Speciation, oxidation state, and reactivity of particulate manganese in marine sediments

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Abstract

Particulate manganese oxides take a significant part in benthic biogeochemical processes of modern marine sediments. Thermodynamics calculations tell us that the reactivity of the different Mn oxides is variable. We describe here a method adapted for marine sediments, which allowed us to extract Mn oxides and determine the mean oxidation state of particulate Mn. Mn oxides are known to be enriched in the oxic layer of marine sediments. We have observed on a continental slope sediment that the oxidation state of particulate Mn changed with depth, within the 8 cm thick oxic layer. Mn(III) oxyhydroxides dominated at the sediment–water interface, and at the bottom of the oxic layer. In between, Mn(IV) oxides were more abundant. Mn(III) oxides are metastable phases which results from the primary oxidation of Mn^{2+}. Mn oxides of the bottom of the oxic layer are enriched in Mn(III) phases because they result from the current in situ oxidation/precipitation of dissolved Mn^{2+} at the oxic–anoxic interface. Mn(III) oxyhydroxides of the surface sediment originate from the precipitation of Mn shortly before settling, presumably in estuaries where redox oscillations are intense. By contrast, Mn(IV) oxides result from the aging of Mn(III) oxyhydroxides during sediment burial. We have tested the reactivity of different types of Mn oxides with ammonia in anoxic environment. The formation of nitrate was observed after 13 days of incubation in experimental units that contained Mn(III) oxyhydroxides, but not in the units that contained Mn(IV) oxides. Therefore, Mn(III) oxyhydroxides may play a major role in the oxidation of ammonia to nitrate in marine sediments.
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1. Introduction

Manganese is the eleventh element in terms of abundance in the earth crust. In marine oxygenated environment, manganese is present in the form of Mn(IV) oxides and Mn(III) oxyhydroxides (Post, 1999). In anoxic sediments, manganese mainly occurs as Mn(II) carbonates and is generally in solid solution with $CaCO_3$. Oxidized forms of Mn are very reactive and have a strong capacity for adsorption of trace metals (Murray, 1975; Stumm and Morgan, 1996). They occur directly in the processes of mineralization of organic matter as electron acceptors in anaerobic environment (Froelich et al., 1979). Marine sediments contain generally an aerobic surface layer enriched in Mn(III,IV) phases. Deeper, these oxides are reduced to soluble Mn(II) (Burdige, 1993). Dissolved Mn(II) can diffuse towards the oxidized zone, where it precipitates again in the form of Mn(III,IV) (Sundby and Silverberg, 1985). It can also reach equilibrium with a carbonate phase and be buried (Middelburg et al., 1987; Mucci, 1988). Therefore, manganese undergoes several redox cycles in the first centimetres of the sediment before being buried (Canfield et al., 1993). The Mn-bearing phases involved during early diagenesis are numerous, and therefore the possible reactions are numerous too.

When organic matter is exported from the photic zone to the oceanic floor, the organic carbon mineralization alters the initial mineralogy and chemistry of deposited particles and interstitial waters. This phenomenon represents the early diagenetic processes. Bacterially mediated oxidation of organic matter is reflected in a well-established depth sequence of redox reactions in which oxygen is reduced near the sediment–water interface, followed by the reduction of nitrate, manganese and reactive iron oxides, sulphate, and finally carbon dioxide (Froelich et al., 1979; Postma and Jakobsen, 1996). Among the many possible redox reactions, Mn oxides get not only involved during organic carbon mineralization, but also in many secondary reactions. Recent studies attach more and more importance to Mn oxides because of their role in the benthic nitrogen cycle. For example, ammonia can be directly oxidized to N_2 or to nitrate by Mn oxide (Luther et al., 1997; Hulth et al., 1999;

Anschutz et al., 2000). In some case, ammonia may be responsible for reduction of all Mn oxides (Hyacinthe et al., 2001). Dissolved iron (Fe^{2+}), sulphur, or nitrite are also reducing agents for Mn oxides (Burdige et al., 1992; Schippers and Jørgensen, 2001; Luther and Popp, 2002). The primary oxidant of Mn(II) can be oxygen, nitrate, or iodate (Aller, 1990; Schulz et al., 1994; Murray et al., 1995; Luther et al., 1997; Anschutz et al., 2000).

In modern marine sediments, Mn(III) phases are mainly MnOOH polymorphs (manganite, groutite, and feitknechtite). The Mn(IV) forms are essentially todorokite, pyrolusite and birnessite (MnO_2). There is also an intermediate form Mn(II/III), hausmannite (Hem and Lind, 1983; Post, 1999). The free energies of formation of the different Mn(III) phases are rather close to each other, but they differ significantly with those of the Mn(IV) phases. Thermodynamics calculations clearly show that reactions of Mn oxide reductions are more favourable with Mn(IV) phases than with Mn(III) phases. The free energy of formation of Mn oxides also depends on the available surface area and the degree of crystallisation of the phase (Burdige, 1993). On another side, the primary oxidation product of Mn(II) generally produces metastable Mn(III) oxyhydroxides (Hem and Lind, 1983). This web of reactions and Mn phases complicates considerably the marine chemistry of manganese. The reactivity of iron oxides toward redox reactions during early diagenesis has been precisely studied (Canfield, 1989). Burdige et al. (1992) showed that the Mn(IV) oxide mineralogy had an effect on microbial and chemical Mn reduction. However, the reactivity of Mn(III) and Mn(IV) phases was generally not distinguished. The oxidation state of Mn in marine sediments was studied in deep sea manganese nodules (Murray et al., 1984; Piper et al., 1984), and reported rarely in pelagic or hemipelagic sediments (Kalhorn and Emerson, 1984; Shimmield and Price, 1986; Canfield et al., 1993). The aim of the present study was to determine the particulate Mn speciation, oxidation state, and reactivity in marine sediments.

In order to determine speciation and oxidation state of particulate Mn, we have combined techniques used to study manganese nodules (e.g. Murray

et al., 1984; Piper et al., 1984) with techniques of chemical extraction. Different chemical extractions processes were optimised to selectively extract from soils or sediments the ferric phases and associated compounds such as phosphorus (e.g. Tessier et al., 1979; Anschutz et al., 1998). We have adapted a similar method for manganesiferous compounds. The studied material comes from modern sediments of the Bay of Biscay and from hydrothermal Red Sea sediments.

In order to better understand the reactivity of Mn with nitrogenous compounds and more particularly with ammonia, we have made an experiment of Mn oxide reduction in anoxic environment. This experience was made in glass vessel to see whether the reduction of various Mn oxides with ammonia was carried out chemically.

2. Methodology development

2.1. Determination of Mn oxidation state in sediments

The Mn oxidation state determination was modified from Murray et al. (1984). Reactive Mn-bearing phases are solubilized with H_2SO_4. Dissolved Mn(III) and Mn(IV) react with iodide (I^-) in acidic solution to give, respectively, 0.5 I_2 and 1 I_2. I_2 forms a complex (I_3^-) with I^- in excess. This complex is then reduced by thiosulphate used for titration. When all I_3^- have reacted, the solution colour and Eh change. The successive reactions are:

$$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O \qquad (1)$$

$$2MnOOH + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + I_2 + 4H_2O \qquad (2)$$

$$I_2 + I^- \Leftrightarrow I_3^- \qquad (3)$$

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} \qquad (4)$$
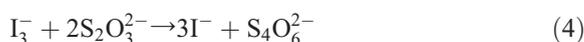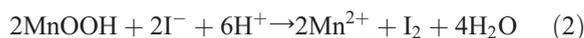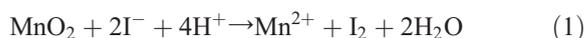
We can estimate the Mn oxidation state by comparing the concentrations of dissolved Mn and iodine. The absence of I_2 production indicates that all the Mn is in Mn(II) form (MnO). If the quantity of produced iodine is equal to Mn, all the Mn is in

Mn(IV) form (MnO_2). The intermediate combinations can be written MnOx, with $1 < x < 2$. The iodine concentration is determined by titration with thiosulphate. It should be noted that some reactive iron present in the sediment is released with the sulphuric acid. Dissolved Fe(III) also oxidizes I^- to iodine. The oxidation number "x" is then calculated according to the following relation:

$$x = 1 + 0.5([Thio] - [Fe(III)])/[Mn] \qquad (5)$$

where [Thio] represents the quantity of thiosulphate used for the titration of iodine. When the proportion of Fe(III) is high, the proportion of iodine that forms from Mn(III,IV) is low. In that case, a small error on Fe(III) determination induces a great error on "x". Therefore, the most accurate values of "x" are obtained when all reactive Mn-bearing phases, and a minimum of Fe oxides are solubilized,. This is why the kinetic of H_2SO_4 extraction on Mn and Fe oxides has been studied.

2.1.1. Kinetic study of H_2SO_4 extraction

The optimal extraction time by H_2SO_4 to dissolve entirely the reactive Mn and a minimum of Fe was determined by kinetics tests on sediments, which contained high concentrations of Mn oxides of identified mineralogy. Fifty milligrams of freeze-dried and homogenised sediment collected in the Atlantis II Deep (Red Sea) were leached with H_2SO_4 as described below. The sample mineralogy was determined by X-ray diffraction (Fig. 1). It contained todorokite as Mn(IV) oxide mineral and manganite, a Mn(III) oxyhydroxide (Anschutz and Blanc, 1995). The sample also contained Fe(III) oxides minerals. The leaching was performed in duplicate. The addition of H_2SO_4 corresponded to the time t_0. One minute later, 1 ml of centrifuged solution was diluted with 2% HCl, for Mn_{H2SO4} and Fe_{H2SO4} concentration measurements. The same operation was realized 2, 5, 10, 15, and 20 min after the H_2SO_4 addition. The results showed that sulphuric acid quantitatively extracted Mn oxides within 2 min and the concentrations of Fe increased during the entire kinetic test (Fig. 1). Thus, the optimal time to extract reactive Mn and a minimum of Fe with H_2SO_4 corresponded to 2 min.
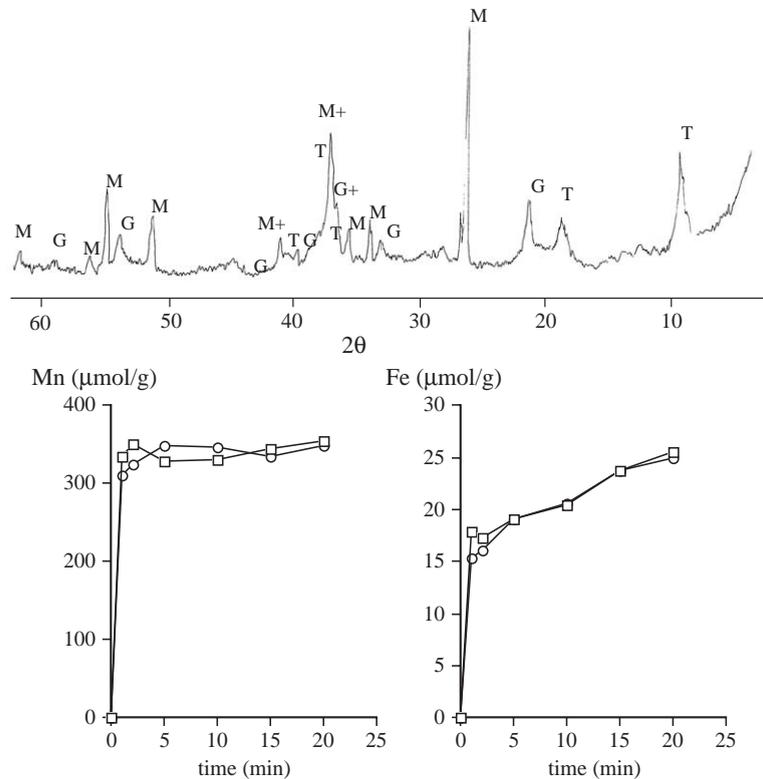
Fig. 1. X-ray diffractogram of the sample of the Atlantis II Deep (Red Sea) used for the kinetics of H_2SO_4 extraction (top). The mineralogy was determined by X-ray diffraction (XRD) analysis of powdered sediment with a Philips PW 1710 diffractometer using CuKα X-Radiation. M: manganite; T: todorokite; G: goethite. Kinetics tests of Mn (bottom left) and Fe (bottom right) extraction by H_2SO_4. Concentrations are expressed in micromole per gram of dry sediment. The leaching was performed in duplicate. Solutions were sampled 0, 1, 2, 5, 10, 15, and 20 min after the H_2SO_4 addition.

2.1.2. Description of the H_2SO_4 extraction

Extractions were performed on freeze-dried and homogenised sediments collected in the south-eastern part of the Bay of Biscay. About 500 mg of freeze-dried sediments were leached with a solution of 1 ml H_2SO_4 (10N), and 10 ml of milli-Q-H_2O during 2 min. Particulate Mn oxides and some Fe oxides are dissolved during this step. Eight milliliters of the centrifuged solution (10 min at 5000 rpm) was then diluted in 10 ml of O_2-free milli-Q-H_2O. A 0.5 ml of NaI–NaOH (6N) was added to the mixture. A yellow coloration appeared because of iodide oxidation with dissolved Mn(III), Mn(IV), and Fe(III). The concentration of iodine was determined by the titration with thiosulphate using a 2 μl resolution automatic titrator. The final solution was diluted in 2% HCl and analysed for Mn_{H2SO4} and Fe_{H2SO4}.

Fe_{H2SO4} results from the dissolution of Fe(II) and Fe(III) phases. To determine the proportion of Fe(III) that was leached, we calculated the difference between measured total extracted Fe, and Fe(II). Fe(II) was measured by the ferrozine method (Stookey, 1970) in a subsample separated before the thiosulphate titration, and the NaI–NaOH addition. Mn_{H2SO4} and Fe_{H2SO4} were measured by flame atomic absorption spectroscopy. When iron concentrations were above the thiosulphate concentrations, the error on "x" became important. In this case, values were not considered.

2.2. Quantification of Mn oxides

The most reactive iron oxide fraction (amorphous "readily microbially reducible" phases) is extracted

with an ascorbate reagent (Ferdelman, 1988; Kostka and Luther, 1994; Anschutz et al., 1998). The kinetics of leaching of Fe(III)-bearing phases with ascorbate has been described by Kostka and Luther (1994). They showed that amorphous Fe(III) phases were extracted quantitatively within 24 h. Hyacinthe et al. (2001), Chaillou et al. (2002), and Rutten and de Lange (2003) showed that the ascorbate reagent was able to extract Mn oxides, but a kinetic study of Mn extraction in natural sediment has never been done.

2.2.1. Description of ascorbate method

The ascorbate reagent consists of a solution of 25 g of sodium bicarbonate and 25 g of sodium citrate in 500 ml of deionised water to which 10 g of ascorbic acid is slowly added to a final pH of 8. About 500 mg of dry sediment is extracted at room temperature with 25 ml of this reagent while shaking continuously. The centrifuged solution is then diluted in 0.2 N HCl for Fe_{Asc} and Mn_{Asc} analysis.

2.2.2. Kinetics of ascorbate extraction

Two kinetic experiments were performed on three samples of dry sediments collected at the station I located at 2800 m depth in the Bay of Biscay (Hyacinthe et al., 2001). The sample OB9I-1 was collected at the surface of the sediment. The sample OB9I-8 came from the depth corresponding to the
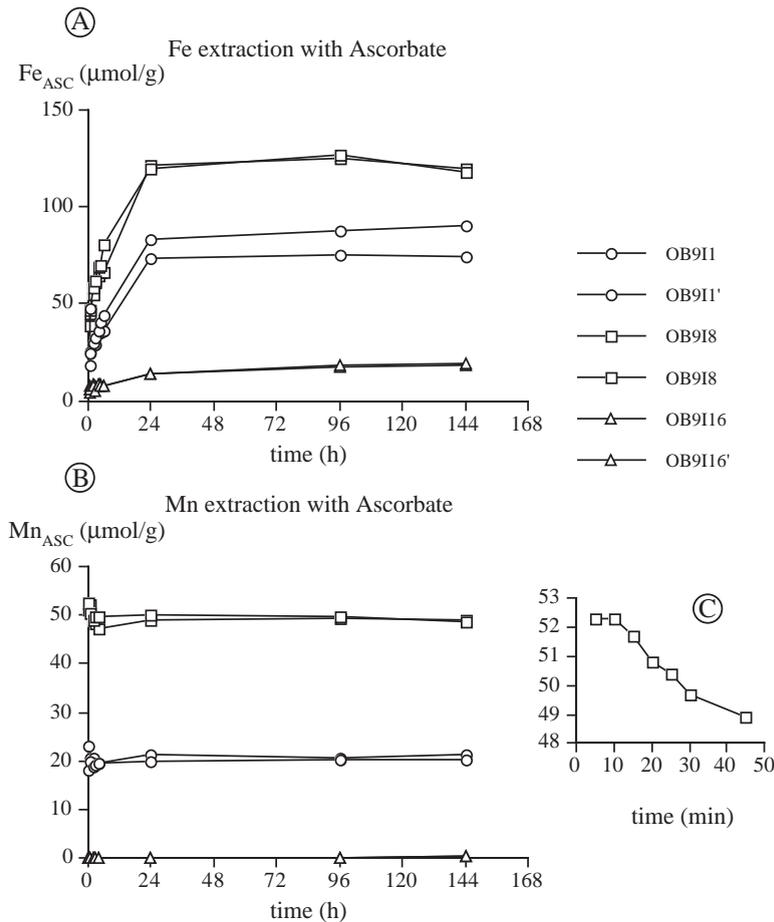
Fig. 2. Kinetics experiment of Fe (A) and Mn oxides (B) extraction by ascorbate. Concentrations are expressed in micromole per gram of dry sediment. The leaching was performed in duplicates on three samples collected at the station I (2800 m depth). Short term kinetic test of Mn oxides extraction by ascorbate in sample OB9I1 (C).

bottom of the oxic layer, at 5 cm below the sediment–water interface. OB9I-16 was collected in the anaerobic zone at 13 cm depth. The leaching was performed in duplicates. The addition of ascorbate corresponded to the time t_0. Half an hour later, every hour during 6 h, and finally after 24 h, 4 and 6 days, 1 ml of solution was centrifuged and diluted with 0.2 N HCl for Mn_{Asc} and Fe_{Asc} concentrations measurements. The results of the Mn_{Asc} kinetic dissolution are shown in Fig. 2 and are expressed in micromole Mn extracted per gram of dry sediment. The samples collected in the oxic layer contained high concentrations of extracted Mn. The duplicates showed that the extraction was very reproducible.

The Mn oxides present in samples OB9I-1 and OB9I-8 were quantitatively extracted in less than 30 min whereas Fe reached a plateau-concentration only after 24 h, as observed by Kostka and Luther (1994). We observed a small decrease of Mn concentrations in the first 6 h. Then, the concentrations increased again to the initial value after 24 h. We have performed a short-term kinetic experiment of ascorbate extraction, in which the Mn concentration of the sample OB9I-8 was controlled every 5 min during 45 min. The experiment showed that the maximum quantity of extracted Mn was reached after 5 min (Fig. 2). This observation suggests that Mn oxides are reduced very rapidly with the ascorbate reagent, and that a part of dissolved Mn(II) produced is momentary trapped until it is totally released after 24 h. Mn(II) is probably adsorbed on reactive Fe(III) oxide phases (Balistrieri and Murray, 1983) until all these oxides are reduced themselves after 24 h.

2.3. Analytical procedures

Fe and Mn extracted from the sediment and the total dissolved Mn and Fe were measured by flame atomic absorption spectroscopy, using aqueous standards. Ammonia was measured by using the flow injection method described by Hall and Aller (1992), and nitrate was measured by the flow injection method of Anderson (1979). The detection limit was 0.5 μmol/l. The accuracy of measurements for nitrate is estimated at 0.2 μmol/l. The accuracy of measurements for NH_4^+ measurements is 2%. Finally, all the nitrate and ammonium analyses were done in duplicate.

3. Application

3.1. Mn distribution and redox state in marine sediments

3.1.1. Material

The sediment cores studied were collected using a multicorer in the south-eastern part of the Bay of Biscay, on the slope of the Aquitaine margin (station B, 550 m) and on flat parts of the canyon of Cap Ferret (station I, 2800 m) during cruise Oxybent-10 in May 2000. These stations were selected because Mn contents were distinct. The top sediment of the station I core was about 4–5 times richer in particulate Mn than the sediment of the station B (Hyacinthe et al., 2001; Chaillou et al., 2002). Sediment core of station I was sliced in thin horizontal sections (0.5 cm for the top 5 cm, 1 cm below, and 2 cm at the bottom) within 1.5 h after core recovery. A sub-sample of each slice was centrifuged under N_2 at 5000 rpm for 20 min to extract pore water. An aliquot of water was filtered (0.2 μm, syringe filter SFCA) and frozen at -25 °C for ammonia analysis, and a second aliquot was filtered and acidified to pH 1.6 with ultrapure HNO_3 for dissolved Mn analysis.

The maximum sedimentation rate at station I was deduced from the slope of the vertical profile of excess ^{210}Pb activity, and the radioactive decay constant (half-life= 22.4 years) according to Chaillou et al. (2002). The excess activity of ^{210}Pb decreased exponentially below 1.5 cm depth (Fig. 3), which suggests that the accumulation rate was constant over time. The maximum sedimentation rate deduced from the data was 0.12 cm/year. The profile of excess ^{210}Pb activity was vertical at the top, and suggests that the sediment was homogenised by bioturbation at the sediment–water interface, down to 1 or 1.5 cm depth.

3.1.2. Profiles of extracted Mn and Fe

The station I was richer in Mn_{H2SO4} and Mn_{Asc} than was the station B (Fig. 3). For both stations, Mn_{Asc} concentrations were lower than Mn_{H2SO4} concentrations, despite the longer time of the ascorbate extraction. However, the shape of the Mn_{H2SO4} and the Mn_{Asc} profiles was the same, with values about 5–10 μmol/g higher for Mn_{H2SO4} concentra-
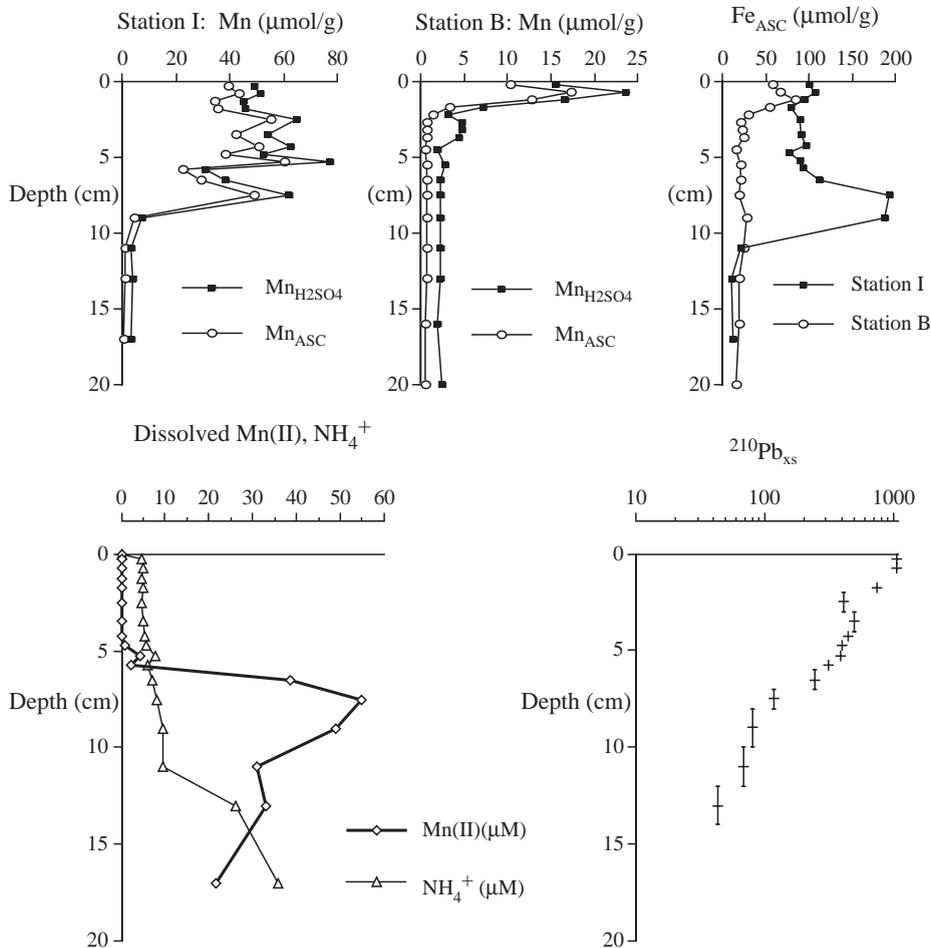
Fig. 3. Vertical distributions of reactive particulate Mn and Fe extracted by ascorbate and H_2SO_4 at stations B (550 m) and I (2800 m). Concentrations of particulate phases are expressed in micromole per gram of dry sediment. Bottom: vertical profiles of Mn(II) and ammonia dissolved in sediment pore waters at station I, and profiles of ^{210}Pb excess activity.

tions. At station B, Mn_{Asc} and Mn_{H2SO4} showed maximum concentrations at 0.75 cm depth with 24 and 17 μmol/g, respectively. The concentrations decreased and reached minimal values below the oxic front (2.2 cm) with 1 and 3 μmol/g. These concentrations remained approximately constant below. Mn_{Asc} and Mn_{H2SO4} oscillated between 35 and 55 μmol/g and 45 and 65 μmol/g, respectively, in the oxic layer of station I sediments. Mn_{Asc} and Mn_{H2SO4} reached minimum concentrations in the anoxic zone, with about 5 μmol/g. Dissolved Mn(II) and ammonia showed low concentrations in the oxic sediment (Fig. 3). Mn(II) was below the detection limit (1 μM) in the top 5 cm. The concentration increased with depth, and

reached a maximum of 55 μM at 7.5 cm depth. Ammonia was below 10 μM in the top 10 cm. The concentration of ammonia increased abruptly at 10 cm, below the depth where Mn_{Asc} was detected.

The concentration of iron extracted by ascorbate (Fe_{Asc}) was always higher than Mn_{Asc} (Fig. 3). Fe_{Asc} concentration reached a maximum of 84 μmol/g in the oxic zone of the station B. Below the oxic front, Fe_{Asc} concentrations decreased abruptly to reach concentrations around 20 μmol/g. At station I, the Fe_{Asc} profile showed high values in the first 10 cm. The maximum value was equal to 192 μmol/g. Deeper, the concentrations decreased to a value of 10 μmol/g.
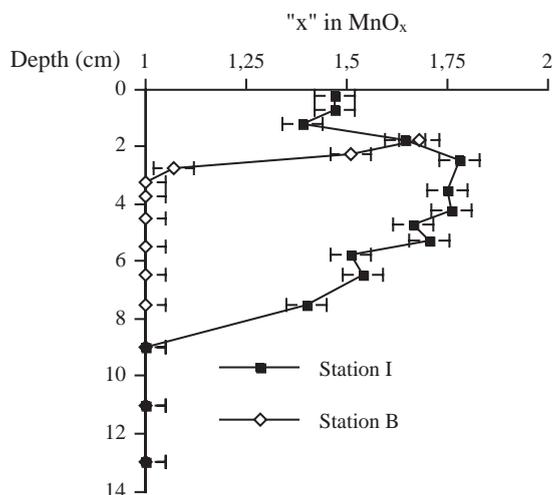
"x" in MnO$_x$

Fig. 4. Vertical profiles of Mn oxidation state ("x" in MnOx) of sediments collected at stations B (550 m) and I (2800 m).

3.1.3. Oxydation state of Mn at the stations B and I

The value of "x" was always above 1 in the layer of sediment enriched with Mn$_{Asc}$ (Fig. 4). The oxidation state was above 1.5 at the top of core B and decreased at the bottom of the Mn$_{Asc}$ enriched layer. At station I, the "x" number was close to 1.5 in the top 2 cm of the core, and at the bottom of the Mn$_{Asc}$ enriched layer, between 6 and 8 cm depth. Between these two layers (2–6 cm), the value of "x" was higher and close to 1.70. Below the Mn$_{Asc}$-rich layer, in the anoxic sediment, "x" was close to 1.

3.2. Experimental study of the reduction of Mn oxides with NH$_4^+$

3.2.1. Synthetic Mn oxide precipitation

The Mn(III,IV)-bearing phases precipitated by mixing 10 g of MnCl$_2$ with 1 l of 1 N NaOH aqueous solution, while bubbling with air. A precipitate formed immediately. Then, the solution stagnated in a glass bottle during more than 1 year. A black precipitate appeared on the glass surface and a reddish brown precipitate formed in the mixture. The precipitate was washed with milli-Q water and recovered by centrifugation. The oxidation state of these artificial Mn oxides was determined according to the method described above. The measurements were performed in duplicates to check the reproducibility of the results, which were in agreement within 3% on

average. The results showed oxidation degrees of 1.48 for the reddish brown precipitate and 1.83 for the black precipitate, indicating that the first one was a Mn(III) phase, and the second one was dominated by a Mn(IV) phase.

3.2.2. Experimental set up

Eight experimental units consisted of 500 ml glass beakers closed up with a rubber cap, that contained 400 ml of anoxic seawater, and no detectable NO$_3^-$ nor Mn^{2+}. Anoxia was maintained by bubbling with N$_2$ during sampling. Table 1 summarizes the content of each unit. Units E3, E4, E5, and E6 contained 614 μmol/l of NH$_4^+$ and 25 mg of the Mn(III) or Mn(IV) oxides. Units E5 and E6 also contained a few mg of wet anoxic sediment in order to supply anaerobic bacteria in the units. E1, E2, E7, and E8 were control units. E1 and E2 allowed us to make sure that the environment was maintained anoxic. E7 and E8 allowed us to check whether the Mn oxides were reduced in the absence of NH$_4^+$, or not. The choice of the NH$_4^+$ concentration coincided to natural high values of ammonium found in marine sediments at depth where the Mn oxides can be in contact with ammonium below the oxic zone. The added mass of Mn oxide was calculated in order to be lower than the amount of ammonium. It corresponded approximately to 500 μmol of Mn. During the experiment, we prepared 18 samplings of 10 ml for each unit in order to analyse the evolution with time of NO$_3^-$, NH$_4^+$ and Mn^{2+} in filtered (0.2 μm) solution. The pH was measured at several sampling times. It remained at 8.0±0.1 during the whole experiment.

Table 1
Composition of the different experiment units used to study the reactivity Mn(III) oxyhydroxides and Mn(IV) oxides with ammonia in anoxic seawater

	Filtered seawater	NH$_4^+$ (614 μmol/l)	Mn(III)	Mn(IV)	Sediment
E1	X	X			
E2	X	X			X
E3	X	X	X		
E4	X	X		X	
E5	X	X	X		X
E6	X	X		X	X
E7	X		X		
E8	X			X	
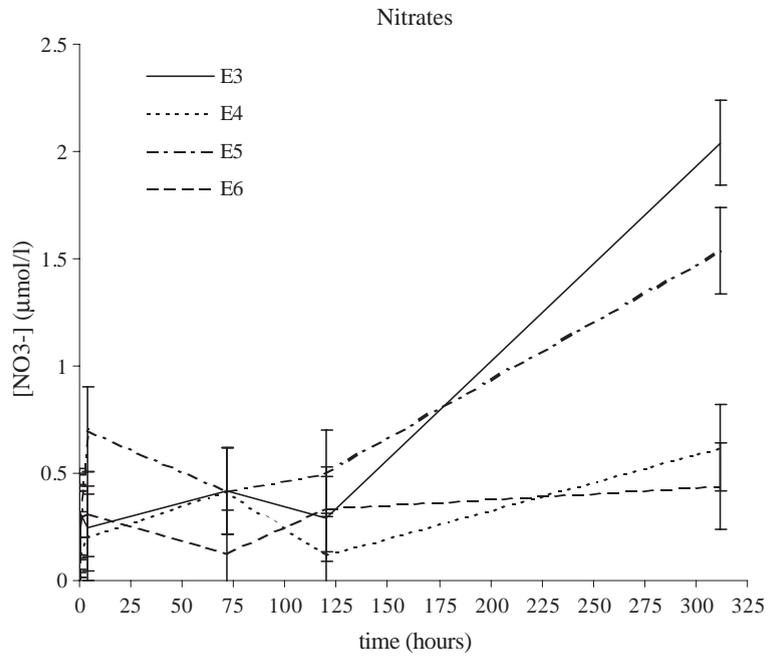
Nitrates

Fig. 5. Variation of nitrate concentrations (μmol/l) with time in the units E3, E4, E5, and E6.

3.2.3. Results

The NO_3^- concentrations of the four blanks never was above our detection limit of 0.5 μmol/l. Nitrate

appeared in the units E3 and E5 that contained Mn(III) oxides and NH_4^+. It was detected after 13 days with concentrations of 2.0 μmol/l in E3 and 1.5 μmol/l in
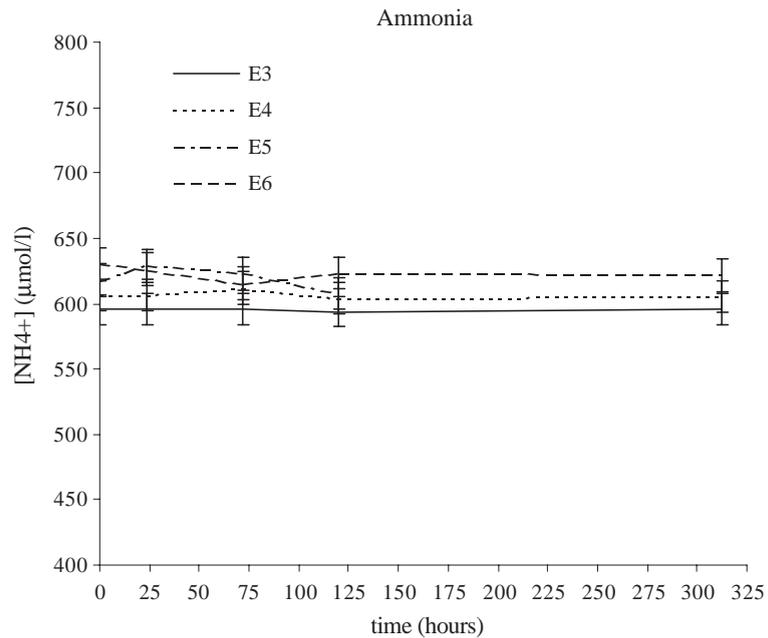
Ammonia

Fig. 6. Variation of ammonia concentrations (μmol/l) with time in the units E3, E4, E5, and E6.

E5. The units E4 and E6 that contained Mn(IV) oxides did not contain NO_3^- at the end of the experiment (Fig. 5). The accuracy of NH_4^+ analysis was 2%, which represents ± 12 μmol/l for a standard concentration of 614 μmol/l. The ammonium concentration of the blank units E1 and E2 remained stable all along the experiment with an average concentration of 617 μmol/l. Ammonium concentration did not decreased significantly in the ammonium and Mn oxide containing units E3 to E6 (Fig. 6). No significant dissolved manganese concentrations, i.e. above the detection limit of 0.5 μmol/l, appeared in the units.

4. Discussion

4.1. The Mn oxidation state determination

The Mn oxidation number is calculated according to the formula: $x = 1 + 0.5$ ([Thio]$-$[Fe^{3+}])/[Mn]. The pure Mn(II), Mn(III) and Mn(IV) phases have respective values of 1, 1.5 and 2. To obtain an accurate "x" value, it is necessary to minimize the dissolution of Fe oxides. Therefore, the time of the H_2SO_4 attack must be minimum. Our kinetic test showed however that 2 min of leaching were necessary to extract the totality of Mn oxides. During this time, a significant part of Fe(III) phases was also dissolved when present. Thus, the method of "x" determination is only accurate for samples enriched in Mn oxides.

4.2. The variations of "x"

The values of "x" were measured accurately in the Mn_{Asc} enriched layer of the stations I and B. At the station I, where the Mn_{Asc} layer is 8 cm thick, we observe vertical variations of the "x" values. Different parameters may explain these variations.

4.2.1. The effects of carbonate and dissolved manganese on "x" values

Sulphuric acid dissolves Mn(III and IV) associated with oxides, but also Mn(II) associated with carbonates. Therefore the variation of the redox state of the particulate Mn located in the oxic layer can be the result of the variation of the proportion of Mn(II)

carbonate rather than the variation of the oxidation state of Mn oxides.

The ascorbate solution extract quantitatively all the Mn(III,IV) phases. Therefore difference between Mn_{H2SO4} and Mn_{Asc} represents the content of Mn(II) phases. This difference remains approximately constant at station I (Fig. 3). Thus, the variation of the observed Mn oxidation state do not depend on a particulate Mn(II) phase.

Mn^{2+} cations are known for their strong adsorption affinity with Mn oxides (Morgan and Stumm, 1964; Murray et al., 1984; Shimmield and Price, 1986). Therefore, Mn_{H2SO4} could contain Mn^{2+} absorbed on Mn oxides, which could account for the experimental measure of "x". In the oxic zone of the station I, the highest "x" value is equal to 1.78, the weakest value is equal to 1.39. If this weakest value would be only due to Mn^{2+} adsorbed on an oxide with the highest "x" ($MnO_{1.78}$) then, the half part of the total extracted Mn should be Mn^{2+} adsorbed on the second half part consisting of the carrier phase, which is impossible. Vertical variations in Mn^{2+} adsorption capacity of the sediment cannot, however, be ruled out, and may explain partly, but not totally, the variation of the total particulate Mn oxidation state. Consequently, neither the carbonates nor the Mn^{2+} adsorbed on Mn oxides can explain all the variations of the Mn oxidation state observed in the oxic layer. These variations must be ascribed to changes in the mineralogy of Mn oxides.

4.2.2. Nature and evolution of Mn oxides with depth

The oxidation state of MnOx is close to 1.5 at the top of the oxic zone of the station I, within the layer mixed by bioturbation, which suggests that the Mn(III) phases dominate. In the middle zone enriched with Mn oxides, between 2 and 6 cm, "x" has a value of 1.70 ± 0.06. This indicates that Mn(IV) phases are mixed with Mn(III) phases. At the bottom of the Mn_{Asc} enriched layer, "x" values are lower or equal to 1.5. Therefore, Mn(III) is dominant in this zone. Consequently, we observe a vertical succession of the oxidation state of Mn oxides within the oxic layer of the sediment of station I.

Mn(II) oxidation proceeds via a number of reactions yielding various oxidation states and mineral forms. Several studies report that the microbial Mn(II) oxidation results in the formation of Mn(IV) oxides without lower valence intermediate (Friedl et al.,

1997; Tebo et al., 1997). However, since environmental conditions of pH, pE, Mn(II) concentration, and temperature affect the Mn minerals that form (see Tebo et al., 1997 for a review), a variety of different Mn oxidation states or mineral forms have been observed in fresh microbial precipitates. The precipitation of Mn(III)-bearing phases is produced mostly from abiotic Mn(II) oxidation. The oxyhydroxide disproportionate slowly (months to years) in a second step to form Mn(IV) oxide, which is the stable form in oxic conditions (Hem and Lind, 1983; Murray et al., 1985). The Mn oxide that appears at the sediment surface of the station I is mostly Mn(III) and can correspond to MnOOH. This metastable oxyhydroxide has not evolved towards Mn(IV) oxide, which suggests that the precipitation of the Mn oxyhydroxides occurred recently. Therefore, the sedimenting Mn-bearing phase do not originated from old primary detrital oxides but rather from freshly oxidized Mn(II). Mn reduction and re-oxidation cycles can occur in the maximum turbidity zone of estuaries (Abril et al., 1999), where oxic/anoxic oscillations because of sediment reworking promote the reductive dissolution of detrital Mn(IV) oxides to dissolved Mn(II), and the oxidative precipitation of Mn to new Mn(III) oxyhydroxides. Such redox oscillation has been confirmed in the Gironde estuary, which represents an important source of detrital material for the Bay of Biscay. The oxidation/reduction of Mn can also occur at the top of the oxic layer of the sediment itself, through a reaction of ammonia oxidation to N_2 by oxygen, by using Mn oxides as a catalyst (Luther et al., 1997; Anschutz et al., 2000). Direct oxidation of Mn^{2+} in the water column can also explain the precipitation of Mn(III) phase.

The bottom of the Mn_{Asc} enriched layer is dominated by Mn(III) forms, which suggests that here again, the precipitation of Mn oxyhydroxides is recent. This level corresponds to the depth where the diagenetic redox cycle of Mn occurs. Mn(III–IV) forms are reduced to Mn(II) by bacteria, or by reducing species such as ammonia, through burial or oscillation of the O_2 front. The profile of dissolved Mn(II) (Fig. 3) shows a peak at this depth, which suggests that the reduction of Mn oxide was in progress. Mn(II) is then reoxidized to Mn(III–IV) oxides in the presence of traces of O_2 or other oxidizing species, such as iodate (Anschutz et al.,

2000). Our data suggests that the precipitation of primary Mn(III) oxyhydroxides dominated.

The presence of Mn oxide with higher oxidation state in the 2–6 cm interval, can result from the aging of primary Mn(III) oxyhydroxide during burial of the sediment, and its transformation to the more stable Mn(IV) oxide in the presence of oxygen. This layer begins just below the bioturbated sediment. The oxidation state of Mn reached its maximum value at 1 cm below the mixed zone. Considering an average sedimentation rate of 0.12 cm year^{-1}, as deduced from the $^{210}Pb_{xs}$ data, 1 cm represents 8 years of particle deposition. Therefore, the oxidation of Mn(III) phases to Mn(IV) oxides is completed in less than 8 years.

4.3. Reduction of Mn(III) and Mn(IV) oxides with NH_4^+

In addition to the metabolic reduction of Mn by bacteria (Froelich et al., 1979), and chemical reduction of Mn oxides with sulphide or Fe^{2+} (Schippers and Jørgensen, 2001), recent studies showed the coupling of Mn and N species during early diagenesis. Ammonium could be directly oxidized by Mn oxides, either in N_2 within aerobic environments (Luther et al., 1997) or in nitrate within the anoxic zone (Aller et al., 1998; Hulth et al., 1999; Anschutz et al., 2000). The ascorbate leaching did not differentiate the various phases of Mn(III–IV). Therefore, it was interesting to test the reactivity of the different types of Mn oxide with ammonia.

4.3.1. Thermodynamic data

Using thermodynamic data from Stumm and Morgan (1996), we observed that during organic matter degradation, Mn(IV) oxides are more reactive than are reactive Mn(III) oxihydroxides. At pH 8 and for one electron transfer (1/4 mol CH_2O) the values of ΔG°_R are −80.1 and −74.1 kJ/mol for γMnO_2 and βMnO_2, respectively, and −69.6, −54.5, and −40.1 kJ/mol for $\beta MnOOH$, $\gamma MnOOH$, and Mn_3O_4, respectively. With regard to the reactivity of Mn(III) and Mn(IV) oxides with NH_4^+ at pH 8, thermodynamic calculations show that NH_4^+ is preferentially oxidized to N_2, first with Mn(IV) oxides and second with Mn(III) oxyhydroxides, and hausmannite. The nitrate production from the oxidation of NH_4^+ with Mn(III,

IV) minerals seems to be favourable at pH 8 for the Mn(IV) species where the ΔG°_R is negative (Fig. 7). The values of ΔG°_R is close to zero for Mn(III) species at pH 8. Therefore, the direction of the reaction will depends on the true activities of dissolved NH_4^+, NO_3^-, and Mn^{2+}. For high values of ammonia and low values of nitrate and Mn^{2+}, such as in our experimental setup, the production of nitrate from ammonia with Mn(III) can be favoured.

4.3.2. Experiment in artificial conditions

During the in vitro experiment, the pH remained close to 8, and Mn^{2+} concentrations were below detection limit. Nitrate did not appear in the four blanks, where Mn oxide was absent. The concentrations of NH_4^+ did not change in the blank units. It means that NH_4^+ was not oxidized independently of MnOx.

The units E4 and E6, which were enriched with Mn(IV) phases, have not revealed a production of

$1/2\,\gamma MnO_2 + 1/3\,NH_4^+ + 2/3\,H^+ \longrightarrow 1/2\,Mn^{2+} + 1/6\,N_2 + H_2O$

$1/2\,\beta MnO_2 + 1/3\,NH_4^+ + 2/3\,H^+ \longrightarrow 1/2\,Mn^{2+} + 1/6\,N_2 + H_2O$

$\gamma MnOOH + 1/3\,NH_4^+ + 5/3\,H^+ \longrightarrow Mn^{2+} + 1/6\,N_2 + 2\,H_2O$

$\beta MnOOH + 1/3\,NH_4^+ + 5/3\,H^+ \longrightarrow Mn^{2+} + 1/6\,N_2 + 2\,H_2O$

$1/2\,Mn_3O_4 + 1/3\,NH_4^+ + 8/3\,H^+ \longrightarrow 3/2\,Mn^{2+} + 1/6\,N_2 + 2\,H_2O$

$1/2\,\gamma MnO_2 + 1/8\,NH_4^+ + 3/4\,H^+ \longrightarrow 1/2\,Mn^{2+} + 1/8\,NO_3^- + 5/8\,H_2O$

$1/2\,\beta MnO_2 + 1/8\,NH_4^+ + 3/4\,H^+ \longrightarrow 1/2\,Mn^{2+} + 1/8\,NO_3^- + 5/8\,H_2O$

$\gamma MnOOH + 1/8\,NH_4^+ + 7/4\,H^+ \longrightarrow Mn^{2+} + 1/8\,NO_3^- + 13/8\,H_2O$

$\beta MnOOH + 1/8\,NH_4^+ + 7/4\,H^+ \longrightarrow Mn^{2+} + 1/8\,NO_3^- + 13/8\,H_2O$

$1/2\,Mn_3O_4 + 1/8\,NH_4^+ + 11/4\,H^+ \longrightarrow 3/2\,Mn^{2+} + 1/8\,NO_3^- + 13/8\,H_2O$
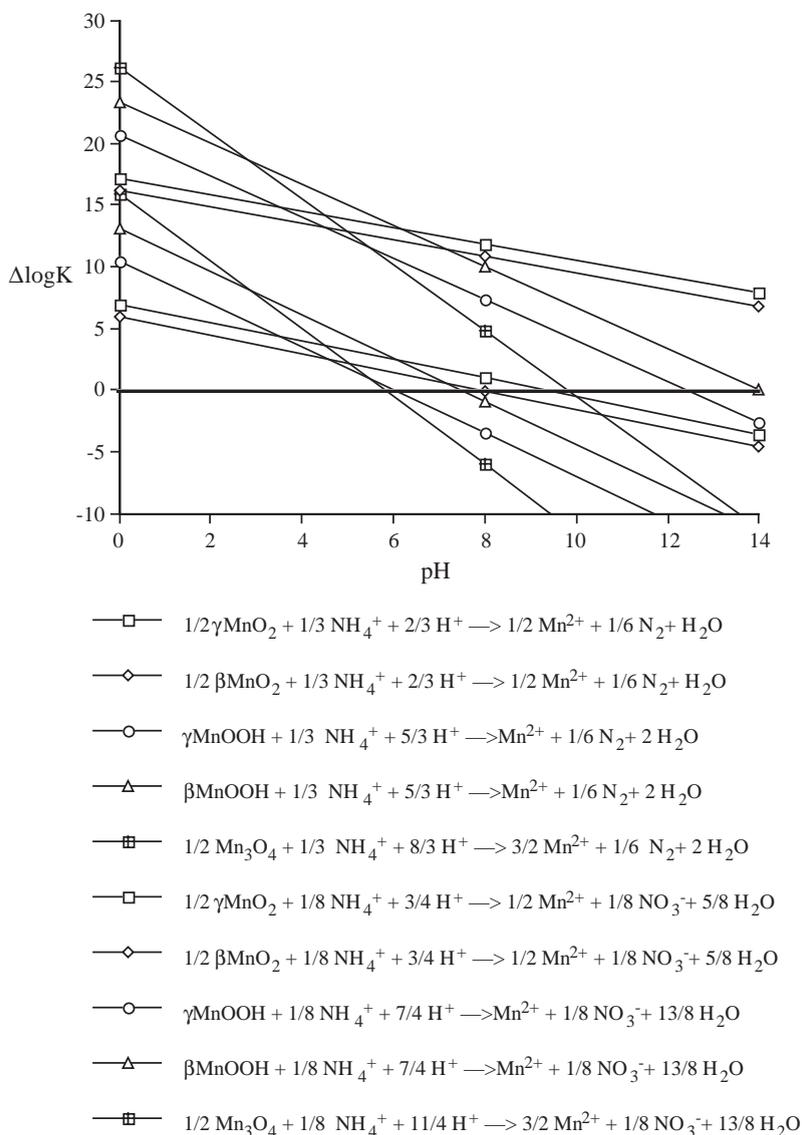
Fig. 7. $\Delta \text{Log}\,K$ vs. pH plots for selected reactions of Mn(III and IV) oxide reduction with ammonia to form nitrate or dinitrogen. $\Delta \text{Log}\,K$ is the total free energy at a given pH. Positive $\Delta \text{Log}\,K$ indicates a favourable reaction. Thermodynamics data come from Stumm and Morgan (1996).

nitrate nor a consumption of ammonia, despite the thermodynamic feasibility. It means either that Mn(IV) cannot react with NH_4^+ to form NO_3^-, or that the kinetics of this reaction is not rapid enough to be detected within 13 days. Low concentrations of nitrate were measured in the presence of Mn(III) oxyhydroxides (E3 and E5) after 13 days. Therefore, nitrate production in anaerobic environment and in the presence of Mn(III) oxyhydroxide happens under artificial conditions.

About 2 μmol/l of nitrate appeared after 13 days in units E3 and E5. The probable source of nitrogen for nitrate formation was ammonia. Since the oxidation of NH_4^+ to NO_3^- occurred only in the oxyhydroxide-bearing units, we can conclude that Mn(III) phases can oxidize NH_4^+ to NO_3^- in anaerobic condition within a short period of time. Thermodynamics calculations indicates that the production of nitrate is theoretically more favourable with MnO_2, but experimental results suggest that the freshly precipitated Mn(III) phase is more reactive. The ΔG_f, of the precipitate was probably different from the value given for pure minerals.

No significant dissolved manganese concentrations appeared in the units. One possible explanation is the adsorption of Mn^{2+} on particles. The adsorption affinity of Mn^{2+} on Mn(III–IV) particles is known to be large (Morgan and Stumm, 1964; Murray et al., 1984; Shimmield and Price, 1986). The stœchiometry of the reaction that involves MnOOH and NH_4^+ indicates a production of 8 Mn^{2+} for 1 NO_3^-. As the measured nitrate concentration is 2 μmol/l in the unit 3, the production of Mn^{2+} should be 16 μmol/l. This concentration represents 6.4 μmol of Mn in the 400 ml of the experimental units. Since the 25 mg of solid manganese introduced in the units correspond to 455 μmol of Mn, it is possible that the 6.4 μmol of Mn^{2+} or 1.4% of total manganese was adsorbed on manganese particles.

A recent study of Mn oxides rich sediment of the Skagerrak basin (Thamdrup and Dalsgaard, 2000) showed that the anaerobic oxidation of NH_4^+ in N_2 or NO_3^- was insignificant and that NH_4^+ could be regarded as the last product of organic N mineralization. Our data show also that the decrease of NH_4^+ concentration was not significant during the experiment. The Mn oxides of the surface sediment of the deep Skagerrak basin consist of Mn(IV) oxides

(Canfield et al., 1993), which are less reactive toward ammonia than Mn(III) phases. According to Aller (1980), the presence of a nitrate peak in the anoxic zone was explained by NH_4^+ oxidation with the oxygen contained in the burrows during bioturbation. It was also suggested that the presence of nitrate in anoxic zone arose from a nitrate infiltration in pore waters during bioturbation from oxic zone towards anoxic zone. However, in some sedimentary deposits, the average distribution of O_2 and NO_3^- were not compatible with an exclusively aerobic nitrification (Sørensen et al., 1987; Bender et al., 1989; Aller, 1990; Murray et al., 1995; Luther et al., 1997; Aller et al., 1998). Hulth et al. (1999) and Anschutz et al. (2000) have observed a coincidence between a NO_3^- peak and Mn^{2+} maximum in anoxic zone, which suggests that Mn oxides were reduced by NH_4^+ to produce Mn^{2+} and NO_3^-. Our experiment shows that this interaction is possible.

5. Conclusion

The quantification of Mn oxides in sediment was carried out according to a technique of chemical extraction: the ascorbate method. This solution leached Mn oxides selectively. However, it did not allow us to differentiate Mn(III) oxyhydroxides and Mn(IV) oxides.

The Mn oxidation state was determined by iodometry. We have optimised this method by taking into account the interference by Fe(III), and by characterizing the optimum time for the leaching. Although additional studies on the effects of pure ferric phases could improve the precision of the method, this titration is reliable and really acceptable in sediments rich in manganese extracted with the ascorbate solution.

The application of these techniques on sediments collected in the Bay of Biscay shows a variation of manganese oxide mineralogy with depth. We observed manganese in the Mn(III) form at the surface of the oxic zone, indicating that the sedimenting Mn oxides did not originated from old primary detrital oxides, but rather from Mn involved in reduction/oxidation cycles shortly before settling. Thermodynamically more stable Mn(IV) oxide dominated in the intermediate oxic layer. It formed

probably from the aging of Mn(III) oxyhydroxide during burial of sediment. Finally, the presence of Mn(III) forms at the bottom of the oxic layer resulted from the oxidation of dissolved Mn(II), which diffused from below.

Experiments that we carried out on synthetic manganese phases showed that manganese oxides reduction by ammonium could generate nitrate in an anoxic environment. Even if thermodynamics indicates that Mn(IV) are the most reactive, it appeared in our experiment that the Mn(III) oxyhydroxides were most reactive. This suggests that the freshly precipitated Mn(III) phase have probably different ΔG_f than have pure minerals. The coupling between the cycles of manganese and nitrogen during early diagenesis seems to be confirmed and should be systematically considered in studies on benthic biogeochemistry.

Acknowledgements

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