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GEOCHEMISTRY

Evidence for the Zircon Origin of Cadmium Anomalies in Bottom Sediments from the Littoral Zone of the Northern Part of Lake Ladoga

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Abstract—The minor-element composition of bottom sediments from the littoral zone of the northern part of Lake Ladoga was studied. Close relationships between the anomalous Cd concentrations in lake sediments and Quaternary glacial formations on the territory of Karelia were shown. A negative correlation of Cd with other heavy metals and a positive correlation with Zr were observed. Most likely, Cd is an impurity in zircons from sandy and sandy loam sedimentary formations on the northern coastal area of Lake Ladoga.

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Cadmium (Cd) is a minor scattered element. The anomalously high concentrations of Cd in atmosphere, soil, water, and bottom sediments (BSs) are often related to the anthropogenic influence on the studied natural objects. The highly toxic properties of Cd for living beings are well known, and, therefore, this heavy metal is among the most dangerous pollutants of the environment. Nonferrous metallurgy, paint and plastic production, the electronic industry, and agriculture provide the basic contribution to environmental contamination with Cd. More than 90% of Cd and its compounds from the total budget of this metal in the natural cycle of matter come to the biosphere from anthropogenic sources [1, 2].

Lake Ladoga, the largest fresh-water reservoir in Europe (17 700 km^2), has a high economic and recreational importance for the northwestern part and the entire Russia [3]. In light of changes in the ecosystem of the lake and the related high anthropogenic influence, ecological and chemical studies of Lake Ladoga are of paramount importance [4].

Study of BSs is an important component of complex limnological investigations. The chemical composition of BSs is an indicator of numerous complex processes of natural and anthropogenic character, which proceed in the catchment area of the lake, as well as in the hydroecological system. Sediments in the coastal zone of large water reservoirs such as Lake Ladoga may be a peculiar depot on the path of migration of various chemical elements including heavy metals to the major part of the lake.

Our study is aimed at understanding the genesis of anomalously high concentrations of Cd in BSs from the littoral zone of the northern part of Lake Ladoga on the basis of ICP-MS analysis.

The field investigations in the North Ladoga area were performed in 2013 and 2014. We studied the surface layer of BSs from the littoral zone (depths of 1–1.5, 3, and 8 m) of Lake Ladoga (Fig. 1).

The samples of sediments were collected using an Ekman bottom grab; the laboratory studies included drying of collected bottom sediments, sieving with a cell size of 2 mm and grinding to a powdered state. The minor-element composition of sediments studied was analyzed on an XSeries-2 ICP-MS mass spectrometer [5, 6]. Computer processing of the data was performed using the Microsoft Excel 2007 and Inkscape 0.48.4 software.

Interest in the study of Cd in BSs from the littoral zone of the northern part of Lake Ladoga was stimulated by the anomalous concentrations of this element (0.66–2.77 ppm) in sediments collected in the area of Lekhmalakhti Bay, Lunkulansaari Island, and Khunuka Peninsula. These concentrations are 2–7 times higher than the regional geochemical background of this heavy metal (0.39 ppm) for BSs of freshwater reservoirs. There is no significant correlation of Cd with Li, which is an indicator of fine granulometric fractions in BSs [7], and basic minor elements and pollutants (Fig. 2), high contents of which are usually typical of shale, aleuritic, and fine-sandy sediments (Kirjavalakhti and Impilakhti bays).

To the contrary, the concentrations of Cd from 0.19 to 0.46 ppm in BSs above the mentioned areas are

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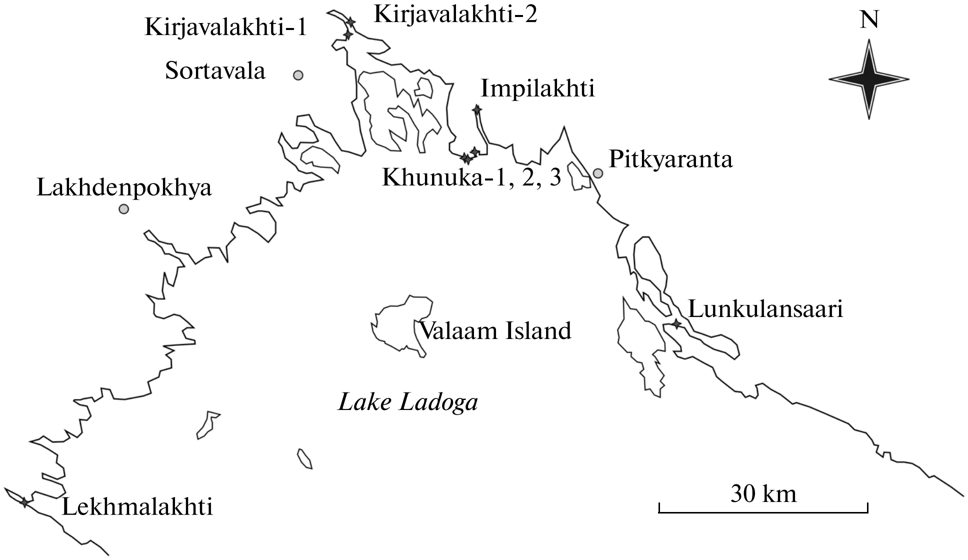

Fig. 1. Schematic map of the studied area. The stations of bottom sampling are indicated by asterisks.

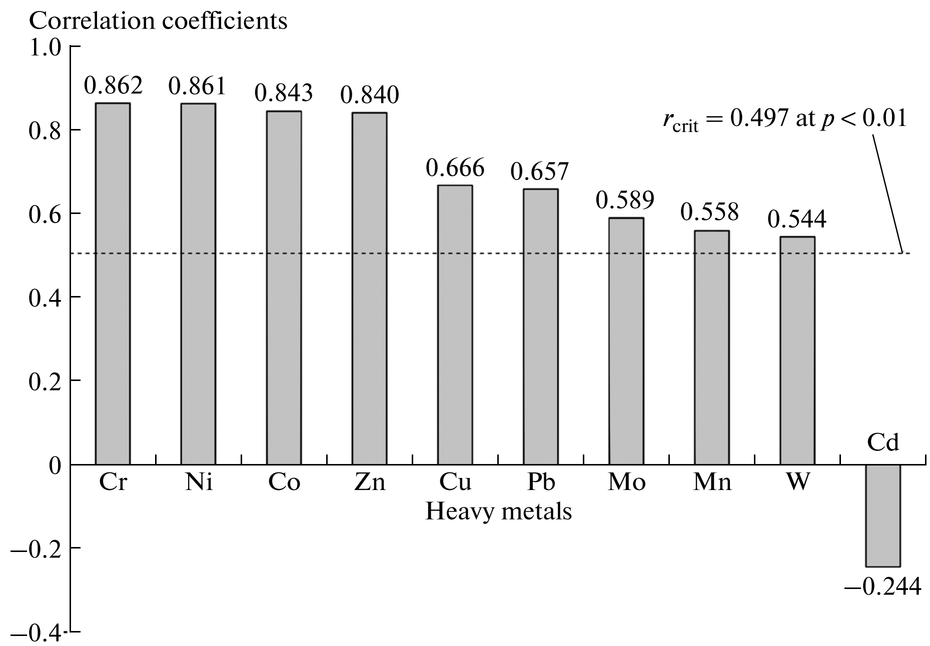

Fig. 2. Correlations between the concentrations of Li and heavy metals in bottom sediments from the littoral zone of Lake Ladoga.

close to the background level, with a median of 0.32 ppm. The high level of accumulation of other heavy metals (Pb, Zn, Cu, and W) in the samples provides clear evidence for the technogenic influence on the hydroecosystem of the North Ladoga area. There is a significant correlation of Cd with Zr in all samples studied ($r_{Cd-Zr} = 0.99$, $p < 0.01$), especially for BSs of Lekhmalakhti Bay, Lunkulansaari Island, and Khunuka Peninsula, where the concentration of Zr in the samples of BSs ranges from 135 to 1998 ppm, with a median of 1116 ppm (Fig. 3).

The behavior of Cd similar to that described above was previously observed during study of BSs from water reservoirs of Petrozavodsk located on the shore of Lake Onega, another large water reservoir in Europe [5, 6]. The studies showed that the high concentrations of Cd had a poor influence on the ecology of the regulated city watercourse, in particular, on the

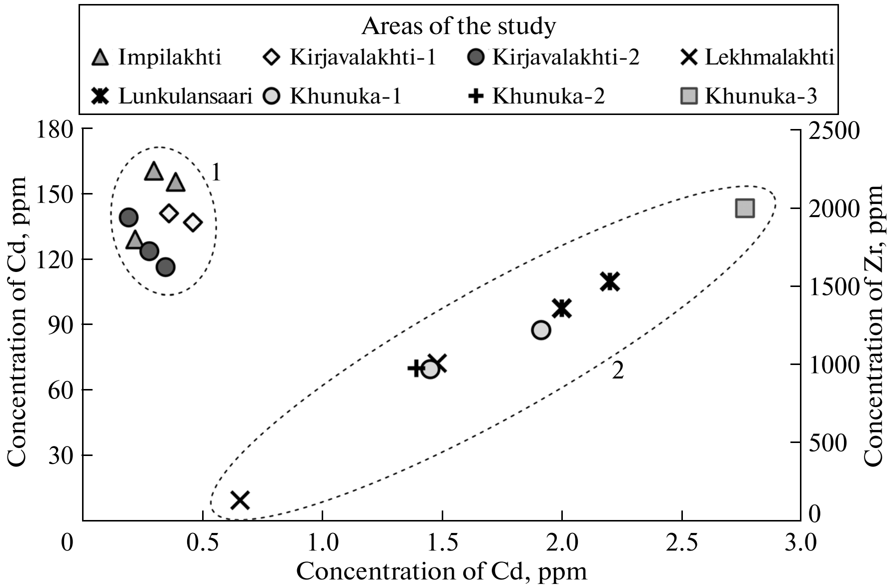

Fig. 3. Cd–Zr binary diagram illustrating the differences in chemistry of two groups of bottom sediments from the littoral zone of Lake Ladoga. The left scale of Zr concentrations is given for points in area (1); the right scale, for points in area (2).

species diversity of diatomic flora of the Lososinka River [8]. The Cd anomaly (4.0 ppm) was registered in BSs from the southern part of Lake Onega. This anomaly is not verified by numerous finds of sphalerite (or other sulfides) in heavy fractions, which does not agree with the classic ideas on the natural isomorphism between Cd and Zn. Note that this sample is represented by sand of lake–glacial origin with a high concentration of zircon $ZrSiO_4$ from the heavy fraction of sediments.

A glacial and most likely zircon "sign" was also registered for Cd anomalies (up to 3.55 ppm) in the horizon of surface–podzolic soils of Karelia abundant on fluvioglacial deposits [9]. Extremely high concentrations of Cd in BSs of the littoral zone of Lake Ladoga, in Lekhmalakhti Bay, Lunkulansaari Island, and Khunuka Peninsula are associated with surface outcrops of sandy and sandy loam (with pebbles and boulders) fluvioglacial Pleistocene formations of the Valdai superhorizon [10]. The shore line in the Kirjavalakhti-1, Kirjavalakhti-2, and Impilakhti areas is composed of Archean and Proterozoic rocks, which stimulates predominant deposition of aleurite and shale in the littoral area of the lake.

The behavior of Cd in BSs from the western part of Lake Ladoga is an insoluble problem in the study of E.A. Petrova [4]. A high concentration (50% and higher) of this minor element was registered in poorly soluble residue in comparison with the bulk concentration of Cd in the samples studied, which may provide evidence for its mineral (zircon?) nature, with account for the significant influence of glacial deposits on the formation of the shore line, littoral zone, and bottom of the western part of Lake Ladoga [10].

Why is Cd associated with zircon?

As is evident from [11], the concentration of Cd in hydrothermal zircons from ore-bearing amphibolite from the Belomorian mobile belt (North Karelia) ranges from 73.7 to 777.6 ppm of mineral grain weight. Such high concentrations of Cd have never been registered in zircons (personal communication of the author of [11]). In this case, Cd is an impurity in Karelian zircons formed during the long-term hydrothermal process, which accompanied intense magmatic and metamorphic activity on the territory 1–3 b. y. ago. The unique finds of native Cd in the North Tirvas deposit in Karelia are also the product of hydrothermal activity in the area of the Koikar structure composed of magmatic rocks [12]. It is mentioned that BSs of the Pacific Ocean enriched in Cd are localized in zones with significant volcanic and hydrothermal activity [13]. More than 60% of natural Cd annually entering the Earth's atmosphere from various sources is controlled by modern volcanism of the planet [1]. The concentration of Cd in magmatic and volcanogenic–sedimentary rocks of the shore line in the studied regions of Lake Ladoga is low, ranging within 0.03–0.51 ppm; however, Fig. 4 shows the correlation between Cd and Zr in the rocks studied.

Because of the high resistence of zircon to weathering, the mentioned correlation is clearer in modern sediments of the Quaternary cover in Karelia, whereas Cd seems to be "conserved" in the isolated mineral system. Most likely, this does not allow Cd to exert a toxic influence on living beings [8]. The study of the benthos of the areas of Lake Ladoga mentioned did not reveal any qualitative or quantitative changes of communities of organisms in the samples with anomalous concentrations of Cd. This phenomenon was observed in other areas of North Russia, in the Komi

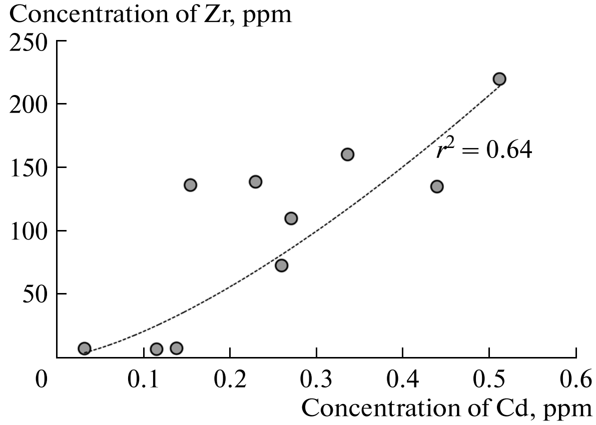

Fig. 4. Correlation between the concentrations of Cd and Zr in native rocks on the shore line of North Ladoga.

Republic. The concentrations of Cd in BSs from the rivers of the basin of the upper and middle reaches of the Pechora River vary from 2 to 30 ppm. Most of the samples of river sediments were collected on the territory of the Pechora-Ilych Nature Reserve, which excludes the anthropogenic nature of such high concentrations of Cd [14]. Because of this, with account for intense exaration glacial activity in northern latitudes stimulating abundance of natural Cd anomalies, the problem discussed in [14] exceeds the limits of the water reservoir, the Lake Ladoga basin, and the entire Karelian region.

Thus, the results of our study provide evidence for the natural origin of Cd anomalies registered in sediments from the littoral zone of the northern part of Lake Ladoga. Among the major factors stimulating intense accumulation of Cd are the volcanic activity on the territory of modern Karelia 1–3 b. y. ago, zircon mineralization with Cd impurities, the resistence of zircon to weathering, and genetic relationships with glacial deposits. It is necessary to be wary with the high concentrations of the heavy metal studied in BSs of Lake Ladoga and not to point unambiguously to its ecological danger.

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