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A new experimental setup for studying the formation of phosphate binding iron oxides in marine sediments. Preliminary results

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Abstract. A new laboratory method is introduced to study the formation of phosphate binding iron(III) oxides at the redox boundary in marine sediments. A sediment core is given a very well-defined oxic-anoxic interface by placing a 0.45 μm filter between the sediment and the overlying water. After a period of $1\frac{1}{2}$ months the filter is covered with a layer of fresh iron oxides, formed by the oxidation of upward diffusing Fe^{2+} from the sediment pore water. The formed iron oxides are investigated by electron probe X-ray microanalysis (EXPMA). With a sediment core from the brackish Baltic Sea the average molar composition of 788 formed particles is $Fe_{1.00\pm0.13}P_{0.55\pm0.06}Ca_{0.37\pm0.04}$ plus unknown amounts of O, H and C. The results show that the particles have a uniform composition, and that calcium plays an important role in the phosphate binding. The laboratory method is a useful supplement to *in situ* sampling for studies of iron oxides.

Introduction

Iron oxides/hydroxides play an important role in natural aquatic systems through their interaction with phosphate (Torrent et al. 1994), organic matter (Tipping 1981; Day et al. 1994), and trace metals (Müller & Sigg 1990). Since the early work of Einsele (1936) many studies have been devoted to the phosphate binding properties of iron oxides. It is generally accepted that iron oxides in the oxidized surface layers of the sediment can serve as a trap for pore water phosphate diffusing upwards (e.g. Krom & Berner 1980; Jensen et al. 1992; Slomp et al. 1998). The phosphate binding can be explained as a ligand exchange process where surface hydroxyl groups on the particulate iron oxides are replaced by phosphate groups (Stumm 1992). Freshly formed iron oxides have a higher phosphate binding capacity than older iron oxides, because the number of binding sites is reduced during the ageing of the oxides (Lijklema 1980). Several studies of naturally occuring phosphate binding iron oxides (henceforth called iron-phosphorus particles) concentrate on the freshly formed particles (Slomp et al. 1996; Mayer & Jarrell 1995; Buffle et al. 1989). The freshly formed particles are normally found at the oxic-anoxic interface in the sediment or the water column, where pore water Fe^{2+} diffusing upwards is oxidized to iron(III) oxide (Buffle et al. 1989). Sampling and analysis of the particles *in situ* can be difficult, because the particles are often present in a low concentration (Slomp et al. 1996). Furthermore, it is not always possible to distinguish between freshly formed particles and old particles coming from sedimenting matter.

These problems are not present in laboratory studies. Here, iron-phosphorus particles are normally formed by adding fresh iron(III) oxides to a phosphate solution (Lijklema 1980; Hawke et al. 1989; Torrent et al. 1994). It is, however, risky to extrapolate from these laboratory experiments to more complex *in situ* conditions, where the oxidation of Fe(II) and phosphate adsorption can take place simultaneously, and result in a co-precipitation of iron and phosphorus.

In this paper we introduce a new laboratory method for studying the formation of iron-phosphorus particles. The method tries to imitate the conditions at the redox boundary in real sediments, as regards the simultaneous supply of dissolved iron and phosphate from below. A sediment core is given a very well defined oxic-anoxic interface by placing a 0.45 μm filter between the sediment and the overlying water. This setup allows the formation of iron-phosphorus particles on the filter surface in high concentrations. Furthermore, the setup allows us to distinguish between freshly formed particles and sedimenting material.

Materials and methods

Our study area is situated in the deepest part of the Arkona Basin in the brackish Baltic Sea. The sampling station (54°56.27′ N, 13°49.90′ E, 47 m water depth) lies in a depositional basin, where mud accumulates at a rate of 2 $mm \cdot a^{-1}$. The sediment and pore water composition in the area is known from earlier and ongoing studies (Laima et al. 1999; Christiansen et al. 1999). The sampling station was chosen because these earlier studies had indicated a substantial upwards diffusion of dissolved iron and phosphate in sediment pore water in the area. Selected data from Laima et al (1999) are included in Figure 1 for information.

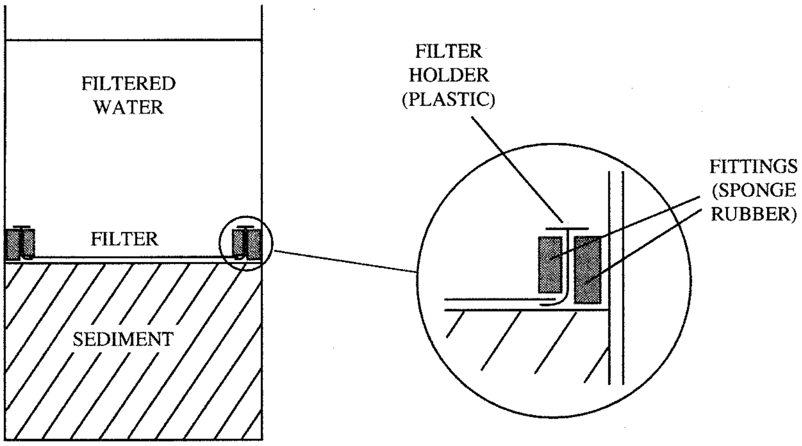

Figure 1. Experimental setup. All fittings/gaskets and components (core liner, filter holder, and filter) fit tightly. The filter holder was constructed from a soft plastic tube stopper (Ø = 5.0 cm) with a circular hole (Ø = 3.5 cm) in the middle. The gaskets required were cut from a 6 mm plate of suitable rubber (see text). The inner gasket kept the filter (Ø = 4.7 cm) pressed firmly down on the filter holder. Positioning was ensured by a few stitches with thread and needle through the inner gasket, the filter and the filter holder in order to avoid possible gaps. The outer gaskets closed the gap between the filter holder (Ø = 5.0 cm) and the core liner (Ø = 5.4 cm). A magnetic stirring bar 5 cm above the filter surface ensured a well-mixed water phase.

Sediment was sampled in June 1997 using a box corer, and subsamples were taken with Plexi glass cylinders (5.4 cm diameter, 20 cm long) retrieving 10 cm of sediment with overlying water.

Sediment cores for pore water analyses were subsampled in $\frac{1}{2}$ or 1 cm slices in a glovebox in argon atmosphere. The slices were centrifugated in airtight containers at 7000 rpm for 30 min. The supernatant was filtered (0.45 μm Sartorius filter) in the glove box and preserved with HCl to pH 2–3. Dissolved phosphate and iron were measured spectrophotometrically – phosphate with the phosphomolybdate method (Murphy & Riley 1963) and dissolved iron with the TPTZ method (Collins et al. 1959). Dissolved manganese in pore water was measured by Flame Atomic Absorption Spectrometry, using the experimental parameters recommended by the manufacturer Perkin Elmer.

For the filter experiment a core without visible macrofauna was chosen. The overlying water was temporarily removed from the sediment core, and a 0.45 μm filter (Mikron Clear, polycarbonate, Ø 4.7 cm) was placed right above ($<$ 1 mm) the sediment surface. The filter was mounted in a homemade filterholder that ensured that all material transported between the sediment and overlying water passed through the filter (Figure 1). Air bubbles entrapped between the sediment and the filter during filter installation were removed with a syringe through the fittings. The fittings or gaskets were made of a suitable sponge rubber that is elastic, impermeable for diffusion, and selfclosing (no holes were left after removal of the syringe).

The overlying water taken from the core was filtered (0.45 μm) and replaced above the mounted filter. The core was then kept with slow stirring (giving a water velocity of approximately 0.5 $\mathrm{cm \cdot s^{-1}}$ near the core liner) in the dark at 4 °C for $1\frac{1}{2}$ months. The oxygen concentration in the water was checked occasionally with an oxygen electrode (Revsbech 1980). The system was open to the atmosphere to allow diffusion of oxygen to the water.

After $1\frac{1}{2}$ months the filterholder was retrieved and the filter was freeze dried. Special care was taken to distinguish between the 'sediment-side' and 'water-side' of the filter. The 'water-side' of the filter was covered with a layer of carbon, and studied by electron probe x-ray micro analysis (EXPMA). Automatic particle recognition was used to allow the analysis of a large number of particles (500–1000), randomly chosen on the filter (Bernard et al. 1989). A data set with X-ray intensities for 12 major and minor elements (Al, Fe, P, Ca, Mg, Mn, Ti, Si, K, S, Na, Cl) were obtained for each particle, using energy dispersive X-ray analysis (EDX). A few particles were also analysed by wavelength dispersive X-ray (WDX).

Samples were taken from the overlying water at the beginning and at the end of the experiment. The samples were filtered (0.45 μm), preserved with HCl to pH 2–3, and analysed for dissolved manganese and iron with Graphite Furnace Atomic Absorption Spectrometry (using the experimental parameters from Slavin et al. 1982 and Sturgeon et al. 1979). Unfortunately the water samples were lost before phosphate analysis took place.

Results

Figure 2 shows results of analyses of phosphate, iron and manganese in pore water from the fresh sampled sediment. For comparison, results from an earlier study at the sampling station are included (from Laima et al. 1999). Using the concentration gradients in the sediment pore water and Ficks law of diffusion, the fluxes of dissolved Fe and P towards the sediment-water interface can be estimated to 7–16 nmol $\mathrm{Fe \cdot cm^{-2} \cdot d^{-1}}$ and 2.5–3.0 nmol $\mathrm{P \cdot cm^{-2} \cdot d^{-1}}$ (Laima et al. 1999; Matthiesen 1998).

During the filter experiment it was noted that the sediment core changed appearance: At the beginning the upper 1 cm of the sediment was light grey, whereas after $1\frac{1}{2}$ month the whole sediment core had turned black. Furthermore, a reddish layer had formed on the water side of the filter. The oxygen content of the overlying water varied between 150 and 250 μM during the

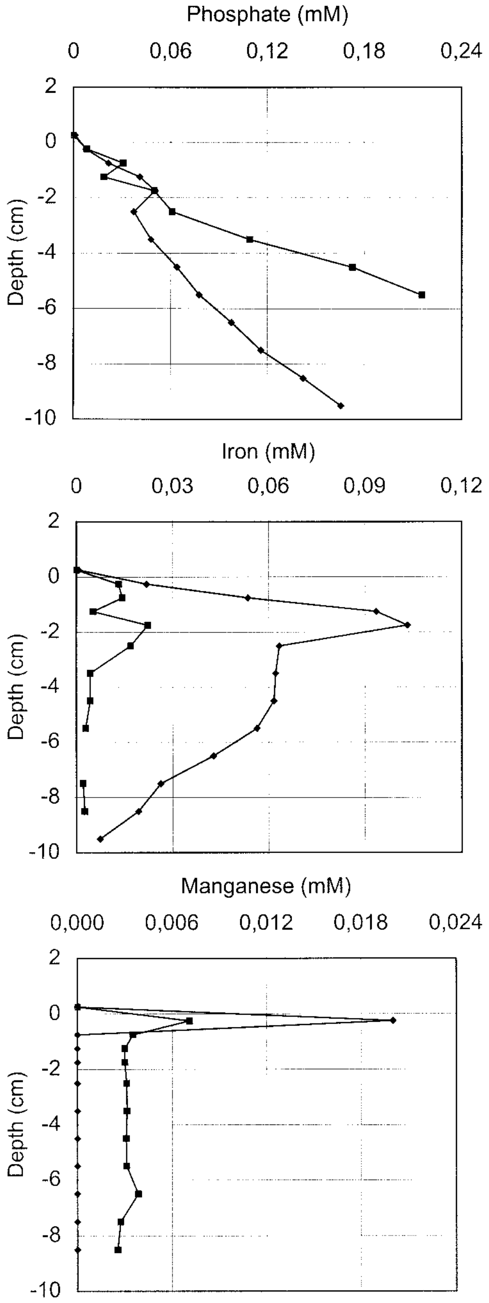

Figure 2(a)–(c). Depth distribution of dissolved phosphate, iron and manganese in sediment pore water at the station. The sediment-water interface is situated at 0 cm depth – concentrations measured in overlying water are shown as points above the interface. ◆: March ’97 (from Mario et al. 1999), ■: June ’97 (this study)

Table 1. Concentrations of dissolved oxygen, iron, manganese, and phosphate measured in the overlying water at the beginning and at the end of the filter experiment.

Unit: μM	O_2	Fe	Mn	Phosphate
Beginning	200	< 1	1	0.5[a]
End	200	< 1	20	n.a.

n.a.: not analysed.

[a] Result obtained from a parallel core.

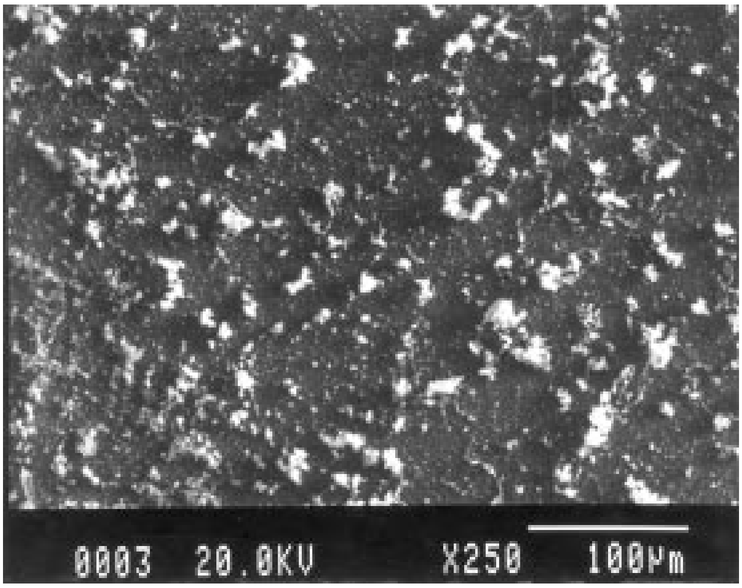

Figure 3. SEM picture of the filter surface after $1\frac{1}{2}$ months.

experiment. The concentration of dissolved manganese in the water rose from 1 μM in the beginning to 20 μM after $1\frac{1}{2}$ months, whereas the concentration of dissolved iron was unchanged (< 1 μM) – Table 1.

A SEM picture of the freezedried filter is shown in Figure 3. Particles of varying sizes were evenly distributed over the filter surface.

Microprobe analysis (EDX) of 788 particles on the filter showed that Fe, P, and Ca were present in all particles. The measured X-ray intensities of Fe, P and Ca were highly correlated (Figure 4). Besides the major elements: Fe, P and Ca, the EDX spectra also showed the presence of Na, Cl, Mg, S, Mn, and Si in a large number of the particles. Na, Cl, Mg, and S most probably derive from seawater solutes precipitated during the freeze drying of the filter and will not be discussed any further. The filters were not rinsed with fresh water

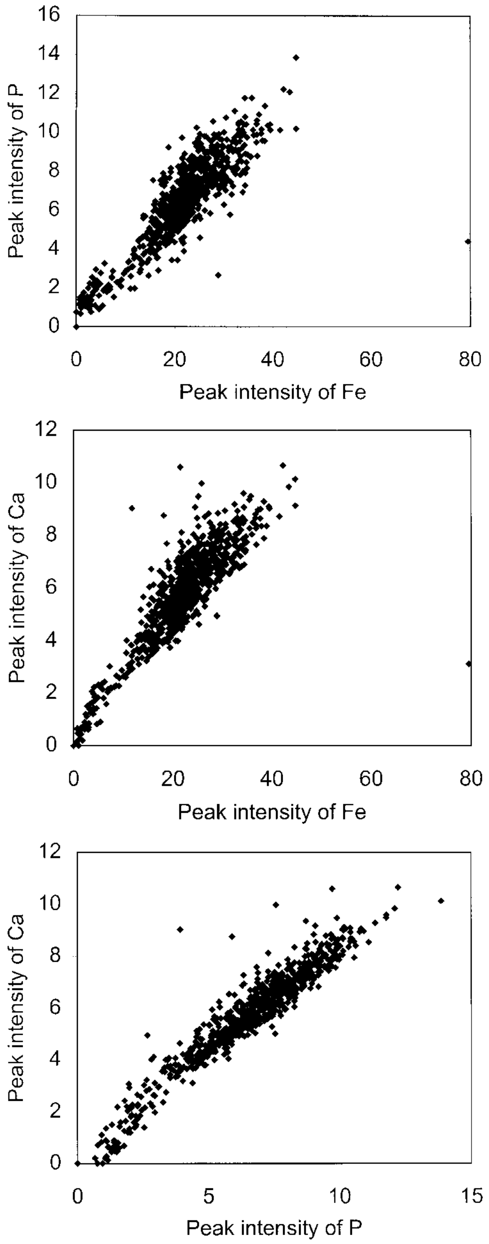

Figure 4(a)–(c). Correlations between EDX peak intensities of P, Fe and Ca in 788 particles on the filter surface. Slope (s), ordinate at origin (y_0) and correlation coefficients (r), computed by least square method, are given in each case. (a) Phosphorus versus iron peak intensities: s = 0.26 ± 0.01; y_0 = 0.68 ± 0.99; r = 0.91. (b) Calcium versus iron peak intensities: s = 0.22 ± 0.01; y_0 = 0.91 ± 0.74; r = 0.93. (c) Calcium versus phosphorus peak intensities: s = 0.82 ± 0.02; y_0 = 0.56 ± 0.46; r = 0.97.

Table 2. The average composition of 788 particles analysed by EDX and 2 particles analysed by WDX.

Weight fraction of oxides (% w/w)			Molar composition[a] (mole)		
Oxide	EDX n = 788	WDX n = 2	Element	EDX n = 788	WDX n = 2
Fe_2O_3	47.6 (6.3)	37.9	Fe	1.00 (0.13)	1.00
P_2O_5	23.2 (2.5)	18.0	P	0.55 (0.06)	0.53
CaO	12.4 (1.4)	9.7	Ca	0.37 (0.04)	0.36
SiO_2	5.3 (2.9)	n.a.	Si	0.15 (0.08)	n.a.
MnO_2	1.3 (1.1)	n.a.	Mn	0.03 (0.02)	n.a.

The numbers in between brackets are the calculated standard deviations (only for EDX). n.a.: not analysed.

[a] Molar composition is calculated from the average weight of oxides, and normalised to 1 mole Fe.

before freeze drying because rinsing could possibly change the particles on the filter.

The quantitative composition of the Fe-P-Ca particles can be estimated from the measured EDX intensities, using the weight of the oxides (as the particles are formed in an oxic environment). It is not possible to quantify the oxygen content of the particles using EDX or WDX analyses. The average composition of the 788 particles is shown in Table 2.

Discussion

Particle formation

Buffle et al. (1989) found Fe-P-Ca particles at the redox boundary in the water column of a eutrophic lake. They suggested that the particles are formed by the oxidation of upwardly diffusing Fe^{2+} (to particulate iron(III) oxides) and coupled sorption of phosphate and calcium. A similar model has been used to describe particle formation at the redox boundary in lake sediments (Deike et al. 1997).

In this experiment the oxidation of upwardly diffusing Fe^{2+} apparently takes place at the filter surface instead of down in the sediment (Figure 5).

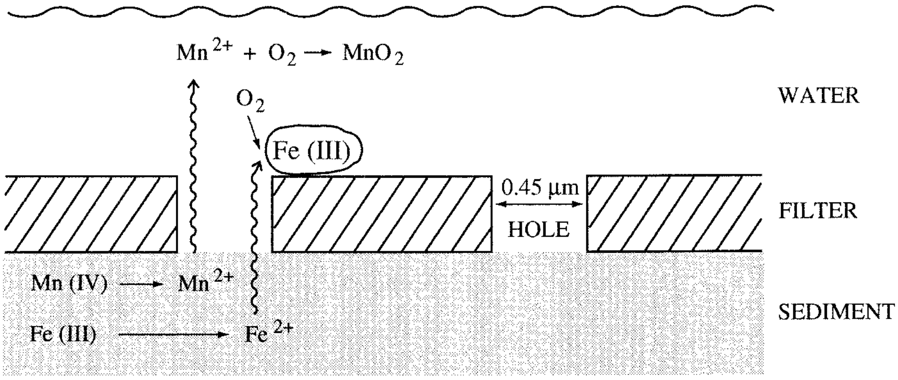

Figure 5. Suggested processes during the filter experiment. Iron and manganese reduction takes place down in the sediment core. The produced Fe^{2+} and Mn^{2+} diffuses up through the filter pores. Fe^{2+} is oxidised at the filter surface, whereas Mn^{2+} diffuses further up into the water column before being oxidised. Phosphate and calcium are not included in this drawing, but they coprecipitate with the iron(III) oxide.

Visual inspection showed, that the redox boundary moved upwards during the experiment, until it coincided with the filter surface. This might be due to a low permeability of the filters used: The filters consist of thin membranes of polycarbonate (5–10 μm thick) with separate channels of diameter 0.45 μm, where the holes only account for approx. 10% of the filter area (Laxen & Chandler 1982). The filter will reduce the diffusive transport of dissolved species between sediment and water, so also the downward transport of oxygen is reduced. With a diminished supply of oxygen to the sediment, reduced Fe^{2+} in the sediment pore water can diffuse upward through the filter before being reoxidized. Particulate iron(III) oxides therefore accumulate on the filter surface, where the particles are easy to investigate.

Not all dissolved Fe^{2+} from the sediment pore water will reach the filter surface. Some of it probably reacts with sulphide from sulphate reduction in the sediment, and precipitates as FeS. This process is indicated by the black color of the sediment at the end of the experiment. The precipitation of dissolved Fe^{2+} can cause a decoupling of the Fe and P cycles in the sediment and result in a considerable release of dissolved phosphate to the overlying water even during oxic water conditions (Matthiesen et al. 1998). Phosphate analysis of the overlying water are necessary to verify this hypothesis, but unfortunately we lost these samples.

Diffusion of dissolved Mn^{2+} across the sediment-water interface is indicated from the concentration gradient between pore water and overlying water at this station (Figure 2). A similar cycle as for iron could therefore be expected for manganese: reduction of particulate manganese(IV) oxides

Table 3. Average composition in Fe-P particles found in some earlier studies. The compositions are normalised to 1 mole Fe.

Reference	Fe	P	Ca	Conditions
Lijklema (1980)	1	0.15–0.25	–	Laboratory experiment with fresh iron oxides (no Ca present)
Buffle et al. (1989)	1	0.25	0.19	Particles sampled at the redox boundary in a fresh water lake
Deike et al. (1997)	1	0.2–0.6	0.05–0.16	Particles sampled in Quarternary sediment (vivianite not included)
This study	1	0.55	0.37	Fresh particles sampled at sediment surface

to Mn^{2+}-ions in the sediment, upward diffusion of dissolved Mn^{2+} in the sediment pore water, and reoxidation of Mn^{2+} at the filter surface. However, the manganese content of particles on the filter is remarkably low. This is probably due to a slow oxidation kinetics of Mn^{2+} compared to the oxidation of Fe^{2+} (Roekens & van Grieken 1983; Wilson 1980). Mn^{2+} diffuses up into the water before being oxidized, whereas Fe^{2+} is oxidized right at the filter surface (Figure 5). This is confirmed by the high concentration (20 μM) of dissolved or colloidal ($<$ 0.45 μm) manganese measured in the overlying water at the end of the experiment.

Particle composition

Figure 4 shows a high correlation between Fe, P and Ca in the newly precipitated particles. This suggests that the particles are formed of chemical compounds with a relatively well-defined stoichiometry. From the EXPMA results the composition can be estimated to $Fe_{1.00\pm0.13}P_{0.55\pm0.06}Ca_{0.37\pm0.04}$ plus O, C, H (not measurable with the used techniques) and minor amounts of Si.

The estimated P:Fe molar ratio of 0.55 is high compared to the phosphate binding capacity reported for pure iron oxides. E.g. Lijklema (1980) reports a maximum binding capacity of only 0.25 phosphate groups per iron in freshly precipitated iron oxides (Table 3). A binding capacity of 0.55 P:Fe can possibly be explained by the Ca content of the particles: the positive Ca^{2+} ion can have a counter-ion effect for the negative phosphate ions, or the formed particles can consist of both a Fe-P phase and a Ca-P phase. XRD studies can possibly give further insight into the exact structure of the particles. A high Ca content was also noted in iron-phosphorus particles sampled at the oxic-anoxic interface in lake sediments (Deike et al. 1997) and in the water column (Buffle et al. 1989). Deike et al. (1997) found Fe:P ratios up to 0.6 in non-vivianite particles (Table 3), and explained the high binding capacity by a coupled adsorption of Ca and phosphate by iron oxides.

It is remarkable that the composition of the particles formed in this experiment is rather constant – the relative standard deviation is only 10–13% (Table 2). This allows the use of more macroscopic methods (such as quantitative chemical analysis of the formed particles) in future studies. For chemical analysis of the particles it will be necessary to separate the 'water-side' of the filter from the 'sediment-side'. This can possibly be achieved by using two filters on top of each other.

Comparison to in situ conditions

The described experimental setup was originally designed with special reference to distinguish between authigenic and sedimenting iron oxides, by eliminating the sedimenting material completely. While this is an advantage in terms of ensuring origin and purity of the formed particles, it also represents a deviation from real *in situ* conditions. It cannot be excluded that the presence or absence of sedimenting material influences the composition and structure of the formed particles. The same applies for the absence of benthic organisms in this study. It will be possible to design future filter experiments where both sedimenting material and benthic organisms are present, for instance by introducing the coreliner, filterholder and filter (Figure 1) in a part of a larger sediment-water microcosm in the laboratory.

It is important to note that the presence of the filter greatly influences the conditions in the sediment below: The sediment becomes anoxic which will of course change the pore water profiles and fluxes of redox sensitive species, just as any aerobic organisms caught below the filter will die. This change from oxic to anoxic conditions is similar to the seasonal changes occuring in several natural sediments (e.g. Jensen et al. 1995). In the filter experiment the change in redox conditions is difficult to avoid, as it is a prerequisite for the whole idea of sampling iron oxides on the filter surface.

Despite deviations from natural conditions, the Fe-P particles formed in this experiment have a composition similar to particles found *in situ* (Table 3). This seems promising for a future use of the setup, though some modifications can be necessary. For instance different filter types and pore sizes could be tested to optimise the setup. A closer control of pH, iron, phosphate, calcium, and oxygen concentration in the overlying water should be included in future studies.

Conclusion

We consider the method described in this paper to be a useful supplementary tool for studying the formation of iron oxides at the redox boundary in sediments. The particles are formed in a high concentration and purity, and can easily be sampled and studied by a range of methods (e.g. quantitative chemical analysis, EXPMA, X-ray diffraction, Mössbauer spectroscopy). At the same time the experimental setup is closer to *in situ* conditions than traditional laboratory studies. The setup can be modified to study the particle formation in different environments, such as different temperatures, pH, oxygen concentrations, and salinities. Further studies with the setup can for instance clarify the role of Ca and Si in the phosphate binding of iron oxides (Deike et al. 1997).

Acknowledgments

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