Phosphate Anion Sorption by the Sediments of Lake Baikal

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Abstract

The behaviour of phosphate anion P_i in the system water−bottom sediments of Lake Baikal is investigated with the help of the radioactive method. The concentration of P_i in water is $0.39 \cdot 10^{-6}$ mol/l, calcium ions $400 \cdot 10^{-6}$ mol/l, pH 7.6. It was established in experiments with $[^{32}P]$ phosphate that with pH changed from 7.6 to 5.6 the distribution coefficient $K_D = [P_i]_{sed}/[P_i]_{sup}$ increases from 6000 to 14 000, while under alkalization to pH 10.5 it decreases to 1500. The data obtained indicate that the main solid phase binding P_i is not hydroxylapatite as it had been considered before but authigenous ferric hydroxide. The concentration of exchangeable P_i in the sediment is $2.3 \cdot 10^{-6}$ mol/l. Sorption of P_i is described by Langmuir's isotherm; the sorption capacity of the sediment is $36.3 \cdot 10^{-6}$ mol P_i/g. After the treatment of the sediment with oxalic acid, which results in the removal of $517 \cdot 10^{-6}$ mol/g Fe, K_D decreases to 417. Since, unlike P_i, the radioactive sulphate is not sorbed by the sediment ($K_D < 60$), it is concluded that P_i binding proceeds according to the chemisorption mechanism but not simple ion exchange. About 200 t of P_i is buried annually in the adsorbed state in the Lake Baikal. This amount is much less than the amount of P_i entering with the water of the Selenga (~1200 t) and carried away with the Angara (~10^3 t).

INTRODUCTION

It was established in the classical works of Mortimer [1, 2] that the phosphate anion in the sediments of lakes in Great Britain is bound by ferric hydroxide. Later this mechanism was also established in the investigations of many other lakes of the zone of moderate climate. The processes involving adsorption and subsequent transformation of the phosphate ion are described in detail in [3]. Accordign to this scheme, the inorganic phosphate P_i is sorbed by ferric hydroxide which is present in the upper oxidized layer. As the sediment gets accumulated, ferric hydroxide that had bound P_i turns out to reside in the zone devoid of any oxygen access; Fe(III) gets reduced by the organic matter present in the sediment. Since Fe(II) salts, including $Fe_3(PO_4)_2$, possess high solubility, Fe^{2+} and P_i ions start to diffuse. The Fe^{2+} ions meet oxygen at the boundary of the oxidized zone; $Fe(OH)_3$ gets precipitated again. As far as P_i is concerned, it can partly migrate following Fe^{2+} and get bound by the diagenetic ferric hydroxide film after the formation of $Fe(OH)_3$, partly enter the reaction with calcium ions thus forming poorly soluble hydroxylapatite. These processes are complicated by biochemical transformations driven by the microorganisms that are present in the sediment.

There is an opinion that sorption of P_i from water by the lake bottom sediments occurs with the participation of ferric hydroxide, though other opinions were formulated with respect to some lakes. For instance, in 1990, the author of [4] came to a conclusion on the basis of thermodynamic calculations that phosphate is present in the sediments of Lake Baikal in the form of hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$.

Indeed, the water of the Baikal is in its chemical composition ($[Ca^{2+}] = 400 \cdot 10^{-6}$ mol/l, total concentration of inorganic phosphate forms (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4) $[P_i] = 0.5 \cdot 10^{-6}$ mol/l, pH 7.6 [4, 5], which corresponds to the ion product $[Ca^{2+}]_{10}[PO_4^{3-}]_6[OH^-]_2 = 10^{-112}$) even

somewhat supersaturated solution of this mineral (the solubility product of pure hydroxylapatite is SP $= 10^{-114}$ [5]).

The authors of [5] paid attention to the fact that, judging from the chemical composition of the water of Lake Michigan ({Ca^{2+}] $= 870 \cdot 10^{-6}$ mol/l, $[P_i] = 0.02 \cdot 10^{-6}$ mol/l, pH 8.2, which corresponds to the ion product $[Ca^{2+}]_{10}[PO_4^{3-}]_6[OH^-]_2 = 10^{-115}$), it is a saturated solution of hydroxylapatite. According to the concept of these authors, due to the excess of calcium ions, changes in the concentration of P_i in water should be unaffected by the disposal of inorganic phosphate into Lake Michigan or by its consumption by phytoplankton. Indeed, in spite of substantial seasonal changes in the concentration of phytoplankton, the concentration of P_i varies only slightly there; it corresponds to the indicated SP value for hydroxylapatite. Milliards dollars are being spent in the USA to remove P_i from purified waste water disposed into the Great Lake, in order to prevent their eutrophication. However, in the opinion of the authors of [5], these expenses are superfluous.

The goal of the present work was investigation of the mechanism of P_i deposition into the sediments of Lake Baikal.

EXPERIMENTAL

Water from the depth of 400 m of the Baikal, submitted by Istok Co. (Irkutsk), was sterilized by filtration, ozonation and UV irradiation. The characteristics of water were described in [6].

The surface sediment was sampled from the Baikal with the help of a shock tube in the southern depression (6 km off Listvyanka settlment) at a depth of 1400 m. The upper layer of the sediment 5 cm thick was mixed and transferred into a double polyethylene bag. In order to sterilize the sediment, the bag was subjected to γ-irradiation (30 thousand rad) with a cobalt unit in the Irkutsk Oncology Centre. The sediment was stored in a refrigerator. In order to provide sterility, the weighed portions of the sediment were taken in a laminar box.

Radioactive chemicals − phosphoric acid labeled with ^{32}P (without support) and ^{35}S sodium sulphate with the specific radioactivity of 360 and 32 MBq/μmol, respectively, − were submitted by the Institute of Reactor Materials (Zarechny city, the Sverdlovsk Region). The working solutions were prepared from these chemicals by adding water.

Other reagents were submitted by Reakhim Co. (Angarsk city). To acodofy suspensions, we used concentrated HCl or 1−10 % acetic acid, 20 % NaOH solution was used for alkalization. A potentiometer with a glass electrode was used to measure pH. When determining the sorption capacity of the sediment with respect to phosphate, we used a working solution of $K_2HPO_4 \cdot 3H_2O$ (2.5 mg/ml) to which a small amount of ^{32}P phosphoric acid was added.

A suspension of the wet Baikal sediment (500 mg, dry mass 100 mg) was mixed at room temperature with a magnetic stirrer with 100 ml of the Baikal water; portions of 100 ml of a diluted solution of the radioactive preparation were added after each 15 min. To determine radioactivity of the supernatant, 1 ml of the suspension was poured in a cone polypropylene test tube 1.5 ml in volume (Eppendorg, Germany), centrifuged for 5 min at the rotation frequency of 5000 rpm in a microcentrifuge of Lina Co. (Angarsk city), then 0.9 ml of the supernatant was sampled into an identical test tube. In the experiments with ^{32}P-phosphate, the tubes with centrifuged supernatant were inserted into a scintillation flask. Radioactivity was measured with the help of scintillation counter RackBeta (LKB, Sweden) according to Cherenkov's procedure. In the experiments with ^{35}S-sulphate, the portions of centrifuged supernatant (50 ml) were deposited onto square pieces of filter paper and dried. Their radioactivity was measured with the help of a toluene scintillator. In reference experiments, the same portions of radioactive preparations were sequentially mixed with 100 ml of the Baikal water, and the radioactivity of the mixture was determined similarly to the procedure of measuring the radioactivity of supernatant from the suspension. The radioactivity of the sediment was calculated on the basis of the difference between radioactivity values for the reference sample and for the centrifuged supernatant.

The treatment of the Baikal sediment (100 mg of dry mass) with 1 % oxalic acid was

carried out by jogging for 30 min at room temperature. The sediment was separated by centrifuging, an aliquot of the supernatant was strongly diluted with 5 % nitric acid, and the concentration of elements were determined with the help of ICP–MS (Element-2, Thermo Finnigan, USA).

RESULTS AND DISCUSSION

We investigated the equilibrium in the system water – bottom sediment of Lake Baikal under the laboratory conditions. As we have already mentioned, the upper layer of the sediment was sterilized by γ-irradiation to exclude the participation of microflora in phosphate redistribution. A weighed 0.5 g portion of wet sterile sediment (with water content 80 %) was mixed with a magnet stirrer with 100 ml of sterile Baikal water [6] monitoring pH. After mixing for 15 min, an aliquot of the suspension was centrifuged. The concentration of inorganic phosphate P_i in the supernatant, determined with the help of a colour reaction with molybdate, was 12 μg/l (0.39 mol/l). Which only slightly differs from the value for the deep water of Southern Baikal (15 μg/l [7]). Then several portions of [^{32}P] phosphoric acid, 7000 Bq each (20 10^{-12} mol), without a support, with the specific radioactivity of 360 MBq/μmol were added consecutively to the suspension at the intervals of 15 min. An aliquot of the suspension (1 ml) was centrifuged, and the radioactivity of the supernatant was measured. A part of the radioactive label passed from the solution to the sediment after each addition.

Investigation of the sorption kinetics showed that as early as 5 min after the addition of the isotope label the radioactivity of the supernatant becomes constant. The results of determination of the radioactivity of supernatant and sediment are shown in Fig. 1. One can see that after the addition of [^{32}P] phosphate both values increased linearly. It should be noted that in this series of experiments the concentration of P_i in the aqueous phase remained constant (0.39 μmol/l) since the amount of phosphate added with the label was negligibly small. The coefficient K_D of phosphate distribution between water and the sediment was determined
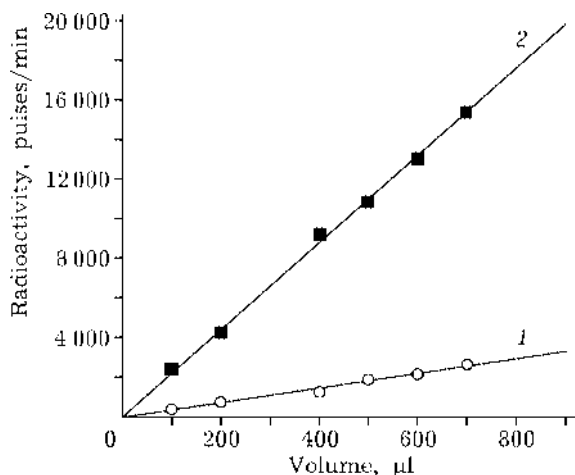

Fig. 1. Increase in the radioactivity of the supernatant (1) and the sediment (2) after the addition of [^{32}P] phosphate without a carrier to the suspension of the sediment (dry mass: 100 g) in the Baikal water (100 ml). Abscissa axis: the volume of [^{32}P] phosphate solution added; $K_D = 6000$, pH 7.6.

on the basis of the slope ratio of the two straight lines (see Fig. 1). According to the definition, $K_D = [P]_{sed}/[P]_{sup}$ (here concentrations are expressed in the same units, for example, in milligrammes per one kilogramme of the sediment and of the Baikal water, respectively). Evidently, $K_D = m_{sup}\alpha_{sed}/(m_{sed}\alpha_{sup})$, where α_{sed}, α_{sup} are radioactivities of the sediment and supernatant, respectively, Bq; m_{sup}, m_{sed} are the masses of the supernatant and the dry sediment, respectively. Mean K_D value determined by us in several experiments was equal to 6000. The concentration of exchangeable P_i in the dry sediment, calculated using K_D values and the equilibrium concentration of P_i in the supernatant, is equal to 2.3 10^{-6} mol/g (72 ppm), which accounts for 5 % of the total P content (1500 ppm) in the reference sample of the Baikal sediment BIL-1 [8].

Hydroxylapatite $(Ca^{2+})_{10}(PO_4^{3-})_6(OH^-)_2$ is formed as a result of the reaction of calcium, hydroxyl and phosphate ions. In order to calculate the pH dependence of the ion product (IP) of hydroxylapatite-related ions that are dissolved in the Baikal water, we used the above-mentioned [6, 7] data on the composition of water: $[Ca^{2+}] = 400$ μmol/l (this value is constant at any depth); for deep water $[P_i] = 0.5$ μmol/l [2], pH 7.6 [6], and hydroxyl ion concentration calculated from the known water
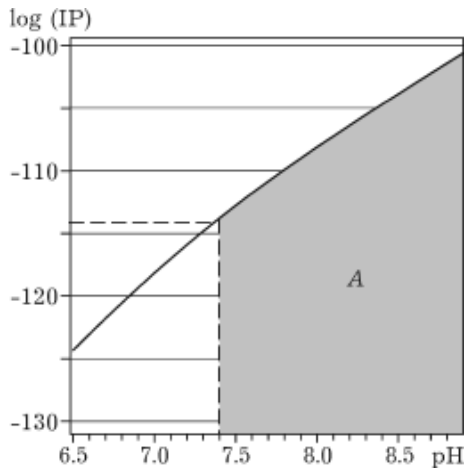
Fig. 2. Dependence of the product of the concentrations of calcium, PO_4^{3-} and hydroxyl ions on pH for the Baikal water (the SP of hydroxylapatite is equal to 10^{-114}): A – the region of hydroxylapatite precipitation; for pH < 7.4, dissolution of the mineral should occur.

Fig. 3. Dependence of K_D for P_i in the system water–sediment on pH. Dark and light circles are the data for two different experiments; broken line is the charge of phosphate z; broken vertical line is pH at which the charge of amorphous ferric hydroxide is equal to zero [10].

ionization constants (pOH = 14 − pH), as well as the concentrations of ions originating from phosphoric acid (K_1 = 0.007486, $K_2 = 6.553 \ 10^{-8}$, $K_3 = 9.52 \ 10^{-13}$ mol/l). The dependence is shown in Fig. 2.

One can see that the ion product decreases with acidification and becomes less than the solubility product of hydroxylapatite at pH < 7.4. Since pH of the Baikal water is equal to 7.6, the results shown in Fig. 1 do not contradict with the assumption that the phase binding P_i in the sediments is hydroxylapatite. In accordance with this assumption, K_D for P_i should sharply decrease with a decrease in pH and increase with alkalization.

A dependence of K_D on pH determined by us in the experiments with [^{32}P] phosphate, similar to the experiments the results of which are shown in Fig. 1, is presented in Fig. 3. One can see that K_D increases within the pH range 9−5. This is an evidence that hydroxylapatite is not the sediment phase in the equilibrium with which the dissolved P_i passes in our experiments because accumulation of hydroxylapatite in the sediment under acidification of the suspension is excluded (accumulation is evidenced by an increase in K_D).

In addition, the dependence of the charge of phosphate anion on pH, calculated from ionization constants, is shown in Fig. 3. One can

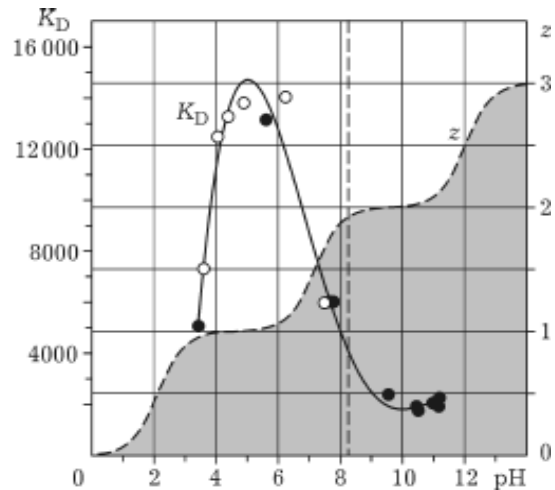see that the maximal binding of P_i with the sediment occurs within the pH range (4−6) in which the charge of phosphorus is equal to −1, that is, in which the relative content of the form $H_2PO_4^-$ is maximal.

As we have indicated above, an alternative to hydroxylapatite as an agent with which P_i dissolved in the Baikal water exchanges is a film of authigenous ferric hydroxide. This film covers the particles of terrigenous suspension in all the water reservoirs containing dissolved oxygen, similarly to the Baikal. The point in which the charge of amorphous ferric hydroxide is equal to 0 corresponds to pH 8.2 [9]. Therefore, the maximal binding of P_i is observed within the pH range in which the charge of ferric hydroxide becomes positive as a result of acidification (see Fig. 3).

We investigated P_i binding by the sediment treated with 1 % oxalic acid for the purpose of removing the authigenous ferric hydroxide. One can see in Fig. 4 that about a half of the total amount of iron is removed. Since oxalic acid removes also other elements along with iron, it affects not only the amorphous authigenous film but also some crystalline phases comprising the sediment. Therefore, Fe content of the hydroxide film can be somewhat lower than the amount of Fe (3.5 %) removed with oxalic acid (see Fig. 4).
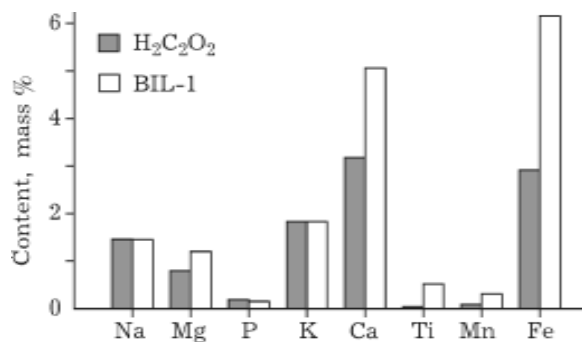
Fig. 4. Content of the elements extracted with 1 % oxalic acid in the Baikal sediment and their total content in BIL-1.

The data on P_i binding by the Baikal sediment treated with 1 % oxalic acid are shown in Fig. 5. One can see that K_D decreases by more than an order of magnitude (to ~400) after treatment. This fact is evidence that P_i binding occurs due to its interaction with easily removed oxalic acid, presumably with the diagenetic phase.

The data obtained allowed us to assume that P_i binding with the hydroxide film covering the particles of the Baikal sediments occurs by means of ion exchange, that is, simple electrostatic interaction between the polycation of ferric hydroxide (at pH below the zero charge point) and the anion of phosphoric acid.

It might be expected that the sediment from Lake Baikal is also able to bind other anions

according to the ion exchange mechanism. In order to examine this possibility, we carried out experiments similar to those described above using [^{35}S] sulphate of high specific radioactivity (without carrier) instead of [^{32}P] phosphate. Unlike for the phosphate anion, the charge of sulphate anion in water is always equal to -2 since it is an anion of a strong acid. It turned out that the sulphate is not sorbed by the sediment (Fig. 6). Therefore, P_i is bound with the sediment by means of chemisorption but not by simple ion exchange.

In order to determine the sorption capacity of the Baikal sediment with respect to P_i, we made experiments in which relatively concentrated solution of twice-substituted potassium phosphate (10.5 mmol/l, 25 mg/10 ml) with [^{32}P] phosphate was added a suspension of 500 mg of the Baikal sediment (100 mg of the dry mass) in the Baikal water (100 ml). The acidity of the medium was unchanged after addition was made. The radioactivity of the sediment at first increased but then, after the sorption capacity was saturated, it became constant.

It turned out that sorption can be described by Langmuir isotherm (Fig. 7). According to Langmuir's model, equilibrium characterized by constant K_L is established as a result of adsorption. In the case under consideration
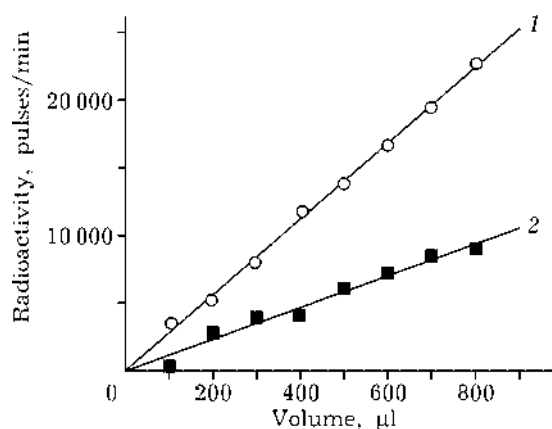
$$K_L = a / \{[P]_{sup}(a_m - a)\}$$

Fig. 5. [^{32}P] phosphate binding with the Baikal sediment washed with 1 % oxalic acid. Abscissa axis: the volume of the solution of [^{32}P] phosphate added to the suspension of the sediment in the Baikal water; ordinate axis: the radioactivity of the supernatant (1) and the sediment (2). The dry mass of the sediment before washing: 100 mg, the volume of the Baikal water: 100 ml, $K_D = 420$.
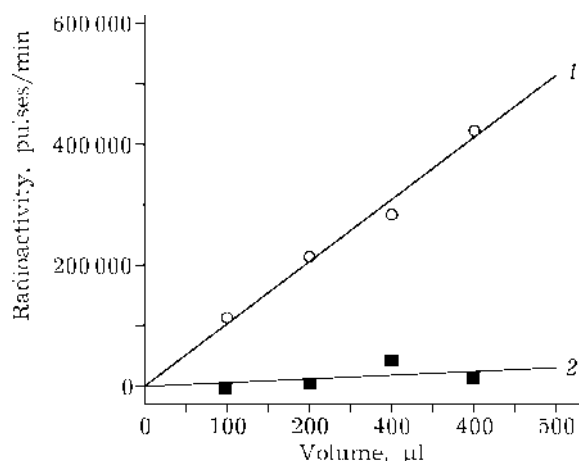

Fig. 6. Investigation of the distribution of [^{35}S] sulphate between the Baikal water and the sediment. The conditions are similar to those used to obtain the data shown in Fig. 1, but instead of [^{32}P] phosphate [^{35}S] sulphate was taken: 1 − supernatant, 2 − sediment. $K_D < 60$.
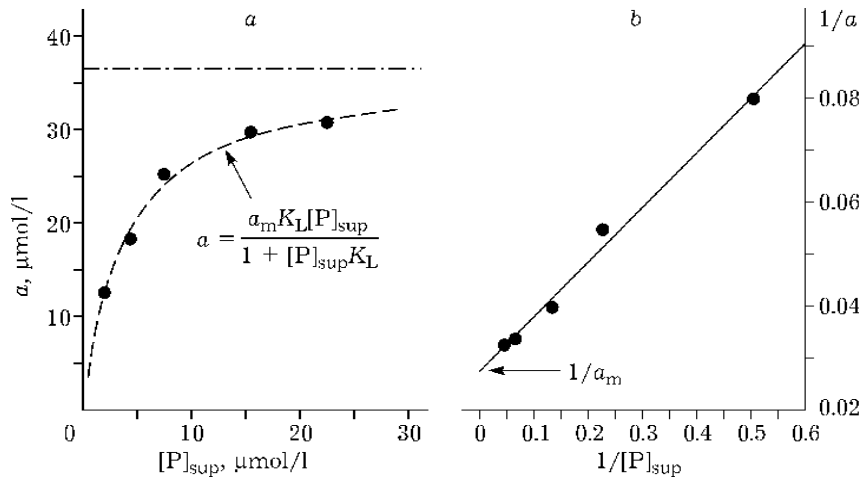
Fig. 7. Determination of the sorption capacity of the Baikal sediment with respect to P_i: a — the dependence of concentration a of P_i adsorption centres in the suspension on P_i concentration in the supernatant (dots); dot-and-dash line: Langmuir isotherm calculated for $a_m = 36.3$ µmol/l and adsorption constant $K_L = 0.262$ l/µmol; b — dependence of $1/a$ on $1/[P]_{sup}$; the straight line was drawn by means of the least squares; the slope ratio is equal to $1/a_m K_L$.

where a is the concentration of free P_i adsorption sites, mol/l of the suspension; a_m is the maximal value of a (in the absence of P_i); $[P]_{sup}$ is the concentration of P_i in the supernatant.

The sorption capacity of the Baikal sediment with respect to P_i, calculated from the determined a_m value, was found to be 36.3 µmol/g (1125 ppm).

It follows from the data presented in Fig. 4 that the content of iron extractable with oxalic acid is 520 µmol/g. So, if oxalic acid extracts iron selectively from the hydroxide film that coats the particles of the Baikal sediments, there is one P_i sorption site in the film per 14 iron atoms. However, this estimation can be overestimated if oxalic acid extracts iron also from the crystal phases. It should be noted that the a_m value is 11 times less than the concentration of calcium ions in the Baikal water, which is one more argument against the hydroxylapatite hypothesis.

At the initial part of Langmuir isotherm for $a \ll a_m K_L = a/a_m [P]_{sup}$. By definition, $a = [P]_{sed} m_{sed}/m_{sup}$. Therefore, in our experiments (for $m_{sed}/m_{sup} = 1000$) $K_D = 1000 K_L a_m = 9501$, which does not too strongly differ from $K_D = 6000$ determined in the experiments in which [32P] phosphate with high specific radioactivity was added to the suspension (see Fig. 1). So, the mechanism of P_i sorption by the Baikal

sediment does not change in principle within a broad concentration of P_i concentrations in the supernatant — from 0.39 to 30 µmol/l, or by a factor of 77.

Our data shown in Fig. 3 allow us to assume the formal scheme of the structure of the complex of ferric hydroxide with the phosphate anion (Fig. 8).

So, the set of the data described above provides evidence that hydroxylapatite is not a phase rapidly binding P_i in the Baikal sediment. The most probable candidate for this role is authigenous film of ferric hydroxide.

As we have already indicated in the Introduction section, P_i binding by the sediments of other lakes was investigated in detail previously. The authors of [9] used a procedure similar to ours and based on the application of [32P] phosphate. They investigated the sediments of four Canadian lakes — Wingra, Mendota, Tomahawk, and Little John. The sediments of the
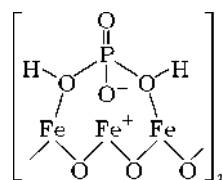

Fig. 8. Formal scheme of binding of phosphate anions with the ferric hydroxide film on the surface of sediment particles.

first two lakes are carbonate, while in the latter two they are non-carbonate. The first, the second and the fourth lakes are eutrophic, while the third one is oligomesotrophic. These authors did not calculate K_D for P_i, but these values can be estimated on the basis of the data presented in the paper: 10 800, 3200, 2500 and 3500, respectively. The exchange of the radioactive phosphate proceeded by 90 % within several minutes. Subsequent slower stages revealed in experiments could be a consequence of phosphate absorption by microorganisms, because, unlike our experiments, the authors of [9] did not sterilize the sediments. An important aspect in the observations of those authors is the fact that P_i binding decreases substantially after a system is transferred into anaerobic conditions, resulting in the reduction of Fe^{3+} to give soluble Fe^{2+}. According to our calculations carried out with the data presented by the authors of [9], K_D of the sediments from the indicated lakes decreased to 520, 700, 83 and 510, respectively, that is, to a value that was obtained by us for the Baikal sediment washed with oxalic acid.

Comparatively broad spread of K_D data for the oxidized sediments from different lakes studied in [9] can be a consequence of their different granulometric composition. Since P_i is sorbed on the authigenous hydroxide film covering terrigenous sediments, K_D should be inversely proportional to the linear dimension of particles.

The dependence of sorption efficiency of the oxidized lake sediments on pH seemingly has not been studied in detail before. However, desorption of P_i in strongly alkaline medium is considered to be a diagnostic evidence of the fact that P_i is sorbed by ferric hydroxide [3] (compare with Fig. 3). Experiments with pure ferric hydroxide [11] showed that P_i is stronger sorbed by this phase at lower pH and weaker at higher pH (9−4), which completely corresponds to our data obtained in the investigation of the Baikal sediments.

It was mentioned in [3] that phosphate in lakes gets bound with iron (III) most likely due to the formation of amorphous ferric phosphate rather than crystal strengite $FePO_4 \cdot 2H_2O$ (compare with [12]). It should be noted that, according to our data, strengite can hardly play a

role of the P_i-binding phase in the Baikal because, similarly to hydroxylapatite, it contains PO_4^{3-} anion and therefore it cannot become more stable in weakly acidic medium (compare with Fig. 3). In addition, the solubility product (SP) of strengite is higher than that of ferric hydroxide.

The data obtained by us are important for the understanding of the role of phosphorus load on the Baikal ecosystem. As we have indicated in the Introduction section, if hydroxylapatite were the bottom sediment phase absorbing phosphate, discharge of an additional amount of P_i would not cause an increase in its concentration in the lake. In other words, it would be not dangerous until its concentration was comparable with the concentration of calcium ions (400 μmol/l), because the lake water could be considered as a saturated solution of this mineral. The facts established by us suggest that this is not the case, at least during the initial rapid stages of binding which proceeds not according to the mechanism of crystal phase growth but according to sorption mechanism. In agreement with this mechanism, hydroxylapatite is discovered not in the oxidized upper layer of the Baikal sediment but in some deeper horizons [13], where its present can be explained by phosphate liberation as a result of Fe^{+3} reduction and the formation of soluble Fe^{2+}. According to the data obtained in the investigation of the sediments from Lake Okichobi, the formaiton of hydroxylapatite after the reduction of Fe^{3+} becomes possible [3] because the solubility of vivianite $Fe_3(PO_4)_2 \cdot 3H_2O$ is rather high. However, the authors of [3] believe that hydroxylapatite cannot be formed in the oxidized layer.

Some data obtained by us also provide evidence against the slow formation of hydroxylapatite in the oxidized upper layer of the Baikal sediments. It follows form the dependence shown in Fig. 7 that an increase in phosphate concentration in the suspension of the sediment in the Baikal water to 30 μmol/l (which is 77 times as high as the concentration of P_i in the lake) does not lead to changes in the mechanism of its binding with the sediment. The concentration of the sites occupied by phosphate in the suspension does not increase but reaches saturation, that is, phosphate does not form a precipitate. Meanwhile, the rate of hydroxylapa-

tite formation with such an increase in phosphate concentration should increase by a factor of 77^n, where n is the number of phosphate anions in the unit cell of hydroxylapatite equal to 6 in the pure mineral. If we assume that hydroxylapatite was formed in the Baikal under such an acceleration within a characteristic time of about a year, its formation in the experiment with $P_i = 30$ µmol/l would occur as soon as within 150 µs. The phosphate did not accumulate in the sediment also in the experiment similar to that the results of which are shown in Fig. 7 but differing form it by higher (by an order of magnitude) concentration of the added P_i (the data are not shown). It is necessary to stress that the ion product $[Ca^{2+}]_{10}[PO_4^{3-}]_6[OH^-]_2$ for many lakes investigated previously many times exceeds the SP of hydroxylapatite. In spite of this, hydroxylapatite does not precipitate in these lakes.

If P_i binding in the Baikal sediment occurs *via* adsorption mechanism, an increase in phosphate discharge into the lake is to cause an increase in P_i concentration in water and finally changes in the trophic character. The rate of bottom sediment accumulation in the Baikal is about 10 mg/cm^2 per year [14]. For $K_D = 6000$ (which corresponds to the concentration of exchangeable P_i equal to 72 ppm and the bottom area of 30 000 km^2), this means that the annual amount of exchangeable P_i buried in the Baikal is about 200 t. This is much less than the arrival of P_i with the water of the Selenga River, the main tributary of the Baikal (about 1200 t) and P_i escape with the water of the Angara River (about 1000 t) [15].

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