Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium

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Abstract—The formation of Fe(III) oxyhydroxide colloids by oxidation of Fe(II) and their subsequent aggregation to larger particles were studied in laboratory experiments with natural water from a freshwater lake and a brackish coastal sea. Phosphate was incorporated in the solid phase during the course of hydrolysis of iron. The resulting precipitated amorphous Fe(III) oxyhydroxide phases were of varying composition, depending primarily on the initial dissolved Fe/P molar ratio, but with little influence by salinity or concentration of calcium ions. The lower limiting Fe/P ratio found for the solid phase suggests the formation of a basic Fe(III) phosphate compound with a stoichiometric Fe/P ratio of close to two. This implies that an Fe/P stoichiometry of ≈2 ultimately limits the capacity of precipitating Fe(III) to fix dissolved phosphate at oxic/anoxic boundaries in natural waters. In contrast to phosphorus, the uptake of calcium seemed to be controlled by sorption processes at the surface of the iron-rich particles formed. This uptake was more efficient in freshwater than in brackish water, suggesting that salinity restrains the uptake of calcium by newly formed Fe(III) oxyhydroxides in natural waters. Moreover, salinity enhanced the aggregation rate of the colloids formed. The suspensions were stabilised by the presence of organic matter, although this effect was less pronounced in seawater than in freshwater. Thus, in seawater of 6 to 33 ‰S, the removal of particles was fast (removal half time < 200 h), whereas the colloidal suspensions formed in freshwater were stable (removal half time > 900 h). Overall, oxidation of Fe(II) and removal of Fe(III) oxyhydroxide particles were much faster in seawater than in freshwater. This more rapid turnover results in lower iron availability in coastal seawater than in freshwater, making iron more likely to become a limiting element for chemical scavenging and biologic production. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The transformation between dissolved Fe(II) species and solid Fe(III) oxyhydroxide phases is central in the cycling of iron in aquatic environments (Stumm and Sulzberger, 1992; Davison, 1993). The behaviour of many other chemical species, including oxyanions such as phosphate and arsenate, alkaline-earth elements and trace metals (e.g., Cu, Zn, and Cd), is linked to the redox dynamics of iron as a result of the scavenging capacity of the precipitating oxyhydroxides (Sholkovitz and Copland, 1982; Ingri, 1985; Sigg, 1985; Belzile and Tessier, 1990; Wheat et al., 1996; Dong et al., 2000). Knowledge of the chemical and colloidal properties of Fe(III) oxyhydroxide phases freshly precipitated in natural water is crucial for understanding the cycling of iron and associated elements. The cycling of iron is also a key topic when dealing with environmental and ecological issues, such as eutrophication and nutrient limitation of biologic processes (e.g., Gunnars and Blomqvist, 1997).

Today it is well documented that particulate Fe(III) oxyhydroxides are formed by oxidation of Fe(II) at oxic/anoxic boundaries in freshwater lakes (Davison and Tipping, 1984) and coastal marine water (Murray et al., 1995; Yao and Millero, 1995). The presence of dissolved species, such as silicate,

phosphate and organic matter, can affect the composition, structure, morphology, and reactivity of the hydrolysis product (Schneider and Schwyn, 1987; Kandori et al., 1992; Deng and Stumm, 1994; He et al., 1996; Deng, 1997; Masion et al., 1997a; Vilgé-Ritter et al., 1999; Mayer and Jarrell, 2000). In freshwater, the oxidation process typically results in colloidal particles having a mean diameter in the range of 0.05 to 0.5 μm (Tipping et al., 1981; Leppard et al., 1988; Pizarro et al., 1995; Lienemann et al., 1999). These colloids are too small to sink at significant rates by gravity, and coagulation processes, therefore, are needed for effective sedimentation. Several reports indicate that the aggregation rate of Fe(III) oxyhydroxide colloids tends to be slow in freshwater, and that their surface properties are controlled primarily by the interaction with organic matter and calcium (Tipping and Ohnstad, 1984; Pizarro et al., 1995; Mayer and Jarrell, 1996). In seawater the settling properties of iron colloids formed in situ are less well studied. Most studies on salinity effects concern river-borne, iron-rich colloids in mixtures of river water and seawater (Mayer, 1982; Fox and Wofsy, 1983; Hunter and Leonard, 1988; Forsgren et al., 1996) or well-defined iron oxide minerals in synthetic solutions (Liang and Morgan, 1990; Ledin et al., 1993).

Examination by electron microscopy has shown that newly formed iron-rich colloids in seawater areas and freshwater lakes frequently contain phosphorus and calcium (Tipping et al., 1981; Bernard et al., 1989; Buffle et al., 1989; Caulkett and Ellis-Evans, 1996; Lienemann et al., 1999; Matthiesen et al., 2001). Sorption experiments in synthetic solutions have revealed that calcium can adsorb to mineral particles of iron

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oxides by complexation reactions with surface hydroxyl groups (Dzombak and Morel, 1990), whereas studies on natural freshwater systems have stressed the influence of organic matter in the sorption process of calcium (Ingri and Widerlund, 1994; Tessier et al., 1996). Few studies, however, have evaluated calcium interactions during the formation of colloidal iron compounds at oxic/anoxic boundaries in natural water (cf. Buffle et al., 1989).

The mechanisms and products of the iron-phosphorus interaction during the oxidation and hydrolysis of iron are of particular interest, since the fixation of dissolved phosphate by settling iron-rich phases strongly affects the geochemical migration of phosphate in aquatic systems (Sholkovitz and Copland, 1982; Stauffer and Armstrong, 1986; Berner et al., 1993; Wheat et al., 1996). Adsorption models have been applied to evaluate the uptake of phosphate by Fe(III) oxyhydroxides precipitated from pore water (Fortin et al., 1993), and phosphate removal from surface waters and wastewater has also been related to formation of discrete basic iron phosphate phases (Tessenow, 1974; Stumm and Sigg, 1979; Luedecke et al., 1989; Fytianos et al., 1998). Still, there is a lack of established equilibrium constants for these compounds (Nriagu and Dell, 1974; Luedecke et al., 1989), which makes it difficult to model and predict their geochemical behaviour. Recent studies involving characterisation of natural iron-rich colloids indicate that the formation of iron-phosphate compounds might be a crucial process in freshwater environments (Buffle et al., 1989; Lienemann et al., 1999). However, these studies are restricted to two eutrophic freshwater lakes, whereas knowledge of colloidal iron-phosphate phases formed in other types of natural waters is lacking.

Here we report a comparative study of the formation, aggregation and settling behaviour of colloidal Fe(III) oxyhydroxide particles newly formed by the oxidation of dissolved Fe(II) in water from a freshwater lake and a coastal sea, respectively. We have characterised the particulate forms of phosphate and calcium associated to the colloidal iron, calling particular attention to incorporation mechanisms and the influence of salinity. Also, we address how our results can help to resolve ecological issues linked to salinity and the geochemical cycling of iron.

2. MATERIAL AND METHODS

2.1. Field Sites and Sampling Procedure

The study area (Fig. 1) is situated ~50-km south of Stockholm, Sweden. It has a fairly homogenous geologic setting and climatology. The Precambrian basement basically consists of sedimentary gneisses and granitoids (Stålhös, 1968, 1979, 1982, 1984), which are often covered by unconsolidated Quaternary drift (Möller, 1969; Persson, 1977; Björnbom, 1981, 1985). The climate is mesothermal and humid (Defant, 1972). The freshwater station (Lake MB) is located in the dimictic Lake Mälaren (Södra Björkfjärden), and the seawater station (Coastal C) at Yttre Hållsfjärden Bay, near the Askö Laboratory, in the adjoining Baltic Sea proper (Fig. 1). Both stations have soft bottoms rich in organic matter. No river empties into the area, and no bottom trawling occurs. Water from Södra Björkfjärden enters the Baltic via a locked canal at the town of Södertälje. In this part of the Baltic, the tide range is negligible (Magaard, 1974). During summer and early autumn, the water column is stratified at both stations, with a thermocline at 15 to 20 m depth. Thus, the principal difference between the two stations is salinity, which is <0.05 ‰S and 5 to 8 ‰S for Lake MB and Coastal C, respectively.
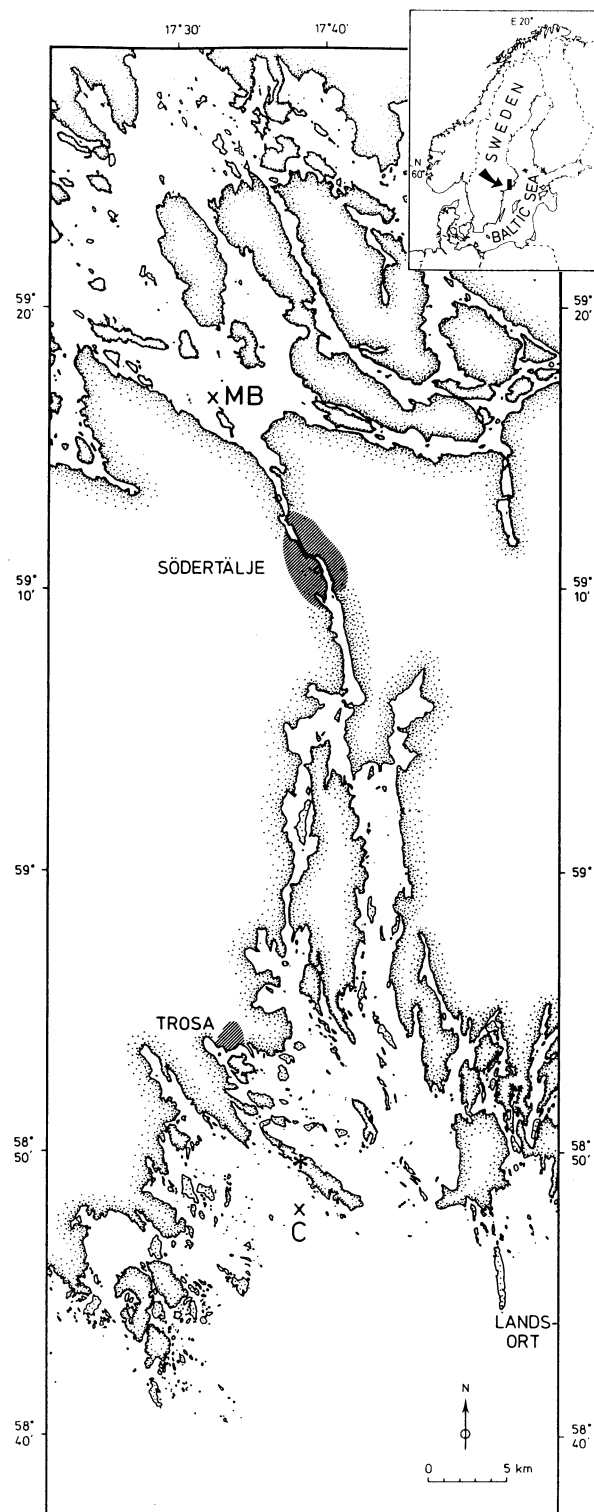

Fig. 1. Map of the study area with the position of the freshwater station Lake MB (MB) and the brackish seawater station Coastal C (C). An asterisk designates the Askö Laboratory.

Water samples were collected at 36 m depth at station Lake MB and 40 m depth at Coastal C on 11 March 1991. A 2-m-long cylindrical

Plexiglas sampler of 20-L volume was used to collect water from a few meters above the bottom. The water samples were stored and transported in 25-L polyethylene carboys. At the laboratory some hours later, the water was transferred to 10-L Pyrex bottles.

2.2. Experimental

To permit comparison of iron dynamics in freshwater and seawater, all experiments were run in parallel at $6 \pm 1°C$, a temperature that corresponds to the deep water in our study area. The oxidation of Fe(II) and the subsequent coagulation/sedimentation processes of the Fe(III) oxyhydroxide formed were studied without interruptions. Total concentrations of 17- to 90-μM Fe and 15-μM P were involved, both within the ranges commonly found in naturally anoxic waters (e.g., Kremling, 1983; Stauffer and Armstrong, 1986). The natural concentration of dissolved silica in the sampled water was 24 μM and 18 μM for Lake MB and Coastal C, respectively. The salinity was 6 ‰S in the brackish seawater collected at Coastal C and <0.05 ‰S in the freshwater of station Lake MB. In addition, a sequence of salinity adjustments were made, i.e., water from Lake MB was modified to 6 ‰S, and likewise, samples from Coastal C were increased to 15 ‰S and 33 ‰S, respectively. The desired salinity and concentrations of iron and phosphate were provided through additions of dissolved salts of FeSO$_4$, KH$_2$PO$_4$, NaCl, KCl, MgSO$_4$, MgCl$_2$, NaHCO$_3$, and CaCl$_2$ (E. Merck, Darmstadt, F.R.G.). Throughout, acid-washed equipment and reagent-grade chemicals were used.

The experiments were carried out in 10-L Pyrex bottles placed in water baths in a dark room of constant temperature and were run in duplicate. In the course of the experiments, temperature, turbidity, dissolved oxygen, pH, and concentrations of iron and phosphate were monitored. Initially, conditions were kept anoxic by bubbling with N$_2$ followed by Ar, both of which were passed through glass filters to disperse the gas. This bubbling resulted in a thorough mixing of the dissolved species. The short anoxic period (a few hours) was interrupted by careful air bubbling, inducing a shift to oxic conditions. The oxidation of Fe(II) in the presence of oxygen resulted in colloidal Fe(III) oxyhydroxide particles. The subsequent coagulation governed the settling rate of the colloidal suspensions. The experiments were terminated after 8 weeks, when the particles were collected by ultracentrifugation (100,000g, 15 min). The particles were washed once in triple-distilled water before being centrifuged again. Finally, the particles were dried at 30°C for 24 h and thereafter kept at room temperature until chemical analyses and characterisation by electron microscopy and X-ray diffraction were completed (usually within 2 to 3 weeks).

The oxidation reaction was found to be first order in dissolved iron, i.e., consistent with the homogeneous rate law described by Stumm and Lee (1961). To compare the observed overall oxidation rates, we calculated the half-life time $t_{1/2}$ $(= k'^{-1} \cdot \ln 2)$, defined by the pseudo-first-order rate expression:

$$-d[\text{Fe(II)}]/dt = k'[\text{Fe(II)}] \qquad (1)$$

which is applicable when pH and partial pressure of oxygen are constant. The oxidation process was regarded as complete when the concentration of dissolved iron fell below 0.5 μM and the concentration of particulate iron reached its maximum. The maximum concentration in particulate iron was set as the starting point for the calculations of settling rate. The second-order removal of particles was calculated from the equation:

$$-d\tau/dt = k \cdot \tau^2 \qquad (2)$$

where k is the second-order constant and τ is the relative change in turbidity. The removal half-time $\tau_{1/2} = 1/(k\tau_o)$ was used to evaluate the time scale of the coagulation process. τ_o is the relative turbidity at the maximum concentration in particulate iron.

Separate oxidation experiments with well-defined synthetic solutions were conducted to evaluate the effect of calcium, organic matter, and salinity on the incorporation of phosphate in the colloids. The experimental procedure resembled that for the natural water, but the sample volume was smaller (1.5-L polyethylene beakers) and the duration of the experiments shorter (3–4 d). These experiments were conducted at room temperature. Inorganic salts of iron and phosphate (Fe(ClO$_4$)$_2$ · 6H$_2$O, KH$_2$PO$_4$ and K$_2$HPO$_4$) were used to create initial dissolved Fe/P

ratios ranging from 0.5 to 22. The total concentrations of iron and phosphate varied within ranges of 30 to 500 μM and 2 to 100 μM, respectively. The synthetic solutions were prepared from purified water (deionized and double-distilled). Three types of solutions were used: synthetic freshwater (1-mM Na$_2$CO$_3$), synthetic 6 ‰S brackish seawater (Lyman and Fleming, 1940), and pure water (only salts of iron and phosphate). pH was kept constant at 7.5 ± 0.5 by small adjustments from HCl and NaOH additions. The particles were washed and collected on a 0.45-μm membrane filter and then dried at room temperature before characterisation by electron microscopy and X-ray diffraction.

2.3. Analytical Techniques

2.3.1. Determination of chemical species

The dissolved fractions of iron and phosphate were defined by ultracentrifugation (100,000g, 15 min) or by serial isopore membrane filtration (0.4 μm + 0.2 μm). Particulate fractions were calculated as the difference between total and dissolved concentrations. Iron was determined by the colorimetric TPTZ method, following Koroleff (1983a). Colorimetric heteropoly blue methods, as modified by Koroleff (1983b,c), were used to determine phosphate and silica. Calcium and magnesium were analysed by flame atomic absorption spectroscopy (AAS), according to the Swedish Institute for Standards (SIS, 1982).

2.3.2. Measurement of dissolved oxygen and pH

Dissolved oxygen was measured with a YSI 54A oxygen meter equipped with a YSI 5739 probe or a WTW Oxi-320m in combination with a WTW 325 probe. The electrodes were calibrated against water-saturated air at the experimental temperature. The pH measurements were made with a WTW pH-95 pH-meter, with a WTW type-E combined pH electrode or a WTW pH-320m equipped with a WTW SenTix-50 probe. The pH electrodes were calibrated using NBS buffer solutions of pH 4 and pH 7 (E. Merck, Darmstadt, F.R.G.). Salinity was measured with an S-C-T-meter, model YSI-33.

2.3.3. Particle removal

To evaluate the aggregation and deposition characteristics of the colloids, the change in turbidity was estimated from time-course measurements, assuming that the relative change in turbidity (τ) reflected changes in the particle concentration of the colloid. Turbidity was recorded with a Hach 18900 Ratio Turbidimeter.

2.3.4. Characterisation of particles

The particulate oxidation products collected at the end of the experiment were examined by X-ray diffraction, using an IRDAB XDC-700 Guinier-Hägg camera (radii: 50 mm). The samples were exposed to Cr radiation (2.2897 Å) for 6 h. Relative elemental compositions (atomic number, $Z \geq Na$) of the particles were determined using a scanning electron microscope (SEM JEOL-820) equipped with an energy-dispersive spectrometer (EDS LINK AN10000). The acceleration voltages used were 15 and 20 kV. The linear correlation between the Fe/P atomic ratio found by the EDS technique and by chemical analysis was highly significant (Fe/P$_{EDS}$ = 1.06 Fe/P$_{chem}$ + 0.31, r = 0.925, n = 22, p < 0.001). Content of carbon and nitrogen in the particles was determined by means of a Leco CHN-900 element analyser.

3. RESULTS

3.1. Oxidation of Fe(II)

The slowest oxidation rate, as demonstrated by a half-life for Fe(II), $t_{1/2} \approx 7$ h, was found in freshwater samples of low pH, whereas the fastest rate, $t_{1/2} \approx 20$ min, was recorded for seawater samples of high pH (Fig. 2). In fact, a strong negative relationship was revealed between the half-life of Fe(II) and pH (Fig. 2). However, increased salinity slowed the oxidation rate
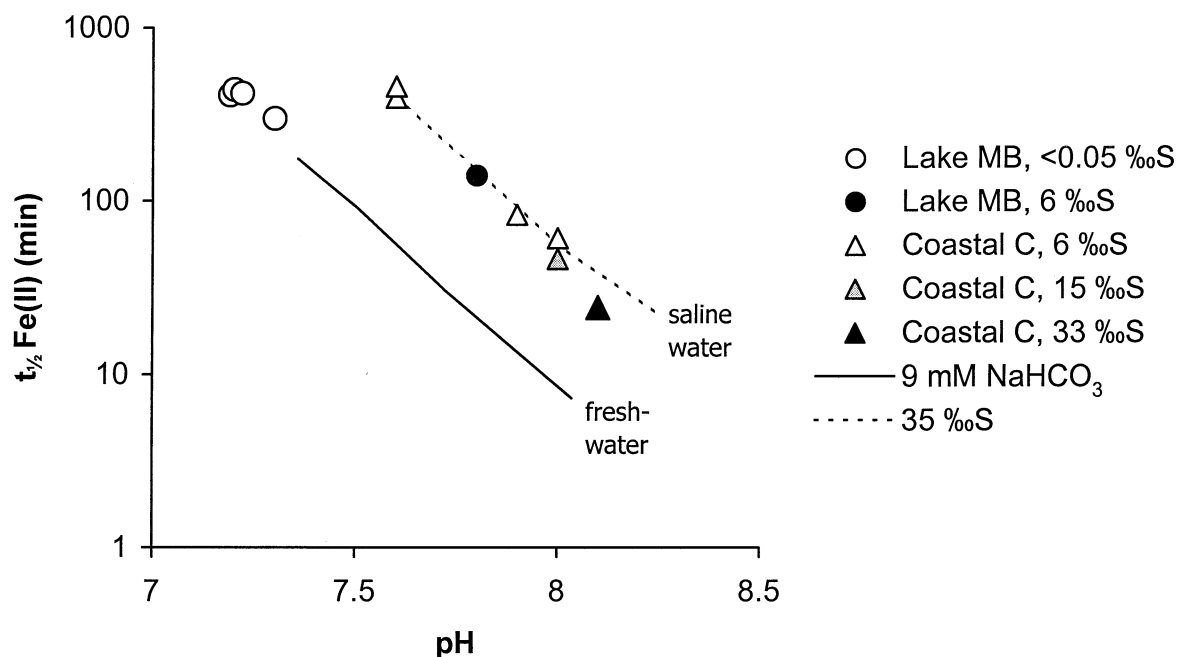
Fig. 2. Half-life time, $t_{1/2}$, of Fe(II) in freshwater and in seawater solutions. The partial pressure of oxygen was 0.21 atm. Temperature $6 \pm 1°C$. For comparison, solid and broken lines denote the half-life relationships reported by Millero et al. (1987) for a temperature of 5°C.

of Fe(II) (Fig. 2) as reported by Millero et al. (1987). The resulting $t_{1/2}$ of brackish seawater samples (6 ‰S) at pH 7.6 corresponded to $t_{1/2}$ of freshwater samples at pH 7.2 (Fig. 2). In freshwater samples with adjusted salinity, i.e., Lake MB 6 ‰S, the half-life of Fe(II) was consistent with the saline samples but was five times longer than expected for a freshwater of this pH (Fig. 2). Still, the higher pH of the seawater solutions often resulted in more rapid oxidation than in the freshwater samples.

At high salinity, our oxidation rates (Fig. 2) were faster than those reported by Millero et al. (1987). We used NBS buffer solutions to define our pH scale. Millero (1986) has shown that this may introduce variability in the results. Instead, a scale based on the total hydrogen ion concentration is preferable for studies in saline media (Dickson, 1984; Millero, 1986). Thus, the difference in oxidation rates (Fig. 2) may be related to the method used to calibrate pH.

3.2. Precipitation of Iron and Phosphate

The oxidation and hydrolysis of iron resulted in precipitation of Fe(III) oxyhydroxides. In this process, the concentrations of particulate iron and particulate phosphate increased congruently (Fig. 3), suggesting coprecipitation. Our results demonstrate that this synchronised precipitation occurs in the natural freshwater as well as in seawater. Previous experiments involving slow oxidation of Fe(II) in 0.01 mol/L $NaNO_3$ solutions suggest a corresponding iron-phosphate precipitation also in synthetic media (Deng, 1997). At initial Fe/P ratios > 2, a full removal of dissolved phosphate was observed. In fact, at an initial dissolved Fe/P ratio of ≈3, the excess of iron was ~30%, and as can be read from Figure 3, all dissolved phosphate had been removed (i.e., transformed into particulate form) when only 70% of the iron had been precipitated.

3.3. Characterisation of the Particles Formed

3.3.1. Oxidation product and identification of elements present in the particles

The oxidation product of Fe(III) oxyhydroxide was amorphous to X-rays. In fact, the iron-containing phase was poorly ordered, even when formed in synthetic media with a relatively large excess of iron (initial Fe/P > 10). In the solid phase of the synthetic solutions, iron and phosphorus were the only significant elements (revealed from EDS analyses), indicating that substances such as calcium or magnesium were nonessential for the incorporation of phosphate. However, precipitates from the natural water samples also contained calcium, silicon, and small amounts of magnesium. From the X-ray diffraction analysis of the natural freshwater and seawater samples, it was possible to trace the typical D-spacing for quartz (3.34 Å), indicating that most of the silicon in these samples originated from detrital bedrock particles. Concordantly, quartz is reported to be abundant in suspended matter in the Baltic Sea (Bernard et al., 1989). Furthermore, all natural samples contained carbon and nitrogen, i.e., no doubt mostly in organic matter. As shown in Table 1, the amounts of carbon and nitrogen were higher in freshwater particles than in those from seawater.

3.3.2. Content of phosphate

The chemical composition of the Fe(III) oxyhydroxide colloids formed was closely related to the initial concentrations of the dissolved species. Both phosphate (Fig. 4) and calcium (Fig. 5) were incorporated in accordance with their relative
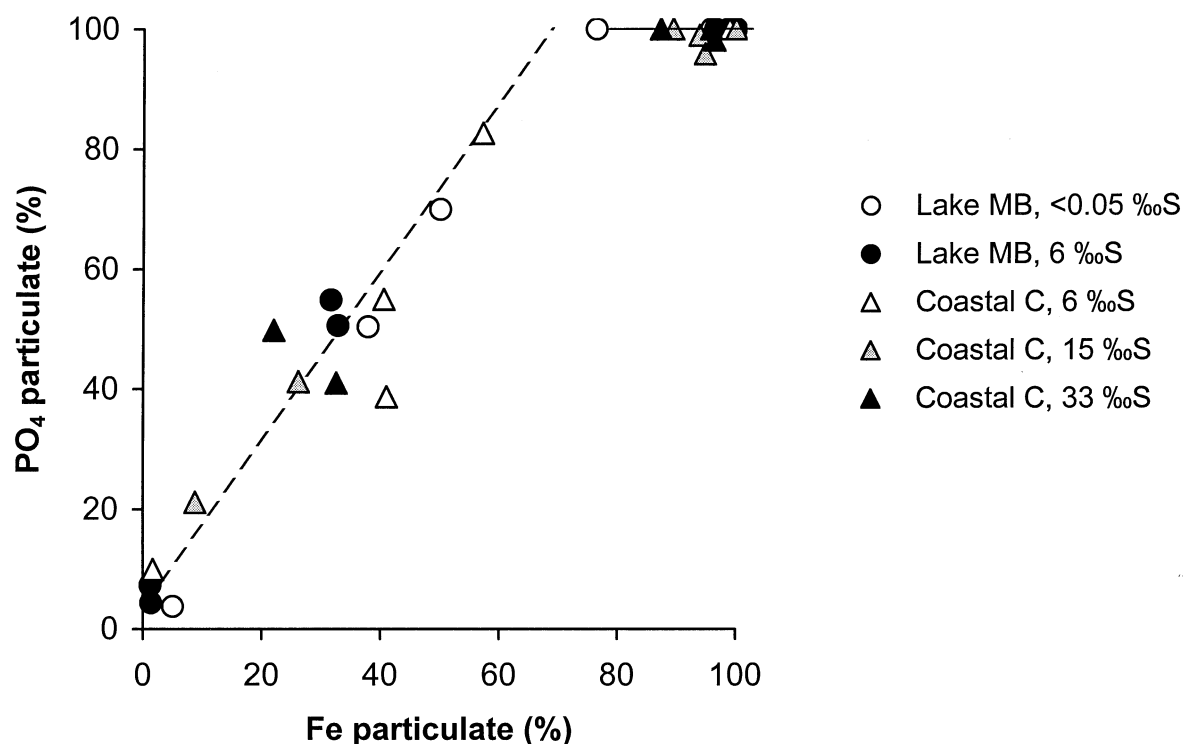
Fig. 3. Particulate phosphate recorded (as percentage of total phosphate) in the course of the oxidation process vs. colloidal Fe(III) oxyhydroxide formed (as percentage of total iron). The starting concentrations of iron and phosphate were ~50 and 15 μM, respectively. Dissolved phosphate was simultaneously transformed into particulate form during the oxidation and precipitation of iron, as indicated by the dotted line, $\%PO_{4\,part} = 1.4\%Fe_{part} + 3.8$, r $= 0.959$, $n = 15$. Data collected after depletion of dissolved phosphate (indicated by a horizontal solid line) are not included in this regression.

initial concentrations, but the resulting content of these two elements seemed to be independent (Fig. 6).

The Fe/P molar ratio of the particles was positively correlated to the dissolved initial Fe/P ratio but with a lower limiting value of ~2 (Fig. 4). Hence, the particles tended to have Fe/P ratios ≥ 2 even at very low initial ratios, whether formed in various natural waters or in synthetic solutions. In fact, the particulate Fe/P ratios of corresponding freshwater and seawa-

ter samples did not differ significantly (see Kruskal-Wallis one-way analysis of variance in Table 1). It is worth noting that among these samples, there were differences in salinity and Fe/Ca ratio (Table 1), as well as in the oxidation rate of Fe(II) (Fig. 2), and the removal rate of the colloids (Table 2). Hence, the particle size and surface properties of the particles formed seemed to be less critical for the iron-phosphorus interaction revealed in Figure 4. Thus, the incorporation of phosphate

Table 1. Elemental composition of the particulate oxidation product, as determined by EDS and combustion analysis. Reported as arithmetic atomic ratios ($\pm$ S.D), except for C and N, which are given as average percentage of dry weight ($\pm$ S.D). Total concentrations of Fe, P and Ca at start are also given.

	Solution Chemistry				Particle Composition			
Sample	Salinity (‰S)	Fe (μM)	P (μM)	Ca (mM)	Fe/P $n = 12$	Fe/Ca $n = 12$	%C $n = 2$	%N $n = 2$
Lake MB	< 0.05	53	15	0.46	3.6 (0.6)[1]	8.7 (0.9)	11.8 (0.3)	0.99 (0.01)
Lake MB*	6	53	14	2.5	3.4 (0.7)[1]	9.5 (0.9)	8.2 (0.8)	0.76 (0.03)
Coastal C	6	52	14	2.5	3.4 (0.2)[1]	9.8 (0.5)	6.2 (1.2)	0.42 (0.06)
Coastal C*	15	51	14	6.4	4.1 (0.7)[1]	7.3 (1.9)	5.9 (0.3)	0.37 (0.01)
Coastal C*	33	50	15	14	4.1 (0.5)[1]	4.3 (0.4)	6.3 (0.6)	0.42 (0.07)
Lake MB	< 0.05	18	15	0.46	2.2 (0.5)	5.4 (1.1)	13.5 (0.6)	1.3 (0.1)
Lake MB	< 0.05	89	14	0.46	6.3 (1.6)	14.9 (2.5)	9.9 (1.2)	1.1 (0.6)
Coastal C	6	18	15	2.5	2.7 (0.8)	6.1 (0.8)	8.4 (1.8)	0.7 (0.1)
Coastal C	6	85	14	2.5	6.4 (0.3)	18.1 (1.2)	7.2 (0.6)	0.55 (0.04)

* Denotes water to which salinity adjustments have been done.

[1] Mean values of these populations did not differ significantly (Kruskal-Wallis test, H $= 9.1$, $n = 60$, p > 0.05).
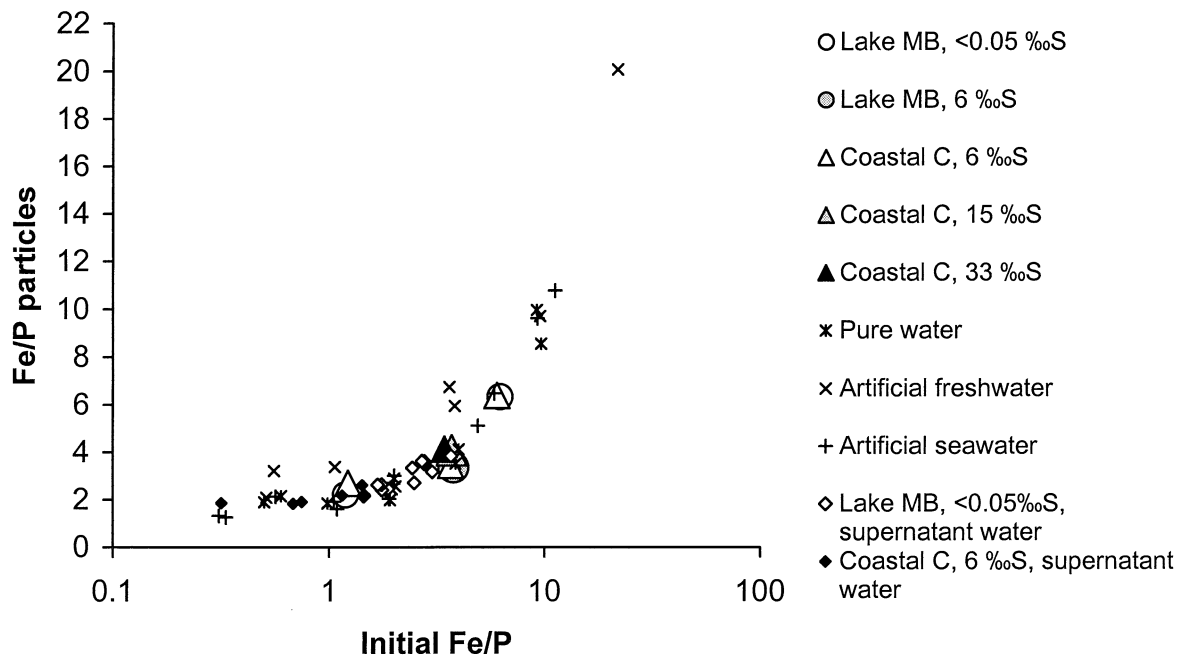
Fig. 4. The Fe/P molar ratio in the particles as a function of the dissolved Fe/P ratio in the initial solution. The particulate Fe/P ratio was determined by EDS, except for samples based on synthetic seawater and particles formed in the supernatant water of sediment cores (Gunnars and Blomqvist, 1997), which were evaluated by wet chemistry methods.

appeared primarily to be governed by the initial dissolved Fe/P ratio.

To evaluate if the Fe/P ratio was a result of stoichiometric incorporation during hydrolysis, we roughly estimated the initial rates of precipitation, i.e., $d[Fe]_{part}/dt$ and $d[PO_4]_{part}/dt$, assuming linear functions as a first approximation. The ratio between the initial slopes indicates that the precipitation rates of phosphate and iron followed an Fe : P stoichiometry of ~ 2 : 1. In accordance with this incorporation stoichiometry, some of the phosphate remained dissolved after precipitation if the solutions had initial Fe/P ratios of < 2. For instance, at an initial iron concentration of 18 μM and a phosphate concen-
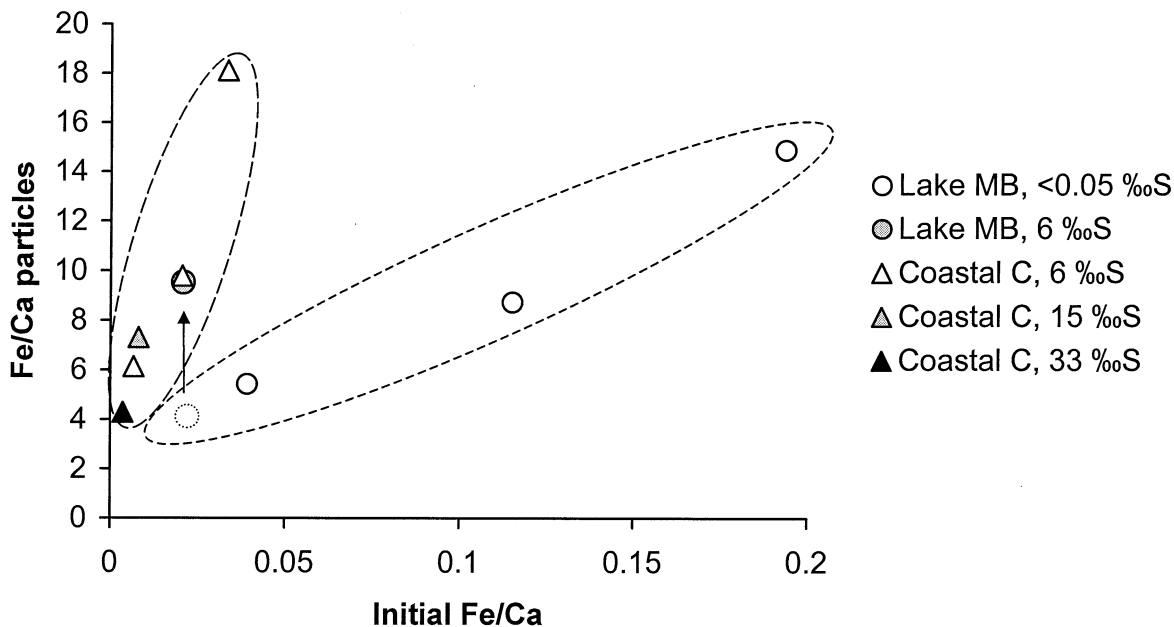
Fig. 5. The Fe/Ca molar ratio in the particles as a function of the dissolved Fe/Ca ratio in the starting solution (cf. Table 1). The arrow denotes an inferred shift in the particulate Fe/Ca ratio of the Lake MB sample when adjusted to 6 ‰S.
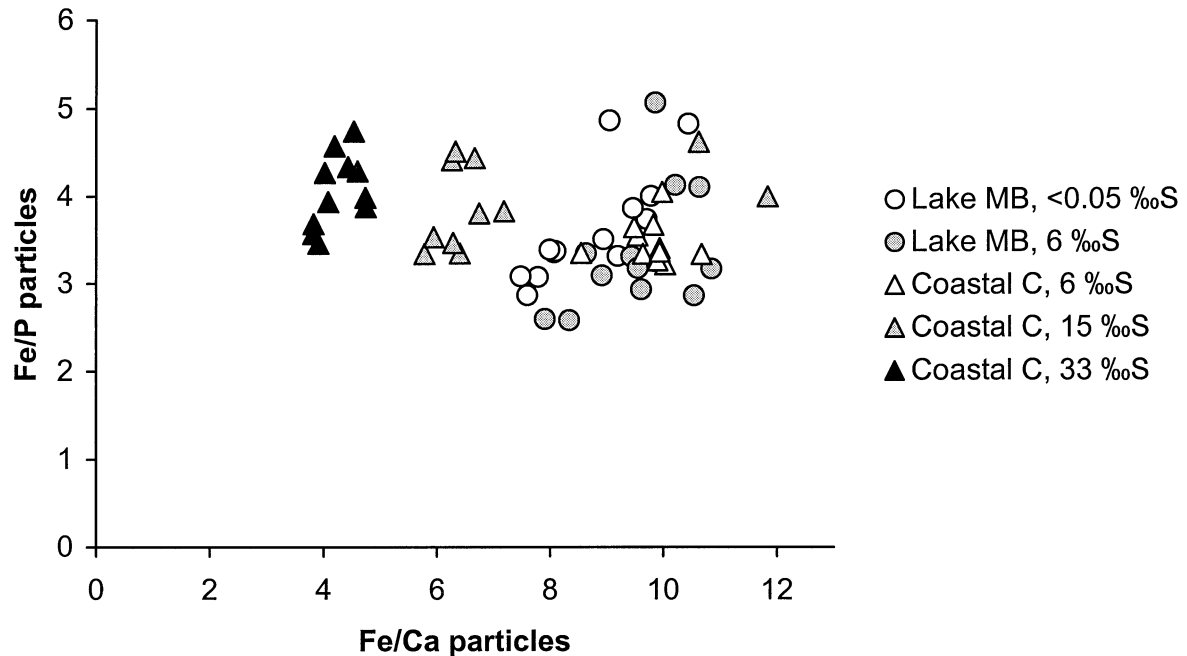
Fig. 6. The Fe/P molar ratio as a function of the Fe/Ca molar ratio in particles produced by oxidation of iron in natural water samples. The initial concentration of iron and phosphate was ~50 and 15 μM, respectively. The average Fe/P ratio of the particles produced was 3.7 $\pm$ 0.1 (arithmetic mean $\pm$ S.E., $n = 60$).

tration of 15 μM, as much as 5 to 6 μM phosphate remained dissolved.

3.3.3. Content of calcium

The Fe/Ca ratio of the particles was correlated to the initial proportions of dissolved iron and calcium, but the regression differed systematically between freshwater and seawater (Fig. 5). In general, the freshwater particles appeared to incorporate calcium more efficiently than did particles formed in seawater. This comparison is, however, restricted by the fact that the initial Fe/Ca ratios were higher in the freshwater samples than in the seawater samples. Interestingly, an induced fivefold increase in calcium concentration of freshwater samples adjusted to 6 ‰S did not result in a corresponding increased in

the uptake of calcium (Table 1). Instead, as marked with an arrow in Figure 5, the resulting particulate Fe/Ca ratio agreed well with the seawater samples. Hence, in addition to the initial Fe/Ca ratio, the calcium uptake appeared also to be related to salinity per se. The Fe/Ca ratio showed a weak negative correlation to the content of magnesium ($r = -0.34$, $n = 47$, $p < 0.05$). However, this result is uncertain due to the low atomic weight of magnesium, which makes it difficult to analyse using the EDS technique.

3.4. Aggregation of Particles

The aggregation of particles was greatly affected by salinity, as shown by a significantly faster aggregation in the brackish seawater samples than in the freshwater suspensions (Fig. 7). In

Table 2. Removal of colloidal particles from the water phase (cf. Fig. 7). Fe is given as the total concentration at start. pH was determined during the coagulation process. r is the correlation coefficient for the second-order rate equation based on linear regression.

Station	Salinity (‰S)	Fe (μM)	pH	Removal Half-Time (h)	Rate Constant k (h^{-1})	r
Lake MB	< 0.05	53	7.4	1200	0.0008	0.900
Lake MB*	6	53	7.8	340	0.0029	0.970
Coastal C	6	52	7.9	57	0.017	0.925
Coastal C*	15	51	8.0	32	0.031	0.836
Coastal C*	33	50	8.1	16	0.062	0.919
Lake MB	< 0.05	18	7.4	910	0.0011	0.969
Lake MB	< 0.05	29	7.4	1000	0.0010	0.732
Lake MB	< 0.05	89	7.3	1000	0.0010	0.922
Coastal C	6	17	8.0	200	0.0050	0.957
Coastal C	6	18	7.9	160	0.0064	0.916
Coastal C	6	85	7.6	100	0.0098	0.974

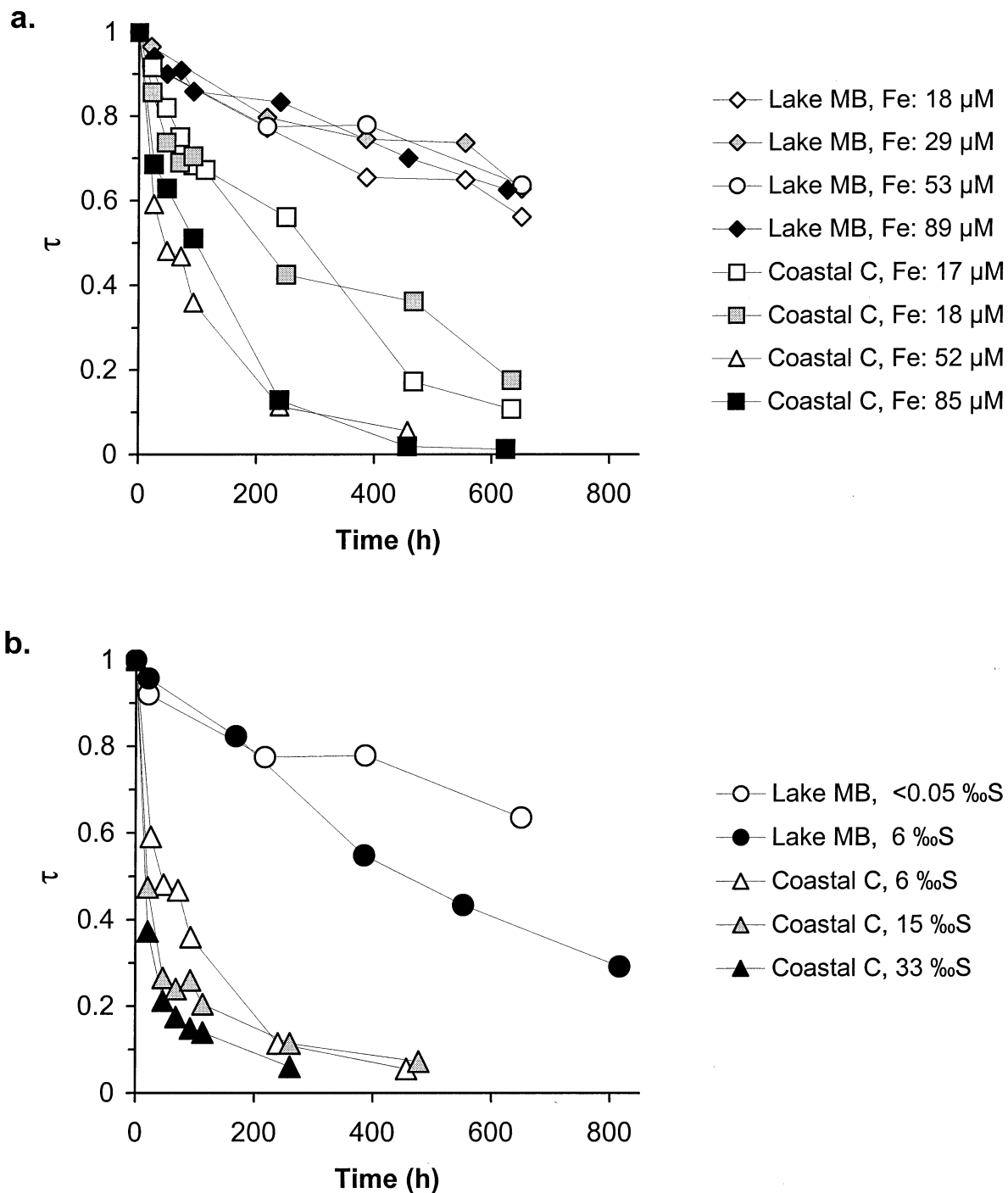* Denotes water to which salinity adjustments have been done.

a.

b.

Fig. 7. (a) Residual turbidity, τ, as a function of time at different initial concentrations of iron. Salinity was < 0.05 ‰S and 6 ‰S in Lake MB and Coastal C, respectively. The starting concentration of phosphate was ~15 μM. (b) Residual turbidity, τ, as a function of time, showing the aggregation and deposition of iron-rich colloids in freshwater and seawater solutions. The starting concentrations of iron and phosphate were ~50 and ~15 μM, respectively.

seawater, the removal rate of the particles was also related to the total concentration of iron, whereas in freshwater suspensions, no such correlation was apparent (Fig. 7a). In the freshwater samples supplied by salt additions, i.e., Lake MB 6 ‰S, a much slower decline was recorded than in natural seawater, i.e., Coastal C 6 ‰S (Fig. 7b), suggesting that the removal rate

was also influenced by other components of the water than the dissolved salts, e.g., organic matter.

The rate of decrease in particle concentration fitted second-order kinetics (Table 2). In the seawater, the removal half-times ($\tau_{1/2}$) varied from 16 h up to 200 h, depending on salinity and the concentration of iron (Table 2). In fact, a salinity-dependent

destabilization was observed in Coastal C samples of Fe of ≈ 50 μM, as revealed by a strong correlation between the second-order rate constant, k, and salinity (r = 0.9997, n = 3, p < 0.05). In the freshwater, $\tau_{1/2}$ was ~1000 h (Table 2). No significant gravitational settling was observed during the first days, and the freshwater suspensions were, therefore, regarded as stable (see Sposito, 1989). In stable suspension, ripening by recrystallization might be a factor enhancing the rate of formation of larger particles (Mayer and Jarrell, 1996). However, in our suspensions the second-order removal mechanism (Table 2), and the lack of characteristic X-ray diffraction patterns, are both inconsistent with significant ripening.

4. DISCUSSION

4.1. Fe(III) Oxyhydroxide Phases Formed in the Presence of Phosphate

The precipitation of Fe(III) oxyhydroxide is known to affect the aquatic cycling of phosphate at scales ranging from the local environment of freshwater lakes (Sholkovitz and Copland, 1982; Stauffer and Armstrong, 1986) to the global Ocean (Wheat et al., 1996). However, more than 60 yr ago, Einsele (1938) observed in laboratory experiments that the resulting Fe/P ratio of newly formed Fe(III) oxyhydroxide is lower when oxidation and precipitation occur in a solution containing phosphate, when compared to Fe(II) that is allowed to oxidize before the addition of phosphate. This observation (see also Mayer and Jarrell, 2000), suggests that the efficiency of the phosphate scavenging might be controlled during the formation of the solid phase.

Frequently, phosphate is present during the oxygenation and subsequent hydrolysis of iron in stratified natural waters, including water of the present study area (Gustafsson, 2000). In our experiments, the iron-rich particles formed in the presence of phosphate tended to have a particulate Fe/P ratio of ~2 even at very low initial dissolved ratios (Fig. 4). This lower-limiting Fe/P stoichiometry of ≈ 2 is too low to be explained by surface adsorption of phosphate on Fe(III) oxyhydroxide. A lower-limiting Fe/P ratio of ≈ 4 was reported by von von Gunten and Schneider (1991) for surface adsorption of phosphate on primary particles of Fe(III) oxyhydroxide (r = 10 Å, pH at 7.5). Thus, an Fe/P ratio < 4, as a result of surface adsorption, seems less likely.

Findings of the present study imply that the incorporation of phosphate into Fe(III) oxyhydroxide takes place at a very early stage of the hydrolysis. This conclusion follows from the correlated precipitation of iron and particulate phosphate (Fig. 3). Combined with a lower limiting Fe/P ratio of ~2 in the solid phase (Fig. 4), our findings are consistent with a growth mechanism stating that the early polymerisation of Fe octahedrons is limited to the dimer stage by complex formation with phosphate (Rose et al., 1996, 1997), and that in a further evolved hydrolysis, basic units consisting of one Fe dimer and one phosphate (i.e., Fe/P = 2) are involved in building up the larger aggregates of Fe(III) oxyhydroxide phosphate (Maison et al., 1997a,b).

From our results (Figs. 3 and 4), we conclude that the interaction pattern corresponds to the formation of an iron-phosphate compound with a stoichiometric Fe/P ratio close to 2. Besides iron and phosphate, this compound is likely to contain hydroxide, oxide, and water ligands. Tentatively, we suggest that the stoichiometric composition complies with the approximate formula: $(H_2O)_z(H)_x[Fe_2(OH)_2PO_4]_y^{x+y}$. This compound, which approaches an Fe : P stoichiometry of 2 : 1, instead of 1 : 1 as in $FePO_4$ (e.g., strengite), is formed in both freshwater and brackish seawater (Fig. 4). Tessenow (1974) reported a similar precipitation pattern, though only in synthetic freshwater solutions. Hence, our results provide experimental evidence that the iron-phosphorus interaction is chemically constrained by an Fe/P stoichiometry of ~2 in natural water, independent of salinity. In addition, the relation in Figure 4 is consistent with observations of particulate Fe/P ratios close to 2 in iron-rich colloids formed under conditions with low initial dissolved Fe/P ratios in the supernatant water of sediment water systems of the Baltic Sea (Gunnars and Blomqvist, 1997), in the water column of the stratified brackish Hallsfjärden Bay (Blomqvist et al., 2000), in freshwater Lake Lugano (Lienemann et al., 1999), and also in interstitial water of experimental sediment water systems of Lake Ursee (Tessenow, 1974).

4.2. Particulate Calcium

It is compelling that the uptake of calcium in the iron-rich particles was more efficient (i.e., lower Fe/Ca ratio) when the particles were formed in freshwater than in seawater (Fig. 5). This finding appears to be related to a calcium uptake through sorption processes. Similarly, experimental studies have shown that an increase in ionic strength from 0.01 to 0.1 mol/L, i.e., corresponding to the ionic strength of freshwater to 5 ‰S seawater, results in a decrease in calcium adsorption on goethite surfaces (Ali and Dzombak, 1996a). However, the coherent pattern in carbon content and Fe/Ca ratio of our particles (Table 1) is intriguing, since it suggests that the uptake of calcium was also related to the adsorption of organic matter. In addition, the freshwater samples had slightly lower pH than the seawater samples (Fig. 2; Table 2), and as adsorption of natural organic matter is favoured by lower pH (Tipping, 1981; Day et al., 1994), this pH difference suggests higher adsorption capacities of calcium and organic matter in the freshwater samples, which is in agreement with our results (Table 1; Fig. 5). Moreover, a calcium sorption related to organic coating could be reduced by salinity. Experimental studies demonstrate that the binding of organic acids onto goethite surfaces is suppressed in synthetic seawater (Balistrieri and Murray, 1987), a phenomenon that might be related to the presence of sulphate competing with the organic acids for the adsorption sites on the surface (Ali and Dzombak, 1996b) or to major cations such as magnesium increasing the fraction of soluble organic complexes (Balistrieri and Murray, 1987). Thus, a reduction of the adsorption density of organic matter also applies to the associated calcium. Our observation of a negative relation between the Fe/Ca ratio and the magnesium content of the particles indicates that the decreased uptake of calcium in seawater could be due to competition from magnesium ions for adsorption sites (van Cappellen and Berner, 1991).

Other reports suggest that the presence of calcium in iron-rich particles can be attributed to the formation of mineral phases, rather than to sorption. Various amorphous iron calcium phosphates, e.g., mitridatite (Moore and Araki, 1977), are reported to precipitate from interstitial water of natural sedi-
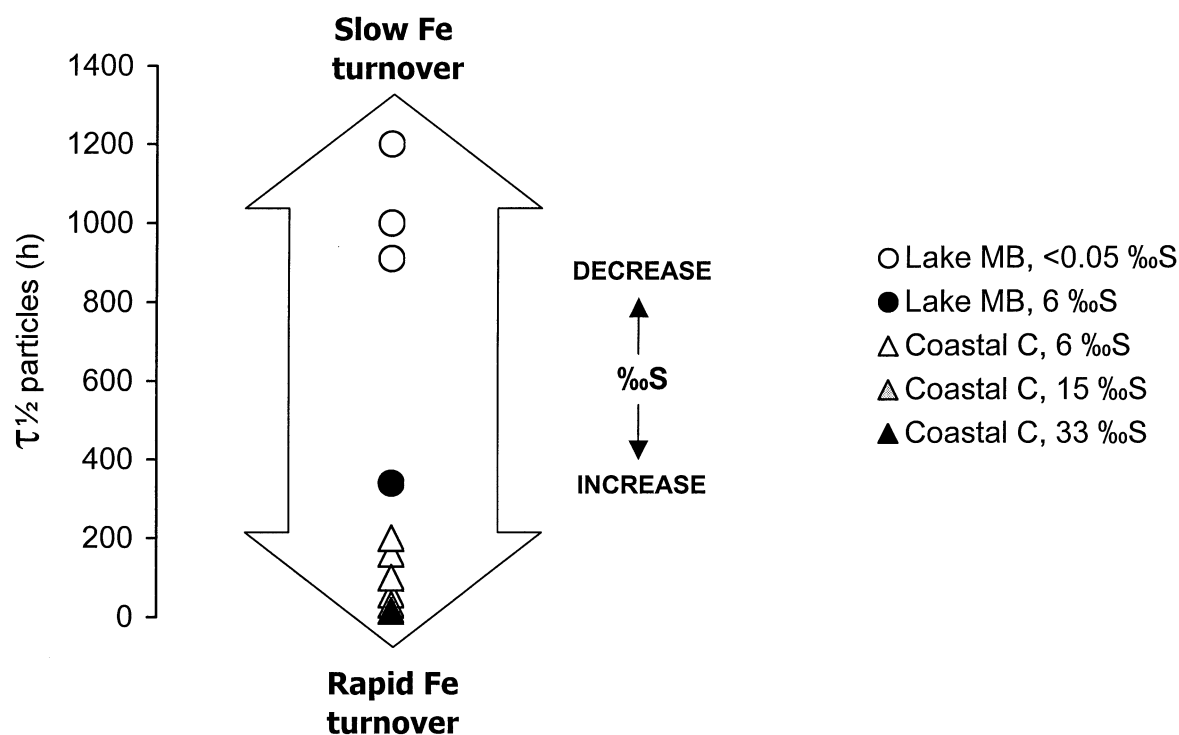
Fig. 8. The slow turnover of iron in freshwater compared to seawater systems. $\tau_{1/2}$ refers to the removal half-time of the iron-rich colloids as defined in Table 2.

ments (Medrano and Piper, 1997). Buffle et al. (1989) inferred a chemical entity from a constant Fe : Ca : P ratio in iron-rich colloids newly formed in a stratified freshwater lake. Also, based on a study of a brackish sediment-water system, Matthiesen et al. (2001) considered calcium important in the formation of iron-phosphate particles. However, our experiments provide no evidence of a discrete authigenic iron-calcium-phosphate phase, or even that the presence of calcium affects the Fe/P ratio (Fig. 4; Table 1). Instead, our results suggest that phosphorus and calcium are incorporated by independent mechanisms (Fig. 6; cf. Figs. 4 and 5).

Clearly, there are arguments suggesting that the uptake of calcium is related to the surface properties of the newly formed particles rather than to the precipitation of inorganic compounds. The uptake might be related to direct binding with surface sites or to the surface coating of organic matter, but in either event, the results presented here indicate that the uptake of calcium by newly formed Fe(III) oxyhydroxides in natural water is reduced by higher salinity (Fig. 5).

4.3. Colloidal Stability

In freshwater and brackish seawater, organic carbon appeared to affect the stability of the iron-rich colloids. First, our results match the stability of suspensions stabilised by organic matter. The stability ratio, $W = \tau_{1/2obs}/\tau_{1/2fast}$ (where $\tau_{1/2obs}$ = observed removal rate and $\tau_{1/2fast}$ = diffusion controlled rate; see Liang and Morgan, 1990) of the freshwater particles (Table 2) was in the range of 500 to 1200. These figures are based on a $\tau_{1/2\ fast}$ of 1 to 2 h at 6°C, as calculated from data reported for

completely destabilized natural iron-rich particles with a mean diameter of 0.3 μm (Tipping and Ohnstad, 1984) and at concentrations of FeOOH corresponding to 20 to 50 μM. The stability ratios of our freshwater samples fit well with the ratios of 10 to 1000 reported for hematite particles stabilised by a coating of organic matter at pH 6.3 in solutions of 0.5 to 1 mM calcium (Liang and Morgan, 1990). Second, the higher carbon content of the freshwater samples compared to the seawater samples (Table 1), seemed to increase the stability of the particles. Particles formed in brackish samples of freshwater origin (Lake MB 6 ‰S) had significantly higher stability ratios than the corresponding seawater samples (Coastal C 6 ‰S), i.e., W = 200 to 300 and W = 30 to 60, respectively. In accordance, Tiller and O'Melia (1993) have demonstrated that an organic coating can have a stabilising effect on heamatite particles at ionic strengths of 0.1 mol/L, but larger amounts of adsorbed organic matter are required to accomplish the same stabilisation at this ionic strength than in freshwater. On the whole, our results suggest that organic matter can affect the colloidal properties of iron-rich particles in freshwater and seawater systems, and as a corollary can also affect the overall transport of iron in these systems.

4.4. Turnover of Iron in Freshwater and Seawater

The turnover of iron was significantly faster in seawater than in freshwater (Fig. 8). This inference is based on the fact that the removal of particles was the slower, rate-determining step in the turnover of iron. The oxidation rate represented by $t_{1/2}$ was fast, on the time scale of some minutes up to 7 h (Fig. 2),

whereas the coagulation process was slow, resulting in removal half-times of from 16 h to 7 weeks (Table 2). Thus, our comparison represents the time scale of iron turnover in water, accounting for oxidation and coagulation processes, but disregarding other processes such as reductive dissolution and biologic filtration. Furthermore, we found that the difference in removal rate was a result primarily of salinity, but that a particle coating of organic matter also contributed to this difference by conditioning for more stable colloids in the freshwater samples (Fig. 7b; cf. discussion above).

Our findings suggest that in freshwater and coastal seawater systems with similar iron supplies, the latter is likely to have a much lower total concentration of iron in its surface water, and much of this due to faster removal (Fig. 8). For example, in stratified parts of the Himmerfjärden estuary, our results suggest an effective removal of the newly precipitated iron within 2 to 3 d, whereas a comparable situation in Lake Mälaren would involve removal rates of ~50 d, thus allowing the concentration of iron particles to increase and develop a well-defined peak in a stratified water column.

4.5. Environmental Links

In aquatic environments, the oxidation of dissolved Fe(II) into Fe(III) oxyhydroxides, and the following aggregation and settling of the iron-rich colloids formed, provide a crucial sequence of reactions with a bearing on several geoecologic phenomena. In addition to iron, the cycling of other associated elements (e.g., phosphorus) is also affected.

The faster aggregation of iron-rich colloids in seawater compared to freshwater (Fig. 7) implies that iron has a shorter turnover time and is less available in marine than in limnic environments (Fig. 8). Frequently, iron has been reported to limit phytoplankton production in various parts of the open Ocean (e.g., Martin and Fitzwater, 1988; Takeda et al., 1995; Behrenfeld et al., 1996; Coale et al., 1996; van Leeuwe et al., 1997; Behrenfeld and Kolber, 1999; Sedwick et al., 1999; Boyd et al., 2000) in certain coastal upwelling areas (Hutchins and Bruland, 1998; Hutchins et al., 1998; Sedwick et al., 2000), and in the Baltic Sea (Staal et al., 1999). In contrast, iron has only occasionally been reported to limit natural phytoplankton populations in freshwater lakes (Schelske, 1962; Elder and Horne, 1977; Wurtsbaugh and Horne, 1983; Hyenstrand et al., 1999). Planktonic diazotrophic cyanobacteria (cyanoprokaryota) are particularly prone to be iron limited (Rueter and Petersen, 1987; Brand, 1991; Rueter et al., 1992), requiring a 60- to 100-fold higher amount of cellular iron in diazotrophy growth compared to balanced cell growth based on fixed nitrogen (Raven, 1988). Hence, the short turnover time and low availability of iron in the marine realm may have been a constraint to the evolution of diazotrophic cyanobacteria. In fact, a single genus (*Trichodesmium*) is today the predominant autotrophic diazotroph in the pelagic marine environment (Capone et al., 1997). It is likewise reported to be iron limited (Rueter, 1988; Paerl et al., 1994).

There appears to exist quantitative differences between the interaction of iron with phosphate in coastal seawater and in freshwater. In seawater, the rapid coagulation and deposition of iron-rich colloids (Fig. 7) implies a short exposure time for later surface adsorption of phosphate by particles having high Fe/P ratios (Fig. 4), i.e., rich in end-standing iron hydroxyl groups (Stumm and Sigg, 1979; Luedecke et al., 1989). Likewise, when proportionally less iron than phosphorus (Fe/P < 2) is supplied from bottom sediments, as reported from coastal marine systems (Gunnars and Blomqvist, 1997), the potential of phosphorus scavenging will be low (Fig. 4). Therefore, these mechanisms, separately or jointly, create a relative shortage of iron in marine systems and, concomitantly, an enhanced availability of phosphate in marine and brackish water. This higher availability of phosphate appears to be a contributory mechanism explaining why the net primary production of coastal marine environments in the temperate zone today is usually limited by nitrogen (Ryther and Dunstan, 1971; Howarth, 1988; Granéli et al., 1990), rather than phosphorus as commonly reported from Recent freshwater lakes (Schindler, 1974, 1977; Hecky and Kilham, 1988; Correll, 1998).

In the chemical evolution of the atmosphere and the ocean, precipitation and deposition of iron in the marine realm has been an overall controlling process, especially in the Precambrian Era (Holland, 1984). Furthermore, over geologic time scales, scarcity of available iron may have been a rate constraint for fundamental life-supporting processes, such as oxygenic photosynthesis and biologic nitrogen fixation in the sea (cf. Falkowski, 1997; Falkowski and Raven, 1997). Thus, the geochemical transformation of dissolved Fe(II) to particulate species of Fe(III) is a key topic for understanding differences in biologic production and biogeochemical cycling between seas and freshwater lakes, both present and past.

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