

The reactivity of iron oxides towards reductive dissolution with ascorbic acid in a shallow sandy aquifer (Rømø, Denmark)

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Abstract

The pool of iron oxides, available in sediments for reductive dissolution, is usually estimated by wet chemical extraction methods. Such methods are basically empirically defined and calibrated against various synthetic iron oxides. However, in natural sediments, iron oxides are present as part of a complex mixture of iron oxides with variable crystallinity, clays and organics etc. Such a mixture is more accurately described by a reactive continuum covering a range from highly reactive iron oxides to non-reactive iron oxide. The reactivity of the pool of iron oxides in sediment can be determined by reductive dissolution in 10 mM ascorbic acid at pH 3. Parallel dissolution experiments in HCl at pH 3 reveal the release of Fe(II) by proton assisted dissolution. The difference in Fe(II)-release between the two experiments is attributed to reductive dissolution of iron oxides and can be quantified using the rate equation $J/m_0 = k'(m/m_0)^\gamma$, where J is the overall rate of dissolution (mol s^{-1}), m_0 the initial amount of iron oxide, k' a rate constant (s^{-1}), m/m_0 the proportion of undissolved mineral and γ a parameter describing the change in reaction rate over time. In the Rømø aquifer, Denmark, the reduction of iron oxides is an important electron accepting process for organic matter degradation and is reflected by the steep increase in aqueous Fe^{2+} over depth. Sediment from the Rømø aquifer was used for reductive dissolution experiments with ascorbic acid. The rate parameters describing the reactivity of iron oxides in the sediment are in the range $k' = 7 \cdot 10^{-6}$ to $1 \cdot 10^{-3} \text{ s}^{-1}$ and $\gamma = 1$ to 2.4. These values are intermediate between a synthetic 2-line ferrihydrite and a goethite. The rate constant increases by two orders of magnitude over depth suggesting an increase in iron oxide reactivity with depth. This increase was not captured by traditional oxalate and dithionite extractions. © 2006 Elsevier Inc. All rights reserved.

1. Introduction

Iron(III) oxides, hydroxides and oxyhydroxides, hereafter collectively referred to as iron oxides, are ubiquitous reactive constituents in soils, sediments and aquifers and may have a profound impact on the composition of groundwater or sediment porewaters. Iron oxides may serve as a terminal electron acceptor in the degradation of organic matter in sediments. In non-sulfidic sediments, more than 70% of organic carbon mineralization in sediments may proceed through the reduction of iron oxides (Canfield et al., 1993; Thamdrup, 2000). In aquifers, iron oxides present in the sediment may constitute an important

redox buffer against the spread of organic pollutants (Heron and Christensen, 1995; Tuccillo et al., 1999).

There are different pathways for reductive dissolution of iron oxide. The reaction may proceed abiotically through reaction with hydrogen sulfide (dos Santos Afonso and Stumm, 1992; Yao and Millero, 1996; Poulton et al., 2004) or various organic reductants and complexing agents (LaKind and Stone, 1989; Sulzberger et al., 1989; Lovley et al., 1991). Alternatively, microbes may catalyze the reaction through dissimilatory iron reduction (Lovley, 1991; Thamdrup, 2000; Luu and Ramsay, 2003). Here, the occurrence of iron oxide as a solid phase constrains its availability as an electron acceptor. Most microorganisms seem to require direct contact between the bacteria and the iron oxide (Arnold et al., 1988; Das and Caccavo, 2000). However, the electron transfer may also be mediated by so-called electron shuttle agents (Lovley et al., 1996; Nevin

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and Lovley, 2000; Rosso et al., 2003). A common feature in laboratory batch incubations is that the reduction process over time becomes inhibited by the produced Fe(II) (Roden, 2004).

The mineralogy of the iron oxides influences the process at several levels. First, ferrihydrite and lepidocrocite are much less stable than goethite or hematite and therefore there will be a major difference in the free energy gain of the reduction process depending on the mineralogy (Cornell and Schwertmann, 2003; Appelo and Postma, 2005). Generally, the energy gain strongly increases towards lower pH (Postma and Jakobsen, 1996). With hydrogen sulfide as reductant, the rate of iron oxide reduction (when normalized to surface area) has been directly related to this difference in energy gain (dos Santos Afonso and Stumm, 1992; Poulton et al., 2004). Similarly, Larsen and Postma (2001) found, for reduction by ascorbate, that the rate normalized to surface area varied for different oxides, which indicates that the mineral structure itself influences the rate. The second aspect is the specific surface area of the iron oxides which generally decreases with increasing stability of the oxides. The specific surface area of ferrihydrite may easily be 10 times higher than that of hematite (Cornell and Schwertmann, 2003) and the reduction rate of an iron oxide is naturally a function of the available surface area. A final complicating aspect is that the mineralogy of the iron oxide may change in the cause of the reduction process. Even small amounts of Fe^{2+} have been found to catalyze the recrystallization of ferrihydrite to goethite or lepidocrocite and the latter mineral may also recrystallize into larger sized crystals (Hansel et al., 2003; Jeon et al., 2003; Pedersen et al., 2005).

The importance of iron oxide mineralogy on microbiologically mediated iron oxide reduction is not clear. Some laboratory incubation studies report that microbes are only able to metabolize poorly crystalline iron oxides such as ferrihydrite at significant rates, but not goethite or hematite (Lovley and Phillips, 1986; Glasauer et al., 2003). However, in other studies microorganisms were able to reduce all iron oxides (Roden and Zachara, 1996; Neal et al., 2003; Bonneville et al., 2004; Hansel et al., 2004; Gonzalez-Gil et al., 2005). Roden and Zachara (1996) argued that the rate of microbial iron reduction depends only on the available surface area of the iron oxides and is independent of the iron oxide mineralogy. However, Bonneville et al. (2004) found that the rate of iron oxide reduction normalized to surface area is also a function of iron oxide mineralogy and can be related to the energy gain of the reaction.

It is generally recognized that part of the pool of iron oxide in sediments is reduced more easily than the remainder (Lovley and Phillips, 1986; Canfield, 1989; von Gunten and Zobrist, 1993; Thamdrup et al., 1994; Heron and Christensen, 1995; Tuccillo et al., 1999; Zachara et al., 2004). Accordingly, the intrinsic reactivity of iron oxides in sediments, i.e. their susceptibility towards reductive dissolution, is an important issue. The traditional assay

towards determining the most reactive iron oxides, also called poorly crystalline Fe-oxides, is by a single step wet chemical extraction in various versions such as HCl hydroxylamine (Lovley and Phillips, 1987; Hines et al., 1997; Poulton and Canfield, 2005), HCl (Tuccillo et al., 1999; Heron and Christensen, 1995) or ammonium oxalate at pH 3 (Schwertmann, 1964; McKeague and Day, 1966; Thamdrup et al., 1994) and these methods are usually calibrated against synthetic iron oxides. By employing such methods it has been found that iron oxide reduction in sediments is strongly correlated to the presence of poorly crystalline iron oxides (Lovley and Phillips, 1987; Thamdrup et al., 1994; Thamdrup, 2000).

In summary, the reactivity of iron oxides will depend on factors like the crystallinity (crystal structure and the crystal size distribution) and will change as the assemblage of crystals becomes partially dissolved. Therefore, a kinetic approach towards the determination of reactivity is preferred and for synthetic iron oxides (Postma, 1993; Larsen and Postma, 2001; Houben, 2003; Roden, 2004) the rate law first proposed by Christoffersen and Christoffersen (1976) has been applied

$$J = \frac{-dn_{\text{cr}}}{dt} = km_0 \left(\frac{m}{m_0} \right)^\gamma g(C) \quad (1)$$

Here, J is the reduction rate (mol s^{-1}), k the rate constant (s^{-1}), m_0 the total sum of reactive iron oxides and $(m/m_0)^\gamma$ a function of the undissolved mineral fraction (both in mol). The exponent γ varies with the crystal structure and the distribution of the crystal population. $g(C)$ describes the influence of the reductant on the rate. In the presence of excess reductant, for example 10 mM ascorbic acid, $g(C)$ becomes a constant, reducing the rate law (1) to

$$\frac{J}{m_0} = k' \left(\frac{m}{m_0} \right)^\gamma \quad (2)$$

Here k' is the product of the rate constant and $g(C)$. The results of such dissolution experiments have shown a variation in initial rate ($m/m_0 = 1$) of two orders of magnitude between a 2-line ferrihydrite and poorly crystalline goethite, while during dissolution of 90% of the crystals ($m/m_0 = 0.1$) the rate decreased by up to three orders of magnitude.

In sediments, iron oxides generally do not occur as a separate mineral phase but rather as an integral component of surface coatings where the predominantly negative surface charged clays and organics are sandwiched with iron oxides that have a predominant positive surface charge (Gu et al., 1994; Perret et al., 2000; Appelo and Postma, 2005). In analogy to a model for the degradation of organic matter (Boudreau and Ruddick, 1991; Boudreau, 1997), the reactivity of Fe-oxides occurring in such a mixture in sediments may be viewed as a reactive continuum described by a distribution function $g(\kappa, t)$ (Postma, 1993). The initial reactivity ($g(\kappa, 0)$) is in this model defined by a Gamma distribution.

$$g(k, 0) = \frac{g_0 k^{v-1} e^{-ak}}{\Gamma(v)} \quad (3)$$

Here, a and v are free fit parameters and $\Gamma(v)$ is the Gamma function. The dissolution of this reactive continuum may then be described by the rate equation (Postma, 1993)

$$\frac{J}{m_0} = \frac{v}{a} \left(\frac{m}{m_0} \right)^{1+\frac{1}{v}} \quad (4)$$

This rate law is mathematically nearly identical to the rate law for a polydisperse population of crystals given above (Eq. (2)) even though the Gamma distribution function treats reactivity by a statistical approach. In other words both the reactivity of synthetic crystal populations and the reactivity of reducible Fe(III) in sediment can be analyzed using the rate law given by Eq. (2). Postma (1993), Roden (2004) and Weiss et al. (2004) presented some data for the reactivity of Fe(III) in sediments. In the following a more extended analysis of the reactivity of iron oxides in aquifer sediments is presented using the kinetic approach and the results are compared with the more traditional assay using chemical extractions.

2. Methods

2.1. Groundwater and sediment sampling

Groundwater was sampled using a drive point piezometer equipped with a 1 cm long stainless steel 50 μ m mesh screen, mounted on a 1.27 cm diameter stainless steel pipe. Samples were collected, using a peristaltic pump, through a 1.5 mm inner diameter stainless steel tube mounted directly behind the screen. The pump pressed the water into a 50 mL syringe and pressure caused by friction of the piston ensured redissolution of any gases. Prior to sampling at each depth the screen and tubing were flushed by pumping 50 mL, corresponding to 1.5 times the volume of the sampling system. The equipment enabled sampling with a 2.5 cm depth resolution.

Sediment samples were obtained by driving a 3 m long stainless steel core-liner (inner diameter 5 cm) into the sediment using a jackhammer. The cores were taken within 0.5 m from the groundwater sampling site. The cores were cut into 5 cm sections and stored in N₂ flushed gas impermeable sealed bags until analysis.

2.2. Water analysis

Water samples were filtered through a 0.2 μ m filter cartridge mounted directly on the sampling syringes. Dissolved Fe²⁺ was determined immediately in the field by spectrophotometry using the ferrozine method (Stookey, 1970). Alkalinity was determined in the field using the Gran titration method. pH, dissolved oxygen and electrical conductivity were determined by electrodes in a flow cell mounted directly on the sampling system. H₂S was also determined in the field (Cline, 1967) but the concentration was always

below the detection limit of 0.5 μ M. Ammonium was determined back in the laboratory spectrophotometrically using Flow Injection Analysis. The analytical precision estimated from repeated analysis is generally within 5%.

2.3. Sediment analysis and reduction experiments

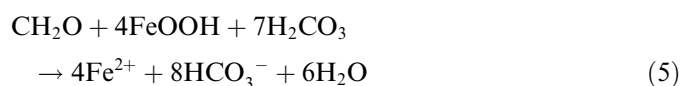
The pool of iron oxides in the sediment were characterized using traditional extraction methods on crushed and air dried sediment samples. For the determination of the amorphous Fe(III) fraction (McKeague and Day, 1966) we used a NH₄⁺-oxalate solution at pH 3 (Schwertmann, 1964) and for the total iron oxide content a dithionite-citrate-bicarbonate (DCB) solution at 80 °C (Mehra and Jackson, 1960).

The reactivity of iron oxides in the sediment was determined by monitoring the release of Fe²⁺ from sediment samples in a ascorbic acid and a HCl solution both at pH 3 (Postma, 1993). 1.1 L anoxic reagent (10 mM ascorbic acid or 1 mM HCl) was prepared and adjusted to pH 3 in a glass reaction vessel and immersed in a 25 °C thermostated bath. Frozen sediment was added to the reactor and did thaw instantaneously. The reactors were stirred with a propeller fitted through the top of the vessel. The pH in the reactor was kept at 3.0 by addition of HCl from a Radiometer TIM 900 titralab in the pH-stat mode. Sampling began less than one minute after sediment addition and was done using an automatic sampler. The samples were filtered in-line through a 0.2 μ m membrane filter and injected directly into glass vials containing a ferrozine solution. A Na-acetate buffer solution was added to the vials and subsequently Fe²⁺ was determined spectrophotometrically (Stookey, 1970).

3. Results

3.1. Groundwater chemistry in the Rømø aquifer

The Rømø aquifer is a pristine shallow sandy aquifer of Holocene age. The groundwater becomes anoxic almost directly below the water table due to the degradation of organic matter. The redox processes related to organic matter degradation in the aquifer have been described in some detail by Jakobsen and Postma (1999) and Hansen et al. (2001). The main terminal electron accepting processes for organic matter degradation in the aquifer are iron oxide reduction, sulfate reduction and methanogenesis. The relative importance of each process varies over short distances and also over time. For this study a site dominated by iron oxide reduction was selected. Fig. 1 presents the water chemistry at this site. The concomitant increases in Fe²⁺ and alkalinity over depth suggest ongoing reduction of iron oxides according to the reaction



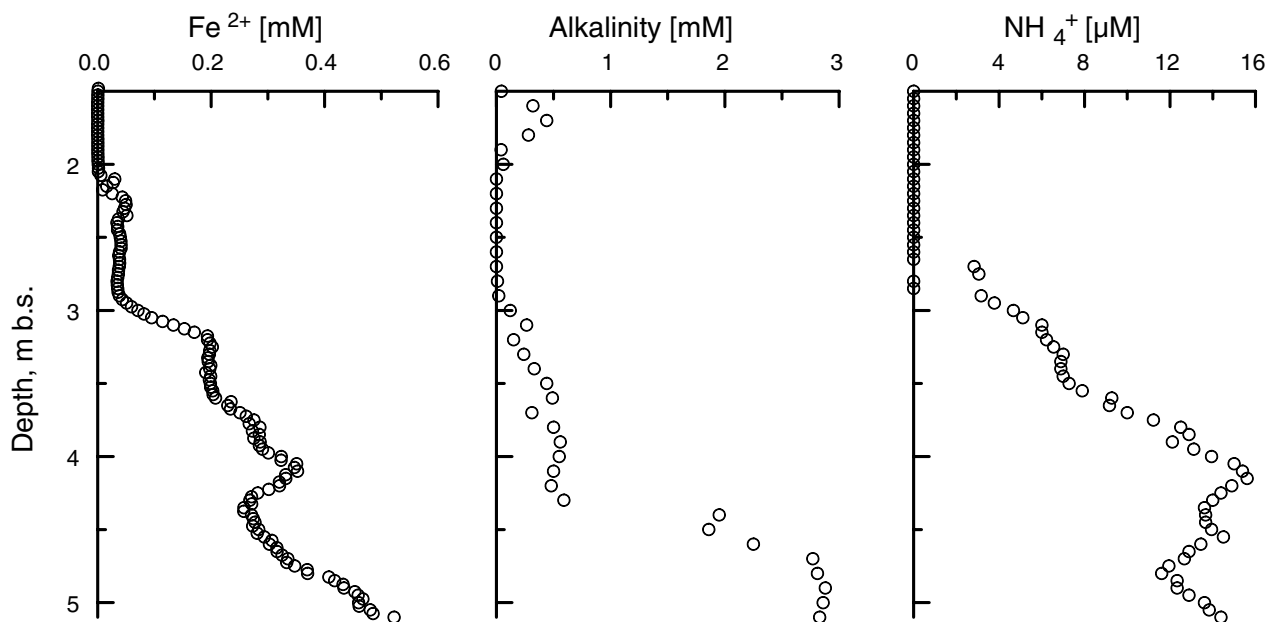


Fig. 1. Selected redox components in groundwater of the Rømø aquifer.

The degradation of organic matter is also indicated by the increase of NH_4 over depth reflecting the release of N-components from sedimentary organic matter. Sulfate reduction was not important at this site as indicated by a near constant SO_4/Cl ratio (not shown). It is therefore unlikely that the precipitation of iron sulfides affects the dissolved iron profiles to any significant extent.

3.2. Reactive iron extracted by oxalate and dithionite

Fig. 2 presents the results from single step sediment extractions using the ammonium-oxalate method (Schwertmann, 1964), designed to extract poorly crystalline iron oxides, including ferrihydrite and lepidocrocite (Schwertmann, 1991), and the dithionite-citrate-bicarbonate

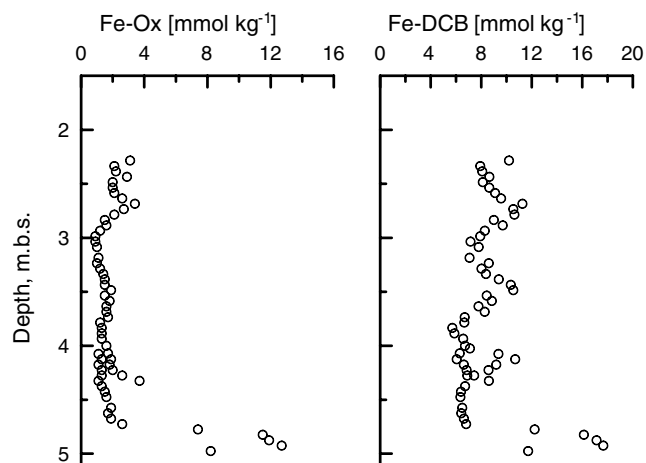


Fig. 2. Iron extracted from Rømø aquifer sediment by a NH_4^+ -oxalate (Fe-Ox) solution at pH 3 and a dithionite-citrate-bicarbonate (Fe-DCB) solution at 80 °C.

(DCB) method for the total content of iron oxides (Mehra and Jackson, 1960; Canfield, 1988). The concentration of iron extracted from the sediment by oxalate (Fig. 2) is highest (~ 3 mmol/kg) in the uppermost part of the aquifer. Below 2.8 m depth oxalate extractable iron decreases to between 1 and 2 mmol/kg without any significant depth trend. However, below 4.6 m depth there is a sudden increase in oxalate extractable iron with values up to 13 mmol/kg. Iron extracted from the sediment by the dithionite (DCB) method is also shown in Fig. 2. The concentration level is around 8 mmol/kg or roughly four times higher than oxalate extractable iron. Also for DCB extractable iron there is a strong increase below 4.6 m depth, up to about 18 mmol/kg. The difference between oxalate and DCB extractable iron is much smaller here, suggesting that iron in the lower part is preferentially present in an oxalate extractable form.

3.3. Reductive dissolution of iron by ascorbic acid

Fig. 3 shows a representative example of the results obtained by leaching the sediment with HCl and 10 mM ascorbic acid, both at pH 3. Immersion of sediment in HCl initially releases Fe(II) very fast. Subsequently the Fe(II) release transforms into a linear increase indicating a constant dissolution rate. The Fe(II) released from the sediment by this treatment could be derived from authigenic Fe(II)-bearing minerals like FeS or FeCO_3 or from hydrolysis and leaching of silicate minerals. Negligible amounts of Fe(III) will be released from iron oxides by this treatment (Larsen and Postma, 2001).

Leaching by ascorbic acid gives a similar behavior with a high initial release that levels off to a linear increase over time which ultimately becomes parallel to the one obtained

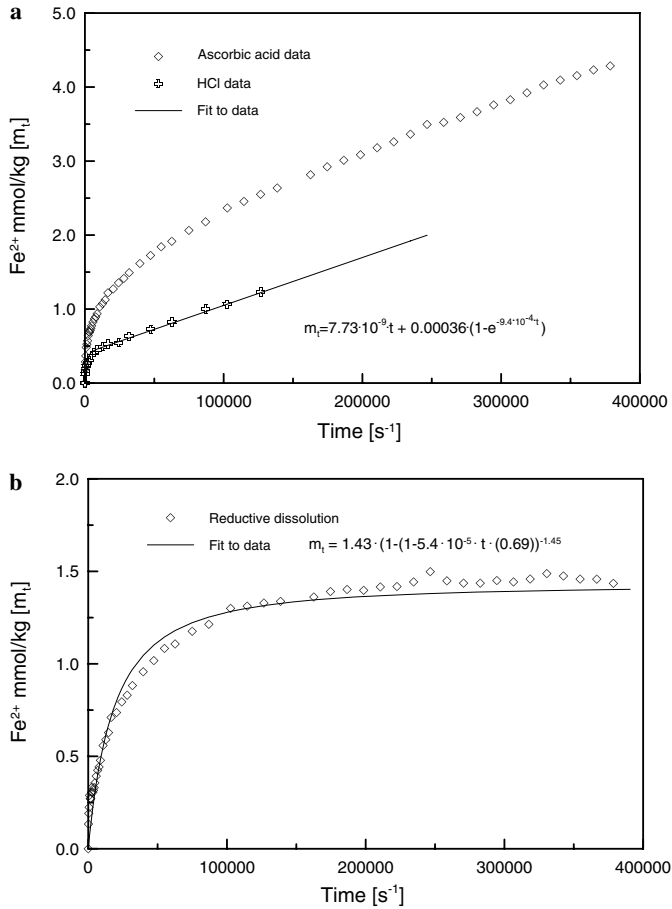


Fig. 3. (a) Release of Fe^{2+} from Rømø aquifer sediment (3.7 m depth) by 10 mM ascorbic acid at pH 3 and a HCl solution at pH 3. (b) Release of Fe^{2+} from sediment by reductive dissolution obtained as the difference between the release in ascorbic acid and HCl.

for HCl leaching. The amount of Fe(II) released by ascorbic acid is about twice the amount released by HCl. Since the pH is the same in both experiments, the higher release

of Fe(II) from the sediment by ascorbic acid must be due to reductive dissolution of Fe(III) in the sediment. The difference between HCl and ascorbic acid released iron is plotted in the lower part of Fig. 3 and therefore represents the reductive dissolution of Fe(III) from the sediment.

The data from the dissolution experiments were fitted to an integrated version of Eq. (2). The integral of Eq. (2) is (Larsen and Postma, 2001)

$$\text{for } \gamma = 1 : \frac{m}{m_0} = e^{-k't} \quad (6)$$

$$\text{for } \gamma \neq 1 : \frac{m}{m_0} = [-k'(1 - \gamma)t + 1]^{\frac{1}{1-\gamma}} \quad (7)$$

The rate law is based on the fraction of undissolved iron oxide (m/m_0) but the experimental data yields the dissolved amount, m_t that equals $m_0 - m$. An independent determination of m_0 is not possible since all known extractants to some degree attack both Fe(II) phases and iron oxides. However, rearranging Eqs. (6) and (7) and substitution of $m_t = m_0 - m$ gives Eqs. (8) and (9) and allows the estimation of m_0 from kinetic data

$$\text{for } \gamma = 1 : m_t = m_0[1 - (e^{-k't})] \quad (8)$$

$$\text{for } \gamma \neq 1 : m_t = m_0[1 - (1 - k'(1 - \gamma)t)^{\frac{1}{1-\gamma}}] \quad (9)$$

Eqs. (8) and (9) enable us to quantify the reactivity of iron oxides in a natural sediment based on the rate law (Eq. (2)) by fitting on m_0 , γ and k' . The γ and k' parameters were estimated through a non-linear fitting procedure while the sum of reactive iron (m_0) was restricted to a value defined by the maximum release asymptotic approached in the dissolution experiment (see Fig. 3).

Using Eq. (9), first a data fit was obtained for the release of Fe(II) by HCl. This data fit, provides values for the iron release by HCl at different times and these values were subtracted from the iron concentrations obtained by ascorbic acid extraction. A rate law for reductive dissolution of iron oxide in the sediment can now be fitted to the new data set

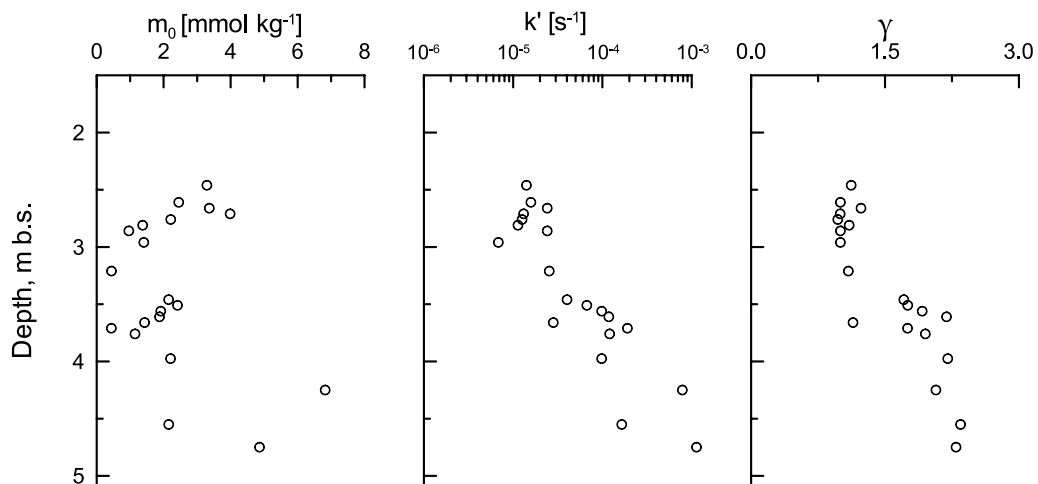


Fig. 4. The reactivity of iron oxides in sediment versus depth, as described by the parameters in rate Eq. (2). m_0 is the initial mass of iron oxide, γ the exponential variable and k' the initial rate constant.

using once more Eq. (9). The data fit provides a quantitative estimate for the reactivity of the pool of Fe(III) in the sediment by the three parameters; here $m_0 = 1.43$ mmol/kg, $k' = 5.4 \times 10^{-5} \text{ s}^{-1}$ and $\gamma = 1.7$.

Similar leaching experiments with HCl and ascorbic acid have been carried out at various depths and the results are shown in Fig. 4. The amount of reactive Fe(III) which was initially present in the sediment has been estimated to be between 0 and 4 mmol/kg, disregarding the two outliers at the greatest depth. The initial rate k' is found to increase two orders of magnitude over depth, from about 10^{-5} to 10^{-3} s^{-1} . The exponential parameter γ increases from around 1.0 to 2.2 indicating an increase in the heterogeneity of the pool of Fe(III) in the sediment.

4. Discussion

4.1. Reactive Fe(III) in the sediments

The reactivity of sedimentary iron oxides are usually described using different selective extraction methods applied along the redox gradient. For example, in marine sediments the decrease of oxalate extractable iron oxides is often interpreted as the depletion of reactive iron oxides with depth (Canfield, 1989; Thamdrup et al., 1994). Comparing dissolution experiments of synthetic iron oxides with sediment data suggest that reactive iron oxides in these sediments are made up of ferrihydrite. However, more recent studies of van der Zee et al. (2003) who used Mössbauer spectroscopy showed that poorly crystalline iron oxides in some sediments may be present as nanogoethite. Larger crystals of goethite are hardly dissolved by oxalate. Similar approach is usually applied in aquifers where the change in pool sizes is investigated along the groundwater flow line. Downstream of landfills, Heron and Christensen (1995) and Tuccelli et al. (1999) found total depletion for 0.5 M HCl and Ti(III)-EDTA extractable iron(III). In soil chemistry the ratio of oxalate extractable iron over DCB extractable iron is often used to track changes in the iron oxide mineralogy (Cornell and Schwertmann, 2003; Poulton and Canfield, 2005). In the Rømø aquifer both oxalate and DCB iron are more or less constant over depth and do not indicate a selective removal of reactive iron oxide by reduction. Still the water chemistry (Fig. 1) shows a steep increase in dissolved Fe^{2+} over depth indicating that the reduction of iron oxides is taking place.

The kinetic approach presented here indicates that the iron oxides in the Rømø aquifer sediment are not as homogeneous as suggested by the depth distributions of the oxalate and DCB fractions (Fig. 2). The ascorbate reduction experiments (Fig. 4) reveal an increase in the reactivity of iron oxide in the sediment over depth, as indicated by the increase in the initial rate (k') of two orders of magnitude and the higher γ values indicate an increased heterogeneity, i.e. the difference between the most and least reactive iron, in the pool of iron in the sediment. These variations in k' and γ are consistent with the removal of the most reactive

iron oxide by reduction as the groundwater migrates downward through the aquifer (Jakobsen and Postma, 1999).

The initial amount of ascorbate reducible iron (m_0) ranges between 1 and 5 mmol/kg (Fig. 4) and is thus slightly higher than oxalate extractable iron but certainly lower than DCB extractable iron (Fig. 2). Strictly, m_0 cannot be compared directly with oxalate or DCB extractable iron because the latter two reflect separate measurements while m_0 is a value derived by the kinetic experiment itself. The ascorbate reduction experiments show a very high initial Fe^{2+} release rate while over time the rate of Fe^{2+} release decreases. This indicates the presence of a small amount of highly reactive Fe(III) while the remainder is less reactive. Most of this change in reactivity must fall within the pool of iron that is also extracted by oxalate. Accordingly, the fraction of iron oxides extracted with oxalate cover a large range in reactivity. The reactivity of the oxalate extractable pool of iron oxides, expressed as variation in initial rate k' , amounts to more than one order of magnitude (Fig. 4). The pool of reducible Fe(III) in the sediment is clearly highly heterogeneous. While most of this heterogeneity falls within the fraction that is extracted by oxalate, the division between oxalate and DCB extractable iron appears somewhat arbitrary. Iron oxides within each fraction may become consumed at different rates and thereby the definition of what is “reactive iron” becomes dependent on the timescale considered.

The approach presented here provides a method to estimate the reactivity of the Fe(III) pool in sediments as a reactive continuum defined by the three rate parameters m_0 , k' and γ . It contrast with results obtained by single step oxalate and DCB extractions that neither capture the strong variation in reactivity within a single sample in the fraction extracted by oxalate, nor the change in reactivity over depth. A kinetically based analysis of the data as presented here accordingly may improve our understanding of the effect of iron oxide reactivity on the process of iron reduction in sediments. At present there are few data for kinetic analysis of sediment ascorbate reduction experiments available for comparison. However, Roden (2004) found for some selected soils and sediments $\gamma = 0.79 - 1.77$, which is about the same range as found here, while k' was 3.0×10^{-7} to 1.6×10^{-6} which is one order of magnitude lower than observed in the Rømø aquifer. The heterogeneity in the reactivity of iron oxides present in sediments may be high. Postma (1993) found $\gamma = 4.7$ for a marine surface sediment while Weiss et al. (2004) even found $\gamma = 5.14$ for a soil.

4.2. Reactivity of Fe(III) in sediments and of synthetic Fe-oxides

The rate laws obtained using Eq. (2) are conveniently displayed as a plot of the logarithm of the unreacted fraction ($-\log m/m_0$) versus the logarithm of the normalized initial rate ($-\log J/m_0$). The results for some selected sediment depths are shown in Fig. 5. Here the y -axis intercept

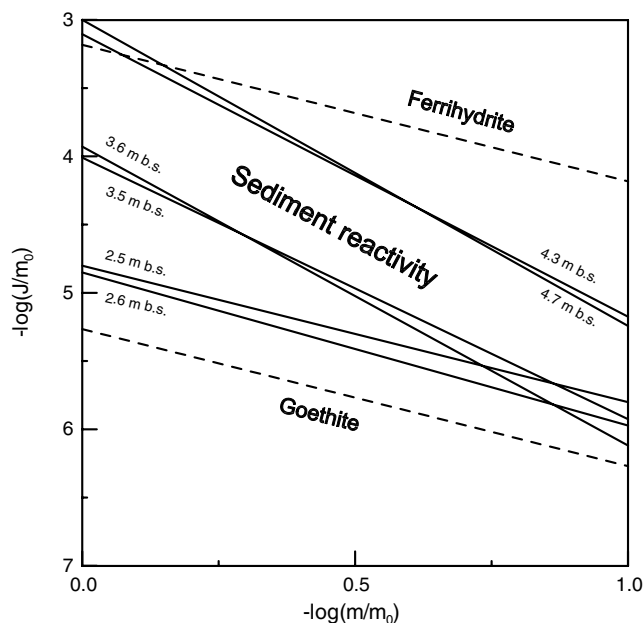


Fig. 5. The reactivity of iron oxides in the Rømø aquifer sediment as compared to the reactivity of the synthetic iron oxides, 2-line ferrihydrite and goethite. J/m_0 is the rate J normalized over initial mass m_0 . m/m_0 is the fraction of iron oxide remaining in the sediment.

is the initial rate k' and the slope of the line for a given sediment depth corresponds to γ . While the variation in initial rate is seen to cover two orders of magnitude, the total range in sediment Fe(III) reactivity varies by three orders of magnitude. Also shown in Fig. 5 are the rate laws obtained by Larsen and Postma (2001) for synthetic ferrihydrite and poorly crystalline goethite which encompass the sediment data quite well. Despite sedimentary iron oxides cover a large range of physical properties (e.g. mineralogy and surface area) the reactivity towards reductive dissolution fall within the same order of magnitude as synthetic iron oxides.

4.3. Importance of sediment Fe(III) reactivity

Thamdrup (2000) showed that the relative contribution of iron reduction to carbon oxidation in marine sediments was almost linearly related to the concentration of poorly crystalline Fe(III) as determined by the oxalate extraction. This suggests Fe(III) reactivity is of major importance for the understanding of carbon cycling in sediments. It is well known that the reactivity of sedimentary organic matter controls the overall rate of organic carbon cycling in sediments (Appelo and Postma, 2005). The question is then how the reactivity of organic matter relates to the reaction rate of iron oxides. Simplified, organic matter degradation proceeds through a two step process. During the initial fermentative step fatty acids and H_2 are produced. These intermediates are subsequently consumed by iron reducing bacteria. If, in a given sediment, the available organic matter has a lower reactivity than the iron oxides, then the fermentative step will control the rate of reduction of iron

oxides and it will proceed as by partial equilibrium in the standard redox sequence (Postma and Jakobsen, 1996). However, when the organic matter has a higher reactivity than the iron oxides then the reactivity of the iron oxides may control the rate of iron oxide reduction. In that case, excess intermediate fatty acids and H_2 will be shunted over to either sulfate reduction or methanogenesis. The reactivity of the sediment iron oxides determines then the predominant terminal electron acceptor.

Our current knowledge concerning rates of iron oxide reduction in sediments is rather low. While for other electron accepting processes, for example sulfate reduction, radiotracer methods are available to measure the rate (Fossing and Jørgensen, 1989), the direct measurement of the rate of iron oxide reduction in sediments is not straightforward. One approach consists of incubating sediments and measurement of the increase of Fe(II) in porewater and sediment over time (Hines et al., 1997; Roden and Wetzel, 1996). Iron cycling through reoxidation is not included in this approach. Alternatively, Canfield et al. (1993) obtained estimates of the rate of iron reduction in sediments as the difference between total organic carbon respiration rates and rates of sulfate reduction, in the absence of other electron acceptors like O_2 and NO_3 . In an aquifer, the rate of iron reduction was obtained by using the Fe^{2+} gradient in combination with the downward rate of water transport (Jakobsen and Postma, 1999). In laboratory experiments Fe(II) was found to inhibit further reduction of iron oxides (Roden, 2004). In experiments where the reduction of ^{57}Fe labeled ferrihydrite during sediment incubation was investigated the reaction product was found to be adsorbed on surfaces rather than forming secondary minerals (Larsen and Koch, 2000). The question of how this applies to in situ iron oxide reduction rates in natural sediments is unresolved. In summary, our current ability to predict more quantitatively the role of iron cycling in sediments is still at a very low level. A more kinetic approach towards understanding the concept of "reactive iron" in sediments might provide a first step towards improving this situation.

5. Conclusions

- (1) The pool of reactive Fe(III) available for reductive dissolution in sediments is heterogeneous and therefore best described kinetically by a reactive continuum model.
- (2) The properties of the reactive continuum can be determined by parallel dissolution in HCl and 10 mM ascorbic acid at pH 3. The difference in Fe(II) release is attributed to reductive dissolution and can be fitted to a Gamma distribution-type rate equation.
- (3) In the Rømø aquifer sediment, the kinetic analysis over depth indicates an increase in the initial rate of over two orders of magnitude as well as an increased heterogeneity in the pool of iron oxide in the sediment.

- (4) The pool of reactive iron present in the sediment determined in this way corresponds roughly to the pool extracted by oxalate in the Rømø aquifer. However, the variation in iron oxide reactivity of more than two orders of magnitude is not revealed by extraction with oxalate.

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