Kinetics of redox cycling of iron coupled with fulvic acid

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ABSTRACT

The kinetics of conversion of iron(III) (hydr)oxides to ferrous iron mediated by fulvic acid have been investigated in order to improve the understanding of the redox cycling of iron at the oxic-anoxic boundary in natural waters. Under the conditions similar to natural waters, fulvic acid is able to reduce the iron(III) (hydr)oxide. The kinetics of the reaction depend on the reactivity of iron(III) (hydr)oxides and the reducing power of the fulvic acid. The rate of reaction is 60 nm/h obtained under following conditions: total concentration of Fe(III) 1.0×10^{-4} M, pH 7.5, fulvic acid 5 mg/L. The rate is considered as a net result of reduction and oxidation in the $> \text{Fe}^{\text{III}}\text{-OH}/\text{Fe}(\text{II})$ "wheel" coupled with fulvic acid. In a real natural water system, reductants other than fulvic acid may be of importance. The results obtained in the laboratory, however, provide evidence that the $\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}(\text{II})$ redox couple is able to act as an electron-transfer mediator for the oxidation of natural organic substances, such as fulvic acid by molecular oxygen either in the absence of microorganisms or as a supplement to microbial activity.

Introduction

Redox reactions of iron, including oxidation of iron(II) accompanied by precipitation, and reduction of iron(III) (hydr)oxides accompanied by dissolution, constitute an important cycle at the oxic-anoxic boundary in natural waters (Davison, 1985). In field investigations, it is frequently observed that a large number of iron-rich particles are accumulated at the oxic-anoxic boundary in marine and freshwater systems (Wells and Goldberg, 1991, Buffle et al., 1988). These iron-rich particles may originate from mononuclear $\text{Fe}^{\text{III}}(\text{OH})_3$, produced from oxygenation of iron(II) and subsequent hydrolysis at the oxic-anoxic boundary (Schneider and Schwyn, 1987, von Gunten and Schneider, 1991). While the iron-rich particles settle into anoxic zone, they can be reductively dissolved to iron(II) at neutral pH (Davison et al., 1980; Wersin et al., 1991). The reductive dissolution of iron(III) (hydr)oxides

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occurring in the anoxic zone is believed to be coupled to the oxidation of various reductants such as naturally occurring organic substances, H_2S (aq), exudates of microorganisms (Werin et al., 1991; Lovley et al., 1991; Dos Santos and Stumm 1992; Sørensen and Jørgensen, 1987; Ottow and von Klotek, 1969; Ghiorse, 1988 and ref. therein). However, many laboratory studies have shown that the reductive dissolution of iron(III) (hydr)oxides by fulvic acid, phenols and oxalate occurs only under acidic ($\text{pH} < 5$) and/or irradiation conditions (Waite and Morel, 1984; Lakind and Stone, 1989; Suter et al., 1991; Siffert and Sulzberger, 1991). The reducing power of humic acid decreases with increasing pH (Szilagyi, 1971). Thus, it is not well-established whether the dissolved ferrous iron found in the anoxic zone of natural waters can be derived directly from the interaction between iron(III) (hydr)oxides and humic substances. The question arises whether humic substances are able to convert iron(III) (hydr)oxides thermally to dissolved ferrous iron species and promote the redox cycling of iron under natural water conditions.

In a recent laboratory study (von Gunten and Schneider, 1991), the oxygenation of iron(II) (0.01 M) was carried out in the presence of TRIS (Tris-(hydroxymethyl)-aminomethane, 0.1–0.5 M, pH 7.5) and in the presence of oxygen between 1.0×10^{-6} – 5.0×10^{-6} M. These conditions (O_2 and pH) are similar to those encountered in the oxic-anoxic boundary in natural waters (Berner, 1981). As shown by von Gunten and Schneider (1991), an oligomeric iron(III) (hydr)oxide was formed where extensive polymerization of iron(III) colloids ($1 \text{ nm} \leq \text{radius} \leq 20 \text{ nm}$) can be prevented by TRIS which most likely formed outer-sphere complexes on the surface of iron(III) colloids. These iron colloids can be readily dissolved by a reductive phenanthroline medium (0.025% phenanthroline and 0.4% hydroxylamine hydrochloride, acetate buffer pH 4.7). The half-time for the dissolution of total iron(III) colloids is about 15 minutes in the reductive medium (von Gunten and Schneider, 1991). Such high reactivity of these iron(III) colloids in terms of rate of reductive dissolution may be similar to that of iron-rich particles observed in natural waters. Although the TRIS medium is unrealistic with regard to natural waters because such a substance does not occur, it can act as an effective scavenger of the primary hydrolytic products formed by the oxygenation of iron(II) (von Gunten and Schneider, 1991; Schneider and Schwyn, 1987).

The objective of this study was to investigate the kinetics of reductive dissolution of iron(III) (hydr)oxides mediated by fulvic acid under the conditions representative of those typically encountered at the oxic-anoxic boundary in natural waters. The conversion rate to iron(II) is determined for iron(III) colloids formed in TRIS medium in the presence of fulvic acid. The effects of freshly prepared and aging solution of fulvic acid are examined on the conversion of iron(III) colloids to iron(II).

Experimental

All chemicals used in this study were analytical grade from either Merck or Fluka Company. All solutions were prepared with doubly deionized water (Barnstead Nanopure). Glassware was cleaned in concentrated HCl and rinsed several times with doubly deionized water. The purity of N_2 used in this study was 99.999%. The trace

amount of O_2 contained in the N_2 was further removed by passing the N_2 through a solution of V(II) with amalgamated zinc (Wersin, 1990).

The pH measurements were carried out using a pH meter (Metrohm 605) with a combined glass electrode (Metrohm). The glass electrode was calibrated using standard buffer solutions of pH 4 and 7 (Merck).

Preparation of iron(III) (hydr)oxides

(1) Iron(III) colloids formed in TRIS medium: Pure CO_2 ($PCO_2 = 1$ atm.) was bubbled through a solution (500 ml) containing 1.0×10^{-2} M $NaClO_4$ and 3.0×10^{-4} M $NaHCO_3$ until a pH value of 4.5 was attained. Then 0.0183 g $Fe(ClO_4)_2 \cdot 6 H_2O$ was added. The initial concentration of iron(II) was 1×10^{-4} M. Oil-free air ($PO_2 = 0.2$ atm.) was then bubbled through the stirred solution until pH 5 was achieved. The pH of the solution was adjusted to pH 7.5 by addition of TRIS buffer. The final concentration of TRIS was 0.5 M. The oxidation of iron(II) ($PO_2 = 0.2$ atm.) proceeded rapidly at about pH 7.5

(2) Preparation of goethite (α - $FeOOH$): goethite was prepared using a method similar to that of Sung and Morgan (1980). The oxide was obtained by hydrolyzing ferric nitrate in a NaOH solution ($Fe/OH = 0.25$, final pH near 12). The suspension of iron(III) (hydr)oxide was left overnight. The iron(III) particles were then repeatedly washed with water, centrifuging the suspension and discarding the supernatant, until the pH reached a value of about 7. The particles were then freeze-dried. The X-ray diffraction pattern confirms that the product obtained is goethite. The surface area is $89 \text{ m}^2/\text{g}$ (geometry estimation by R. Giovanoli, University of Bern).

Preparation of the solution of fulvic acid

The fulvic acid, obtained from the International Humic Substances Society, was prepared from the Suwannee River, Georgia, U.S.A. The characteristics of the fulvic acid are reported elsewhere (Thurman and Malcolm, 1983).

Doubly-deionized water (50 ml) was de-oxygenated by purging with nitrogen for 30 minutes. Fulvic acid was then dissolved to give a fulvic acid concentration of 0.1 mg/ml.

Dissolution of iron(III) (hydr)oxides by fulvic acid

The colloids of iron(III) (hydr) oxide (28.5 ml, TRIS medium) were transferred into a flask with a full volume 30 ml. The colloids were carefully purged with nitrogen about 10 minutes to eliminate dissolved oxygen. Then, 1.5 ml fulvic acid (0.1 mg/ml, freshly prepared or stored in the dark at 20°C) was added and mixed well with the colloids. The final concentrations of iron(III) as iron(III) (hydr)oxide and fulvic acid were 10^{-4} M and 5 mg/L, respectively. The flasks with the same experimental conditions, i.e. $Fe(OH)_3(s)$ 1×10^{-4} M, fulvic acid 5 mg/L, were carefully capped to avoid entrapment of air. The flasks were then simultaneously immersed in water in a dark

container to minimize the oxygenation of iron(II). The dissolution of goethite by fulvic acid followed the same procedure described above. The final concentrations of iron(III) as α -FeOOH and fulvic acid were 10^{-4} M and 5 mg/L, respectively.

A glove-box filled with nitrogen (nitrogen was circulated into the box for about one hour before sampling) was used for sampling in order to prevent oxygenation of iron(II). The sampling was carried out at intervals during the dissolution experiment. Each sample was taken from one of the flasks immersed in water in the dark container and each flask in the dark container was used for only one sampling. In the case of iron(III) (hydr)oxide formed in TRIS medium, sample aliquots (10 ml) were directly transferred into a 25 ml flask because the colloids ($1 \text{ nm} \leq \text{radius} \leq 20 \text{ nm}$, von Gunten and Schneider, 1991) were too small to be filtered by a $0.01 \text{ }\mu\text{m}$ cellulose nitrate membrane (the smallest pore size membrane available in our laboratory). In the case of goethite, the sample can be filtered through a $0.1 \text{ }\mu\text{m}$ cellulose nitrate membrane prior to analyzing the filtrate for iron(II) and total iron.

Analytical methods

The phenanthroline method was used to determine the concentration of ferrous and total iron (Tamura et al., 1974; Deng, 1992). The measurement of ferrous iron was completed within 5 minutes in order to minimize the slow reduction of ferric iron by phenanthroline.

Results

Kinetics of reductive dissolution of iron(III) (hydr)oxides by fulvic acid

In order to simulate the conditions of the oxic-anoxic zone in natural waters, the dissolution of the iron colloids produced by oxygenation of iron(II) (1×10^{-4} M) in TRIS medium (0.5 M, pH 7.5) was performed in a closed system at pH 7.5 in the presence of 5 mg/L fulvic acid. The kinetics of the conversion of iron(III) colloids to iron(II) was followed by measuring ferrous iron produced (Fig. 1). The rate of the conversion is 6×10^{-8} M/h obtained from the slope of the curve in Fig. 1 during the period of 25 days. The result shows explicitly that the fulvic acid is able to reduce the iron(III) (hydr)oxide formed in the presence of TRIS to iron(II) under conditions similar to the oxic-anoxic boundary in natural waters. However, it is difficult to distinguish whether most of the iron(II) produced remains on the surface of the colloids or actually enters the solution because the iron(III) colloids are too small to be filtered by a $0.01 \text{ }\mu\text{m}$ cellulose nitrate membrane. Under the same experimental conditions, neither dissolved iron(II) nor iron(III) can be detected by the phenanthroline method in goethite (α -FeOOH) – fulvic acid system within 25 days.

Decrease of the reducing power of fulvic acid as a consequence of aging

Figure 2 illustrates that the reducing power of fulvic acid with respect to freshly formed iron(III) colloids (TRIS medium) is significantly different in two cases: one is

Fig. 1. Reductive conversion of iron(III) (hydr)oxide formed in TRIS medium (0.5 M) to iron(II) by fulvic acid: formation of $\text{Fe}(\text{OH})_3(\text{s})$ (0.01 g/L): $\text{Fe}(\text{II})_0$ 1.0×10^{-4} M, $\text{PO}_2 = 0.2$ atm., pH 7.5; • reductive conversion in a closed system: fulvic acid 5 mg/L, pH 7.5, 20 °C

Fig. 2. Comparison of the reducing power of fulvic acids (FA) to iron(III) (hydr)oxide: formation of $\text{Fe}(\text{OH})_3(\text{s})$ (0.01 g/L): $\text{Fe}(\text{II})_0$ 1.0×10^{-4} M, $\text{PO}_2 = 0.2$ atm., TRIS 0.5 M, pH 7.5; reductive conversion: fulvic acid 5 mg/L, pH 7.5, 20 °C. (a) FA solution freshly prepared; (b) FA solution stored in the dark at room temperature (20 °C) for 2.5 months

a freshly prepared fulvic acid solution; the other is a fulvic acid solution stored in the dark at room temperature (20 °C) for 2.5 months. The latter seems to have lost most of its reducing power presumably due to slow oxidation of reducing functional groups by dissolved oxygen. This result suggests that the structure of fulvic acid may change continuously during its storage. It may also imply that the structures of humic acids could be changed during their isolation from natural samples.

Discussion

Reactivity of iron(III) (hydr)oxides with fulvic acid

The results presented above show that the ferrous iron can only be detected for the iron(III) colloids (TRIS medium)-fulvic acid system. Neither dissolved ferrous nor ferric iron are detectable in goethite-fulvic acid system during the period of 25 days. The observations suggest that the structure of an iron(III) (hydr)oxide plays an important role in the iron redox cycling at least in a laboratory scale. As proposed by Wehrli et al. (1990), the reactivity of a metal center on the surface at a given pH is likely to increase with the number of terminal ligands. In the case of iron(III) (hydr)oxide, the groups such as $> \text{Fe}(\text{OH})_2$ and $> \text{FeOH}$ may react faster with solutes at solid/water interface than the groups $> \text{Fe}-\text{OH}-\text{Fe} <$. Thus, the difference in reactivity of goethite and the iron(III) colloids (TRIS medium) in terms of the dissolution kinetics may be accounted for by the difference in the concentration of active endstanding groups on the surface (Deng, 1992; Deng and Stumm, 1992). The high reactivity of the iron(III) colloids formed in TRIS medium may plausibly be interpreted by their large surface area ($1 \text{ nm} \leq \text{radius} \leq 20 \text{ nm}$, von Gunten and Schneider, 1991) with a high proportion of active terminal $-\text{OH}$ groups. Correspondingly, a high reductive dissolution rate of the iron(III) colloids can be expected when a high concentration of iron(III)-fulvic surface species is achieved with suitable coordination arrangements (Wieland et al., 1988). Therefore, the extent of endstanding $> \text{Fe}-\text{OH}$ groups per iron(III) ion on the surface most probably determines the reactivity of iron(III) (hydr)oxides.

Kinetic description of $> \text{Fe}^{\text{III}}-\text{OH}/\text{Fe}(\text{II})$ redox cycling coupled with fulvic acid

A reaction sequence with regards to the redox cycle of iron has been proposed by Stumm and Morgan (1981). The $\text{Fe}(\text{III})-\text{Fe}(\text{II})$ redox couple acts as an electron-transfer catalyst for the oxidation of natural organic substances such as fulvic acid by oxygen:

The rate law for the oxygenation of iron(II) in aqueous solution in the neutral pH range ($\text{pH} > 5$) has been established in previous studies (Stumm and Lee, 1961; Stumm and Morgan, 1981):

$$\text{Rox} = -d[\text{Fe}(\text{II})]/dt = k_{\text{H}}[\text{Fe}(\text{II})][\text{O}_2(\text{aq})]/[\text{H}^+]^2 \quad (4)$$

where Rox (M/h) denotes the rate of oxygenation of iron(II); k_{H} is the rate constant ($1.8 \times 10^{-10} \text{ M h}^{-1}$) at 20°C . $[\text{Fe}(\text{II})]$ and $[\text{O}_2(\text{aq})]$ are the concentrations (M) of

Fig. 3. Kinetic description of $> \text{Fe}^{\text{III}}\text{-OH}/\text{Fe}(\text{II})$ redox cycling coupled with fulvic acid type of natural organic substances (total iron(III) as $\text{Fe}(\text{OH})_3(\text{s})$ 1×10^{-4} M, fulvic acid 5 mg/L, pH 7.5, 20°C)

iron(II) and the dissolved oxygen, respectively; $[\text{H}^+]$ is the concentration of proton (M). When pH is 7.5, $k_{\text{H}}/[\text{H}^+]^2 = 1.8 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$.

When the rate of oxygenation of iron(II) is slow in comparison to iron(III) reduction by the organic substance, a relatively high-steady state concentration of iron(II) can be maintained in the system as long as the organic substance is not fully oxidized. Thus, the reaction rate ($6 \times 10^{-8} \text{ M/h}$) obtained in Fig. 1 is considered as a net result of reduction and oxidation in the $> \text{Fe}^{\text{III}}\text{-OH}/\text{Fe}(\text{II})$ "wheel" coupled with fulvic acid, i.e. the net reaction rate ($R_{\text{net}} = \text{rate of reduction (Rred)} - \text{rate of oxygenation (Rox)}$). The value of the net reaction rate was obtained in the close system under following conditions: $\text{Fe}(\text{OH})_3(\text{s})$ 0.01 g/L (Fe(III) total 10^{-4} M), pH 7.5, fulvic acid 5 mg/L, 20°C . The overall reaction is rather slow and depends on the reactivity of the iron(III) (hydr)oxides and the reducing power of the fulvic acid.

The scheme of the redox cycle of iron with kinetic consideration is depicted in Fig. 3. The figure is highly schematic and the rate given is qualitative indicating how the $> \text{Fe}^{\text{III}}\text{-OH}/\text{Fe}(\text{II})$ redox couple is able to act as an electron transfer mediator for the oxidation of fulvic acid by oxygen. In real systems, reductants other than fulvic acid may be operative (decomposition intermediates of the respiration processes, $\text{H}_2\text{S}(\text{aq})$, exudation products of algae). Thus, Fig. 3 may present a generalizable model for the iron redox cycling occurring at the oxic-anoxic boundary in natural systems.

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