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Biomorphic structures in ferromanganese nodules

G. Lysyuk
Institute of Geology RAS, Syktyvkar, Russian Federation (lol310776@gmail.com)

Manganese oxides, which are widespread and of great practical importance, are formed and transformed by an active role of microorganisms. Finely dispersed Mn oxides are the most abundant in oceanic ferromanganese nodules (FMNs) and in products of weathering on land. Nanosized phases in pelagic FMNs from the Pacific Ocean and the shelf zone of Baltic Sea were objects of this investigation.
Numerous relics of planktonic organisms often replaced by Mn oxide as coating films were iden¬tified in the inner zones of FMNs. X-ray amorphous Mn oxides are widespread in FMNs. As follows from SEM examination, these phases are mineralized glycocalyx. Experiments on high-temperature transformations made it possible to identify this phase as todorokite, and SEM images indicate that todorokite was formed under the influence of bacterial activity. A cyanobacterial mat detected in the interlayer space of nodules is additional evidence for the participation of bacteria in nodule growth and the formation of finely dispersed Mn minerals. The chemical composition of this cyanobacterial mat is as follows (wt%): 48.35 MnO, 6.23 $Fe2O_3$, 8.67 MgO, 5.05 $A12O_3$, 4.45 SiO_2, 3.63 NiO, 2.30 Na2O, 2.19 CuO, 1.31 CaO, and 0.68 K2O.
The SEM examination of the inner zones of FMNs allowed detection of numerous biofilms in the interlayer space of nodules. These biofilms are composed of fusiform, rod-shaped, and coccoid bacteria and their filamentary cover. The bacterial mass is composed of (wt %) 28.34 MnO, 17.14 $Fe2O_3$, 7.11 SiO_2, 2.41 CaO, 7.90 TiO_2, 1.74 Na2O, 1.73 $Al2O_3$, 1.30 MgO, 1.25 P2O5, 1.25 SO_3, 0.68 CoO, 0.54 CuO, 0.53 NiO, and 0.50 K2O. Thus, the chemical composition of cyanobacteria and bacterial mass of biofilms corresponds to Mn oxides.
Inclusions of native metals were found in FMNs and Mn-bearing zones of weathering. Numerous copper red and brass yellow metal lamellae, flakes, and dendrites in FMNs were identified by a microprobe as native copper and intermetallic compounds of Cu and Zn (brass yellow grains). Fe-Cu compounds and pure Fe are less abundant. In addition, sporadic grains of native Al and Zn were found. The occurrence of native metals can beexplained by segregations of organic matter that served as microscopic domains with highly reducing conditions.
Electron microscopic investigations displayed presence of many inclusions with high concentration of radioactive elements ($Y2O_3$ up to 2.19%, ThO_2 from 5.45% up to 7.09%, UO_3 from 36.28% up to 50.72%, PbO from 9.96% up to 13.96%, $Ce2O_3$ up to 1.24%). Besides this, nano-scale thorite grains with globular structure were found out (content of V2O5 – 0.97-4.80%, $Ce2O_3$ – 1.09-4.21%, $Nd2O_3$ – 1.24-5.81%, ThO_2 – 19.27-31.99%).
We can propose that lamination of Fe-Mn minerals provided capture of radioactive particles in consequence of high active area and to enough hollow space in frame structure. High sorption properties of FMN of the shelf zone of Baltic Sea allow to use them as indicators of environmental changes for ecological monitoring.
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