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N-compound reduction and actinide immobilisation in surficial fluids by Fe(II): the surface $\equiv Fe^{III}OFe^{II}OH°$ species, as major reductant

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Abstract

Soluble Fe(II) is an important reductant in anoxic surficial fluids, due to fast redox kinetics of the Fe(II)/Fe(III) couple. However, its availability is limited in neutral and alkaline pH range by the solubility of FeS(s), $Fe_3(PO_4)_2$, $FeCO_3(s)$ and other Fe(II) rich minerals. The adsorption of Fe(II) on a variety of mineral phases has been studied. It is shown that, provided enough surface area is available, adsorption is completed before the onset of precipitation, leading to Fe(II) surface species which are able to reduce compounds present in solution in a very efficient way. The abiotic reduction of a variety of N rich compounds (nitrites and nitrobenzenes) by sorbed Fe(II) has been reported in the literature. The observed initial rate of such reduction reactions is shown to be proportional to the $\equiv Fe^{III}OFe^{II}OH°$ species concentration, in the same manner that the homogeneous oxygenation rate of Fe(II) is proportional to $Fe(OH)_{2(aq)}°$ concentration. The electron transfer in these reactions, appears to occur dominantly via an outer sphere mechanism. In contrast, the abiotic reduction of inorganics, such as U(VI) and Tc(VII), by sorbed Fe(II) involves inner sphere electron transfer mechanism. In the case of uranium reduction, three kinetic steps can be distinguished: the adsorption of the uranyl ion (formation of an inner sphere surface complex), followed by two reductive steps which lead to the formation of a $UO_2/Fe(OH)_3$ mixed solid phase. These surface-catalysed reduction reactions may have led to the formation of uranium mineral ores and to the removal of uranium from reducing surface waters. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: Surface catalysis; Reduction; Fe(II); Nitrobenzene; Uranium; Magnetite; Lepidocrocite

1. Introduction

Chemical reactions can have a major influence on the transport of organic and inorganic solutes. Considerable advances have been made in developing a coherent set of thermodynamic data for describing the solution and mineral behaviors in water–rock systems. Redox (oxidation–reduction) reactions may cause transformation of organic compounds, and changes of speciation of inorganic solutes, that have a marked effect on transport properties. For example Cr(VI) and U(VI) can be mobile in groundwater because they are relatively weakly adsorbing and their aqueous species, mainly as CrO_4^{2-} and $UO_2(OH)_2°$ species in the neutral pH range, are soluble. However Cr(III) and U(IV), if uncomplexed, should be highly retarded in groundwater due to extensive sorption and precipitation. Dissolved Fe(II)

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has long been used to reductively precipitate chromium in water treatment plants and contaminated groundwaters (Kent et al., 1994). On the other hand, reductive dehalogenation and reduction of nitro and azo functional groups of organic compounds can be performed by Fe(II) porphyrins and lead to products that have greater mobility than their parent compounds (Zora et al., 1974; Schwarzenbach et al., 1990). These reductive reactions are however limited in neutral and alkaline pH range by the solubility of FeS(s), $Fe_3(PO_4)_2$, $FeCO_3(s)$, etc.

Fe(II) present within, or sorbed on, mineral particles is highly reactive even at high pH. Reduction of nitrite ions to N_2O by Fe(II) sorbed on lepidocrocite was studied by Sorensen and Thorling (1991). Cui and Eriksen (1996) documented the reaction with pertechnetate ions, precipitated as TcO_2 by Fe(II) sorbed onto magnetite. Chromate ions were precipitated by Fe(II) present in biotite, goethite or magnetite (Eary and Rai, 1989; Ilton and Veblen, 1994; Deng et al., 1996). In these experiments Fe(II) is usually present in large excess with respect to surface reactive sites, and this hinders a mechanistic interpretation of the data.

In the present work, we compare the reduction kinetics of nitrogen (V) (as 4-chloronitrobenzene) and uranium(VI) (as uranyl ions) by adsorbed Fe^{2+} ions. Only data obtained with Fe(II) surface coverage lower than a monolayer are discussed. The sorption of Fe(II) on hematite and magnetite is described within the framework of the constant capacitance model. Kinetic laws expressed in terms of Fe(II) surface species have been obtained, and contrasting electron transfer mechanisms for uranyl ions and nitrobenzene are discussed.

2. Material and methods

2.1. Materials and experimental methods

Two iron oxyhydroxides, magnetite (Fe_3O_4) and hematite (α-Fe_2O_3), were synthesized as suspensions (Taylor et al., 1987; Sorensen and Thorling, 1991). The full experimental methods can be found in the original papers (Liger et al., 1998; Klausen et al., 1995). Careful experimental design was necessary in order to reduce oxygen concentrations to

trace levels. In particular, all experiments were conducted in sealed serum flasks or titration reactors, which were purged numerous times with oxygen-free argon before starting the experiment (see details in Liger et al., 1998).

In ferrous iron sorption experiments aliquots of mineral stock suspension and Fe(II) stock solution were added using a syringe. The pH was adjusted either by a series of buffers, for magnetite, or by potentiometric titration, for hematite. Once equilibrium was reached a sample was withdrawn and filtered via a 0.2 or 0.05 µm a pore membrane, for magnetite and hematite, respectively. Fe(II) concentration was measured photometrically after complexation with either FerroZine or orthophenanthroline, with measurements made at 562 nm and 510 nm, respectively.
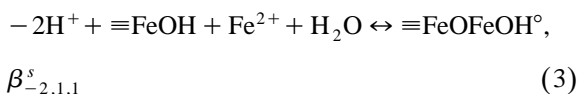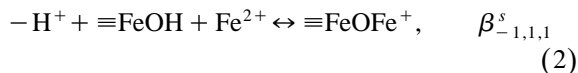
Reduction kinetic experiments were performed for fixed values of pH and initial Fe(II) aqueous concentration $[Fe(II)]_o$. An aliquot of the oxidant (Ar–NO_2 or UO_2^{2+}) stock solution was added to the Fe(II)/mineral suspension and the kinetics were followed by subsequent sampling at regular intervals. The samples were filtered as indicated above and acidified, before analysis by HPLC (for Ar–NO_2 and its metabolites) or laser induced fluorescence (for uranium). In the Ar–NO_2 experiment, Ar–NO_2 and its metabolites do not accumulate onto the particles. In the U case, however, products and reactants of the reaction remained fully sorbed on the particles. Analysis of the unreacted adsorbed uranyl was achieved by flushing the filter cake by 5 volumes of 0.5 M $NaHCO_3$ solution, a technique shown to specifically desorb U(VI). The U concentration in the filtered solution was then measured as indicated above.

2.2. Equilibrium model for H^+ and Fe^{2+} adsorption

The adsorption and desorption of protons and divalent metal ions on iron oxyhydroxides are generally fast reactions, as demonstrated by pressure jump studies (Yasunaga and Ikeda, 1986), and may thus be assumed to be at equilibrium. They are described by the general equation:

$$p H^+ + q(\equiv FeOH) + r Fe^{2+}$$
$$\leftrightarrow H_p(\equiv FeOH)_q Fe_r^{p+2r}, \qquad \beta_{p,q,r}^s \qquad (1)$$
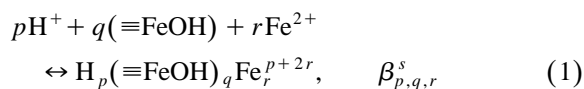
where $\equiv$FeOH symbolizes a surface reactive site. Provided $[Fe(II)]_o$ is significantly lower than the total concentration of surface sites $[\equiv FeOH]_t$, the adsorption of Fe^{2+} onto ferric (hydr)oxide surfaces results in the formation of two Fe(II) surface complexes (Liger et al., 1998):

$$-H^+ + \equiv FeOH + Fe^{2+} \leftrightarrow \equiv FeOFe^+, \qquad \beta^s_{-1,1,1} \tag{2}$$

$$-2H^+ + \equiv FeOH + Fe^{2+} + H_2O \leftrightarrow \equiv FeOFeOH°,$$
$$\beta^s_{-2,1,1} \tag{3}$$

It must be noted that $\beta^s_{p,q,r}$ are (intrinsic) conditional constants which must be corrected for the coulombic energy of the charged surface in order to obtain the corresponding intrinsic constants:

$$\beta^s_{p,q,r(\text{int})} = \beta^s_{p,q,r} e^{((p+2r)F\psi/RT)} \tag{4}$$

where ψ is the surface potential. Within the scope of the constant capacitance model, the surface potential is related to the surface charge by (Schindler and Stumm, 1987):

$$\kappa\psi = \frac{F}{s \cdot C_s}\Big(\Sigma p \beta^s_{p,q,0(\text{int})} e^{-(pF\psi/RT)}[H^+]^p$$
$$\times [\equiv FeOH]^q + \Sigma(p+2r)$$
$$\times \beta^s_{p,q,r(\text{int})} e^{-((p+2r)F\psi/RT)}$$
$$\times [H^+]^p [\equiv FeOH]^q [Fe^{2+}]^r \Big) \tag{5}$$

where κ is the specific capacitance (C V^{-1} m^{-2}), s is the specific surface area (m^2 g^{-1}) and C_s the concentration of solid in g l^{-1}. The equilibrium constants $\beta^s_{p,q,r(\text{int})}$ and $\beta^s_{p,q,0(\text{int})}$ were evaluated with the aid of the computer program GRFIT (Ludwig, 1992).

3. Results and discussion

3.1. Fe(II) adsorption onto mineral particles

Adsorption of the ferrous ion onto hematite and magnetite occurs over two pH units, between pH 5.5

and pH 7.5 (Fig. 1), as is also observed for a variety of minerals such as clays, silica, anatase and other iron hydroxides (Wehrli, 1990; Zhang et al., 1992; Liger et al., 1997c). Adsorption is therefore completed in conditions undersaturated with respect to $Fe(OH)_2(s)$. Supersaturation for ferrous hydroxide occurs at pH 7.65 for $Fe(II) = 10^{-4}$ M ($pK^s_{Fe(OH)_2} = 16.7$; Smith and Martell, 1976). The Fe^{2+} ion adsorbs to the positively charged surface as the zero points of charge is $pH_{PZC} \approx 6.8$ and 8.4 for hematite and magnetite, respectively (Liger et al., 1998; Regazzoni et al., 1983). Thus, it may be assumed to form an inner sphere complex with ferric oxide surfaces. The formation of multinuclear surface complex did not have to be assumed, at the surface coverages considered in the present paper (see discussion on this point in Liger et al., 1998). Model curves were obtained with the intrinsic constants listed in Table 1.

Comparison of hematite and magnetite surface reactivities toward Fe(II) is not straightforward (since different values of s and $[Fe(II)]_o$ have been used in the two sets of experiments) and is best obtained via the surface complexation modelling exercise. The Constant Capacitance Model was chosen since all experiments were performed at constant ionic
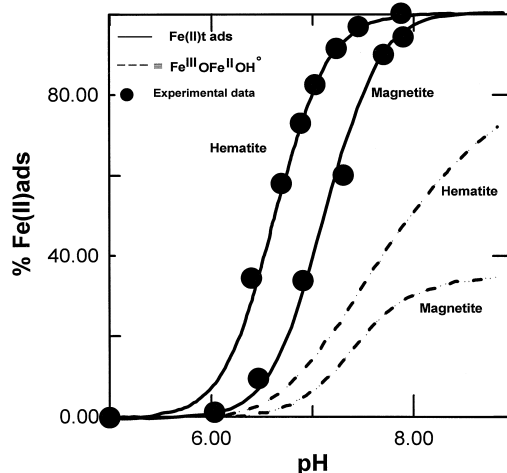

Fig. 1. Adsorption of Fe(II) on hematite (filled squares; Liger et al., 1997a) and magnetite (empty squares; Klausen et al., 1995). Solid lines are model curves (see text). Dotted line represents the $> Fe^{III}OFe^{II}OH°$ species contribution.

Table 1
Log $\beta_{p,q,r}$ values for the two investigated minerals (magnetite and hematite) and their respective adsorption of Fe(II)

	Magnetite	Hematite
Site nm^{-2}	2.13[a]	2.07
C_s (g l^{-1})	0.55[b]	0.53
s (m^2 g^{-1})	56	109.3
κ (F m^{-2})	1.0	1.98
log $\beta_{1,1,0}$	6.26[a]	8.08
log $\beta_{-1,1,0}$	-7.32[a]	-8.82
log $\beta_{-1,1,1}$	-1.05	-1.15
log $\beta_{-2,1,1}$	-9.0	-10.05

Acid base properties ($\beta_{p,1,0}$ values) were obtained for magnetite by fitting the data from Regazzoni et al. (1983) and for hematite from Liger et al. (1998). The Fe(II) surface complexation constants ($\beta_{p,1,1}$ values) were obtained for magnetite by fitting Klausen et al. (1995) data and for hematite from Liger et al. (1998). The model used is the Constant Capacitance model (see text).
[a]From Regazzoni et al., 1983 and Turner, 1995.
[b]0.2 g l^{-1} in k_{obs} determination experiments.

strength and because UO_2^{2+} (Manceau et al., 1992) and Fe^{2+} form inner-sphere surface complexes with the mineral surface under study. Comparison of $\beta_{-1,1,1}$ and $\beta_{-2,1,1}$ values for magnetite and hematite in Table 1 suggests that Fe(II) has a higher affinity for the magnetite surface.

Heterogeneous hydrolysis of Fe(II) starts around pH 6.5 (Fig. 1) whereas the pK_1 value for homogeneous hydrolysis is equal to 9.5 (Smith and Martell, 1976). Therefore, as often reported for divalent metal ions, the mineral surface enhances the hydrolysis of Fe(II). This heterogeneous hydrolysis has been shown to enhance the rate of Fe(II) oxygenation in an auto catalytic phenomenon identified by Tamura et al. (1976). We shall now study the effect of surface enhanced hydrolysis on the oxidation of Fe(II) by two other oxidants, namely nitrobenzene and uranyl ions (Fig. 2).

3.2. Reduction of N-rich compounds

The reduction of 4-chloronitrobenzene (Ar–NO$_2$) does not occur in presence of either dissolved Fe^{2+} or suspended magnetite, but does occur when both are present with (Ar–NO$_2$) in suspension (Klausen
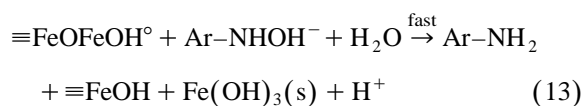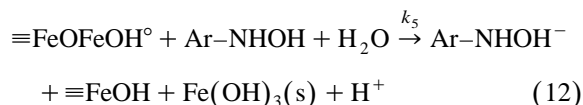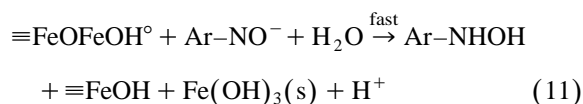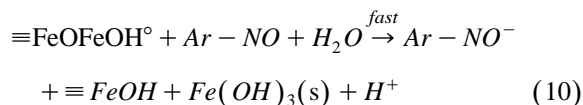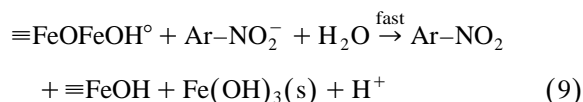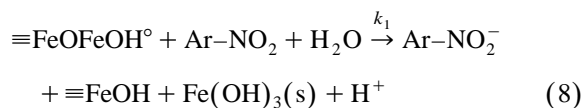
et al., 1995). The initial reaction has been shown to be first order with respect to Ar–NO$_2$:

$$\frac{d[Ar-NO_2]}{dt} = -k_{obs}[Ar-NO_2] \qquad (6)$$

Comparison of k_{obs} values reported by Klausen et al. (1995) with $\equiv$FeOFeOH° concentrations computed on the basis of their sorption data (Fig. 1 and Table 1) indicates that (Fig. 3):

$$k_{obs} = k_1[\equiv FeOFeOH°] \qquad (7)$$

with $k_1 = 22$ mol^{-1}l s^{-1} After this initial step, and prior to the formation of the amine, only one intermediate species was observed: 4-chlorophenylhydroxylamine (Ar–NHOH, Fig. 4). No evidence for adsorption of any intermediate species could be found, since at each kinetic step the sum of Ar–NO$_2$, Ar–NHOH and Ar–NH$_2$ aqueous concentrations remains constant and equal to $[Ar-NO_2]_o$ (Klausen et al., 1995). Accordingly, of the six electron transfer involved in the reduction of Ar–NO$_2$, only two (Eqs. (8) and (12)) are rate limiting. The remaining four electron transfer (Eqs. (9)–(11) and (13)) must be fast. Therefore, the reaction scheme may be (Fig. 4):
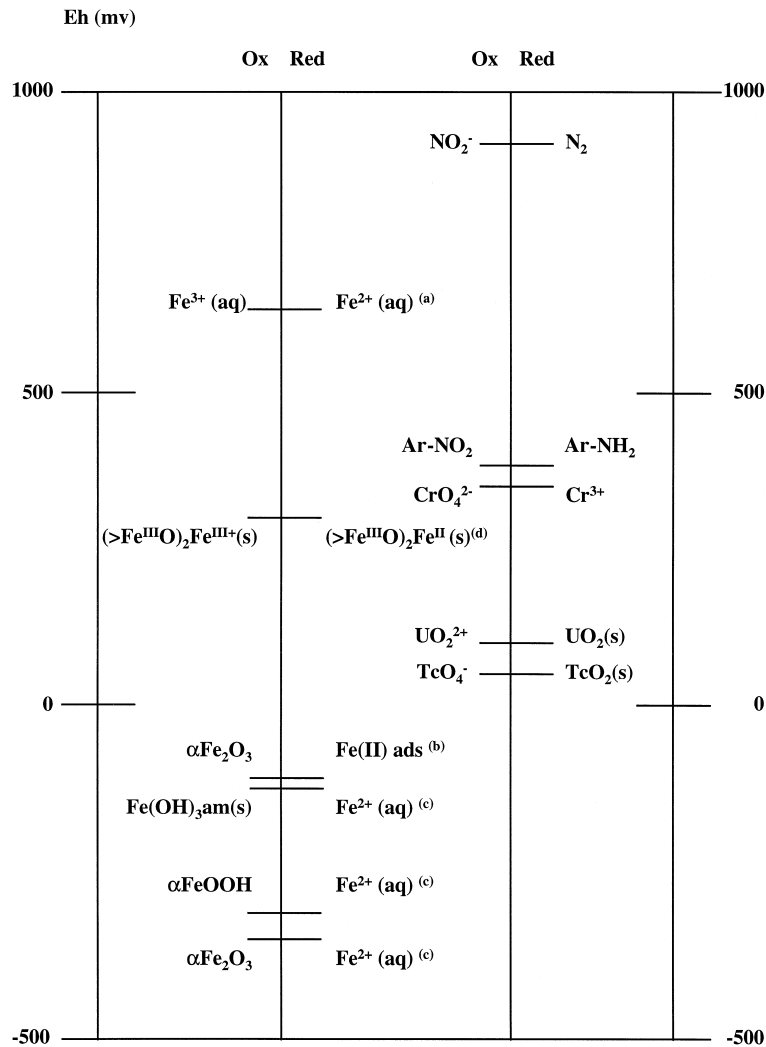
$$\equiv FeOFeOH° + Ar-NO_2 + H_2O \overset{k_1}{\rightarrow} Ar-NO_2^-$$
$$+ \equiv FeOH + Fe(OH)_3(s) + H^+ \qquad (8)$$

$$\equiv FeOFeOH° + Ar-NO_2^- + H_2O \overset{fast}{\rightarrow} Ar-NO_2$$
$$+ \equiv FeOH + Fe(OH)_3(s) + H^+ \qquad (9)$$

$$\equiv FeOFeOH° + Ar-NO + H_2O \overset{fast}{\rightarrow} Ar-NO^-$$
$$+ \equiv FeOH + Fe(OH)_3(s) + H^+ \qquad (10)$$

$$\equiv FeOFeOH° + Ar-NO^- + H_2O \overset{fast}{\rightarrow} Ar-NHOH$$
$$+ \equiv FeOH + Fe(OH)_3(s) + H^+ \qquad (11)$$

$$\equiv FeOFeOH° + Ar-NHOH + H_2O \overset{k_5}{\rightarrow} Ar-NHOH^-$$
$$+ \equiv FeOH + Fe(OH)_3(s) + H^+ \qquad (12)$$

$$\equiv FeOFeOH° + Ar-NHOH^- + H_2O \overset{fast}{\rightarrow} Ar-NH_2$$
$$+ \equiv FeOH + Fe(OH)_3(s) + H^+ \qquad (13)$$

Fig. 2. Representative redox couples at pH = 7 with $[Fe(II)]_t = 1.6 \ 10^{-4}$ M and $[ox] = 5 \ 10^{-7}$ M. (a) Pourbaix, 1963; (b) Liger et al., 1998, (c) Stumm and Sulzberger, 1992.

At each site, there is only one electron available. The semiconductor properties are probably not important since the band-gap is large and electrons probably remain trapped on the sorbed Fe^{2+} ions. The raw product of the reaction is an Fe(III) atom sorbed onto hematite, which has been shown by Mössbauer spectroscopy to be in an amorphous ferric oxide surface structure (Ambe and Ambe, 1990). Four electron transfer steps must be fast. This is a considerable number of electrons and it is unlikely that these electron transfer steps proceed via the formation of

inner sphere surface complexes, especially since each surface Fe(II) site provides only one electron. The electron transfer must therefore involve an outer sphere mechanism as observed in the case of Fe(II) oxygenation (Wehrli, 1990).

3.3. Prebiotic time organics synthesis

The above-mentioned reduction mechanism has important implications not only for present day de-

contamination processes (metabolites are discarded in water and therefore attention must be paid to their potential toxicity), but also for mechanisms involved in the early development of life during the Archean. At that time low P_{O2} prevailed in the atmosphere and the composition of the archean atmosphere was dominated by CO_2, H_2, H_2O and N_2, with in some places presence of a more reducing atmosphere (with CH_4 and NH_3 instead of CO_2 and N_2) due to local gas production from crustal reservoirs (Oro et al., 1990).

Although lightning strikes has been invoked to account for the prebiotic synthesis of amino acids (Miller, 1953; Miller and Van Trump, 1981), thermodynamics indicate that glycine for instance can be synthesized from a CO_2–H_2–N_2 atmosphere (with, e.g., $P_{CO_2} = 0.1$ atm, $P_{H_2} = 0.001$ atm and $P_{N_2} = 10^{-0.097}$ atm) in presence of the Fe(II) rich olivine mineral fayalite, when goethite and silicic acid are formed as by products (Wagman et al., 1982). However, such reactions are typically slow, rate limited by the specific surface area of the Fe(II) mineral. They may have been dramatically enhanced by Fe(II) present not within a mineral but adsorbed at the surface of mineral particles. The archean ocean is
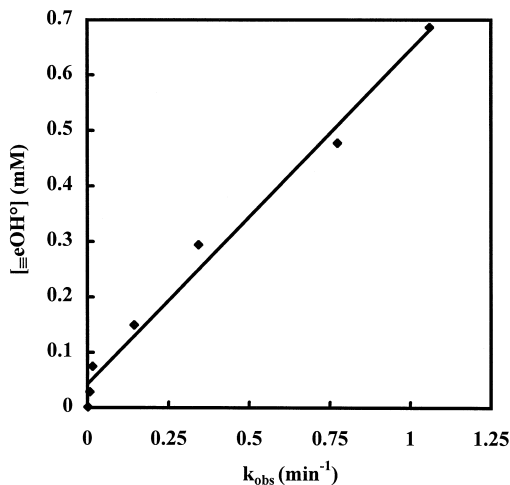

Fig. 4. Reduction at pH 7.0 and 25°C of 50 μM 4-chloronitrobenzene in presence of 17 m^2 l^{-1} magnetite and an initial concentration of 2.3 mM Fe(II). Crosses: 4-chloronitrobenzene, filled circle: 4-chlorophenylhydroxylamine and filled triangle: 4-chloraniline (data from Klausen et al., 1995). Solid line is a model curve ($k_1 = 23$ M^{-1} s^{-1}, $k_2 = 2.8$ M^{-1} s^{-1}; [> FeOFeOH°]$_o$ = 3.6 10^{-4} M, [Ar–NO$_2$]$_o$ = 4.6 10^{-5} M).

Fig. 3. Dependance of pseudo first order rate constant k_{obs} for the reduction of 50 μM 4-chloronitrobenzene (Klausen et al., 1995) on the concentration of > $Fe^{III}OFe^{II}OH°$ surface species, in suspensions of 11.5 m^2 l^{-1} magnetite and Fe(II) intial concentration of 1.5 mM.
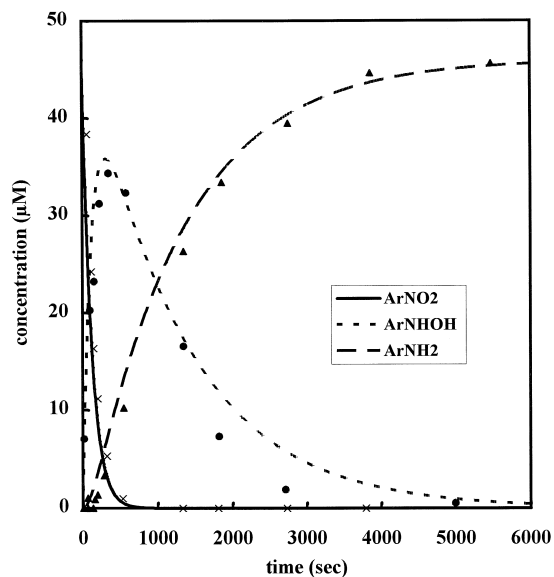
believed to have been rich in Fe(II), with concentrations as high as 7 ppm (Holland, 1973; Holland, 1984). Mineral surfaces may have therefore catalyzed two critical reaction steps in the synthesis of organics in prebiotic times: (i) the reduction of N-rich compounds by Fe(II), as shown above, and (ii) the polymerization of the reaction products (Cairns-Smith, 1982).

3.4. Reduction of uranium and U mineral ore formation

The homogeneous reduction of UO_2^{2+} by aqueous Fe^{2+} at 296.15 K does not occur within three days, even in pH conditions where $UO_2(s)$ and $Fe(OH)_3(s)$, products of the reaction, are thermodynamically more stable than the reactants (Fig. 5, top curve). In presence of hematite particles, however, the reaction proceeds within hours (Liger et al., 1997b). At least three steps can be distinguished.
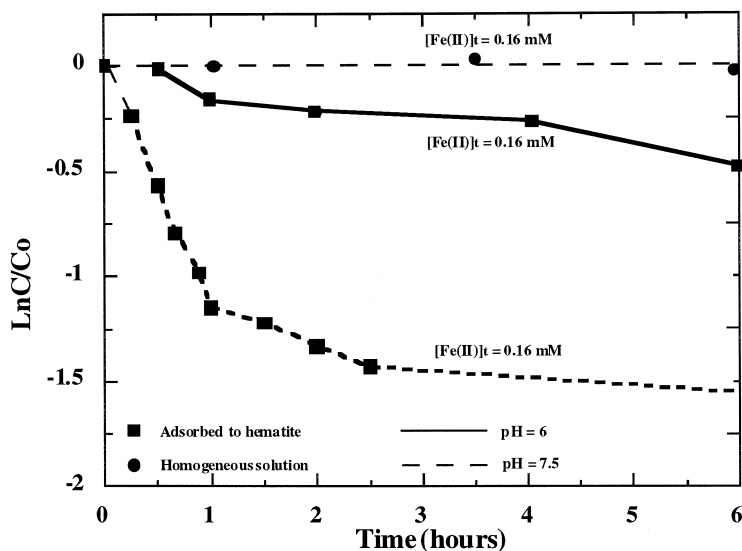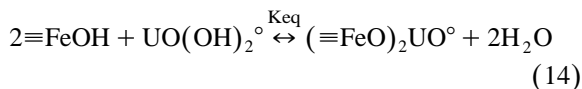
Fig. 5. Natural logarithm of the relative concentration (C/C_o) for uranyl vs. time at various $[U(VI)]_o$ and at pH 7.5 (dotted lines) or 6.0 (full line).

In the first step, nearly 100% of the aqueous U(VI) present in solution as the neutral $UO_2(OH)_2^\circ$ species is adsorbed onto the hematite surface, described by the reaction:

$$2\equiv FeOH + UO(OH)_2^\circ \overset{Keq}{\leftrightarrow} (\equiv FeO)_2 UO^\circ + 2H_2O \quad (14)$$

Within the next 10 h, these adsorbed uranyl ions are reductively transformed to surface $UO_2(s)$, as identified by a diagnostic 800 cm^{-1} IR absorption band (Liger et al., 1998), in a reaction which in the initial stages can be described by a first order process with respect to U(VI) (Fig. 5):

$$\frac{d[U(VI)]_{ads}}{dt} = -k_{obs}[U(VI)]_{ads} \quad (15)$$

The k_{obs} values obtained at different pH and $[Fe(II)]_o$ experimental conditions lead to the following kinetic rate law (Liger et al., 1998):
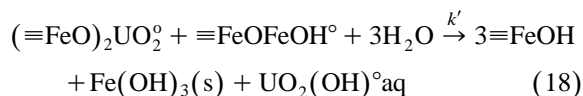
$$k_{obs} = k[Fe(II)]_o[OH^-] \approx k[Fe(II)]_{ads}[OH^-]$$
$$\approx k[\equiv FeOFe^+][OH^-] = k'[\equiv FeOFeOH^\circ] \quad (16)$$
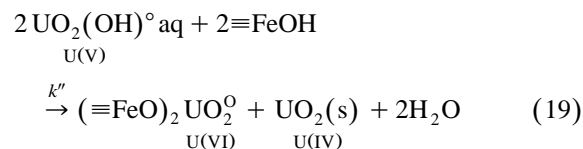
The form of this kinetic law is similar to that re-ported by Millero for the oxidation of Fe(II) by oxygen (Millero et al., 1987):

$$\frac{d[Fe(II)]}{dt} = -kP_{O_2}[OH^-]^2[Fe(II)]$$
$$= -k_1 P_{O_2}[Fe(OH)_2^\circ] \quad (17)$$

a reaction well known for the auto catalytic effect of the $Fe(OH)_3(am)$ product formed during the reaction. This auto catalytic effect has been observed in the 6.0 to 7.5 pH range (Tamura et al., 1976), i.e., in the pH range where Fe(II) is expected to be adsorbed onto $Fe(OH)_3(am)$ and to be present as $\equiv FeOFeOH^\circ$ species. Eqs. (15) and (16) are compatible with a two step reaction. First the formation of an intermediate unstable U(V) species:

$$(\equiv FeO)_2 UO_2^\circ + \equiv FeOFeOH^\circ + 3H_2O \overset{k'}{\to} 3\equiv FeOH$$
$$+ Fe(OH)_3(s) + UO_2(OH)^\circ aq \quad (18)$$

followed by a disproportionation reaction (19):

$$2\,UO_2(OH)^\circ\,aq + 2\equiv FeOH$$
$$\underset{U(V)}{}$$
$$\overset{k''}{\to} (\equiv FeO)_2 UO_2^\circ + UO_2(s) + 2H_2O \quad (19)$$
$$\underset{U(VI)}{} \quad \underset{U(IV)}{}$$

In this reaction, both the oxidant and the reactants are present as inner-sphere surface complexes. One can therefore assume that the electron transfer occurs via an inner sphere electron transfer. The product of the reaction is expected to be a $UO_2(s)/Fe(OH)_3(s)$ solid solution. Uranium mineral ores formed at redox fronts, such as those from Poços de Caldas (Brazil) and Catahoula (Texas) (Galloway, 1978; Waber, 1991) and uranium deposits in estuaries (Barnes and Cochran, 1993) may all have been formed by the mechanism described by Eqs. (18) and (19). The U was probably deposited from oxidizing diagenetic solutions percolating in the redox zone where they met with sorbed Fe^{2+} ions, still present as magnetite or ripidolithe in these mineral ore deposits.

4. Conclusion and perspectives

Ferrous iron is an important species in reducing surficial fluids (e.g., organic rich aquifers and flooded soils) and surface waters (e.g., estuaries and stratified lakes and fjords) and the Fe(II)/Fe(III) couple controls for the redox potential of most groundwaters (Grenthe et al., 1992). Above pH 5.5, Fe^{2+} starts to be adsorbed onto particles and this adsorption is completed, on most mineral phases, around pH 7.5, i.e., before the onset of precipitation. Above pH 6.5 a significant part of sorbed Fe(II) is present as an hydroxylated surface complex, $\equiv Fe^{III}OFe^{II}OH°$. This hydrolyzed surface species is a very effective reductant towards uranyl ion and 4-chloronitrobenzene. The observed reduction rates are proportional to the $\equiv Fe^{III}OFe^{II}OH°$ concentration. A similar increase of reaction rate upon hydrolysis of divalent ions has been reported in the hydrolysis of organics by Cu(II) (Smollen and Stone, 1997) and in the reductive precipitation of Tc(IV) (Cui and Eriksen, 1996). Furthermore when granulated iron is used as reactive barrier in an aquifer to dechlorinate TCE and PCE or to precipitate chromate ions, measured redox potential indicate that the reductant is not zero valent iron but rather the $\equiv Fe^{III}OFe^{II}OH°$ species studied in the present paper, i.e., Fe(II) sorbed on the corrosion layer present at the surface of granulated iron (Charlet et al., 1998).

Electron transfer mechanism appears to be different for the organic and the inorganic reactants stud-

ied here. In the case of Ar–NO_2 (as for O_2 and NO_2^-), the electron transfer is most likely outer sphere and products are not retained by the solid phase, which acts merely as source of electrons. On the contrary reduction of U(VI) (as well as Cr(VI) or Tc(VII)) leads to unsoluble solids which may then form solid solutions with the $Fe(OH)_3(am)$ formed in the same reaction. These solid solutions have been observed in Poços de Caldas (Bruno et al., this issue) and the proposed mechanism may have led to such U mineral ore formation.

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