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Chapter

Study of Deep-Ocean Ferromanganese Crusts Ore Components

Alla A. Novakova and Dmitrii S. Novikov

Abstract

A complex layer-by-layer morphology and phase analysis of a ferromanganese crust aged about 70 million years, extracted from the rise of the Magellan Mountains of the Pacific Ocean, was carried out using several physics methods: digital optical microscopy, scanning electron microscopy with high resolution, X-ray fluorescence and diffraction analysis and Mossbauer spectroscopy. This analysis showed that the crust is an association of several minerals with various dispersion and crystallization degree, between which fossilized bacterial mats with Fe- and Mn- oxides are located. These phenomena indicate the biogenic nature of the crust. Changes in the crusts phase composition from the lower layer to the upper layer indicate changes in the external environmental conditions during their formation.

Keywords: Ferromanganese Crusts, X-ray analysis, Scanning electron microscopy, Mössbauer spectroscopy, Bacterial activity

1. Introduction

Ferromanganese crusts were first discovered at the bottom of the Pacific Ocean. The crusts samples were taken on board by the English ship "Challenger" and described in 1873 during the first complex oceanological expedition in the history of world science. However, until the middle of the XX century, only the chemical composition of crusts was analyzed. It was found out that ferromanganese crusts consist of up to 20% Mn, 15% Fe and 0.3–2.5% Co. In addition, they can contain complexes of noble, non-ferrous, rare and rare earth metals (up to 70 elements). All this data obtained stimulated further complex investigations on the topic. Many expeditions, mainly in the Pacific Ocean, were conducted to find and obtain ferromanganese crusts by USSR, USA, Germany, China, Japan and other countries in 1970–1980. Currently, crusts are found in all oceans, including the Arctic Ocean. They are often spread on basalts and clastic volcanic rocks in the depth range of 400–7000 m. The crusts are relatively thin continuous covers lying on the slopes of seamounts of volcanic origin. The thickness of the crusts can reach 26–40 cm. The crusts age is usually determined by Be, U, and Os – isotope dating methods [1]. The average age reaches several tens of millions of years. The most common crustal growth rates found in all oceans vary between 2 and 4 mm/mln.yr.

Researchers of ferromanganese crusts have always had 2 questions: 1) where do the colossal masses of manganese and iron come from to the places where the crusts form? and 2) what is the mechanism of the crusts formation and why does it differ a lot from the usual bottom depositions? Until the middle of the XX century, the idea of hydrogenic mineralization (the deposition of metals from the oceanic water) prevailed. It is known that the flow of substances from various sources into the ocean water is dynamically balanced by their removal to the bottom depositions. Thus, the salt composition of ocean water remains stable. However, model experiments and real observations did not reveal the deposition of large amounts of iron and manganese to the ocean floor. In the second half of the XX century, more attention was paid to the underwater volcanic eruptions, mantle fluid flows and post-volcanic hydrothermal activity i.e. processes that are actually recorded, which may be the main suppliers of metals for the oxide ferromanganese ores formation. Accordingly, the volcanogenic-sedimentary type of mineralization was identified.

By the end of the 1990s, marine geologists, microbiologists, and micropaleontologists had developed and validated the biological concept of ferromanganese oxide ore formation. According to this concept, crusts are considered as products of the vital activity of bacterial communities that can oxidize divalent iron and manganese compounds and precipitate metal oxides in a crystalline or amorphous form on the cell surface or even within the cell, as well as in the matrix of biological films [2, 3]. The biological concept of oxide ferromanganese ore genesis has been brilliantly confirmed by scanning electron microscopy [4].

Developing and fossilizing biofilms (0.5 to 2 microns thick or more) form bacterial mats with a multilayer structure: stand-alone bundles of biofilms separated by cavities, clusters of filamentous bacteria, and layers of glycocalyx. Therefore, in bacterial mats, dense, massive micro-layers and porous, loose ones are distinguished. It is bacterial mats that form columnar stromatolites of ferromanganese crusts, which are the ore components. During the entire time of stromatolite growth (millions of years), extreme events periodically occurred (underwater volcanic eruptions, tectonic phenomena, global glaciation, etc.) that affected the vital activity of microorganisms and were imprinted in the crustal sections by the formation of interlayers with different types of columns (the thickness and density of columns as well as their growth direction changed, and bushy branches were formed) [5]. At the same time, the growing crusts, having a high porosity and a fine structure, demonstrate a large sorption capacity. As a result, they are saturated with complexes of non-ferrous, rare and rare earth metals. The biofilm matrix contains a significant concentration of polysaccharides with a negative charge. Due to this, metal cations are able to accumulate on the surface of the extracellular polymer matrix, forming strong complexes. These processes can explain the mechanism of enrichment of ferromanganese crusts with the ore-compound metals [6].

The structure, composition and genesis of ferromanganese crusts have been studied by scientific laboratories in many countries for more than 50 years (since their industrial significance was discovered). However, the nature of the oxide ferromanganese ore formation has not been fully revealed yet. This is due to the fact that the crusts are very complex in composition and structure layered formations. The nanoscale oxide ore components of biogenic origin are also the significant part of the crusts composition in addition to numerous clastic and dispersed minerals formed as a result of volcanic activity. Therefore, it is obvious that the study of such objects requires subtle chemical and physical methods of studying their composition, structure and morphology, which appeared only at the end of the XX century. This work is devoted to such research.

2. Analysis of ferromanganese crusts phase composition and morphology

A characteristic feature of ferromanganese crusts is their layered structure, which shows a history of their origin and growth. If the crust is sliced, one can usually observe from 3 to 5 layers with an average thickness of 2–3 cm, differing in structure, physical properties and composition of components. Usually, the lower layers of the crust are dense and strong, while the upper layers are more porous and brittle. It is possible to consistently trace the processes of ore accumulation and global changes in the external conditions for the formation of ferromanganese crusts by studying the composition and structure of these layers.

2.1 Object of study

Figure 1 shows a section of the crust studied in our work, isolated at a depth of 1200 m from the surface of the guyot of the Magellan Mountains of the Pacific Ocean. This crust has a special feature: it has a "relic" layer (R) of pre-existed crusts that underlies the main section and situated on the weathered basalt. The thickness of the R – layer reaches 8 cm. The stratification of the crust section was carried out by marine geologists M. Melnikov and S. Pletnev (from the Institute of Oceanology, Gelendzhik). The layers are named (below): I-1, I-2, II and III, which were formed in the time intervals indicated on the geochronological scale placed to the left of the crust.

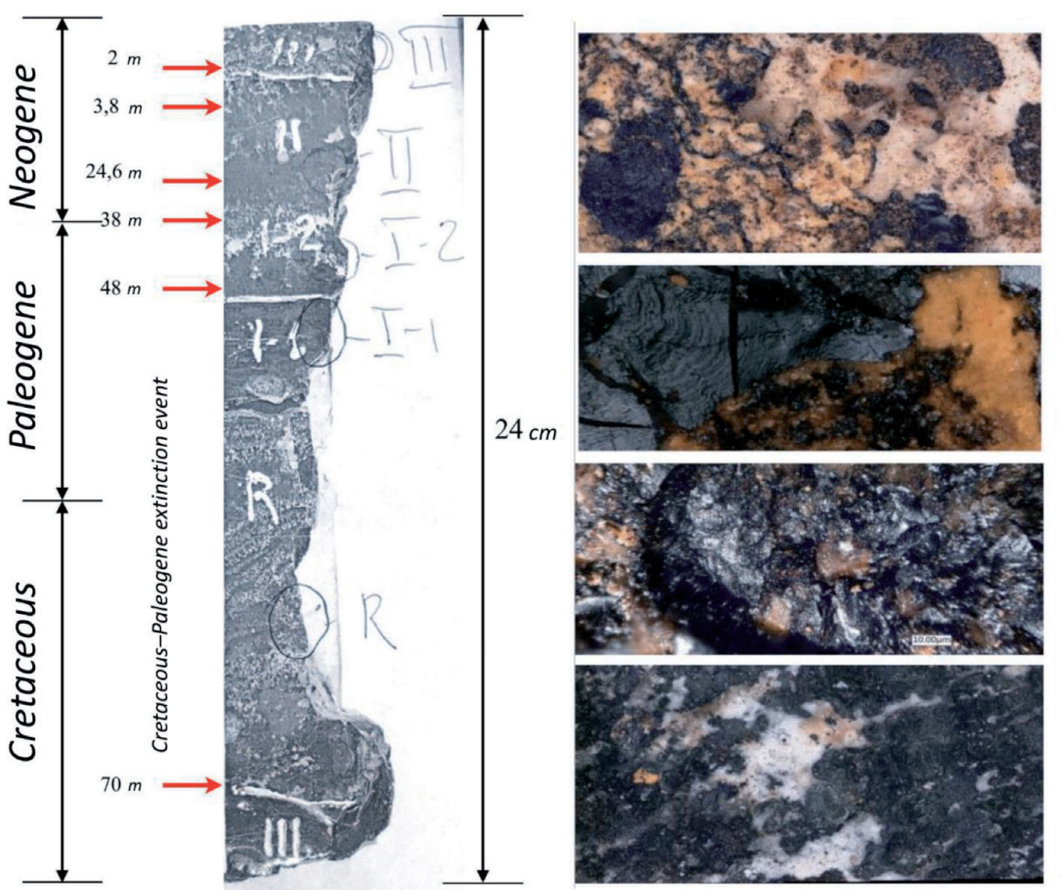


Figure 1.
Section of the studied sample of the ferromanganese crust, compared with the geochronological scale (in the interval of 70 million years). Optical images of the various layers are on the right.

The method of layer-by-layer studies of the crust was as follows:

1. Color optical images were obtained from all layers of the crust section using the Keyence VHX – 5000 digital optical microscope which allows us to record changes in the phase composition of the crust from layer to layer.

2. A TESCAN VEGA scanning electron microscope was used to study the morphology and relative position of various crystal phases, as well as to search for traces of bacterial activity that leads to the growth of ore formations

3. The elemental composition of each layer at individual points along its surface was determined using a portable X-ray fluorescence analyzer SciAps X-200, which has a collimated X-ray beam with a diameter of less than 3 mm. These results were then mathematically processed to obtain the average elemental composition for each layer of the crust.

4. The results of the elemental composition were entered into the High Score Plus program of the PANalytical Empyrean X-ray diffractometer, which was used for X-ray diffraction analysis to determine the nature of ore and accessory minerals, and assess accompanying growth of ore formations.

5. The Mössbauer spectra were taken and analyzed for each layer to clarify the phase composition of the ultrafine iron-containing compounds that make up the thoracic component. Mathematical processing of the obtained Mossbauer spectra made it possible not only to determine which iron oxide compounds are contained in each layer of the crust, but also to trace quantitative and qualitative changes in their composition during the transition from one layer to another.

2.2 Experimental microscopy results

The surface layers of the ferromanganese crust analysis performed by digital optical microscopy (**Figure 1**) showed that they consist of associations of a large number of minerals with different degrees of crystallization and dispersion. There is also an increase in yellowish-red inclusions from the lower layer I to the upper layer III. These inclusions correspond to iron oxide compounds (goethite, hematite, etc.), i.e., there is an increase in the iron-ore component from the lower layer of the crust to the upper one, and the proportion of accessory minerals decreases. It is difficult to analyze the content of the manganese-ore component in the crust layers by this method, since manganese oxides are very dark, and it is hard to distinguish them from other dark-colored phases. However, we were able to identify an interesting region that has a colomorphic structure, which is most likely formed by manganese oxides (**Figure 2a**) by examining the sample from the R-layer in detail [7].

We examined this region of the R-layer using a scanning electron microscope (**Figure 2b**) to clarify the assumption about the manganese nature of the colomorphic structure. The Energy Dispersive analysis performed on the electron microscope allowed us to obtain a picture of the distribution of chemical elements in this region of the R-layer (**Figure 3**). The analysis shows that manganese and oxygen occupy the same positions in the colomorphic structure, which indicates that they are combined in the form of manganese oxide. At the same time, calcium and phosphorus also occupy identical positions, which indicates that they are connected in a common structure, most likely apatite. No iron compounds were found in this area.

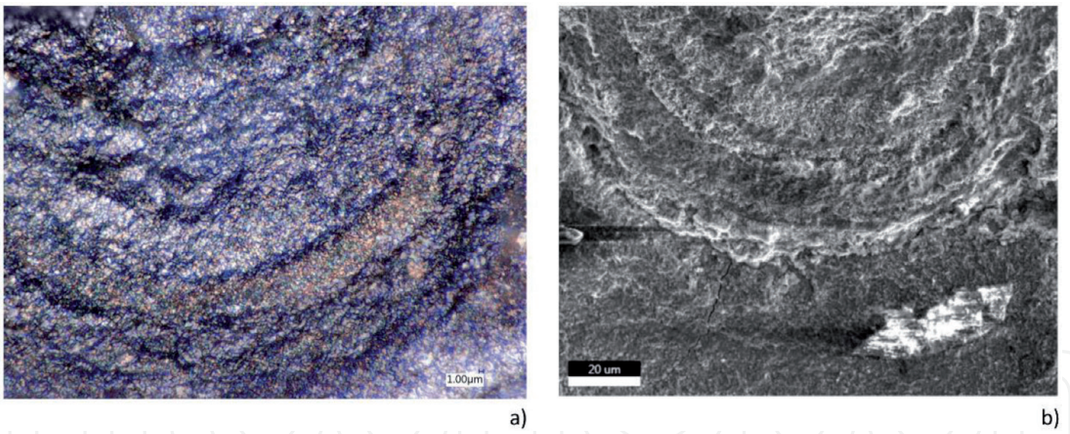


Figure 2.
Optical (a) image of a colomorphic structure on the surface of the R-layer and electron microscopic image (b) of the same structure.

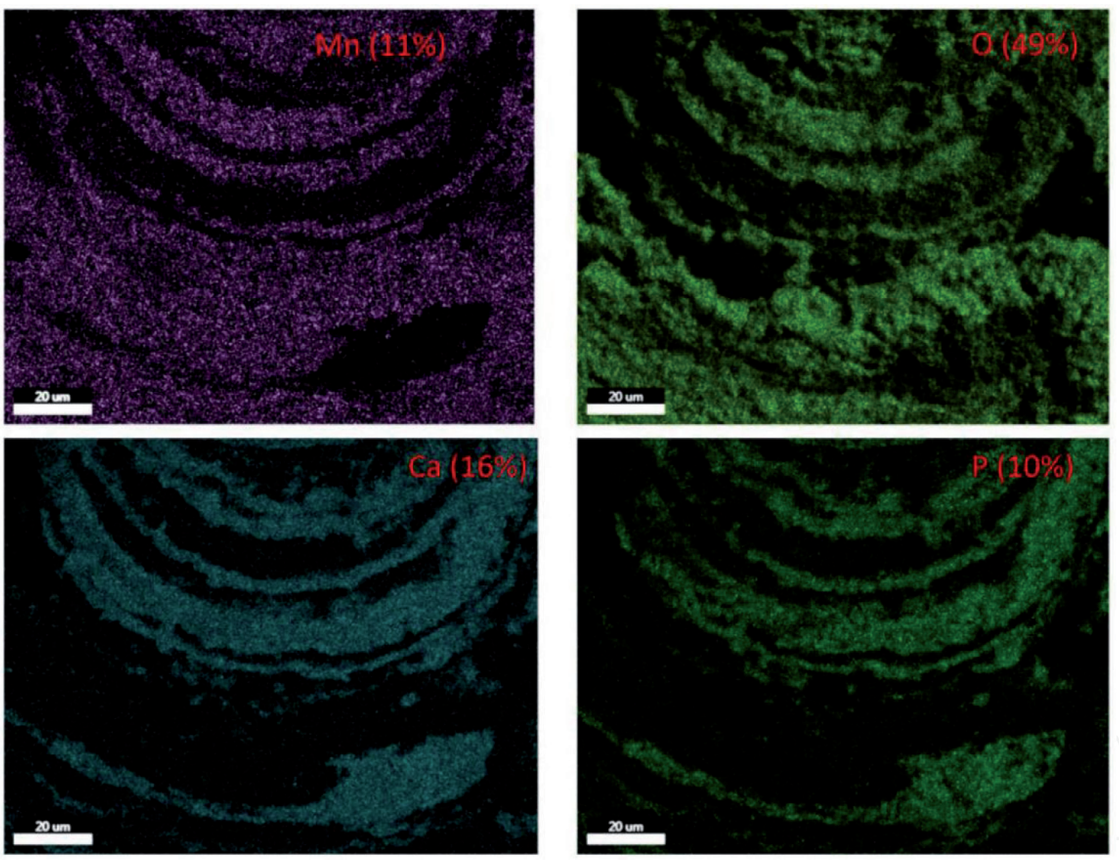


Figure 3.
Distribution of chemical elements in a colomorphic structure on the surface of the P-layer and their percentage.

By increasing the magnification of the scanning microscope (x10, 000), we were able to see columns of stromatolites, layers of bacterial mats with fossilized bacteria, and microcrystals of accessory minerals (**Figures 4** and **5**).

2.3 X-ray investigation results

Elemental analysis of each layer of the studied crust was carried out at 8 separate points of its surface area (a surface area was selected, which will later be analyzed using an X-ray diffractometer) using the SciAps X-200 analyzer. The built-in camera made it possible to obtain an image of the analyzed area of the sample and accurately determine the measurement point of the X-ray spectrum.

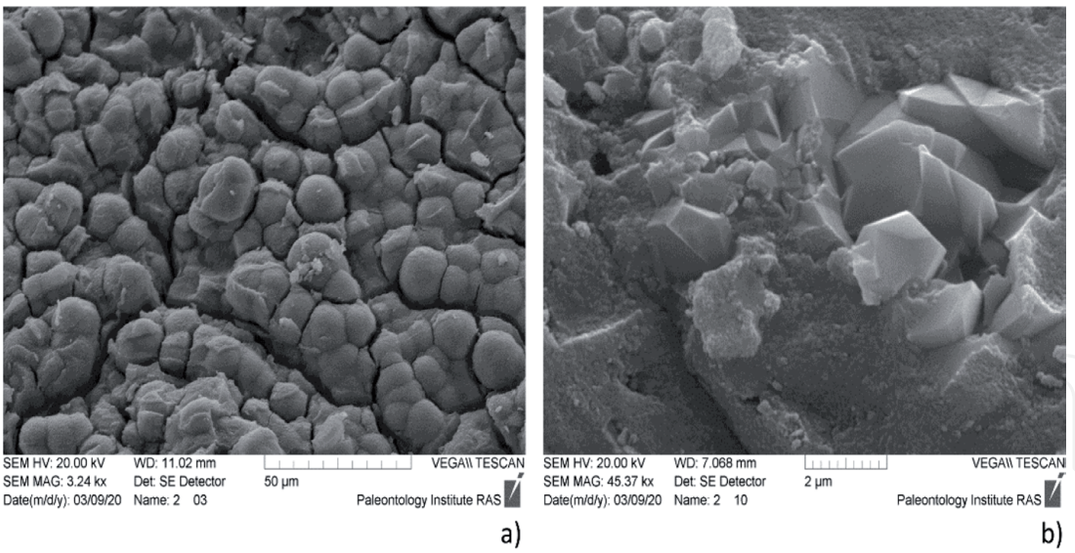


Figure 4.
Micrographs of the ferromanganese crust with different magnifications: (a) numerous columns of stromatolites are seen (top view); (b) microcrystals of apatite lying on bacterial mats.

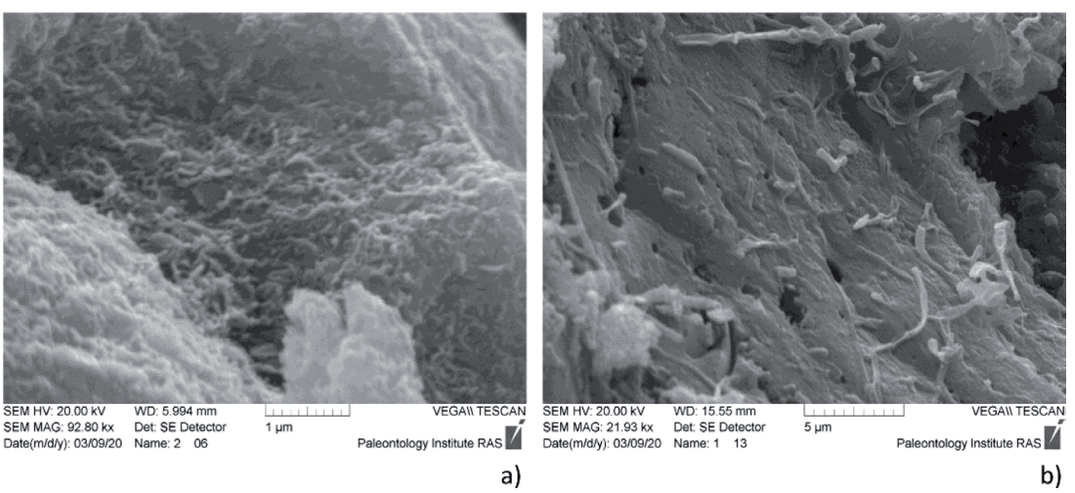


Figure 5.
Micrographs of bacterial mats: (a) a mat completely covered with filamentous bacteria; (b) a mat with void zones formed by cyanobacteria.

Mathematical processing of the obtained data allowed us to find out the elemental composition of each layer under study, the numerical data of which are presented in **Table 1**.

According to **Table 1**, up to 20 different elements – metals, as well as phosphorus and silicon-were found in each layer of the studied crust. The average mass ratio in the crust is dominated by Fe (%), Mn (%), and P (%). Si and Al are also present in significant amounts. All these data were used to conduct a layer-by-layer phase analysis of the studied crust.

Figures 6–**8** shows X-ray diffractograms of all layers of the studied crust. The diffractograms were decoded for all phases, but we reverse special attention (highlight in the diffractograms) on Fe and Mn oxides. The main mineral phase in the relict layer (**Figure 6a**) is Fluorapatite, as well as minerals (calcium silicate, corundum, pargasite and pyrosmalite). Fe and Mn oxides compounds are detected in **Figure 6b**.

It is extremely difficult to perform a quantitative phase X-ray analysis of the studied layers of the ferromanganese crust: they consist of associations of a large number of minerals and nanoscale, often amorphous, oxide compounds of iron and manganese.

Sample	R	I-1	I-2	II	III
Al	3.78	1.02	2.17	4.33	3.49
Bi	0.11	0.09	0.00	0.00	0.00
Co	0.28	0.00	0.00	0.00	0.00
Cr	0.00	0.07	0.04	0.13	0.00
Cu	1.64	0.86	0.81	0.75	0.76
Fe	13.06	40.17	37.33	25.74	45.11
Mg	2.15	0.66	1.12	1.00	1.58
Mn	44.81	46.53	33.47	20.64	30.63
Mo	0.11	0.26	0.10	0.03	0.12
Nb	0.03	0.04	0.03	0.07	0.02
Ni	5.16	2.27	1.38	2.06	1.42
P	36.44	0.00	25.82	26.69	9.70
Pb	0.27	1.21	0.62	0.28	0.44
S	0.00	0.00	0.00	1.66	0.00
Sb	0.00	0.12	0.05	0.08	0.00
Si	2.68	2.94	3.97	11.00	8.63
Sn	0.00	0.09	0.00	0.08	0.04
Ti	2.75	2.08	1.79	3.00	1.44
V	0.88	0.37	0.31	0.49	0.21
W	0.08	0.07	0.08	0.09	0.07
Zn	0.91	0.65	0.43	0.48	0.42
Zr	0.46	0.78	0.68	0.74	0.60

The lines of the main elements of the ore component Fe and Mn are highlighted in color for clarity of their change from layer to layer.

Table 1.
Elemental composition obtained by means of X-ray fluorescence analysis.

As a result, the X-ray reflexes of oxides are very weakened and broadened in comparison with the reflexes of minerals of microcrystals. Their intensity is often comparable to the error limit of the method (2%). Therefore, we performed only to qualitative analysis.

The observed broad peaks of Mn- oxides were deciphered by introducing todorokitis and unstable buserite, which explains significant increase in the intensity and area of the peaks in the previously identified diffractogram angles: 35° - 37° and 63° - 67°. Iron oxides on diffraction patterns (**Figures 6–8**) are represented by goethite and hematite.

2.4 Mossbauer spectroscopy

More accurate studies of nanoscale iron oxide compounds in different layers of CMC can be carried out by the method of Mössbauer spectroscopy on the Co^{57} isotope. Due to its selectivity (only the Fe^{57} nuclei reflexes are recorded in the spectra), the method makes it possible to separate iron-containing minerals from the total mineral mass. According to the parameters of the Mössbauer spectrum. It is possible to determine the valence state of iron, the symmetry of its local neighborhood from the Mössbauer spectra parameters and therefore to determine the iron-containing

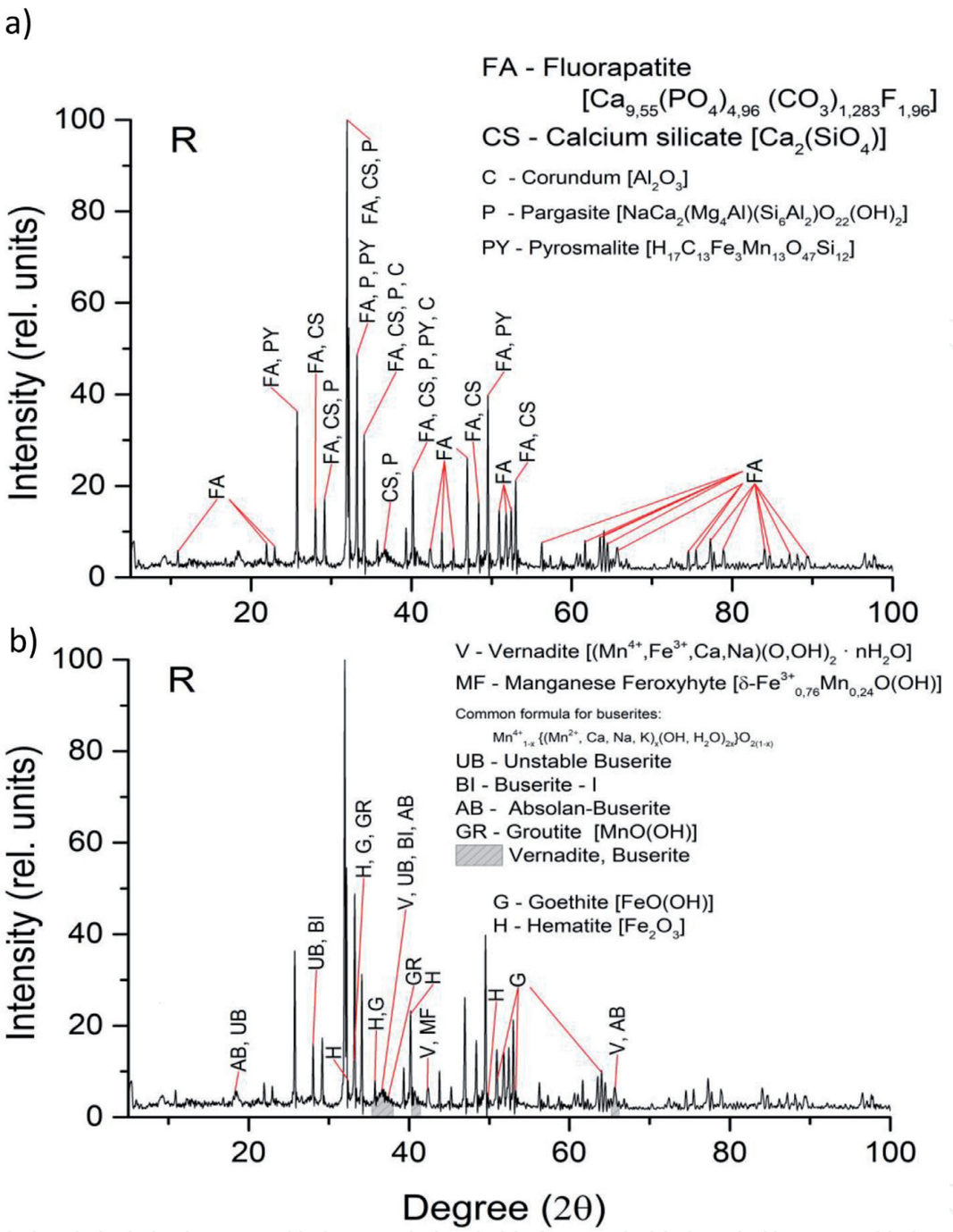


Figure 6.
X-ray diffractogram of the relic layer of the ferromanganese crust: (a) analysis of minerals components; (b) analysis of Fe- and Mn- oxides.

mineral [8], as well as to estimate the particle sizes of iron compounds from the temperature dependence of Mössbauer spectra [9, 10].

We performed the Mossbauer investigation of all the Iron-manganese crust layers (**Figure 1**) at room temperature. Five spectra of the different layers are presented in **Figure 4**.

All the spectra are broadened paramagnetic doublets, which indicates the superparamagnetic state of the iron oxide particles [11]. Mathematical processing of the spectra made it possible to decompose them into components corresponding to various iron oxides. Thus, a layer-by-layer quantitative phase analysis of the iron compounds of the studied crust was carried out. The figure shows that the smallest effect value (4.6%) is observed in the relic layer. There are significantly fewer iron-containing minerals in R-layer than in layers I. 1 and I. 2 (7.4% and 6.8%), in which

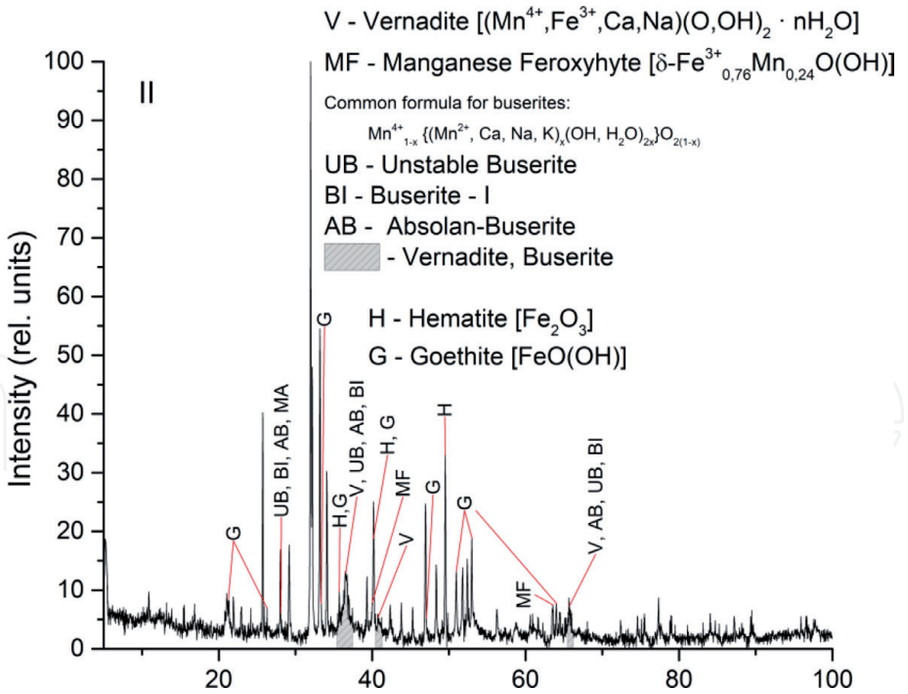


Figure 7.
X-ray diffractograms of layer I-1, I-2.

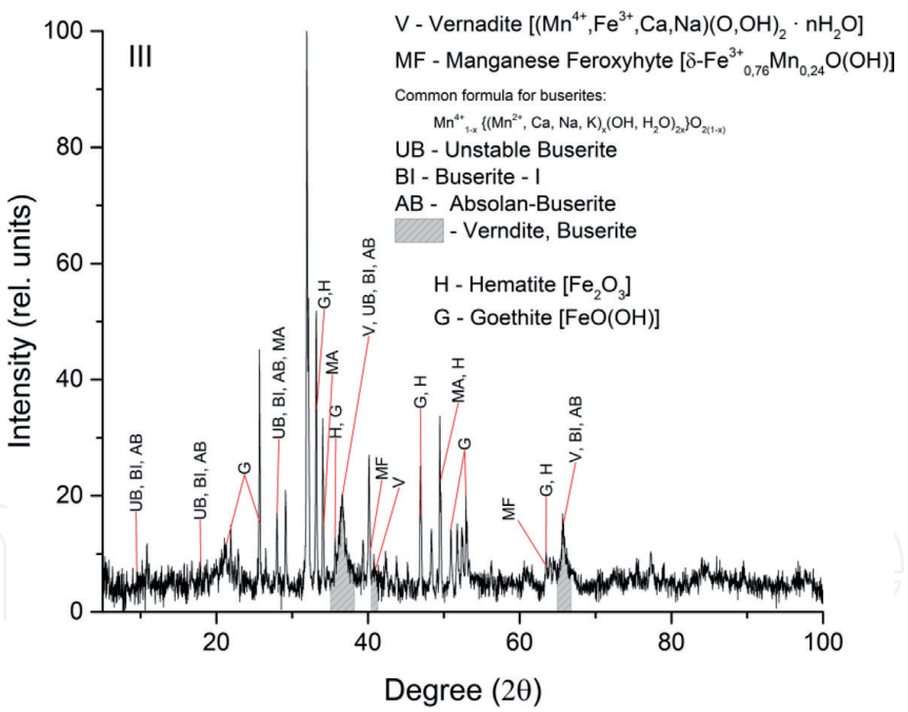


Figure 8.
X-ray diffractograms of layer II, III.

bacterial activity is already observed. The R-layer phase compositions differs from the subsequent layers: in addition to trivalent oxides, it contains amorphous ferrihydrite ($5Fe_2O_3$. $9H_2O$) and divalent (FeO) wustite. In the subsequent layers I. 1 and I. 2, only trivalent iron oxides are present, which is explained by the active activity of iron-oxidizing bacteria. A comparative analysis of the Mossbauer spectra taken at room and nitrogen temperatures allowed us to estimate the size of these superparamagnetic particles. They are lesser than 7 nm for goethite, and lesser than 5 nm for hematite. The obtained estimate of the particle sizes of goethite and hematite corresponds to the sizes of biogenic nanoparticles [12]. Results are shown in **Figure 8**.

Based on the results obtained, it is possible to trace the changes that occurred in the crusts over millions of years and make assumptions about the changes in the external conditions of their formation (**Figures 9** and **10**).

Since the main source of iron in the crusts was the products of volcanic eruption and collapsing basalts, the iron presented in the base of the crust in a metallic or divalent state. After that, under the influence of oxidizing bacteria, iron ions are oxidized to a trivalent state. This explains the presence of low concentrations of divalent wustite in the relict layer and the high content of trivalent iron in the composition of nanosized oxides: amorphous ferrihydrite, goethite, and hematite. In the subsequent layers I-1 and I-2, in which iron-oxidizing bacteria are active and ore-bearing stromatolites appear, an increase in the magnitude of the effect of the goethite and hematite phases is observed, with goethite as the most intensive phase.

In layer II, one can notice significant changes that have occurred with the iron oxides in the crust. Probably, during the global glaciation corresponding to the age of this layer (3.8–2.4 million years), other types of bacteria appeared with changes

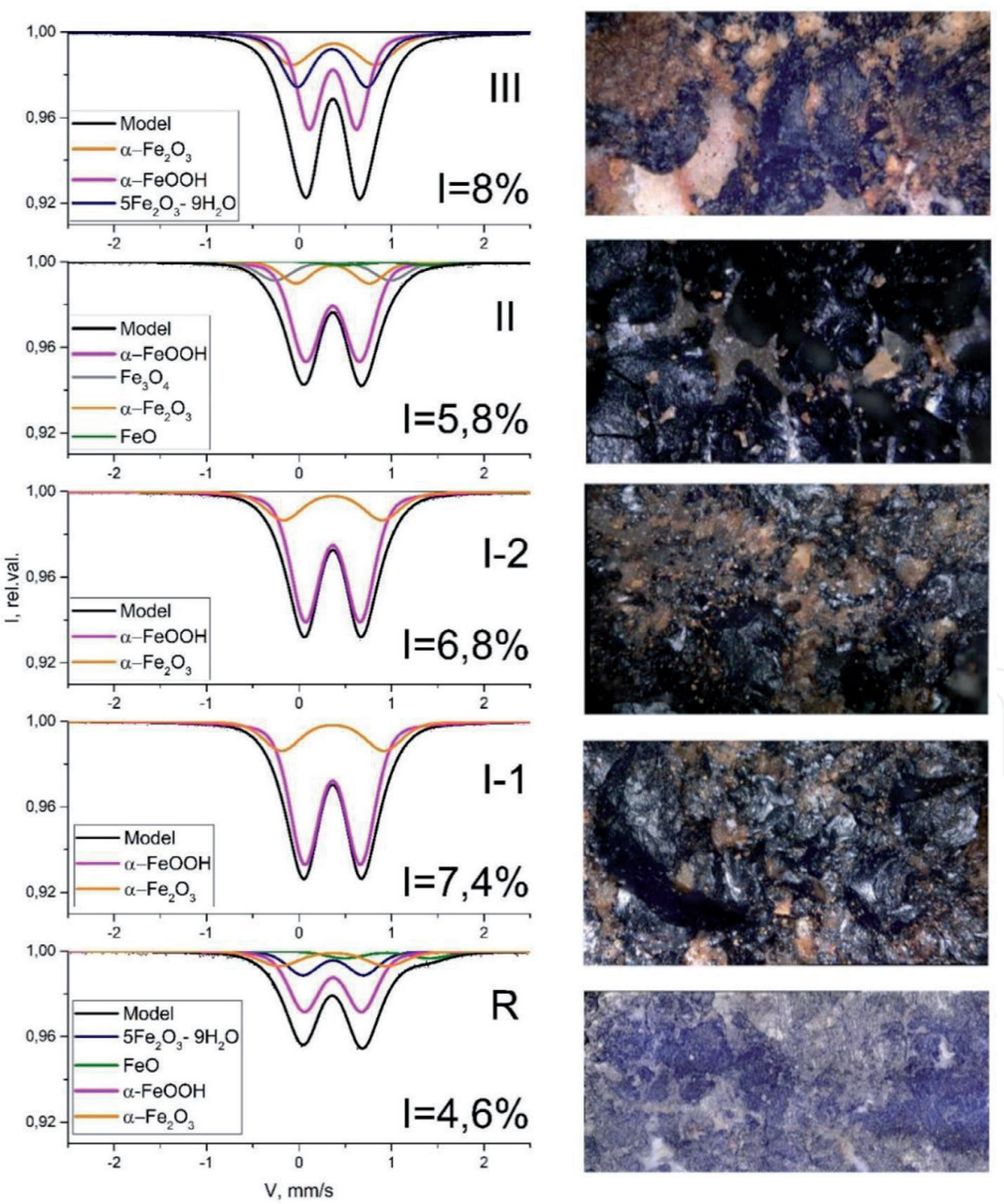


Figure 9.
Mössbauer spectra of various layers of the crust.

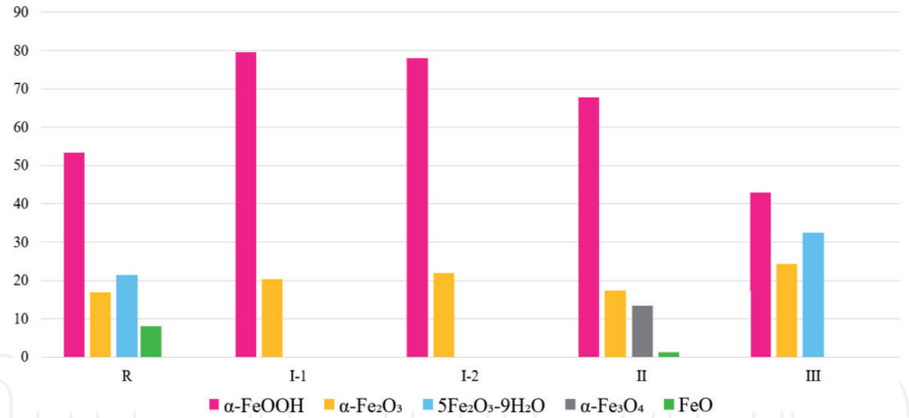


Figure 10.
Quantitative phase composition diagrams of all layers of the studied crust.

in external conditions (changes in pH, temperature, environmental composition, including a large content of decaying endangered organisms). It leads to the trivalent iron contained in nanoscale goethite and hematite transformation to divalent in wustite and partially divalent in magnetite.

In layer III, the phases of goethite and hematite are again observed. Probably, by the time of the formation of this layer, the reduction processes in the environment stopped and the colonies of oxidizing bacteria began to work actively again.

3. Conclusion

A comprehensive layer-by-layer analysis of the ferromanganese crust showed that the crust is practically a composite consisting of clastic and volcanogenic micron-sized minerals and stromatolites, consisting of fossilized biofilms filled with nanoparticles of iron and manganese oxide compounds, which are bacteria waste products. The lower layers of the crust are very dense: they contain many clastic minerals, and ore-bearing stromatolites grow between them. During the growth of the crust, bacteria constantly carry out their vital activity, therefore stromatolites grow continuously, occasionally changing their direction and shape under the influence of external conditions. And minerals: apatite, quartz and others come to the place of crust growth only occasionally - after a volcanic eruption. Therefore, the proportion of the iron-ore and manganese-ore components increases from the lower crust layer to the upper layer, which is almost entirely composed of these components. This leads to the fragility of the upper layers of the crust.

Experimental methods have provided objective evidence of the biogenic nature of the ore components of ferromanganese crusts. And the method of Mössbauer spectroscopy, first applied to these objects, made it possible to obtain a quantitative phase analysis of iron ore components in different layers of the crust. Based on this analysis, it was possible to trace how the composition of iron oxides changes in different layers of the crust, depending on changes in external conditions.

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