

The biogeochemical system of chemical elements distribution in the hydrosphere

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The chemical elements composition of the oceanic water is a result of substance migration and transformation on river-sea and ocean-atmosphere boundaries. Stability of these processes is the main condition of the hydrosphere ecosystems stability. Detailed studies revealed three types of chemical element distribution in the ocean: 1) Conservative: concentration normalized to salinity is constant in space and time; 2) Nutrient-type: element concentration in the surface waters decreases due to the bio-consumption; and 3) Litho-generative: complex character of distribution of elements, which enter the ocean with the river runoff and interred almost entirely in sediments. The correlation between the chemical elemental compositions of the lithosphere and ocean is relatively weak ($r = 0.68$) while for river and oceanic water it is high ($r = 0.94$).

In our presentation, we shall show intensities of global migration and average concentrations in the ocean in the coordinates $\lg C_{\text{ocean}} - \lg \tau_{\text{ocean}}$, where C_{ocean} is an average element concentration and τ_{ocean} is its residence time in the ocean. In this plot elements form groups reflecting the similarity of their properties. The System indicates an existence of the relationship between three main geochemical parameters of the dissolved forms of chemical elements in the hydrosphere: 1) average concentration in the ocean, 2) average concentration in the river runoff and 3) the type of distribution in oceanic water. This allows using knowledge of two of these parameters to gain theoretical knowledge of the third. Finally, the mean concentrations of elements and patterns of their distribution in the ocean can be used to determine pre-techno-generative concentrations of elements in the river runoff [1, 2, 3].

[1] Korzh (1974), *Journal de Recherches Atmospheriques*, **8**(3-4), 653-660. [2] Korzh (2008), *J. Ecologica* **15**, 13-21. [3] Korzh (2012), *Journal of water science and its practical application* **1**, 56-62.

Accumulation mechanisms and bonding of high-tech metals in marine ferromanganese crusts

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Marine ferromanganese crusts (Fe-Mn crusts) are abundant throughout the global ocean and provide a potential economic resource for a wide range of rare metals for high technology applications. Understanding the geochemical processes that govern the interactions of these rare metals with natural Fe-Mn oxides has far reaching implications that span the range from global-ocean geochemical balances to the development of new techniques for extractive metallurgy. In our project we used synchrotron-based XANES spectroscopy to assess oxidation states in natural samples and samples in which metals were sorbed onto synthetic and natural Fe and Mn oxides. EXAFS spectroscopy was used to resolve the local structure around the metals in these same samples. We focussed on the metals Te, Pt, Mo, Zr, and Pb.

Our results confirm that Te is largely Te(VI) in Fe-Mn crusts and predominantly bound to FeOOH by inner-sphere complexation. For most model compounds, most Te(IV) transformed into Te(VI) during sorption. These data confirm that oxidative surface adsorption is the process responsible for the extremely high enrichment of Te in crusts (up to about 200 ppm) as compared to seawater. Since Pt concentrations are too low in natural Fe-Mn crusts, we investigated Pt only on sorption samples. As for Te, the results suggest that during uptake of Pt(II) from seawater a surface oxidation to Pt(IV) on the crusts takes place, explaining the high enrichment of Pt in crusts (up to 1-3 ppm). Of the model compounds, especially Mn oxide was very effective in oxidizing Pt(II). Molybdenum (as Mo(VI)) shows a strong association with the Mn oxide phase of crusts, while in sorption and sequential leaching experiments it also strongly binds on FeOOH. Lead displays a complex distribution, especially in phosphatized crusts, where it seems to form insoluble phosphate compounds. Zirconium was found to be bound as Zr(IV) to both FeOOH and MnO₂ phases, in contrast to the expected predominant binding to FeOOH. A more detailed evaluation of the spectra is presently carried out to resolve open questions.