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Geochemical and Mineralogical Studies of Fe-Mn Nodules and Crusts from the White Sea: Potential Role of Benthic Fauna in their Formation

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Sediments from the deep part of the White Sea are enriched in Mn (up to 5%), despite the fact that they are mainly terrigenous in origin. Comprehensive geochemical investigations conducted in this area correspond to the period of 1920-60's (Nevessky et al., 1977), but there are very few recently published data.

In summer of 1999 during cruises of R/V *"Professor Vladimir Kuznetsov"* samples from the five stations in the Kandalaksha Bay of the White Sea were collected by multiple corer. Contents of REE, Mo and W were determined by ICP-MS (VG Plasmaquad) and Fe, Mn, Al by AAS. Labile forms of these elements were analysed after the extraction of samples by 1 M $NH_2OH*HCl$ + 35% CH_3COOH during 4 hour period. The mineral composition and internal structure of Fe-Mn aggregates were determined by reflecting microscopy and analytical transmission electron microscopy.

Fluffy surface layer and more dense underlying sediment form an important geochemical interface, where microbial processes of Fe and Mn oxidation are most active. Different Fe-Mn aggregates were found at this interface: flat ferruginous concretions (19.2% Fe), Mn micro-concretions (28.4% Mn), Mn crusts on the shells of bivalves *Portlandia arctica* and *Yoldia hyperborea* (26% Mn), Fe-Mn oxide films on the tubes of polychaete *Pectinaria hyperborea*, and spherical Fe-Mn concretions (up to 37% Mn). Mineralogical studies have shown that analysed ferruginous concretion consists of poorly ordered 2-line ferrihydrite. Form of oxide particles points to their bacterial origin. Mn micro-concretions and tubes of *Pectinaria* contain vernadite and Fe-vernadite, Mn-crusts on bivalves and spherical Fe-Mn concretions consist of poorly ordered birnessite with admixture of Fe-vernadite and ferrihydrite. Chemical composition, mineralogy and structures of Mn nodules show that they can grow from Mn crusts previously formed on bivalves. Manganese crusts on live *Portlandia* reach 3 mm in thickness. Assuming that the age of mollusc can hardly be more than 10 years, growth rate of Mn crusts is estimated as >0.3 mm/year.

Bulk contents of REE in Fe-Mn aggregates are lower than in associated sediments. Sediments are characterized by a smooth REE pattern, which is in general shale-like except of (light REE)/(heavy REE) slope whereas all Fe-Mn aggregates are relatively depleted in cerium. Increased LREE/HREE ratio of sediments can be inherited from the composition of source rock provenance, which consists predominantly of acid rocks. Negative Ce anomaly reflects probably diagenetic rather than hydrogenous origin of oxides of Fe and Mn. Distinctive positive Eu anomaly in the composition of *Pectinaria* tubes is probably due to the high content of feldspars in tube material. Though contents of Fe and Mn are lower in these tubes than in associated sediments, the major part of these elements present in tubes are in the form of very reactive oxides. Tube walls are built mainly from sandy particles, which are not significant carriers of most REE except of Eu. Therefore, negative cerium anomaly, which is typical for diagenetic oxides, appears, because it is not masked by shale-like pattern of REE sorbed onto clay minerals. In acid hydroxylamine extracts negative Ce anomaly is more distinctive and Eu does not show anomalous distribution, because the extraction releases REE mainly from poorly crystallized oxide phases.

Unlike REE, molybdenum enriched Fe-Mn crusts and concretions of the White Sea (up to 734 ppm). Strong correlation between Mo and Mn contents was observed for oxide aggregates and surface sediments (r=0.998, n=10). The parameters of the regression curve are within the range of calculated parameters of Mo-Mn correlation in oceanic Fe-Mn nodules (n=276) and Mn crusts (Strekopytov, 1998). Strong Fe-P correlation was observed for the hydroxylamine-extractable fraction of samples, average P/Fe molar ratio is about 0.4 that can point out the presence of separate iron-phosphate phase.

Observation of the material, which was dredged by detritus sledge, has shown that Fe-Mn encrustations forms on the surface of living organisms rather than on rock debris, which is abundant at the bottom of the White Sea. This indicates the essential role of benthic organisms in the accumulation of iron and, especially, manganese and, therefore, in the formation of Fe-Mn concretions.

Nevessky EN, Medvedev VS & Kalinenko VV, *The White Sea: Sedimentogenesis and Holocene development. Moscow, Nauka*, (1977).
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