GEOCHEMISTRY

Cadmium and Zinc in Namibian Shelf Phosphorites

G. N. Baturin

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Cadmium, one of the most hazardous toxicants, is accumulated in phosphorites more actively than all other microelements. According to [1], the average Cd content in phosphorites is 18 ppm, which is 60 times higher than the average concentration in clays. Therefore, a complex technology of phosphorite processing was implemented to remove Cd for the ecological safety of phosphorite fertilizers [2, 3].

Cadmium and zinc, members of Group II in the periodic table, usually occur together in natural objects (in particular, phosphorites). At the same time, these elements are often considered separately in the geochemistry of phosphorites. For example, data on Zn are absent in several works devoted to the behavior of Cd in phosphorites [4–6].

The Cd and Zn distribution has been investigated in detail for Late Cretaceous Cd-rich phosphorites of Israel [7, 8]. In reduced varieties of these phosphorites, Cd is correlated with Zn and pyrite is associated with Cd-rich sphalerite [7]. Phosphorites of Morocco are less well studied [9].

Comparable data on other phosphorites are scanty. Therefore, it is expedient to continue comprehensive investigations of phosphorites of various types.

Thus, analysis of the Zn/Cd ratio in Recent and Pliocene–Pleistocene phosphorites of the Namibian shelf, which represent the youngest sediments with the signature of primary formation environment [10], is an interesting task.

We studied recent phosphorite nodules and micronodules of different grades of lithification, phosphatized coprolites of sea lions, and enclosing diatom oozes. Pliocene–Pleistocene phosphate samples include phosphorite nodules, phosphatized coprolites and shell casts, as well as phosphate-rich and phosphate-poor sands.

Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117997 Russia; e-mail: gbatur@geo.sio.rssi.ru

The author of the present communication collected samples of recent phosphorites and sediments on the inner Namibian shelf during Cruise 4 of the R/V *Akademik Kurchatov* (1968) and Cruise 26 of the R/V *Mikhail Lomonosov* (1972). Pliocene–Pleistocene phosphorite samples from the inner Namibian shelf were taken under the supervision of O.V. Kolosov with the participation of M. Bremner and his team of researchers from Cape Town University during Cruise 4 of the R/V *Professor Logatchev* (1992). A part of this material was placed at our disposal for further investigation.

The gravel-size nodules, phosphate shell casts, and phosphatized coprolites were chosen for analysis in the course of examination of bulk samples. Grain size fractions were separated by sieving. Phosphate grains were extracted from diatom oozes under binocular microscope.

The typical chemical composition of samples was studied by conventional methods of chemical analysis in laboratories of the Shirshov Institute of Oceanology. Contents of Zn, Cd, and Fe were determined by the ICP-MS method at the Analytical Certification Center of the Fedorovskii All-Russia Research Institute of Mineral Resources.

The results obtained show that the Zn content varies from 2.6 ppm in recent nodules to 348 ppm in recent coprolites, while the Cd content varies from 0.22 ppm in recent nodules to 51 ppm in recent diatom oozes.

Data on the average content of components suggest the following conclusion (table). Recent diatom oozes, which host the growing phosphorite nodules and micronodules (grains), are enriched in organic matter (C_{org} 6.9%) and P (P_2O_5 0.90%) and, particularly, Cd (35 ppm). At the same time, they are slightly depleted in Zn (70 ppm) relative to the typical sedimentary rock. It is worth noting that the average C_{org} content is 0.74% in sediments of the World Ocean [11], while contents of Zn and Cd in pelagic sediments are equal to 130 and 0.3 ppm, respectively [12].

In the slightly phosphatized diatom ooze (P_2O_5 6.33%), the average contents of C_{org}, Zn, and Cd are 1.5–2 times lower, relative to the nonphosphate variety

Average chemical composition of samples (wt %) and Zn and Cd concentrations in them (ppm)

P_2O_5	CaO	SiO_2	Al_2O_3	Fe_2O_3	CO_2	C_{org}	Zn	Cd	Zn/Cd	Number of samples
Recent diatom ooze
0.90	7.1	43.0	3.0	1.5	2.85	6.9	70	35	2.2	8
Recent phosphatized mud
6.33	9.45	35.53	1.5	0.81	1.95	3.70	29	28	1	4
Loose phosphorite nodules from diatom oozes
24.7	39.0	6.84	0.47	0.32	5.14	1.60	17.3	4.4	5.5	5
Dense phosphorite nodules from diatom oozes
31.13	48.15	0.08	0.03	0.06	6.06	0.98	64	2	31	6
Loose coprolites from diatom oozes
28.92	47.7	0.17	0.03	0.3	4.0	1.33	182	4.7	48	4
Dense coprolites from diatom oozes
30.9	49.5	0.2	0.1	0.10	7.25	0.80	80	2.7	30	3
Phosphate grains and sandy fractions from diatom oozes
29.4	49.2	3.5	0.55	0.56	5.2	1.30	2.60	17	15.2	5
Nodules from Pliocene–Pleistocene phosphate sands
32.3	50.8	1.80	0.5	1.30	4.8	0.82	34	3.2	15	4
Phosphatized shell casts from phosphate sands
30.0	48.0	3.9	0.76	1.44	5.40	0.96	53	5.4	9.5	3
Lithified coprolites from phosphate sands
32.69	52.4	0.40	0.05	0.29	6.07	1.03	72	26	4.3	2
Phosphate-poor sands
9.40	46.2	8.56	1.4	1.7	27.22	1.2	34	7.1	5.5	4
Phosphate sands and fraction 1–0.5 mm
25.64	42.6	8.5	1.8	2.7	6.6	1.98	34	20	3.2	3

(3.7, 29, and 28 ppm, respectively). Loose phosphorite nodules, representatives of the next stage of prograde phosphatization, are enriched in P_2O_5 (up to 24.7%). Correspondingly, the nodules are 1.5–2 times depleted in C_{org} (1.6%) and Zn (17 ppm) and six times depleted in Cd (4.4 ppm).

In dense phosphorite nodules, which are compositionally similar to counterparts from phosphorite deposits in ancient marine sediments on continents, the average P_2O_5 content is as much as 31.13%, while contents of C_{org} and Cd decrease to 0.98% and 2 ppm, respectively. At the same time, the Zn content decreases to 2.6 ppm in some samples and increases to 86 ppm in other samples (average 64 ppm). Consequently, the average Zn/Cd ratio increases from 1–2 in nonphosphate and phosphatized diatom oozes to 5.5–31 in loose and dense phosphorite nodules.

Average contents of other components also vary in the course of phosphatization. Contents of the struc-

tural elements of apatite increase significantly. For example, the CaO content increases from 7.1 to 48.15%, while the CO_2 content increases from 2.85 to 6.06%. At the same time, the content of silica represented by biogenic opal decreases from 43% to 0.08%. This process is accompanied by a decrease in contents of Al_2O_3 (from 3 to 0.03%) and Fe (from 1.5 to 0.06%).

Phosphatization of recent coprolites is accompanied by a similar pattern of compositional variation. Contents of P, Ca, and CO_2 increase, while contents of C_{org}, Fe, Zn, and Cd decrease.

Phosphate grains and sandy fractions extracted from diatom oozes are mainly composed of the apatite phase, as suggested by the high P_2O_5 content (29.4%). However, in contrast to nodules, the phosphate grains contain an appreciable amount of nonphosphate admixtures, such as biogenic opal (3.5%), Al_2O_3 (0.55%), and Fe (0.56%). According to the SEM data [13], Fe is primarily represented by pyrite. Relative to lithified nod-

ules, the Zn content in phosphate grains is four times higher (260 ppm), while the Cd content is 7.5 times higher (17 ppm).

Samples of Pliocene–Pleistocene phosphorite sands of the gravel fraction from the inner Namibian shelf represent typical phosphorites with 30–32.69% P_2O_5 and 48.0–52.4% CaO.

Phosphorite nodules contain a minor admixture of SiO_2 represented by diatom remnants and quartz (1.8%) and pyrite (1.3% recalculated on the Fe_2O_3 basis). In general, the phosphorite nodules are compositionally similar to the lithified nodules in recent diatom oozes on the inner shelf. Relative to the diatom oozes, the phosphorite nodules are two times depleted in Zn (64 and 34 ppm, respectively) and slightly enriched in Cd (2.0 and 3.2 ppm, respectively).

The phosphatized shell casts are nearly identical to the phosphorite nodules in terms of chemical composition. However, the shell casts are slightly enriched in Zn (53 ppm) and Cd (5.4 ppm).

Like recent coprolites from diatom oozes, coprolites from phosphate sands are characterized by extremely low contents of SiO_2 (0.40%), Al_2O_3 (0.05%), and Fe (0.29%). Contents of Zn and Cd are 72 and 26 ppm, respectively.

Phosphate-poor and phosphate-rich Pliocene–Pleistocene sands are characterized by P_2O_5 and CO_2 contents of 9.40–25.64 and 27.72–6.60%, respectively, because the phosphate-poor sands contain a significant admixture of coquina.

The Zn content is similar in both types of sand (34 ppm), whereas the Cd content is three times higher in the phosphate-rich sand (20 ppm) relative to the phosphate-poor variety (7.1 ppm). The Zn/Cd ratio varies from 15 (nodules) to 9.5 (shell casts), 4.3 (coprolites), and 1.7 (phosphate sands); i.e., the Cd content becomes one order of magnitude higher than the Zn content.

Thus, the studied material is characterized by the following degrees of variation: Zn 134 times, Cd 232 times, and Zn/Cd 76 times. Variation ranges of average values are as follows: Zn 17.3–260 ppm, Cd 2–35 ppm, and Zn/Cd 1–48. Thus, the degree of variation in Zn and Cd contents and Zn/Cd ratio reaches 15, 17.5, and 48 times, respectively. This fact testifies to the absence of correlation between Zn and Cd in the course of Recent and Pliocene–Pleistocene phosphate accumulation on the Namibian shelf.

Here, similarity in the behavior of Zn and Cd is manifested in the fact that their concentrations decrease in the following three series: diatom oozes–phosphatized oozes–loose nodules; recent loose coprolites–dense coprolites; and Pliocene–Pleistocene coprolites–shell casts–nodules.

Dissimilarity in their behavior is expressed in different intensities of decrease in concentrations. For example, the Zn content becomes two times lower in the first

and third series, while the Cd content becomes 8–11 times lower. Moreover, the Zn content increases four times and the Cd content decreases two times in the course of transition from the recent loose nodules to the dense varieties. Relative to the phosphate-rich sand, the phosphate-poor variety is characterized by the presence of Zn partly related to carbonates and the association of Cd with organic matter.

The main distinctive feature is as follows: Zn is not apparently concentrated in the process of phosphatization. Relative to the average value for sedimentary rocks, the Zn content is only two times higher in the loose coprolites and three times higher in the recent phosphate grains. The Zn content is lower in all other samples. In contrast, the Cd content in diatom oozes (sources of phosphorus for nodules) is two orders of magnitude higher than the background value for sedimentary rocks. In all other cases, the Cd content is tens of times higher. The Zn/Cd ratio varies from 320 in sedimentary rocks [14] to 430 in pelagic sediments [12] and 1–48 in the studied material.

The mode of occurrence of Cd and Zn in phosphorites is diverse. According to [2], Cd can enter the crystal lattice of apatite. This assumption is not supported by the extremely high variation range of the Cd/P ratio. The average $Cd/P_2O_5 \times 10^4$ value varies from 40 in diatom oozes to 0.06–4.4 in recent phosphate grains. A similar pattern is observed in Cretaceous phosphorites of Israel (0.41–5.40) [8].

The role of sulfides is more significant in this respect. Results of five microprobe analyses indicate that phosphorites of Israel contain unique sphalerite inclusions with the following average composition (%): Zn 60.6, Cd 4.7, and S 31.4 [8]. It should be emphasized that sphalerite inclusions are unknown in phosphorites of other regions. Pyrite nodules in phosphorites of Israel contain 0.3–0.5% Zn and 0.03–0.08% Cd.

In samples from the Namibian shelf repeatedly investigated by scanning and transmission electron microscopes [15], sphalerite has not been detected even by the microdiffraction method. At the same time, framboidal pyrite globules (up to 10–20 μm across) are abundant (figure). However, the depletion of lithified sediments in total Fe (Fe_2O_3 0.06–0.56%) suggests a generally low content of pyrites in recent phosphorites. In Pliocene–Pleistocene nodules hosted in sands, the total Fe content is more than 1–2%. Therefore, one cannot rule out that a part of Cd and Zn in phosphorites of the Namibian shelf is bound with pyrite. Let us recall that the phosphatization of recent diatom oozes and the formation of nodules is accompanied (although with a variable intensity) by a decrease in contents of both Cd and Fe.
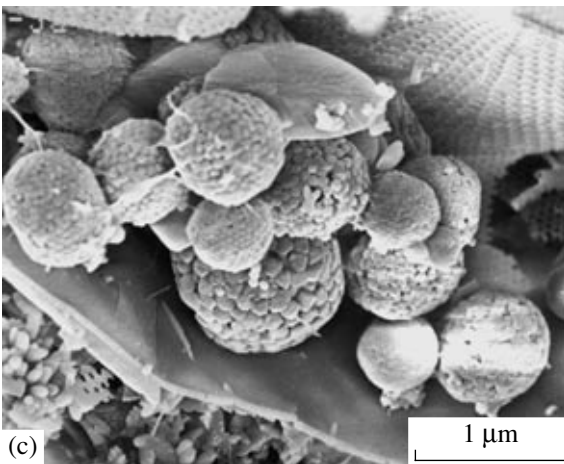
It is worth noting that the recent phosphate grains (mainly lithified to a moderate degree) are four times enriched in Zn and 8.5 times enriched in Cd, relative to the dense phosphorite nodules. Contents of Zn are similar in Pliocene–Pleistocene sands and phosphorite
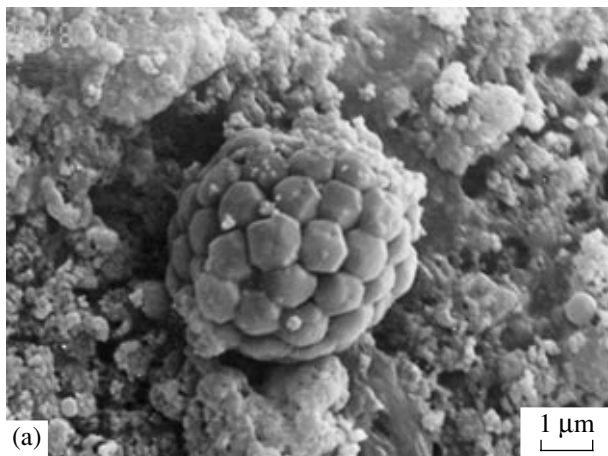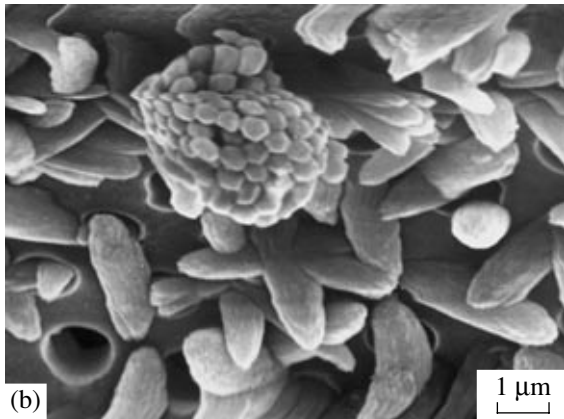
Globular pyrite in recent phosphorite nodules from the inner Namibian shelf. (a) Pyrite globule in colloform phosphate mass of the soft loose nodule; (b) pyrite globule associated with phosphate crystallites on the surface of diatom algae cast in slightly lithified nodule; (c) globular pyrite aggregate on the fragment of diatom algae cast.

nodules. However, the Cd content is six times higher in the sands. Hence, the accumulation of Cd and Zn (to a lesser extent) is governed by the specific surface of phosphate aggregates that serve as sorbents of heavy metals from the interstitial and, probably, near-bottom waters.

Zinc and cadmium, which fulfill some biogenic functions, are assimilated by plankton. After the death of plankton, Cd and Zn continue to accumulate in the biological suspension and organic-rich bottom sediments of the surface layer. At the same time, sulfate reduction in sediments promotes the formation of pyrite with isomorphic admixtures of Zn and Cd. In some cases, zinc minerals with Cd admixture can also form. The possibility of the formation of minerals with CdS composition in such an environment is an open issue.

The process described above is mainly governed by organic matter. This fact is supported by the maximal Zn content (average 35 ppm) in diatom oozes that host the recent phosphorite nodules with the C_{org} content of 5–12.5% (in some places, up to 20% or more [4]).

In Moroccan Cretaceous black shales with phosphorite intercalations and abundant C_{org} (up to 3–14%), the Zn and Cd contents are as high as 1154 and 178 ppm, respectively (average 466 and 50 ppm, respectively). In phosphorites, the average Zn and Cd contents decrease to 380 and 25 ppm, respectively [9]. In Cretaceous phosphorites of Israel, the average Zn and Cd contents in the reduced variety are 1448 and 98 ppm, respectively. In the oxidized variety, the contents are 208 and 5 ppm, respectively [8].

However, correlation between contents of C_{org}, Cd, and Zn are missing the recent and ancient phosphorites, except in the case of some reduced sedimentary sections [7]. This can be related to two reasons. First, lithification and, particularly, redeposition of phosphorites is accompanied by the decay of organic matter. However, the residual organic matter can accumulate more intensely heavy metals and retain their primary reserve. Second, the release of heavy metals in the course of redeposition of phosphorites can be accompanied by their resorption on the phosphate material, clay minerals, and iron oxides [7]. Therefore, the organic matter can play a significant (and even major) role as an ingenuous accumulator of heavy metals in both black shales and phosphorites.

ACKNOWLEDGMENTS

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