Vertical distributions of interstitial phosphate and fluoride in anoxic sediment: Insight into the formation of an authigenic fluoro-phosphorus compound

KEN'ICHI SASAKI,* SHINICHIRO NORIKI and SHIZUO TSUNOGAI

Laboratory of Marine and Atmospheric Geochemistry, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan

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In order to investigate the chemical form of authigenic phosphate compounds being precipitated in coastal sediments, the vertical distributions of dissolved phosphate and fluoride in pore water from the sediments of Funka Bay (Japan) were determined for the period from April 1997 to July 1998. The phosphate concentration in surface sediment pore water was typically 0–5 μM and increased up to 40–60 μM at 70 cm depth below the surface. In spring and summer, small maximums higher than 100 μM were found at a depth of around 20 cm, probably resulting from decomposition of organic matter and/or desorption of phosphate from the ambient sediment particles under anoxic conditions. Seasonal and vertical variations in the fluoride concentration of the pore water were in the range 53–74 μM . We found an inverse relationship between interstitial phosphate and fluoride concentrations, suggesting precipitation of an authigenic fluoro-phosphorus compound with a P/F atomic ratio of around 1/3 in the sediment. Formation of such a compound will greatly contribute to the global sink of phosphate from the ocean.

INTRODUCTION

Phosphate (P) is an essential nutrient for living organisms, and limits the rate of photosynthetic productivity in the natural ecosystem. Uncertainty remains concerning the chemical mechanism by which phosphate is removed from the ocean and into coastal sediment. Phosphorus in sediments exists in three main chemical forms, authigenic minerals (Jahnke *et al.*, 1983; Baker and Burnett, 1988; Froelich *et al.*, 1988; Rittenberg and Berner, 1993; Schuffert *et al.*, 1994, 1998), organic form (e.g., Filipek and Owen, 1981) and adsorbed on sediment particles (Krom and Berner, 1981; Sundby *et al.*, 1992; Jensen *et al.*, 1995). Inorganic phosphorus, which is synthesized authigenically in pore water, generally accounts for around 70% of the total reactive phosphorus in marine sediment (Filippelli, 1997).

Phosphorus in organic matter accounts for 10–40% of total phosphorus in coastal marine sediment (Morse and Cook, 1978; Krom and Berner, 1981; Filipek and Owen, 1981; Kamatani and Maeda, 1989) but is preferentially released during decomposition of the organic matter (Ingall and Van Cappellen, 1990). Organic phosphorus hence acts as an important secondary sink for phosphorus from the ocean. Though dissolved reactive phosphate released to pore water can be adsorbed on sediment particles, it is easily desorbed and dissolved into pore water under anoxic conditions (Watanabe and Tsunogai, 1984) and does not form an effective sink for phosphorus. Thus authigenic phosphorus minerals in sediment are the main sinks for phosphorus from the ocean (Sundby *et al.*, 1992; Filippelli, 1997; Louchouart *et al.*, 1997). Rittenberg (1992) pointed out that the extraction techniques used for identification of

*Corresponding author (e-mail: kasaki@ees.hokudai.ac.jp)

authigenic minerals also released background phosphorus associated with calcium carbonate, clays like smectite and biogenic apatite. For this reason it has been difficult to identify authigenic minerals that may act as potential P sinks in marine sediments.

It is known that some marine phosphate precipitates as a carbonate fluorapatite (CFA) in marine sediment (Jahnke *et al.*, 1983; Baker and Burnett, 1988; Froelich *et al.*, 1988; Schuffert *et al.*, 1994, 1998). The phosphorus to fluorine (P/F) atomic ratio of CFA has been reported to be in the range 2/1–5/1 (Parker, 1975; Burnett, 1977; Jahnke, 1984; Gulbrandsen *et al.*, 1984; Baker and Burnett, 1988; Froelich *et al.*, 1988). Although it has been suggested that CFA forms in reductive non-phosphogenic sediment (Sundby *et al.*, 1992; Lyons *et al.*, 1996; Louchouart *et al.*, 1997), the existence of CFA has not been confirmed in such sediment. Phosphorus contents of marine sediment are generally less than 1000 ppm making the contents difficult to analyze by either nondestructive analysis (such as X-ray diffraction) or isolation of the mineral for chemical analysis (e.g., Ruttenberg and Berner, 1993). Thus the chemical composition of authigenic phosphate minerals in marine sediment have not been clearly defined. Despite the existence of inorganic phosphorus minerals in marine sediment, pore water is often found to be supersaturated in phosphorous with respect to CFA (Berner, 1980). This fact suggests that sub-equilibrium in the liquid-solid system has been achieved with respect to some other phosphate minerals.

In this study, we try estimating the phosphorus to fluorine atomic ratio in authigenic minerals from the distribution of interstitial chemical components in anoxic marine sediment from Funka Bay, Japan. The P/F atomic ratio is often used to calculate the burial flux of phosphorus (Lyons *et al.*, 1996; Reimers *et al.*, 1996) and hence to calculate the effective phosphorous sink. The vertical and seasonal variation in dissolved reactive phosphate in marine sediment pore water will yield information concerning the precipitation of authigenic phosphate minerals in the sediment.

The knowledge derived from this study can hence contribute to elucidation of the behavior of not only phosphorus but also fluorine in the ocean.

SAMPLING AND METHODS

Study area

Funka Bay, located in the southwest of Hokkaido, Japan, covers an area of 2.3×10^3 km² with an average water depth of 60 m (Fig. 1). Two distinct water masses occupy the bay each year. One is Oyashio Water ($S < 33.0$, $T < 2^\circ\text{C}$) which enters into Funka Bay in early spring and remains through summer. The other is Tsugaru Warm Water ($S > 33.8$, $T > 6^\circ\text{C}$) which enters in autumn and remains until the following spring. The temperature of the bottom water is approximately 4 to 8°C (Ohtani and Kido, 1980).

Blooms of phytoplankton (predominantly diatom assemblage) are observed in March or April every year (Tsunogai and Watanabe, 1983). A large flux of settling particles has been observed in sediment trap experiments during this period (Noriki *et al.*, 1985). The total accumulation rate of sediments near the center of the bay is 0.2 cm/yr (Matsumoto and Togashi, 1980). In summer, the water column is stratified (this is apparent from CTD data) and the concentration of dissolved oxygen in the bottom water is about 3 ml/l, which is

Fig. 1. Location of Funka Bay (St. 30; $42^\circ15' \text{N}$, $140^\circ36' \text{E}$; water depth 91 m).

lower than that in other seasons (Table 1). The concentration of dissolved reactive phosphate in pore water varies seasonally as a result of variations in the redox condition of the marine sediment (Watanabe and Tsunogai, 1984).

Sampling

Sediment cores were collected at a central part of Funka Bay, Station 30 (42°15' N, 140°36' E; water depth of 91 m, Fig. 1) using a gravity corer with an acrylic tube (55 mm I.D. and 1 m long). The core samples were 50–70 cm in length. The small sampling holes (i.d. = 4 mm) for pore water extraction were prepared on the core tube and covered by plastic tape during coring. Two or more sediment core samples were taken every observation, and observations were performed 10 times from April 1997 to July 1998 (Table 1). After retrieving the core sample on shipboard from sea bottom, the sediment core tubes were immediately placed upright in an ice water bath. Samples of bottom water were collected using a Niskin bottle from a water depth of approximately 90 m.

Pore water extraction

Pore water extraction was performed in a thermostatic room ($6 \pm 1^\circ\text{C}$) by the method described

by Jahnke (1988). This method squeezes pore water from sediment core without direct exposure to air. After removing the corer to the thermostatic room, the pore water samples were extracted from the sampling holes into plastic syringes through a $0.45 \mu\text{m}$ Millipore filter by compressing the core using pistons at both the top and bottom ends of the core tube. The length of the sediment section (X , cm) from which the pore water sample was obtained was calculated based on the amount of pore water and the water content of the sediment according to the following equation,

$$X_i = Y_i \cdot S^{-1} \cdot \{1 + (\rho_w/\rho_s) \cdot (1 - W_i)/W_i\}, \quad (1)$$

where Y_i (cm^3) is the volume of pore water collected from the sampling port number i , S (cm^2) is a cross section of the core, ρ_w and ρ_s (g/cm^3) are the densities of pore water and sediment particles, respectively, and W_i is the water content of the sediment at the depth of the port. In this study the ρ_w and ρ_s are assumed to be $1.0 \text{ g}/\text{cm}^3$ and $2.5 \text{ g}/\text{cm}^3$, respectively. The sum of pore water volume from all ports is more than 95% of an ideal volume calculated from the distance of the piston movement.

Experiments of artificial change in the chemical state of sediment

An experiment exposing the sediment sample to air was performed using the following procedure. Each core collected from April to July 1997 was divided into 2.5 cm sections under an atmosphere with an air temperature of $6 \pm 1^\circ\text{C}$ in a thermostatic room. The sediment sample was kept for 3 hr in a plastic bag with air. The sample was then packed into a 50 ml plastic syringe with filter paper and glass wool. Pore water was squeezed from the sample by mechanically compressing the syringe (Manheim, 1968). The pore water was immediately filtered using a $0.45 \mu\text{m}$ Millipore filter and was stored in a 5 ml plastic syringe.

An experiment on the dilution of the pore water was done using one of the sediment cores collected in April 1998 using the following method. All procedures were performed in a nitrogen gas

Table 1. Observation date and concentrations of dissolved oxygen and phosphorus in the bottom water

Date	PO_4 (μM)	DO (ml/l)	Coring
1997/03/18	1.57	6.17	—
1997/04/14	2.31	4.88	○
1997/05/12	1.58	4.29	○
1997/06/16	1.32	—	○
1997/07/09	1.25	5.40	○
1997/07/30	1.97	3.00	—
1997/08/20	1.97	3.62	○
1997/09/09	2.08	—	—
1997/10/05	2.34	—	—
1997/11/06	1.82	5.13	○
1997/12/04	2.12	3.69	—
1998/02/25	1.12	6.73	○
1998/03/12	1.14	7.00	—
1998/03/23	1.27	6.10	○
1998/04/21	1.51	—	○

atmosphere to avoid oxidation of the sample. The core was sectioned into 2.5 cm pieces that were then packed into a 50 ml plastic centrifuge tube in a room kept at a temperature of 6°C. The tube was centrifuged at 2000 rpm for 10 min. Up to 5 ml of supernatant liquid was removed into a 5 ml plastic syringe. Approximately 10 ml of reducing artificial seawater was added to the residue. After mixing well, the tube was kept in an air bath at 6°C for about 10 hr. The tube was again centrifuged and the supernatant solution was removed to another 5 ml syringe. The residue was dried in a drying oven at 60°C for 3 days. The dilution ratio of the pore water was calculated from the weight of the sample measured during each step of the procedure. A solution of reducing artificial seawater for dilution of pore water was prepared according to the following method. The dissolved oxygen in the artificial seawater was purged by bubbling nitrogen gas through the solution for 20 minutes. Sodium sulfide was added to the solution under a nitrogen gas atmosphere. The solution produced has approximately 5 μM of sulfide concentration and no phosphate and fluoride. The Eh value is approximately -250 mV.

Chemical analyses

The concentrations of dissolved phosphate and fluoride in pore water were determined by molybdenum blue colorimetry (Strickland and Parsons, 1972) and lanthanum-alizarin complexone colorimetry (Greenhalgh and Riley, 1961), respectively. The oxidation-reduction potential of the sediment was measured with a platinum electrode (relative to a standard hydrogen electrode) during the sectioning of a core. The platinum electrode was inserted into the sediment to a depth of 2.5 cm from the core top. After the measurement, the top 2.5 cm of the core was removed and the Eh value of the next 2.5 cm of core was measured. The pH value of the pore water was measured using a glass electrode, calibrated to NBS standards. Dissolved oxygen in the bottom water was determined by the Winkler titration method. The concentrations of dissolved calcium and magnesium in the pore water were determined

using acetylene flame atomic absorption spectrometry (Model Z-8000, HITACHI Inc.).

RESULTS

Seasonal and vertical variations of interstitial phosphate and fluoride

Vertical profiles of dissolved reactive phosphate (DRP) in pore water are illustrated in Fig. 2. The seasonal variation of DRP in the pore water of Funka Bay was described and discussed in detail by Watanabe and Tsunogai (1984). Our observations were consistent with their results. The interstitial DRP concentration in the surface sediment was lower than 5 μM , which is nearly the same as that found in the bottom water (Table 1). Below this layer, the DRP concentration increased up to 40–60 μM down to the base of the core. Furthermore the DRP concentration exhibited seasonal variations with values higher than 160 μM for the sub-surface layer (10–20 cm) just after the spring bloom (April) and in summer (July and August).

Under oxygenated conditions the DRP concentration might decrease by its adsorption to sediment particles (probably metal oxyhydroxides such as FeOOH), and increase in the anoxic environment through its release back into the pore water (Krom and Berner, 1981; Sundby *et al.*, 1992; Jensen *et al.*, 1995). Watanabe and Tsunogai (1984) found an increase in alkalinity in pore water with the high concentration of DRP and stated that it is due to an increase in dissolved sulfide resulting from sulfate reduction. They explained that the maximum DRP found was a result of desorption of phosphate from sediment particles during the development of reducing conditions in the sub-surface layer. We observed the Eh value in the sediment and also found it to show a seasonal variation in the sub-surface layer (Fig. 3). The value in this layer was from 0 to -50 mV in February (winter) and decreased to around -200 mV in April. A redox cycle of iron in sediment acts as a pump enriching interstitial phosphate (Froelich *et al.*, 1988) and is important as a phosphate source for the formation of authigenic phos-

Fig. 2. Vertical profiles of phosphate concentrations in the pore water extracted from the sediments without direct exposing to air. The arrow indicates the concentration in the overlying water.

Fig. 3. Vertical profiles of oxidation-reduction potential (Eh) of the sediment. The arrow indicates the value in the overlying water.

phate minerals.

Vertical profiles of dissolved fluoride (DF) concentrations in the pore water are shown in Fig. 4. The DF concentration in the 5 cm surface layer varied seasonally from 61.6 to 74.6 μM with an average of 10 observations being 68.8 μM ,

roughly the same as that of the overlying seawaters (approximately 68 μM). Higher DF concentrations in the surface layer were found during the period from April to July. In other months, lower DF concentrations were observed. Below this layer, DF concentration varied in the range 53.6–68.0 μM and the amplitude of seasonal and vertical variations of DF concentration was smaller than that of the interstitial DRP concentration. The lower DF concentration was chiefly found in the sub-surface layer during spring and summer corresponding with a higher DRP concentration. Such lower concentrations of DF in the pore water of marine sediments have been reported for other coastal regions (Ruttenberg and Berner, 1993) and for a saline water lake (Lyons *et al.*, 1996). In these observations, contemporaneous high concentrations of DRP in the pore water were also found.

Artificial changes in DRP and DF with altering chemical state of sediment

Vertical profiles of DRP concentration in pore water, which was collected from sediment exposed to air, were illustrated in Fig. 5. These concentrations are up to 3 times smaller than those measured *in situ* (Fig. 2). Bray *et al.* (1973) also re-

Fig. 4. Vertical profiles of fluoride concentrations in the pore water extracted from the sediments without direct exposing to air. The arrow indicates the concentration in the overlying water.

Fig. 5. Vertical profiles of interstitial phosphate (a) and fluoride (b) concentrations in the pore water extracted from aerated sediments (filled symbols). For the comparison, the *in situ* value from simultaneous observation (Figs. 2 and 4) was also shown (open symbols). The arrows indicate the concentrations in the overlying water.

ported that DRP in anoxic sediment decreased by oxidation during sample handling under air. Adsorption coefficients for phosphate in oxygenated sediment are 10–1000 times larger than those found in anoxic sediment (Krom and Berner, 1980). The decrease in DRP with oxidation of sedi-

ment should be due to adsorption of phosphate to the ambient sediment particles. In the pore water we analyzed, we found DF concentrations much higher than those from *in situ* pore water and those from bottom water.

Table 2. The result of the pore water dilution experiment. Release of phosphate (ΔP) and fluoride (ΔF) from 50 g of wet sediment during the experiment and the $\Delta P/\Delta F$ ratio.

Depth (cm)	ΔP (μmol)	ΔF (μmol)	$\Delta P/\Delta F$ (mol/mol)
25–30	0.341	0.728	0.47
30–35	0.200	0.711	0.28
35–40	0.124	0.732	0.17
40–45	0.063	0.633	0.10
45–50	0.115	0.939	0.12
50–55	0.221	0.831	0.27
Average			0.23 ± 0.14

In the pore water dilution experiment, we can calculate the concentrations of DRP and DF just after addition of the reducing seawater from the dilution ratio and the initial concentrations of DRP and DF. After 10 hours, concentrations of DRP and DF have significantly increased up to 1.3 and 1.5 times respectively, compared to the concentrations recorded just after dilution. This observation indicates that phosphate and fluoride were released from the sediment particles to the pore water by dilution of the pore water. Changes in concentrations of DRP (ΔP) and DF (ΔF) ranged from 2 to 10 μM and from 15 to 25 μM , respectively. The $\Delta P/\Delta F$ atomic ratio from the pore water dilution experiment was calculated to be 0.23 ± 0.14 (Table 2).

DISCUSSION

Factors controlling dissolved fluoride distribution in pore water

We found seasonal variations of DRP concentration and Eh value in the sub-surface layer (around 10–20 cm depth) of marine sediment. This fact indicates that phosphate was released from sediment particles during the development of reducing conditions in this layer and the observations are consistent with the results of Watanabe and Tsunogai (1984). The concentration of DF varied in a roughly opposite sense to the variation in concentration of DRP.

There are three possible mechanisms to explain the seasonal and vertical variations in DF concentration in pore water including: (1) incorporation into and release from calcium carbonate (Carpenter, 1969; Rude and Aller, 1994), (2) adsorption onto and desorption from metal oxyhydroxides (Rude and Aller, 1993), and (3) precipitation of authigenic minerals such as carbonate fluorapatite (CFA) (Carpenter, 1969; Froelich *et al.*, 1983, 1988; Jahnke *et al.*, 1983; Ruttenger and Berner, 1993; Rude and Aller, 1994).

Fluorine is incorporated into calcium carbonate during precipitation of the mineral. If the seasonal variation of the DF concentration is caused by incorporation and release from calcium carbonate, a variation in the concentration of dissolved calcium in the pore water should be simultaneously observed. Measurements of interstitial calcium concentration in the marine sediment pore water were found to be nearly constant both seasonally and vertically ($10.0 \pm 0.2 \text{ mM}$), no significant variations in calcium concentration were found. Assuming calcium carbonate could incorporate around 500 ppm of fluorine (Carpenter, 1969), this would explain a maximum of only 1.3 μM of the possible DF variation estimated from the range in error (2σ) for Ca determination. Inorganic carbon content in the surface sediment down to 50 cm depth was extremely low (less than the detection limit (0.08 wt%) of C/S analyzer (model EMIA 820, HORIBA Inc.), our unpublished data). This suggests that no or little calcium carbonate was authigenically precipitated from pore water in the Funka Bay sediment. Thus the first option (1) could not be the main process responsible for the variation of fluoride concentration in the pore water.

The adsorption/desorption of DF on metal oxyhydroxides is affected by the amount of such oxides in the Funka Bay sediment particles and the degree of fluoride dissociation in the pore water (Rude and Aller, 1993). In the 2.5 cm surface layer, the Eh value in the sediment remained at +50~+100 mV (sub-oxic condition) throughout our observation. Large seasonal variation of the

Eh value was observed below this layer to 20 cm depth (Fig. 3). Sub-oxic conditions were found in February while reducing conditions developed in March. The concentration of metal oxyhydroxides decreases under reducing conditions. This process might result in an increase in the interstitial fluoride concentration during anoxic conditions and a decrease during oxygenated conditions. Magnesium concentration and pH value in pore water influences the formation of an Mg^{2+} - F^- ion pair and dissociation of hydrofluoric acid. The interstitial magnesium concentration was approximately constant (53.5 ± 12.3 mM) in all layers during all seasons. The seasonal and vertical change in the pore water's pH value was negligible (7.4 ± 0.1) except in the upper 10 cm of core. At pH 7.2–7.5, the adsorption efficiency of fluoride onto ferric oxyhydroxide is suppressed in the presence of dissolved magnesium (Rude and Aller, 1993). As there is limited variation in the chemical forms of DF, the effect of dissolved Mg in controlling DF concentration can be negligible. In the surface layer, the adsorption process can explain why the variation in DF concentration is consistent with variation in Eh. On the other hand, seasonal variation of DF in the sub-surface layer displays the opposite trend to the variation expected from the redox condition of the sediment. Hence the second option (2), whereby DF is controlled by adsorption/desorption on metal oxyhydroxides, cannot explain the large variation of DF in the sub-surface layer.

The third mechanism (3), precipitation of authigenic PF-bearing minerals, seems to be the most reasonable to explain the seasonal and vertical variations of the interstitial fluoride concentration (Reimers *et al.*, 1996). Lower DF concentrations in pore water were found associated with higher DRP concentrations. If the observed decrease in DF concentration was caused by formation of a mineral containing phosphorus, then the inverse relationship between these ions indicates saturation with respect to a fluoro-phosphorus compound. The compound should dissolve when the pore water becomes undersaturated with respect to the fluoro-phosphorus compound. In our

experiment exposing the sediment to air, we found a decrease in DRP and an increase in DF (Fig. 5). The decrease in DRP leads to undersaturation with respect to a fluoro-phosphorus compound, thus the mineral should dissolve and restore saturation conditions. The increase in DF in our experiment suggests dissolution of such a compound does occur.

P/F ratio of authigenic compound from pore water chemistry

Principal minerals containing PO_4 and F, which can precipitate in marine sediments, are carbonate fluorapatites (Berner, 1980) and/or their precursors (Gulbrandsen *et al.*, 1984). These minerals are formed by association of dissolved ions in pore water; namely Ca^{2+} , Mg^{2+} , Na^+ , PO_4^{3-} , F^- , OH^- and CO_3^{2-} . Assuming the formation of such minerals occurs in the Funka Bay sediment, we define the chemical reaction as follows:

and,

$$[\text{Ca}]^a[\text{Mg}]^b[\text{Na}]^c[\text{PO}_4]^g[\text{F}]^h[\text{OH}]^i[\text{CO}_3]^j = K_{ip}, \quad (3)$$

where K_{ip} is constant at saturation. Any ions not contained in the above equation may not be major components of the compound (at least for carbonate fluorapatite, Gulbrandsen *et al.*, 1984), and are neglected. The concentration of sodium, which is a major cation in seawater, was assumed to be constant in the surface sediment. Concentrations of calcium and magnesium ions were found to be constant both seasonally and vertically (Mg: 53.5 ± 12.3 mM; Ca: 10.0 ± 0.2 mM).

The pH in pore water of the layer deeper than 10 cm below surface was nearly constant (7.4 ± 0.1), suggesting little variation in the OH content of the pore water in this layer. In the upper 70-cm layer, the concentration of dissolved inorganic carbonate in pore water varies by up to a factor of

2.5 (from 2000 to 5000 $\mu\text{mol/l}$) (Kato *et al.*, unpublished). In contrast, the DRP concentration of pore water in this layer varied by a factor of more than 100 (from several micro-mole/l up to 170 μM). This variation in DRP concentration is significantly greater than that found for the other measured components (OH and CO_3). Hence we can assume that the concentrations of the other ions involved in Eq. (3) are negligible compared to the concentrations of DRP and DF. Accordingly Eq. (3) can be simply rewritten as follows,

$$[\text{PO}_4]^g [\text{F}]^h = A_{\text{sat}} (= \text{constant}), \quad (4)$$

$$\log[\text{F}] = -(g/h) \times \log[\text{PO}_4] + (1/h) \times \log(A_{\text{sat}}), \quad (4')$$

where A_{sat} is a constant for an apparent ionic product at saturation.

Figure 6 shows the DRP to DF plot on a logarithmic scale involving data on the seasonal vari-

ation of pore water in Funka Bay (Figs. 2 and 4) and from the experiment involving sediments exposed to air (Fig. 5). The slope of the data indicates the ratio of g/h (as defined in (4')), is equal to the phosphorus to fluorine (P/F) atomic ratio in a fluoro-phosphorus compound (Eq. (2)). Because the pore water from the surface 5 cm may be strongly affected by exchange with bottom water, we exclude this data in the following consideration.

The fitting line is calculated to be

$$\log[\text{F}] = -(0.30 \pm 0.03) \times \log[\text{PO}_4] - (5.4 \pm 0.1) \quad (5)$$

$$r = 0.70, n = 268$$

by a least squares method (Fig. 6). Dashed lines in Fig. 6 show the confidence limit ($P = 0.05$) of the line fit. The slope of the line is -0.30 ± 0.03 . The data indicates that the phosphorus to fluorine atomic ratio (i.e., g/h) in the authigenic mineral is

Fig. 6. A logarithmic scale plot of fluoride to phosphate of pore water from surface sediment of Funka Bay (small dots). Solid line is a simple regression curve ($\log[\text{F}] = -(0.30 \pm 0.03) \times \log[\text{PO}_4] - (5.4 \pm 0.1)$). Cross and triangle symbols show data from Long Island Sound (Ruttenberg and Berner, 1993) and from Jellyfish Lake (Lyons *et al.*, 1996), respectively.

around 1/3. Data for pore water in anoxic sediments was extracted from the literature (Ruttenberg and Berner, 1993; Lyons *et al.*, 1996) and were also plotted in Fig. 6 and found to be consistent with the line fit. This fact indicates that an authigenic fluoro-phosphorus compound having a P/F atomic ratio of approximately 1/3 is formed in some anoxic sediments lying under saline water.

In our experiment adding reducing seawater to the sediment, we found release of phosphate (ΔP) and fluorine (ΔF) from sediment particles to pore water, and a ΔP to ΔF atomic ratio of 0.23 ± 0.14 was calculated (Table 2). The ΔP to ΔF atomic ratio is consistent with the P/F atomic ratio of an authigenic fluoro-phosphorus compound (0.30 ± 0.03) estimated from variations in the DRP and DF of pore water found above. The pore water dilution leads to undersaturation with respect to a fluoro-phosphorus compound, and would result in dissolution of the compound.

Concentrations of DRP and DF in the bottom water were less than $3.0 \mu M$ and around $68 \mu M$, respectively. The ionic product of DRP and DF in the bottom water is less than that at saturation, thus,

$$[\text{DRP}]^g \cdot [\text{DF}]^h < (3.0 \times 10^{-6})^{0.3} \cdot (68 \times 10^{-6})^1 \\ = 1.5 \times 10^{-6} < A_{\text{sat}} (3.5 \times 10^{-6}). \quad (6)$$

In order to achieve saturation in the bottom water, DRP must be increased to approximately $50 \mu M$. Thus,

$$[\text{DRP}]^g \cdot [\text{DF}]^h = (50 \times 10^{-6})^{0.3} \cdot (68 \times 10^{-6})^1 \\ = 3.5 \times 10^{-6} = A_{\text{sat}}. \quad (7)$$

When the interstitial DRP exceeds $50 \mu M$, the DF concentration varies according to Eq. (5). The pore water from surface sediment, which was strongly affected by bottom water, was found to be undersaturated with respect to the compound. A condition necessary to form the fluoro-phosphorus compound is that interstitial phosphate concentration exceeds $50 \mu M$ as a result of either decomposition of organic matter and/or the redox

cycle of iron in the sediment.

The P/F atomic ratio of phosphorite synthesized in the laboratory was 2/1–3/1 (Jahnke, 1984). Carbonate fluorapatite (CFA) in phosphogenic sediments had an average P/F atomic ratio of 2.5/1 (Froelich *et al.*, 1988). Thus, the P/F atomic ratio of a fluoro-phosphorus compound estimated here in Funka Bay sediments is considerably different from that of CFA. Gulbrandsen *et al.* (1984) pointed out the possibility of the existence of CFA precursors from a laboratory experiment to synthesize CFA. The formation of a fluoro-phosphorus compound indicated by the analysis of pore water from Funka Bay sediments could be just such a precursor to CFA. The supersaturation with respect to CFA found in the sea's bottom water can be explained by the deposition of a first CFA precursor, which readily dissolves causing supersaturation.

Burial fluxes of inorganic phosphorus in sediments have often been estimated using the downward flux of interstitial fluoride multiplied by the P/F atomic ratio in the phosphate minerals, which is assumed to be CFA having an average P/F atomic ratio of 2.5/1 (Reimers *et al.*, 1996). Using the 0.30 ± 0.03 of the P/F atomic ratio estimated here, the burial flux of inorganic phosphorus was estimated to be 5–10 times lower. Coastal sediment is one of the main sinks of phosphate in the ocean (accounting for more than 50% of the whole ocean phosphate budget: Filippelli, 1997; Schuffert *et al.*, 1998). It is necessary to consider the removal of phosphorus by a new phosphate mineral, which forms a precursor to formation of CFA, in order to fully understand the cycle of phosphorus in the ocean.

CONCLUSIONS

Based on the distributions of dissolved phosphate and fluoride in the pore water extracted from the sediments of Funka Bay, we investigated the authigenic precipitation of phosphorus and fluoride in coastal sediments. We found an apparent inverse relationship between phosphate and fluoride concentrations. This suggests that interstitial

phosphate reacts with interstitial fluoride and precipitates as a fluoro-phosphorus compound. The P/F atomic ratio of the authigenic fluoro-phosphorus compound was estimated to be around 1/3 from the relationship between variations in dissolved phosphate and fluoride. The atomic ratio was consistent with the range of $\Delta P/\Delta F$ atomic ratios estimated from an independently performed pore water dilution experiment and is significantly different from the P/F atomic ratio for carbonate fluorapatite. It is important to consider the formation of this material, a possible CFA-precursor, when the removal of phosphorus from the ocean is evaluated.

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REFERENCES

- Baker, K. B. and Burnett, W. C. (1988) Distribution, texture and composition of modern phosphate pellets in Peru shelf muds. *Mar. Geol.* **80**, 195–213.
- Berner, R. A. (1980) *Early Diagenesis. A Theoretical Approach*, 168–174, Princeton Univ. Press.
- Bray, J. T., Bricker, O. P. and Troup, B. N. (1973) Phosphate in interstitial waters of anoxic sediments: Oxidation effects during sampling procedure. *Science* **180**, 1362–1364.
- Burnett, W. C. (1977) Geochemistry and origin of phosphorite deposits from off Peru and Chile. *Geol. Soc. Amer. Bull.* **88**, 813–823.
- Carpenter, R. (1969) Factors controlling the marine geochemistry of fluorine. *Geochim. Cosmochim. Acta* **33**, 1153–1167.
- Filipek, L. H. and Owen, R. M. (1981) Diagenetic controls of phosphorus in outer continental-shelf sediments from the Gulf of Mexico. *Chem. Geol.* **33**, 181–204.
- Filippelli, G. M. (1997) Controls on phosphorus concentration and accumulation in oceanic sediments. *Mar. Geol.* **139**, 231–240.
- Froelich, P. N., Kim, K. H., Jahnke, R., Burnett, W. C., Soutar, A. and Deakin, M. (1983) Pore water fluoride in Peru continental margin sediments: Uptake from seawater. *Geochim. Cosmochim. Acta* **47**, 1605–1612.
- Froelich, P. N., Arthur, M. A., Burnett, W. C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.-H., Roe, K., Soutar, A. and Vathakanon, C. (1988) Early diagenesis of organic matter in Peru continental margin sediments: phosphorite precipitation. *Mar. Geol.* **80**, 309–343.
- Greenhalgh, R. and Riley, J. P. (1961) The determination of fluorides in natural water with particular reference to seawater. *Anal. Chim. Acta* **48**, 213–218.
- Gulbrandsen, R. A., Roberson, C. E. and Neil, S. T. (1984) Time and the crystallization of apatite in seawater. *Geochim. Cosmochim. Acta* **48**, 213–218.
- Ingall, E. D. and Van Cappellen, P. (1990) Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments. *Geochim. Cosmochim. Acta* **54**, 373–386.
- Jahnke, R. A. (1984) The synthesis and solubility of carbonate fluorapatite. *Amer. J. Sci.* **284**, 58–78.
- Jahnke, R. A. (1988) A simple, reliable, and inexpensive pore-water sampler. *Limnol. Oceanogr.* **33**, 483–487.
- Jahnke, R. A., Emerson, S. R., Roe, K. K. and Burnett, W. C. (1983) The present day formation of apatite in Mexican continental margin sediments. *Geochim. Cosmochim. Acta* **47**, 259–266.
- Jensen, H. S., Mortensen, P. B., Andersen, F. O., Rasmussen, E. and Jensen, A. (1995) Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Limnol. Oceanogr.* **40**, 908–917.
- Kamatani, A. and Maeda, M. (1989) Distribution and budget of phosphorus in Tokyo Bay. *Chikyukagaku (Geochemistry)* **23**, 85–95.
- Krom, M. D. and Berner, R. A. (1980) Adsorption of phosphate in anoxic marine sediments. *Limnol. Oceanogr.* **25**, 797–806.
- Krom, M. D. and Berner, R. A. (1981) The diagenesis of phosphorus in a nearshore sediment. *Geochim. Cosmochim. Acta* **45**, 207–216.
- Louchouart, P., Lucotte, M., Duchemin, E. and de Vernal, A. (1997) Early diagenetic processes in recent sediments of the Gulf of St-Lawrence: phosphorus, carbon and iron burial rates. *Mar. Geol.* **139**, 181–200.
- Lyons, W. B., Lent, R. M., Burnett, W. C., Chin, P., Landing, W. M., Orem, W. H. and McArthur, J. M. (1996) Jellyfish Lake, Palau: Regeneration of C, N,

- Si, and P in anoxic marine lake sediments. *Limnol. Oceanogr.* **41**, 1394–1403.
- Manheim, F. T. (1968) Disposable syringe techniques for obtaining small quantities of pore water from unconsolidated sediments. *J. Sediment. Petrol.* **38**, 666–668.
- Matsumoto, E. and Togashi, S. (1980) Sedimentation rate in Funka Bay, Hokkaido. *J. Oceanogr. Soc. Jpn.* **35**, 261–267.
- Morse, J. W. and Cook, N. (1978) The distribution and form of phosphorus in North Atlantic Ocean deep-sea and continental slope sediments. *Limnol. Oceanogr.* **23**, 825–830.
- Noriki, S., Ishimori, N. and Tsunogai, S. (1985) Regeneration of chemical elements from settling particles collected by sediment trap in Funka Bay, Japan. *J. Oceanogr. Soc. Jpn.* **41**, 113–120.
- Ohtani, K. and Kido, K. (1980) Oceanographic structure in Funka Bay. *Bull. Faculty, Fisheries Hokkaido Univ.* **31**, 84–114.
- Parker, R. J. (1975) The petrology and origin of some glauconitic and glauco-conglomeratic phosphorites from the South African continental margin. *J. Sedimentary Petrol.* **45**, 230–242.
- Reimers, C. E., Ruttenger, K. C., Canfield, D. E., Christiansen, M. B. and Martin, J. B. (1996) Porewater pH and authigenic phases formed in the uppermost sediments of the Santa Barbara Basin. *Geochim. Cosmochim. Acta* **60**, 4037–4057.
- Rude, P. D. and Aller, R. C. (1993) The influence of Mg^{2+} on the adsorption of fluoride by hydrous oxides in seawater. *Am. J. Sci.* **293**, 1–24.
- Rude, P. D. and Aller, R. C. (1994) Fluorine uptake by Amazon continental shelf sediment and its impact on the global fluorine cycle. *Cont. Shelf. Res.* **14**, 883–907.
- Ruttenger, K. C. (1992) Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* **37**, 1460–1482.
- Ruttenger, K. C. and Berner, R. A. (1993) Authigenic apatite formation and burial in sediments from non-upwelling continental margin environments. *Geochim. Cosmochim. Acta* **57**, 991–1007.
- Schuffert, J. D., Janke, R. A., Kastner, M., Leather, J., Sturz, A. and Wing, M. R. (1994) Rate of formation of modern phosphorite off western Mexico. *Geochim. Cosmochim. Acta* **58**, 5001–5010.
- Schuffert, J. D., Kastner, M. and Jahnke, R. A. (1998) Carbon and phosphorus burial associated with modern phosphorite formation. *Mar. Geol.* **146**, 21–31.
- Strickland, J. D. H. and Parsons, T. R. (1972) *A Practical Handbook of Sea Water Analysis*. 2nd ed., Bull. Fish. Res. Bd. Can., 167.
- Sundby, B., Gobeil, C., Silverberg, N. and Mucci, A. (1992) The phosphorus cycle in coastal marine sediments. *Limnol. Oceanogr.* **37**, 1129–1145.
- Tsunogai, S. and Watanabe, Y. (1983) Role of dissolved silicate in the occurrence of phytoplankton bloom. *J. Oceanogr. Soc. Jpn.* **39**, 231–239.
- Watanabe, Y. and Tsunogai, S. (1984) Adsorption-desorption control of phosphate in anoxic sediment of a coastal sea, Funka Bay, Japan. *Mar. Chem.* **15**, 71–83.