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FERROMANGANESE ORE FORMING PROCESSES IN THE INDIAN OCEAN AS A CHARACTERISTIC FEATURE OF OCEANIC SEDIMENTOGENESIS

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ЗАЛІЗО-МАРГАНЦЕВЕ РУДОНАКОПИЧЕННЯ ІНДІЙСЬКОГО ОКЕАНУ ЯК ХАРАКТЕРНА РИСА ОКЕАНІЧНОГО СЕДИМЕНТОГОНЕЗУ

Generalized data about morphology, distribution, chemical and mineralogical compositions of ferromanganese deposits of the Indian Ocean such as: concretions, microconcretions, crusts, and crust's similar sediments were presented. Manganese ore accumulation process in all its forms, as a characteristic feature of oceanic sedimentogenesis, by reexamination of existing data about mineralogical composition of oceanic ferromanganese deposits was newly evaluated. Mineralogical types of ferromanganese deposits were determined on the basis of mineralogical analysis, determination of mineralogical associations and crystal- chemical features of minerals, which constitute these deposits.
Keywords: mineralogical and chemical composition, ferromanganese deposits, the Indian Ocean.

Наведено узагальнюючі дані з розповсюдження, морфології, хімічного і мінерального складу залізо-марганцевих утворень Індійського океану: конкрецій, мікроконкрецій, корок, коркоподібних утворень. Переосмислення наявних даних про мінеральний склад океанічних залізо-марганцевих утворень дозволяє по-новому оцінити марганцеве рудоутворення у всіх його проявах, як характерну рису океанського седиментогенезу. Аналіз мінерального складу утворень різного генезису дозволив виділити їх мінеральні типи, грунтуючись на мінеральних асоціаціях і кристалохімічних особливостях мінералів, що їх складають.
Ключові слова: мінеральній склад, залізомарганцеві утворення, Індійський океан.

INTRODUCTION

Ferromanganese deposits are currently among the World Ocean's mineral resources, which attract special attention because they are the source of cuprum, nickel, cobalt and manganese and some other elements. Ferromanganese deposits are divided into ferromanganese concretions, crusts and microconcretions and can be of different origin (hydrogenetic, diagenetic and hydrothermal). The main attention was focused on the study of crusts and concretions of the Pacific Ocean. The deposits of the Indian Ocean are less studied (Skornyakova et al., 1989, Skornyakova et al., 1990, Smetannikova et al., 1991, Shyukov et al., 2001, Bogdanova et al., 2008, Banakar et al., 2000, Chiranjeeb Sarkar et al., 2008). The main attention was addressed to ferromanganese concretions while data about microconcretions and crusts are rather scarce in works dedicated to the Indian Ocean.

Intensive study of geology of the World Ocean for more than half a century has yielded in many discoveries, which in many aspects changed old notions about geology of the planet in general. However, the main theoretical questions in the problem of oceanic ore genesis have not been solved yet. Moreover, the interest somehow has decreased recently and practical aspects connected with extraction of the mineral deposits of the ocean bottom have become more actual.

At the present ferromanganese concretions, microconcretions and crusts are considered as one unit of the oceanic sediment and ore genesis. The study of the problems of oceanic ore genesis requires clarification of all of its results including crusts and microconcretions.

Crusts grow only as the result of direct precipitation of hydrogenic and/or hydrothermal matter from oceanic water; concretions originate either from direct precipitation or a diagenetic supply from surrounding deposits and interstitial water.

Microconcretions, which can be encountered in pelagic sediments more often than concretions, originate from diagenetic nourishment from surrounding sediments and interstitial water.

Existing notions about origin of various forms of ferromanganese deposits (sedimentological, diagenetic and hydrothermal) reflect, first of all, information about the source of ore matter and in less degree reveal mechanisms of origin of these ores (Shnyukov et al., 2001, Suchkov, 2012, Shkolnik et al., 2012).

STUDY AREA, METHODS AND RESEARCH OBJECT

Samples of ferromanganese deposits were collected in the course of survey in the Indian Ocean (Scientific Research Vessel «Antares», leg № 1, 2, 3, 5; Scientific Research Vessel Feodosiya»). Detailed investigations of mineralogical and chemical compositions, morphology and inner structure were carried out. The object of this research is the samples of ferromanganese concretions, buried concretions, microconcretions and ferromanganese crusts and crusts-like deposits of the Central and

Western-Australian basin, Eastern-Indian ridge and the area of triple junction of Middle Indian ridges of the Indian Ocean. The classification of these deposits which is used in Odessa University is listed in Shnyukov et al. (2001).

The main characteristics of the mode of occurrence, morphology, chemical and mineralogical compositions of the studied ferromanganese deposits of the Indian Ocean are listed in previously carried out research (Suchkov et al., 1988, Smetannikova et al., 1991, Suchkov et al., 1991, Suchkov et al., 2000, Shnyukov et al., 2001, Suchkov, 2012).

The study of inner structure of ferromanganese deposits was carried out by analyzing of polished sections under the binocular. X-ray diffractometry method was applied in order to study mineralogical composition. The diffractometer DRON-3 was used. Chemical composition of ferromanganese deposits was determined by means of atomic absorption method, using the ASS-3 equipment.

Determination of the phases and quantitative analysis of mineralogical phases' composition was carried out on the basis of high quality diffraction data.

Enhanced methodic for diagnostics of manganese minerals was used (Suchkov et al., 1988, Skornyakova et al., 1989, Smetannikova and Frank-Kamenetskiy, 1989). This methodic is based on different behavior of manganese hydroxide's crystal lattice when these minerals experience dehydration under the influence of increasing temperature.

RESULTS AND THEIR ANALYSIS

Ferromanganese deposits of the Indian Ocean have characteristic chemical composition and can be distinguished by the mineralogical composition. Variations of chemical and mineralogical composition of these deposits in the frame of one type as well as in different regions of the Indian Ocean can be observed.

Concretions with the large globular structure of the surface (type I) can be encountered in the Central basin of the Indian Ocean. These deposits are characterized by high ratios of Mn/Fe (>4) and have cuprum-nickel geochemical specialization (sum of Cu, Ni, and Co is up to 2%). Ore material consists of manganese phase with layered structure and labile interlayer space (mixed layer asbolan-buzerit, buzerit).

Concretions with fine globular structure of the surface (type II) are widely distributed and can be encountered within eastern part of the Indian Ocean (the Central, Western-Australian basin, Eastern-Indian ridge). Average ratio values of Mn/Fe (>1.5) as well as cobalt-nickel geochemical specialization (sum of Cu, Ni, Co content is up to 2%) are the main characteristic features for these deposits. Ore substance consists of manganese phase with layered structure and labile interlayer space (buzerit, mixed layer asbolan-buzerit). Hydrated mineral type represented by not stable buzerit can be encountered in the outer zones of the concretions.

Concretions with smooth structure of the surface (type III) are spread on the surface of all Indian Ocean, but their matter composition varies in the western and eastern parts of the ocean. In the western part of the ocean concretions are characterized by low ratios of Mn/Fe (<1, rare the value is up to 1.4) and low content of Cu, Ni and Co (sum <1%), in concretions of the eastern part of the ocean, values of Mn are not significantly higher than Fe content (<1.5) and not high values of Cu, Ni and Co (sum < 1.5%) have cobalt-nickel geochemical specialization. In the western part of the ocean these concretions consist of vernadite (which has pseudobedded crystal structure) and gothite. In the eastern part, the concretions of this type consist of vernadite and manganese hydroxide with layered structure (not stable buzerit, mixed layer asbolan-buzerit).

Zonality in chemical and mineralogical composition can be observed in some ballstones. From the outer layers of concretions toward the nucleus decrease of content of such elements as manganese nickel and cuprum content is observed along with increment of iron content. These changes are connected with the variations of non-metal material in zones of grows of the concretions; with iron concentration in muddy and siliceous matter, as well as with enrichment with iron of initial phases of ore matter. Thus, in the outer layers of concretions of the Central basin the quantity of ore substance is 64.8%, close to the nucleus zones its concentration decreases to 46.8 %. The distribution of minerals has concentric zonal character in ferromanganese concretions, in some ballstones and vertical asymmetry in the variation of mineralogical composition can be observed as well. Outer zones of concretions consist of the most hydrated kinds of manganese minerals which are characterized by less perfect crystal structure (not stable buzerit and buzerit I). The central zones of concretions and zones, which are close to the centre are constituted by more steady mineral phases with regular crystal structure (buzerit II, mixed layered asbolan-buzerit). Such type of the distribution of the minerals within some ballstones can be explained by solid phase transformations of manganese phases (Suchkov, 2012).

Buried horizons of concretions are wide spread in general in the Indian Ocean and were described within many fields, which are covered with concretions. The quantity of buried horizons is up to 4 and they are often correlated with the boundary between different lithological types of sediments. Morphology of buried concretions is very similar to those concretions, which lie between the sediments and water as showed the data obtained from the same stations. The dominant size of buried concretions is 10-40 mm, also, concretions with size up to 60 mm can be encountered. Concretions with globular and rounded shape with knobby surface are dominant. Chemical composition of buried concretions is not different much from those, which lie on the surface of the bottom. Mineralogical composition of buried concretions is represented by 10 Å manganese minerals with layered structure (mixed layer asbolan-buzerit, buzerit II) and vernadite in the eastern part of the ocean. Vernadite and gothite are the main minerals of the buried concretions in the western part of the ocean (area of the triple junction of mid-ocean ridges). Stability of phase composition of the material of buried concretions is a characteristic feature of deposits in a sedimentary sequence. In general the characteristic feature of buried concretions is absence of zoning in the distribution of manganese minerals. Mineralogical composition of buried concretions corresponds to mineralogical composition of nucleolus part and areas, which lie close to the nucleolus area of concretions, which lie on the bottom surface.

Microconcretions are widespread in the bottom sediments of the Indian Ocean. Maximum content of microconcretions is correlated with mud and siliceous-clayey mud in the eastern part of the ocean. Microconcretions are interbedded with calcinated and clayey-calcinated sediments and often can be found together with horizons of metalliferous deposits in the western part of the ocean (the region of the triple junction of mid-ocean ridges). The dominance of multi-nucleus micro clots and botryoidal forms is a characteristic feature of microconcretions. Besides irregular botryoidal forms microconcretions can be encountered in a form of tubes in the western part of the ocean. Chemical composition of microconcretions of the eastern part of the ocean are attributed to nickel-manganese geochemical specialization and can be characterized by considerable dominance of manganese over iron (Mn/Fe > 0.5, up to 18) and high content of Cu, Ni and Co (sum >3%), in general because of nickel (2% and more). Microconcretions of the western part of the ocean are mostly ferriferous and content of ore elements is close to previously discovered concretions in this area. The presence of such mineral as bernessit in microconcretions, along with common for concretions bezerite and asbolan-buzerit is noted in the eastern part of the ocean. The quantity of burnessit down in the sediemntological section becomes higher which can be connected to diagenetic transformations. The composition of the microconcretions in the western part of the ocean is the same as in the other parts of this area (vernadite and gothite).

Ferromanganese crusts in the Indian Ocean are distributed in all studied regions and cover the tops and lopes of mountains. Boulders and gravel and highly changed basalts are the main sediments which cover these areas. The thickness of these deposits is up to 4 cm (up to 5 cm in the area of the triple junction of mid-ocean ridges). Crusts which are underlain by lithified bottom sediments (filipsite and sepiolite) were discovered in the Central basin of the Indian Ocean (the area of Indrani fault). The shape of the crusts is determined by the shape of the substratum and the contact of the ore matter and the substratum is sharp. The surface is even and macrorelief of the surface is knobby. The crusts have thin-layered structure in the section. The crusts of the eastern part of the Indian Ocean are of manganese-iron type (Mn/Fe 0.7-1.5) and in the comparison with the concretions of this area the crusts are depleted with Cu and Ni, and content of Co is up to 0.5 % and they can be attributed to cobalt-depleted type. The crusts of the western part of the ocean have ferriferous composition (Mn/Fe 0.5-0.8) and low concentrations of Cu, Ni and Co. Ore matter of the crusts consists of vernadite.

Ferromanganese crust-like deposits are encountered in the western slope of the Eastern-Indian ridge. They have flattened shape or shape of irregular form with horizontal-layered or breccias-like structure. Ore substance of these deposits according to their structural, chemical and mineralogical properties can be divided into two groups: sedimentological and hydrothermal origin (Suchkov et al., 1991). Ore matter of the first group consists of about 10 minerals with layered type of crystal structure and mobile interlayer space (buzerit, mixed layer asbolan-buzerit). Ore material of the second group consists of bernessit (which has layered type of crystal structure) and by manganese minerals with tunnel type of crystal structure (pirolyuzit and todorokit).

DISCUSSION AND CONCLUSIONS

Currently ferromanganese concretions, microconcretions and crusts are considered as the sequence of one uniform sediment- and ore-genesis processes.

Crusts grow mainly as the result of direct precipitation of hydrogenetic and/or hydrothermal matter from oceanic water, concretions are formed under the influence of direct precipitation and as a sequence of diagenetic supply from surrounding sediments and interstitial water. Microconcretions, which can be encountered in pelagic sediments more often than concretions, originate from diagenetic nourishment from surrounding sediments and interstitial water. Accumulation of such elements as nickel, cuprum and cobalt in hydroxides of manganese and iron may occur due to sorption (Novikov et al., 1990). Contribution of microorganism function into the processes of concretion and microconcretion formation can be essential (Shkolnik et al., 2012). On the one hand, microorganisms can locally change physicochemical parameters of minerogenesis's environment, and on the other hand, microorganisms are able to concentrate non-ferrous metals.

Analyses of existing hypothesis of origin of ocean ferromanganese deposits was carried out by Shnyukov et al., (2001), where was suggested that sedimentological and sediment – diagenetic processes play an important role in origin of ferromanganese deposits of the Indian Ocean. The sources of ore forming components are ridge zones of the ocean, from where ore material is transcended by bottom currents. Apparently, in addition to the sources of endogenous matter, magmatism and hydrothermal activity should be added. Hydrothermal activity and magmatism take place outside spreading zones in the Indian Ocean (Eastern-Indian ridge, the area of Indrani fault in the Central basin etc.).

Previously carried out research of ferromanganese deposits of different origin in the Indian Ocean showed that the most widespread manganese minerals are 10 Å minerals with the layered type of structure (not stable buzerit, buzerit I, buzerit II, mixed layer asbolan-buzerit), bernessit, todorokit and pirolyuzit. The two latter can be encountered only in hydrothermal sedimentary crusts of the Eastern-Indian ridge. Gothite can be observed among the minerals of iron in some ores. It was revealed that every type of ferromanganese deposits (with a certain characteristic of chemical composition, morphology and inner structure) is characterized by a certain set of manganese minerals. Thus, the probability to encounter one or the other type of manganese hydroxide and its crystal-chemical features can be used as typomorphic indicator of ferromanganese deposits.

The distribution of different types of ferromanganese deposits in the Indian Ocean according to their chemical composition and mineralogical association data are depicted in the figure 1. Analysis of the distribution according to mineralogical associations and peculiarities of ore's chemical composition make it possible to group mineralogical types of oceanic ferromanganese deposits of the Indian Ocean. These groups are as follows:

<u>The first group</u>. Microconcretions which have the best organized crystal-chemical phase with layered type of the crystal structure (bernesite and as an admixture – buzerit with layered type of the crystal structure as well). These deposits are distributed in the Central and Western-Australian basins. Concretions of the Central basin have large globular structure of the surface (type I), their main components are manganese hydroxides with layered type of the crystal structure and mobile interlayer space – buzerit, mixed layer asbolan-buzerit. Ferromanganese deposits of this mineralogical type originate due to diagenetic supply of ore matter from the surrounding sediments and interstitial water.

<u>The second group</u> consists of the concretions with fine globular structure of the surface (type II) which are spread in the Central and western-Australian basins and on the slopes of Eastern-Indian ridge. Manganese hydroxides with layered type of the structure and mobile interlayer space (bezerit and mixed layer asbolan-buzerit) are the main ore minerals of this mineralogical type. These deposits have mixed sedimentologic – diagenetic nature.

<u>The third group</u> is represented by concretions with smooth structure of the surface (type III) and crusts, which are wide spread in the Central and western-Australian basin and slopes of Eastern-Indian ridge. The main ore phase of these deposits is vernadite, which crystal structure is pseudobedded, manganese and iron cations have not even disposition in this structure. These deposits have sedimentological origin and the source of ore matter is marine water.

<u>The fourth group</u> consists of concretions, microconcretions and crusts which are distributed in the area of the triple junction of mid-Indian ridges. This

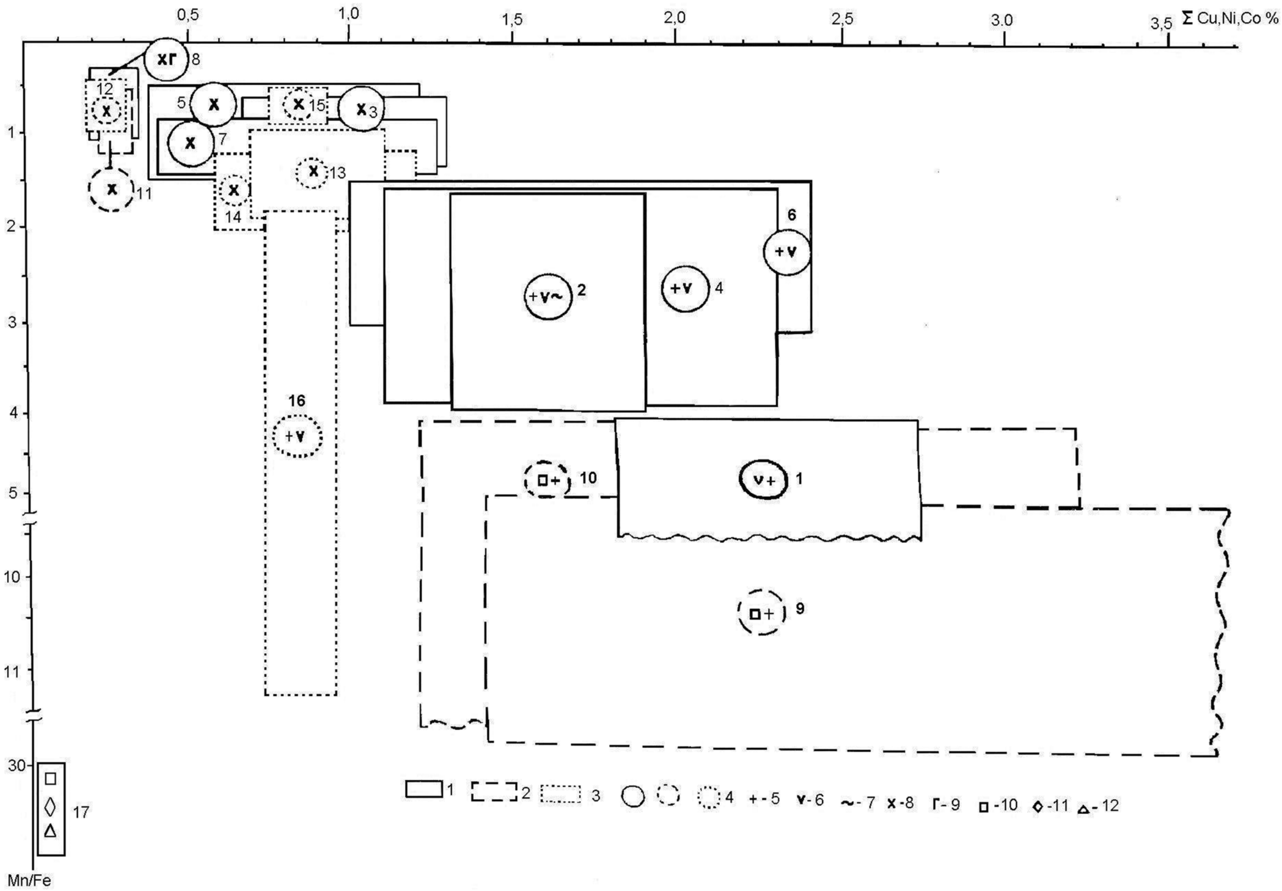

Fig. 1. Chemical and mineralogical composition of ferromanganese deposits of the Indian Ocean
1. concretions; *2.* microconcretions; *3.* crusts; *4.* mineralogical composition; *5.* buzerit I; *6.* asbolan-buzerit; *7.* buzerit II; *8.* vernadite; *9.* goethite; *10.* bernessit; *11.* todorokit; *12.* pyrolyusite.
Zone of distribution and types of ferromanganese deposits: *1-3* – concretions of the Central basin; *1* – I type (large globular structure of the surface); *2* – II type (fine globular structure of the surface); *3* – III type (smooth structure of the surface); *4,5* – concretions of the Western-Australian basin; *4* – II type; *5* – III type; *6-7* – concretions of the Eastern-Indian ridge; *6* – II type; *7* – III type; *8* – concretions of III type of the area of the triple junction of mid-ocean ridges; *9-11* microconcretions; *9* – the Central basin; *10* – the Western-Australian basin; *11* – the area of junction of mid-ocean ridges; *12-15* – crusts; *12* – area of junction of mid-ocean ridges; *13* – the Central basin (southern part); *14* – the Central basin (the Indrani fault area); *15* – the Eastern-Indian ridge (central zone); *16-17* – crust-like deposits of the western slope of the Eastern-Indian ridge; *16* – ore substance of hydrogenetic – sedimentological origin; *17* – ore material of hydrothermal genesis.

deposits consist of vernadite with pseudobedded crystal structure. Gothite is present as an admixture. These deposits have sedimentological and sediment-diagenetic nature. Differences of mineralogical and chemical composition of these deposits from the deposits of previous group are explained by the regional differences of ore matter from western and eastern parts of the Indian Ocean (Shnyukov et al., 2001).

Special place belongs to crust-like deposits of the western slope of the Eastern-Indian ridge. These deposits form the fifth group. The deposits create ore matter of two groups: the first one is represented by manganese minerals with layered structure and mobile interlaminar space – buzerit, mixed layer asbolan-buzerit. By the contrast with similar deposits of this area latter minerals are considerably enriched with manganese. Ore matter of the second group is represented by ordered phase with layered type of the crystal structure – bernessit, as well as by minerals with tunnel type of crystal structure – pirolyusit and todorokit. This ore matter is characterized by considerable enrichment with manganese and minute content of Cu, Ni and Cu. Ore matter of such composition has a hydrothermal origin, and the process of formation of the ore matter of the first group was under the influence of dilution of hydrothermal material, i.e. the genesis is mixed – sedimentological – diagenetic.

Thereby, mineralogical types of ferromanganese deposits, which were marked out, create following genetic sequence. Sedimentological (hydrogenous) deposits (concretions and crusts), which consist of iron and manganese hydroxides with irregular pseudobedded structure. Sedimentological – diagenetic ore deposits (concretions) are formed by manganese hydroxides with laminated type of crystal structure and mobile interlaminar space – buzerit, mixed-layer asbolan-buzerit. Diagenetic ore deposits (concretions and microconcretions) are formed by manganese hydroxides with layered type of crystal structure and mobile interlaminar space (buzerit, mixed-layer asbolan-buzerit) as well as arranged hydroxides with layered structure – bernessit. Hydrothermal sedimentary ore deposits are characterized by the presence of ordered layered hydroxides (bernessit), and also by separate manganese minerals with tunnel type of crystal structure. We suggest in this row an increment of the degree of order of manganese hydroxides even up to occurrence of the minerals with tunnel type of crystal structure from sedimentological deposits to diagenetic and hydrothermal ores.

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