (Bondietti et al., 1993; Biber et al., 1994; Paige et al., 1997a; Eick et al., 1999) and an accelerating effect (Bondietti et al., 1993; Eick et al., 1999) has been observed but which conditions favour one effect over the other remains unclear.

This study shows that the presence of arsenic, at an As/Fe molar ratio less than 0.005, in ferrihydrite and lepidocrocite does not alter the reduction rate during reductive dissolution in ascorbic acid at pH 3 (Fig. 2, Table 1). The

potential effect of an adsorbed anion on the dissolution rate must depend on the fraction of surface sites that is occupied by the anion. The As/Fe ratio can be used as an approximation of the As/surface site ratio to compare the results of this study with those of previous studies. Since previous studies (Bondietti et al., 1993; Biber et al., 1994; Paige et al., 1997a; Eick et al., 1999) have generally used significantly higher As/Fe molar ratios (0.002–5.6), the insensitivity of the reduction rate towards trace amounts of arsenate is attributed to the low arsenate concentration employed here.

4.2.2. Release of arsenic during abiotic dissolution of iron oxides

The release of arsenate with Fe^{2+} is incongruent during the reductive dissolution of both ferrihydrite, lepidocrocite and goethite (Fig. 3). Paige et al. (1997a) also reported incongruent release of arsenate and iron during proton assisted dissolution of ferrihydrite with As/Fe ratios between 0.03 and 1.0.

The release of arsenate from ferrihydrite is significantly delayed compared to Fe^{2+} (Fig. 3). Apparently the arsenate remains adsorbed onto the ferrihydrite surface until the surface area and thereby the number of surface sites becomes too small to contain all the arsenate. During continued dissolution adsorbed arsenate decreases while aqueous arsenate increases in accordance with Fig. 4. Dixit and Hering (2003) determined a sorption density of arsenate on ferrihydrite of 2.6 sites per nm^2 at pH 4, assuming a specific surface area of $600 \text{ m}^2/\text{g}$ for ferrihydrite. If we use the same sorption density under our experimental conditions, at pH 3, we can estimate that at maximum 1% of the surface sites is covered with arsenate at the beginning of the experiments. Consequently the ferrihydrite surface will not become saturated with arsenate until 98% of the ferrihydrite has dissolved. However, our results (Fig. 4) show that arsenate is already released from ferrihydrite to the solution when approximately 50% of the oxide has dissolved. This may be due to competitive anion adsorption between arsenate and the ascorbate (10 mM).

The release of arsenate from goethite resembles that from ferrihydrite (Fig. 4). Given the smaller surface area of goethite, compared to ferrihydrite, saturation of the surface with arsenate is expected to occur earlier in the dissolution experiment for goethite than for ferrihydrite at an equal arsenate content. However, for both iron oxides the arsenate is released when approximately 50% of the iron oxide is dissolved. This could be caused by the lower “mobile” arsenate pool in the experiments with goethite, since initially only 40% of the arsenate is found as adsorbed arsenate while the rest resides within the goethite structure.

The sorption behaviour of arsenate during dissolution of lepidocrocite clearly differs from that of ferrihydrite and goethite since arsenate is released very rapidly from lepidocrocite (Figs. 3 and 4). The adsorption of arsenate on iron oxides is strongly pH dependent, with increasing adsorption at decreasing pH (Bowell, 1994; Manning

et al., 1998; Raven et al., 1998; Dixit and Hering, 2003). The pH at which the net surface charge is zero i.e. the point of zero charge (PZC) is 7.8–7.9 for ferrihydrite, 6.7–8 for lepidocrocite and 8.9–9.5 for goethite (Parks and de Bruyn, 1962; Cornell and Schwertmann, 2003). Based on these PZC values it seems questionable whether a difference in PZC alone can account for the different sorption behaviour of lepidocrocite.

Lepidocrocite consists of double chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedra running parallel to the *c*-axis. The double chains share edges with adjacent double chains and each chain is displaced by half an octahedron with respect to its neighbour, thus forming corrugated sheets of octahedra. Assuming that arsenate adsorbs to lepidocrocite by complexes resulting from bidentate corner sharing between AsO_4 tetrahedra and edge sharing pairs of FeO_6 octahedra (Randall et al., 2001), possible sites for the adsorption of arsenate are along the *b*- and the *c*-axis (Cornell and Schwertmann, 2003). Since lepidocrocite crystals are extended along the *c*-axis, the latter surface is expected to be more important for the adsorption of arsenate. Larsen and Postma (2001) found that the mechanism for reductive dissolution of lepidocrocite in 10 mM ascorbic acid is etch-pitting of the crystals parallel to the *c*-axis. This could be expected to increase the number of surface sites, but the results show that instead it eliminates surface sites for the adsorption of arsenate as reductive dissolution occurs.

4.3. Transformation of iron oxides

The least stable iron oxides may undergo phase transformations into more stable phases (Cornell and Schwertmann, 2003). The transformation product depends on the pH, the temperature of the system, and the presence of foreign ions (Schwertmann and Murad, 1983). Under oxic conditions, goethite and hematite are thermodynamically the most stable iron oxides and they are therefore the end members of many transformation pathways. Under anoxic conditions, in the presence of Fe^{2+} , ferrihydrite and lepidocrocite may transform into goethite, lepidocrocite, magnetite and green rust (Tamura et al., 1983; Jolivet et al., 1992; Tronc et al., 1992; Ona-Nguema et al., 2002; Hansel et al., 2003; Pedersen et al., 2005).

4.3.1. Transformation of iron oxides

In this study, ferrihydrite was transformed into lepidocrocite and goethite at a low Fe^{2+} concentration and into goethite and magnetite at a high Fe^{2+} concentration, as evidenced by the XRD measurements. Lepidocrocite transformed into magnetite at a high Fe^{2+} concentration and remained lepidocrocite at a low Fe^{2+} concentration.

In the experiments with ferrihydrite, Lepi0 and Lepi0.001a, isotopic equilibrium is reached for the ^{55}Fe and bulk Fe between the aqueous and non-aqueous phases (Fig. 7). This suggests the recrystallization of the iron oxides to proceed by dissolution of the original phase and precipitation of a new phase, induced by the catalytic

action of Fe^{2+} . Pedersen et al. (2005) suggested a mechanism where $\text{Fe}(\text{II})$ exchanges for $\text{Fe}(\text{III})$ in the terminal octahedral positions and the added electron then facilitates the disintegration of the iron oxide.

During the recrystallization of Lepi0.001b and Lepi0.005, no redistribution of ^{55}Fe was observed despite a complete recrystallization of lepidocrocite to magnetite at the higher Fe^{2+} concentrations. This indicates a solid phase transformation of lepidocrocite to magnetite. Such a topotactic transformation of lepidocrocite to magnetite has previously been reported by Sudukar et al. (2003).

4.3.2. Incorporation of arsenic in the recrystallized phase

Paige et al. (1994, 1996) studied the transformation of ferrihydrite coprecipitated with arsenic at As/Fe molar ratios between 0 and 0.075, at 60 or 70 °C and pH 12, and concluded that arsenate is not incorporated into the product phase. Similar results have been found for phosphate by Paige et al. (1997b). In contrast, Sun et al. (1999) found arsenic to become incorporated in the structure of the product during the transformation of ferrihydrite with an As/Fe molar ratio of 0.01, at pH 12 and at 70 °C. Also Ford (2002) concluded that arsenic is retained in the transformation product of ferrihydrite coprecipitated with arsenic in the As/Fe molar ratio range 0–0.07 due to the inability to extract arsenic in 0.4 M HCl. Here the transformation took place at pH 6 and 40 °C.

Our data provides more direct evidence concerning the fate of arsenate during the transformation of ferrihydrite and lepidocrocite because radiotracers allow us to separate between adsorbed arsenic and arsenic incorporated in the crystal. Figs. 8 and 9 demonstrate how the adsorbed fraction of arsenic decreases with time as ferrihydrite and lepidocrocite are recrystallized, at pH 6.5 and 25 °C, into more crystalline phases. This decrease is only observed when a recrystallization occurs and is absent when the original iron oxide remains unaltered. No separate arsenic phases were detected in the XRD diffractograms as expected considering the low arsenic content of the samples.

The relative incorporation of ^{73}As into the recrystallization products versus the relative release of ^{55}Fe is displayed in Fig. 10. Here the release of ^{55}Fe is used as an indicator for the extent of recrystallization of ferrihydrite. The line indicates when the incorporation of ^{73}As equals the release of ^{55}Fe . Fig. 10 illustrates how the incorporation of ^{73}As into the crystalline product only occurs during the final stage of the recrystallization process. Perhaps this indicates that arsenic remains preferentially adsorbed onto the ferrihydrite until the surface of ferrihydrite becomes too small to adsorb all the arsenic.

4.3.3. Effect of arsenic on the transformation rate

The presence of foreign ions, either coprecipitated with ferrihydrite, adsorbed onto the ferrihydrite surface or present in solution, may influence the rate of transformation (Cornell and Schwertmann, 1979; Gálvez et al., 1999; Schwertmann et al., 2000; Campbell et al., 2002; Ford,

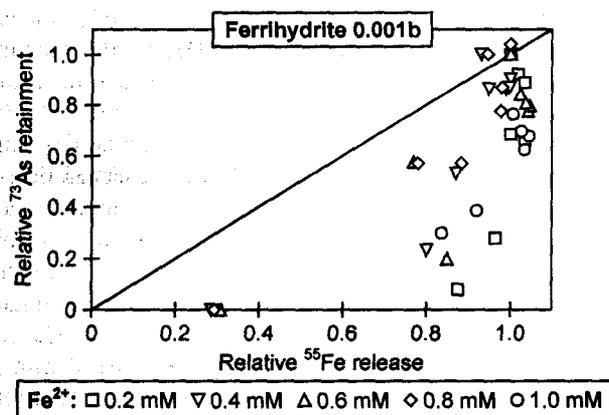


Fig. 10. The relative incorporation of ^{73}As as a function of the relative release of ^{55}Fe during transformation of ferrihydrite 0.001b. The straight line indicates when the incorporation of ^{73}As equals the release of ^{55}Fe .

2002; Alvarez et al., 2005). Both arsenate and phosphate have been found to retard the recrystallization rate (Paige et al., 1996, 1997b; Sun et al., 1999; Ford, 2002). Arsenic is believed to retard the transformation of ferrihydrite in a similar way as hydroxyl-carboxylic acids (Sun et al., 1999) for which Cornell and Schwertmann (1979) suggested a model where ferrihydrite becomes stabilized by the anion linking of two or more units of ferrihydrite, thereby forming a network of particles resistant to both aggregation and dissolution.

The initial rate of recrystallization of the iron oxides has been calculated (Fig. 11) as the slope of a line through the first data points for ^{55}Fe release (Fig. 6). The initial transformation rate of ferrihydrite is found to be slightly related to the Fe^{2+} concentration, while it is unaffected by the arsenic content. This result contradicts earlier findings showing an inhibiting effect of arsenate on the transformation rate of ferrihydrite (Sun et al., 1999). Part of the discrepancy may be due to the low arsenic content used in this study. Furthermore Ford (2002) and Paige et al. (1996) provoked ferrihydrite recrystallization by heating,

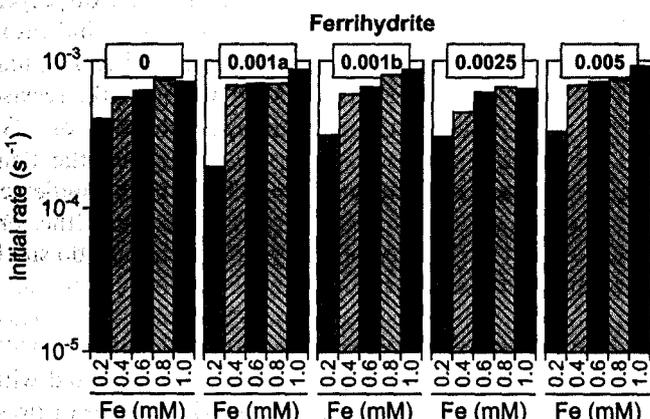


Fig. 11. Initial recrystallization rate of ferrihydrite containing arsenic in the As/Fe molar ratios varying from 0 to 0.005 and at various Fe^{2+} concentrations.

while in this study recrystallization was catalysed by the addition of Fe^{2+} . A comparison of the recrystallization rates shows that the rates in this study are four orders of magnitude higher than those found by Ford (2002) at an As/Fe molar ratio of 0.005. Apparently the driving force for recrystallization is much higher when provoked by the presence of Fe^{2+} as compared to heating.

4.4. Implications for natural environments

Our results demonstrate that the association of arsenic with iron oxides varies with the mineralogy. For ferrihydrite and lepidocrocite most arsenic remains associated with the surface but in goethite and magnetite arsenic is to a larger extent incorporated in the structure. The difference has major implications for arsenic mobilization in aquifers. While adsorbed arsenic may be mobilized by competitive anion exchange with phosphate (Acharyya et al., 1999, 2000) or carbonate (Appelo et al., 2002; Anawar et al., 2004) this is not the case for structurally incorporated arsenic. Therefore more information is needed on arsenic speciation in sediments in order to evaluate the mobilization mechanisms.

The reduction of iron oxides has also been suggested as a mechanism for arsenic mobilization to groundwater which has been supported by correlation plots between Fe and As (Nickson et al., 2000; BGS and DPHE, 2001; McArthur et al., 2001; Bose and Sharma, 2002; Horneman et al., 2004; van Geen et al., 2004). However, our results show that a congruent release of arsenic and iron during reductive dissolution of iron oxides cannot be expected. While arsenate is repelled from lepidocrocite, it adsorbs strongly onto ferrihydrite and goethite and is only released once the surface area of the iron oxide has become too small to adsorb all the arsenate. In accordance herewith, Swartz et al. (2004) proposed that the aqueous arsenic concentration in a Bangladesh aquifer is controlled by a limited capacity of the iron oxides to further adsorb arsenic.

The phase transformation of ferrihydrite and lepidocrocite into more crystalline Fe(III) oxide phases or magnetite results in the incorporation of arsenic into the structure of the crystalline product. In the field this process may be important as e.g. oxic river sediment becomes incorporated in a sedimentary floodplain sequence and develops into an anoxic aquifer with groundwater containing Fe^{2+} . The transformation of ferrihydrite and lepidocrocite, to which arsenate is adsorbed, into more stable Fe(III) oxides could be an important trapping mechanism for arsenate in natural sediments.

5. Conclusions

With ferrihydrite and lepidocrocite, arsenate is mainly associated with the iron oxide surface and is not incorporated into the crystal lattice. However, with goethite 70% of the arsenate was bound so strongly to the oxide that it

did not easily desorb. The presence of trace amounts (less than 5‰) of arsenate in or on ferrihydrite, lepidocrocite and goethite does not affect the reactivity towards reductive dissolution in 10 mM ascorbic acid. During reductive dissolution arsenate remains adsorbed to ferrihydrite and goethite until the surface area is too small to retain the arsenate, whereas there is a rapid release of arsenate from lepidocrocite.

During recrystallization of ferrihydrite and lepidocrocite in an Fe²⁺ solution arsenic becomes bound more firmly to the product phase. The rate of recrystallization depends on the Fe²⁺ concentration but is unaffected by the presence of arsenate in the studied range.

Acknowledgments

This research was supported by the Danish Natural Science Research Council. We thank Hans Christian Bruun Hansen at KVL for help and guidance with the X-ray diffractograms and two anonymous reviewers for their comments.

Associate editor: George R. Helz

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