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THE EARLY STAGES OF FERROMANGANESE ORE GENESIS ON THE GUYOTS OF THE MAGELLAN SEAMOUNTS (THE PACIFIC OCEAN)

Fe-Mn crusts play an important role in marine mineral-deposit research because of their widespread occurrence and high concentrations of valuable and rare metals. Most Fe-Mn crust deposits occur on the tens of thousands of seamounts found in the ocean. Data on the structure, texture, composition, age, and deposit characteristics will help define which factors are key for the creation of mineral accumulation and which combination of factors leads to the formation of potentially economic concentrations of metals. In this paper, we address the structure and characteristics of the oldest Fe-Mn crust stratigraphic sections (Late Cretaceous and Paleocene) collected from the Magellan seamounts.

A complete section of the crusts on the Magellan Seamounts includes four layers, each 2–4 cm thickness: the Late Paleocene (?)–Early Eocene layer I-1, the Mid-Late Eocene layer I-2, the Miocene layer II and the Quaternary layer III. In some cases, the main CMC section is underlain by relict layers. The chemical and mineral composition of the layers was determined both by X-ray diffraction and precision methods; concentrations of the main ore components and phosphorus were determined by the methods of classical chemistry.

The age of 12 samples was determined, the mineral composition of four, the chemical composition of 22 samples. The results of the relict layers analysis allow to distinguish two groups of samples among them. Among the relict layers, two age ranges are established — the second half of Late Cretaceous (R_1) and the first half of Paleocene (R_2).

High concentrations of barium, lithium, gallium, and zinc suggest that hydrothermal sources could be the source of the material. But not through direct delivery, but via the phase of transfer of sea bottom water.

Thus, the analysis of lithological and geochemical parameters and fossil fauna of foraminifera in the relict layers of the Magellan Seamounts ore section indicates two stages of their formation: Late Campan–Maastricht and Early Middle Paleocene. The discreteness of the formation of relict layers in time once again proves that the sharply changing environmental conditions controlled the growth of the CMC ore section.

Keywords: ferromanganese crusts, guyots of Magellan seamounts, Late Cretaceous and Paleocene.

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Introduction

A complex interaction of geological, biological, and hydrological processes takes place over the elevated areas of the ocean floor, which may control ore formation on the surface of seamounts. Studies demonstrate that the formation of ore crusts on the surface of guyots is a very long process, discrete in time [3, 5]. One of the objects is cobalt-rich manganese crusts on underwater elevations and mountains. This is a new type of solid minerals that surpasses land deposits in terms of a few chemical elements. The crusts often form solid covers of iron and manganese hydroxides, which lie on the outcrops of rocks on the surface of seamounts. In the most promising areas, the thicknesses of these covers reach 10–15 cm. The contents of the main components, %: Mn — 21–23, Fe — 16–18, Co — 0.5–0.6, Ni — 0.4–0.5, Cu — 0.1–0.2 [3]. In general, the crusts contain more than 70 elements of the Mendeleev's periodic system, of which Mo, TR, Pt, Te, Tl, etc. are considered as associated beneficial components.

To date, the number of studied in detail sections of ore crusts, and the data on the history of their formation, is insufficient to accept or deny the existing hypotheses of their origin. The introduction of new techniques in the practice of marine geological work offers great opportunities in the search and assessment of ore reserves in deep-water areas of the bottom of the oceans. In the north-western part of the Pacific Ocean, one of the promising areas for CMC mining is the guyots of the Magellan seamounts (Fig. 1). The Magellan seamounts — an arched chain of volcanic seamounts — divide the East Mariana Basin into the Pigafetta and Saipan troughs. In the west, they border the Mariana system of deep-sea trenches, and in the southeast — with the elevations of the Great Caroline and Marshall Islands. The linear length of the Magellan Seamounts of 1300 km and their location on an ancient section of the oceanic crust have long attracted the attention of researchers as an object for constructing various geodynamic modelling. The mineralization of the Magellan Seamounts region is spotty. It is due to the differentiated development of the crusts with different mineralization parameters and variations in the weight concentrations of ferromanganese nodules (FMN) in the intermountain depressions (Fig. 2). CMC are developed on the exposed surfaces of bedrocks, while FMN are confined to the zones of development of non-lithified sediments. The ores are localized within the seamounts at depths of 900 to 3500 m, on the surfaces with slopes of 0–5° to 12–20°. On steeper slopes, the formation of crusts is weak developed. The substrate of the crusts may be rocks of various compositions, exposed on the surface of the bottom. The thickness of the crusts varies over a wide range: from the first millimeters to the first tens of centimeters. Today, the crusts with a thickness of >4 cm are considered commercially valuable. The average thickness in the richest ore deposits is 10–12 cm. The CMC have a layered structure. A complete section of the crusts on the Magellan Seamounts includes four layers (Fig. 2), each 2–4 cm thick: the Late Paleocene (?) — Early Eocene layer I-1, the Mid-Late Eocene layer I-2, the Miocene layer II and the Quaternary layer III [5]. At the same time, in some cases, the main CMC section is underlain by relict layers, their age is estimated in a wide range. They have a mosaic-block structure and, in general, are rather heterogeneous in structure and composition. We have pre-established two-time intervals for the formation of the relict layer — Late Cretaceous and Paleocene. The accumulation of new data on CMC of the Magellan seamounts, especially by drilling cores, allows a closer look at the early stages of their formation. This report focuses on the structural features, the age and

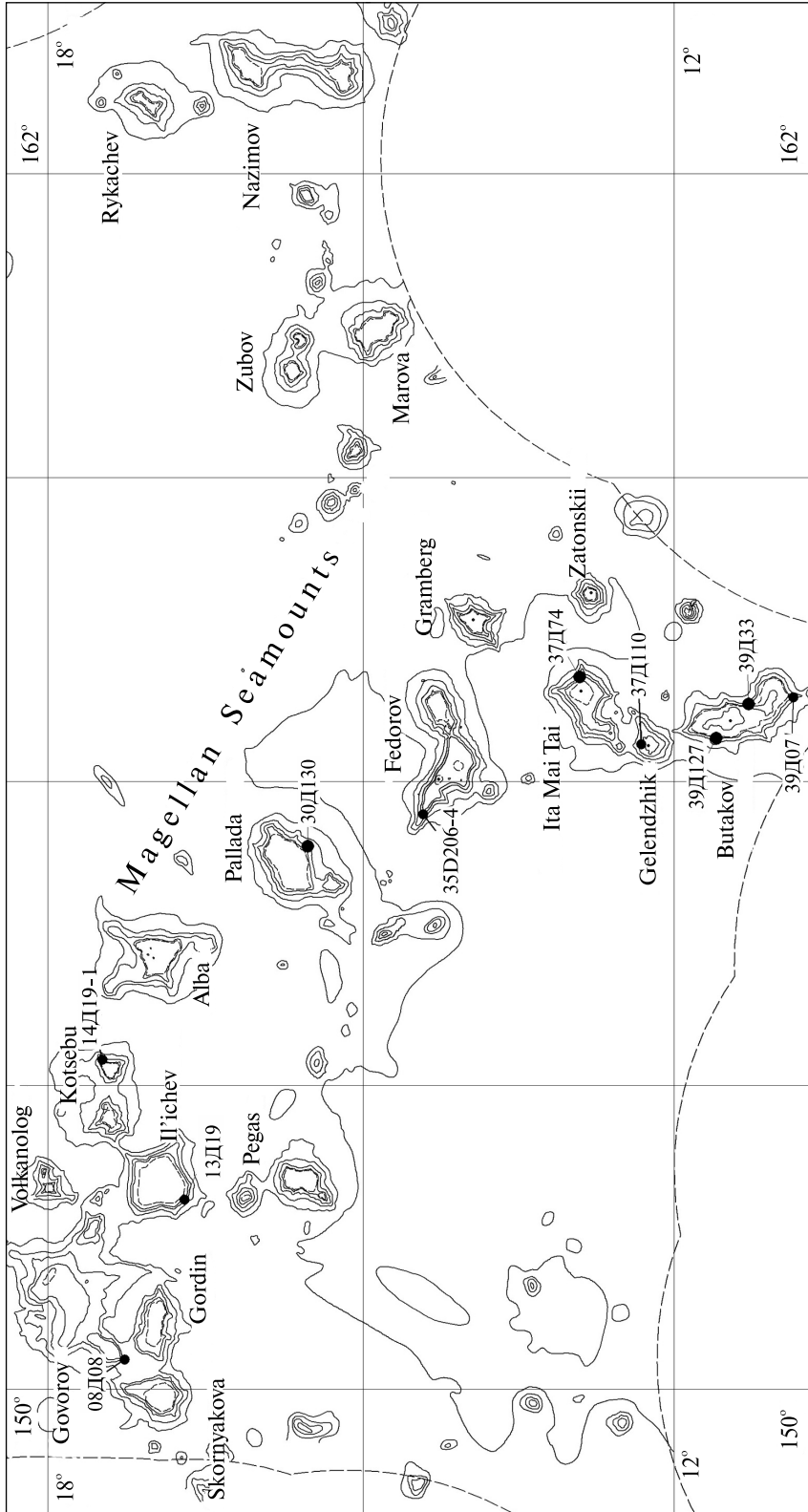


Fig. 1. The position of the guyots of the Magellan Seamounts

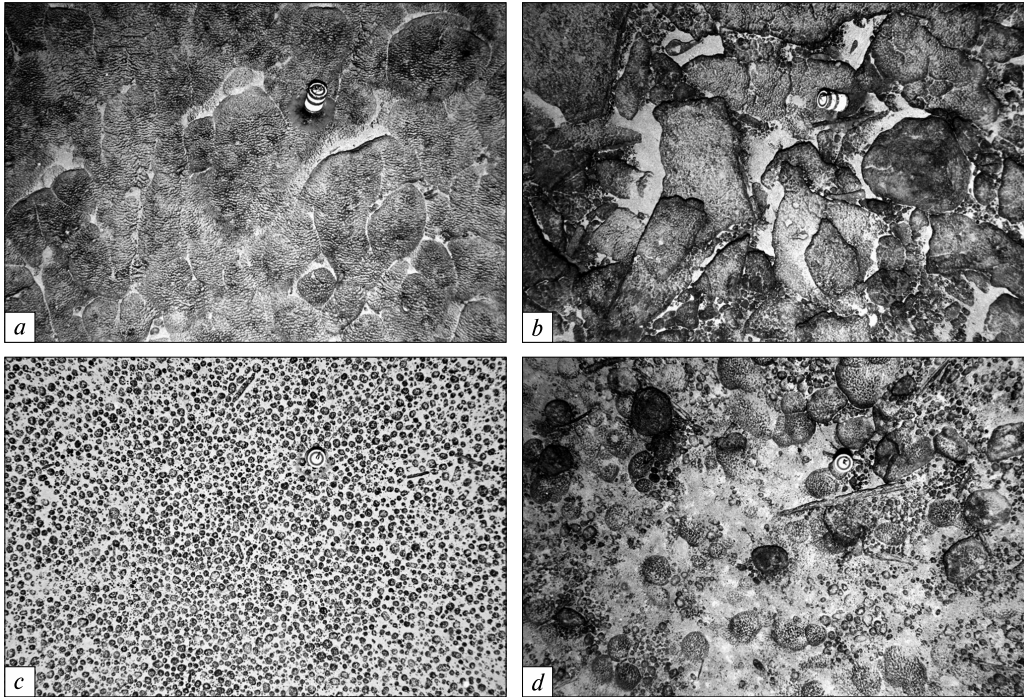


Fig. 2. Different types of mineralization within the range according to the results of photo profiling: *a* — continuous undamaged crust coverings free from sediment, 08F23, 12:24:23; *b* — crust covers of medium and high degree of disturbance, 08F29, 16:21:31; *c* — fraction nodule field from 3 to 6 cm on the surface of the peak plateau, 08F25, 13:06:29; *d* — small and boulder nodules associated with the cover of crusts, 08F41, 07:36:22

the conditions of formation of the most ancient layers of the ore section. They are interesting due the fact that they were formed in the most warm and shallow-water conditions compared to the layers I-1, I-2, II and III.

Materials and Techniques

Regular expeditions to the Magellan Seamounts had been carried out by the Dalmorgeologiya Company up to 1996 [4, 5, 11 etc.]. Since 2000, the work has been carried out by the SSC Yuzhmorgeologiya (after 2016, JSC Yuzhmorgeologiya) on board the R/V Gelendzhik targeted at the search and evaluation of the mineral reserves of cobalt-manganese crusts. The vessel is specialized in conducting geological and geophysical works in the ocean and is equipped appropriately. The comprehensive work during the expeditions was based on the following methods: bathymetric survey with a multi-beam echo sounding, geoacoustic, magnetic and photo-television profiling [4]. The bathymetric survey was carried out by a multi-beam echo sounder EM 12 S-120 by the Norwegian company Simrad.

The photo-television profiling was performed using the original Neptune photo installation at an average speed of 1.0 to 1.2 knots. The shooting interval was selected depending on the speed of the vessel and ranged from 30 to 40 seconds, which ensured the inter-frame distance of not more than 30 m. The shooting distance from the bottom was 5.0 ± 0.2 m.

Stone material from the bottom was sampled using drags and a submersible drilling rig. We have compiled a representative collection of sedimentary rocks including layered crusts, from different guyots. Biostratigraphy methods (foraminifera, nanoplankton, corals, mollusks, etc.) made it possible to determine the age of the recovered rocks.

These studies allowed forming a general knowledge of the topography, structure of the oceanic crust, sedimentary strata of intermountain basins and mountain structures. We have obtained the information on the morphology and geological structure of the guyots, also on the composition, structure, and development of the ferromanganese formations. The facial features and regularities of the distribution of crusts and nodules, their structure and composition were studied at individual polygons (Fig. 2). By the results of drilling (over 300 stations) in the study area, a vast occurrence of cobalt-manganese crusts and their actual thickness was estimated.

The chemical and mineral composition of the layers was determined both by X-ray diffraction and precision methods (All-Russian Institute of Mineral Raw Materials). Concentrations of the main ore components and phosphorus were determined by the methods of classical chemistry (JSC Yuzhmorgeologiya).

Results and Discussion

During geological sampling of the ore crusts from the Magellan seamounts, about 40 samples containing relict layers were described; this approximately corresponds to the frequency of occurrence in about 2% of the sampling stations. The frequency of occurrence in the studied in detail guyots may be higher: on the Fedorov and Ita-Mai-Tai guyot — about 3%, on the Gramberg and the Butakov guyots — more than 5%; but it may also be lower: on the Alba guyot it is less than 0,5 %. For various reasons, not all the above samples were possible to be fully studied. So, the age of 12 samples was determined, the mineral composition of four, the chemical composition of 22 samples. The results of the relict layers analysis allow to distinguish two groups of samples among them. Visually, one of the groups is very similar in appearance to the layer I-1, that is, it has a thin-layered texture of ore material, numerous interlayer and secant phosphate veins, but with the difference that the layer is divided into blocks that can be unfolded relative to each other, separated from the main section by layers of non-metallic material and large clastic fragments. The substance of the layer itself acquires a steel-grey color (due to the saturation with the phosphate component) against the blue-black color of the layer I-1. The thickness of such relict layers varies from 1 to 7 cm, on average 3.1 cm.

In the second group of samples the ore material is composed of the columns which are relative to the similar formations in the layers I-2, II and, to some extent, in the layer III. The columns are usually vertically oriented and saturated with a phosphate component. Therefore, the relict layer has a lighter color than the layers I-2 and II. The phosphate component makes fine layering of the columns clearly distinctive and marks the horizons traced from column to column. Layers of this type are also divided into blocks separated by phosphate veins, often unfolded relative to each other. Their thickness varies from 1 to 11 cm with an average of 4.3 cm.

Among the relict layers, two age ranges are established — the second half of Late Cretaceous (R_1) and the first half of Paleocene (R_2). The first one was found in the crusts of the Butakov guyot in the eastern link of the Magellan Seamounts and the Zubov guyot relatively close to it, belonging to the Marshall Islands rise. The Paleocene age interval

was found in the crusts of the guyots of the western link of the Magellan Seamounts.

In the core of the well on the Butakov guyot, an interlayer of planktonogenic limestones in the range of 14.0–20.5 cm separates the layers I-I and R₁ (Fig. 3). The relict layer substrate is a modified volcanoclastic rock. The limestone is dated, according to planktonic foraminifera, to Middle and Late Maastrichtian (the *Abathomphalus mayaroensis* zone with the participation of the species index and *Globotruncanita sub-spinosa* (Pessagno), *Globotruncanita stuartiformis* (Dalbiez)), which suggests that the relict layer is not younger than it. Given the previously obtained data on the relict layer, we can assume that it is not older than Late Campanian [2, 3].

In the relict layer of R₂ crusts on the breccias from the Zubov guyot, a complex of foraminifers of the transition layers of Maastrichtian and Early Palaeocene with the participation of single shells of the species *Abathomphalus mayaroensis* (Bolli) and *Subbotina pseudobulloides* (Sub.) was established. Apparently, this relict layer was formed at the beginning of Early Paleocene. Earlier we repeatedly pointed out that in the sedimentary rocks of Magellan Seamounts there are signs of completion of the formation of a “Santo — Maastrichtian” complex at the beginning of Early Paleocene [3].

A relict layer of the Kotzebu guyot crusts, which is located on reefogenic limestones, is dated to the beginning of Late Paleocene (Planorotalites pzedomenardii zone). The ore formations sampled on the Ilyichev guyot correspond to the same age.

The mineral composition of the lower relict layer R₁ (Campanian — Early Maastrichtian) differs significantly from the overlying layers of crusts of the main section. The content of asbolan and “5Å-mineral” is high here. Vernadite is probably present in comparable amounts. The impurities contain todorokite and bernessite. Phosphates and carbonates make up the non-metallic part. The predominant mineral in iron hydroxides is finely dispersed goethite. Ferroxylite and ferrihydrite are in subordinate amounts [4].

Table. Chemical composition of cobalt-rich manganese crusts layers of the Magellan Seamounts

| Component | Crust layer composition | | | | | | |
|-------------------------------|-------------------------|----------------------|-----------|------|----|-------|------|
| | Layer R ₁ | Layer R ₂ | Layer I-1 | | | | C, % |
| | | | C, % | V, % | n | C, % | |
| Iron | 15.1 | 5.4 | 12.40 | 22 | 89 | 11.17 | |
| Manganese | 19.41 | 8.96 | 21.95 | 15 | 89 | 17.96 | |
| Cobalt | 0.276 | 0.112 | 0.41 | 23 | 89 | 0.32 | |
| Nikel | 0.280 | 0.484 | 0.42 | 29 | 89 | 0.45 | |
| Copper | 0.056 | 0.214 | 0.117 | 31 | 88 | 0.143 | |
| P ₂ O ₅ | 9.73 | 15.53 | 6.93 | 38 | 84 | 9.74 | |
| Molybdenum | — | 0.02 | 0.065 | 16 | 18 | 0.046 | |
| TiO ₂ | 1.54 | — | 0.79 | 66 | 37 | 0.72 | |
| Zinc | — | 0.062 | 0.073 | 22 | 22 | 0.064 | |
| Lead | — | 0.052 | 0.184 | 22 | 22 | 0.105 | |
| Mn/Fe | 1.8 | 1.33 | 1.85 | 26 | 89 | 1.68 | |

Note. C — average content, V — coefficient of variation, n — sample. The R₁ and R₂ analyses were

The Paleocene (R_2) layers are closer also by mineral composition to the composition of the layer I-1, that is, vernadite and ferroxigite predominate in association with apatite (francolite); however, impurities of asbolan, todorokite, and bernessite are quite common [3]. The chemical composition of the relict layers is characterized by high concentrations of carbonates and phosphates and by sharply lower concentrations of metal components (see table). Against this background, relatively high nickel and copper contents can be noted, their contents are the same as in some overlying layers.

Some geochemical indicators allow us to draw more interesting conclusions. Thus, the manganese module (Mn/Fe) lies in the general trend of decreasing the index up the crust section. The same can be said about the Co/Ni ratio — on the contrary, it lies in the general trend of increasing the indicator from foot to roof and, accordingly, in the relict layer it is minimal (0.54). The Co/Cu ratio has a minimum due to lower cobalt concentrations, and the Ni/Cu is high, but not maximum, as the behavior of concentrations of these components across the layers is not unidirectional.

The composition of the two types of relict layers is different in a certain way. The material of a layer built by the columnar structures demonstrates the maximum of the manganese module (2.65) and the minimum of the Co/Ni (0.52) and Co/Cu (1.76) ratios. However, the variability of the last two coefficients is very high. The values of the coefficients in the relict layer R_2 , similar in appearance to the layer I-1, are completely different from the coefficients of the layer I-1, but also differ from the values of R_1 . The main difference is in the value of the manganese module (1.33), which is as low as in the upper layers of the section of crusts II and III, characterized by increased iron content. The coefficients associated with non-ferrous metals are generally similar to the coefficients in the R_1 layer, considering lower nickel concentrations, which determine the correction of the values of these coefficients.

To summarize, one could say that among the relict layers, we single out two varieties different in age, structure, and composition. As for single samples, there are inter-

| Layer I-2 | | Layer II | | | Layer III | | |
|-----------|-----|----------|------|-----|-----------|------|-----|
| V, % | n | C, % | V, % | n | C, % | V, % | n |
| 26 | 106 | 17.10 | 14 | 131 | 17.69 | 10 | 139 |
| 20 | 107 | 22.35 | 13 | 131 | 23.67 | 13 | 140 |
| 31 | 107 | 0.52 | 24 | 131 | 0.65 | 24 | 140 |
| 31 | 107 | 0.50 | 22 | 131 | 0.47 | 22 | 140 |
| 27 | 107 | 0.168 | 27 | 131 | 0.103 | 45 | 140 |
| 47 | 97 | 1.60 | 74 | 123 | 1.21 | 65 | 128 |
| 26 | 21 | 0.046 | 21 | 43 | 0.050 | 20 | 59 |
| 56 | 51 | 1.82 | 17 | 60 | 1.77 | 18 | 64 |
| 23 | 21 | 0.071 | 13 | 37 | 0.063 | 25 | 38 |
| 36 | 21 | 0.122 | 16 | 37 | 0.150 | 16 | 38 |
| 25 | 106 | 1.35 | 25 | 130 | 1.34 | 19 | 139 |

performed in samples of 39B1/1—5s and 13D16-3h respectively.

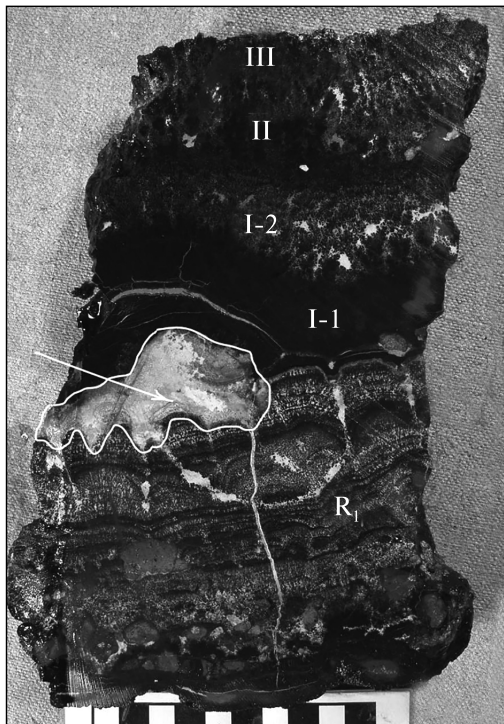


Fig. 3. The age of formation of individual layers of the ore section of the Magellan Seamounts: layer R_1 — Late Campanian-Early Maastrichtian, layer I-1 — the Late Palaeocene-Early Eocene, layer I-2 — the Mid-beginning of Late Eocene, layer II — the Mid (?) — Late Miocene and layer III the Eopleistocene. The white arrow indicates a limestone phenocryst dating from the Maastrichtian age

sections that, at very small sample volumes, leave a significant part of uncertainty. Even the layers with a distinct appearance do not always have an expected age. Thus, in the sample from the Alba guyot, the relict layer R_2 , similar in appearance to the layer I-1, is dated by Maastricht. There are much more such intersections with the chemical composition, especially in the nickel and copper contents. It is no accident that the variability of the coefficients remains high.

Therefore, one must on to accumulate factual material and to hope for confirmation of the earlier constructions. Returning to the question from which we started this report — about more detailed characteristics of the process of ore genesis at individual stages — we may draw certain conclusions. A different mineral and, especially, chemical composition of the relict layers may indicate a different nature of the composing material. High concentrations of barium, lithium, gallium, and zinc suggest that hydrothermal sources could be the source of the material.

But, of course, not through direct delivery, but via the phase of transfer of sea bottom water. This hypothesis explains also the low occurrence of the layer — it began forming not over the entire area of exposed bedrock, as it will occur later during the formation of the main crust section, but locally, in the areas close to the expected hydrothermal vents.

The ore deposition mechanism could have a more pronounced biochemical character, at least in Campanian-Maastricht. Such a mechanism, however, could form the main section, however, for relict layers, such assumptions are most justified. New data on fossilized stromatolite algae indicate their great role in the formation of CMC and FMN during intensification of hydrothermal processes [1]. The Paleocene (R_2) relict layers were formed under conditions to a certain extent like the conditions for the formation of the layer I-1, which caused some similarity of appearance. But in the period between the formation of the layers R_2 and I-1, there were probably some tectonic and oceanological events that caused a partial destruction of the surfaces and local interruptions in the formation of the ore section. It was during the transition period from Cretaceous to Cenozoic that a global crisis was noted in the development of the organic world, which is often associated with the fall of a large asteroid or intense trappian volcanism [2].

Thus, the analysis of lithological and geochemical parameters and fossil fauna of foraminifera in the relict layers of the Magellan Seamounts ore section indicates two stages of their formation: Late Campan-Maastricht and Early Middle Palaeocene. The discreteness of the formation of relict layers in time once again proves that the sharply changing environmental conditions controlled the growth of the CMC ore section.

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РАННІ СТАДІЇ ЗАЛІЗОМАРГАНЦЕВОГО РУДОГЕНЕЗУ НА ГАЙОТАХ МАГЕЛЛАНОВИХ ГІР (ТИХИЙ ОКЕАН)

Fe-Mn рудні кірки грають важливу роль серед океанічних родовищ корисних копалин через їх значне поширення і високі концентрації поліметалів і рідкісних земель. Більшість рудних кірок залягає на поверхні десятків тисяч підводних гір в океані. Дані по структурі, текстурі, хімічному складу і віку кірок дозволяють виявити, які з факторів є ключовими для концентрацій промислових скупчень мінеральної речовини. В даній статті наведені структури будови і хіміко-мінералогічні характеристики найбільш древніх стратиграфічних шарів рудних кірок (пізня крейда і палеоцен), відібраних і вивчених на Гайотах Магелланових гір.

Повний розріз кори на Магелланових горах включає чотири шари, кожен завтовшки 2–4 см: пізньопалеоценовий (?)–ранньоеоценовий I-1, середньоеоценовий I-2, міоценовий II і чет-

вертинний III. У деяких випадках основна ділянка КМЦ підстеляється реліктовими шарами. Хімічний і мінеральний склад шарів визначався як за рентгенівською дифракцією, так і точними методами; концентрації основних рудних компонентів і фосфору визначалися методами класичної хімії.

Визначено вік 12 зразків, мінеральний склад — 4 зразків, хімічний склад — 22 зразків. Результати аналізу реліктових шарів дозволяють виділити серед них дві групи проб. Серед реліктових шарів встановлені дві вікові групи — друга половина пізньої крейди (R_1) і перша половина палеоцену (R_2).

Високі концентрації барію, літію, галію і цинку дозволяють припустити, що джерелом матеріалу можуть бути гідротермальні джерела. Але не через пряму доставку, а через фазу перенесення морської донної води.

Таким чином, аналіз літологічних і геохімічних параметрів і викопної фауни форамініфер в реліктових шарах рудного розрізу Магелланових гір вказує на дві стадії їх формування: Пізній кампан-маастрихт і ранній-середній палеоцен. Дискретність утворення реліктових шарів за часом ще раз доводить, що різкі зміни умов навколишнього середовища контролювали ріст рудного розрізу КМЦ.

Ключові слова: залізомарганцеві корки, гайот Магелланових підводних гір, пізня крейда, палеоцен.