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Biofilms and Biominerals in the Lateritic Weathering Crust as Exemplified by the Central Bauxite Deposit (Siberian Platform, Russia)

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Abstract: The study of lateritic bauxite by electron microscopy revealed abundant products of interaction between organic matter and minerals. Abundant biomineral films of different genesis and composition were found, including Al, Fe, Al-Fe, Al-Si, Al-Fe-Si, sorbed rare and rare-earth elements (REE). The evolution of these films from amorphous to crystallized and the conversion into druse crystals of gibbsite, hematite, kaolinite etc. was traced. New data were obtained on mineralization of deposits of wood, roots, biofilms and bacteria in tropical conditions. Mono- and multilayer films were identified. Different composition biofilms occurred before and after seasonal monsoon rains. The mineral composition of the films is influenced by micro-local conditions and the introduction of chemical elements, including rare and rare-earth elements, with capillary water during the dry seasons. The products of biomineralization are microscopic in size, but are of universal and global importance to all weathered rocks and associated bauxite deposits.

Keywords: lateritic bauxite; organic matter; biofilms; REE; supergene minerals

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1. Introduction

All processes of destruction of parent rocks and formation of supergene minerals occur in close interaction with living and dead organic matter. The formation of minerals through biomineral films are material traces of the work done by the biota in the process of bauxite formation. In nature, weathering crusts are the biggest accumulators of nano- and micro-sized mineral particles in amorphous, crypto- and micro-crystalline states. The study of weathering crust minerals is extremely difficult because of their small size and shape. In the process of lateritization, the parent and associated rocks containing an increased amount of certain chemical elements and minerals are concentrated and become economically profitable [1].

Bauxite is a rock composed of aluminum hydroxide minerals: gibbsite—$Al(OH)_3$, boehmite—AlO(OH) and diaspore—AlO(OH). Bauxite contains impurities of Fe oxyhydroxides (FeO(OH) and hematite Fe_2O_3), titanium (rutile and anatase—TiO_2) as well as kaolinite and quartz. Under favorable economic parameters, bauxite is an aluminium ore. Bauxite is the ultimate weathering product of aluminosilicate rocks of all composition and genesis. Preserved in situ, it is called lateritic bauxite [1]. When eroded, redeposited and concentrated in other areas of accumulation, bauxite is called sedimentary bauxite. Lateritic bauxites are formed in hot, alternately humid tropical climates, in conditions of relatively calm tectonic regime, and on smooth positive relief forms, in conditions of abundant water exchange and mass development of biota [2]. Lateritic bauxites crown the zonal profiles of the weathering crust. In the upper part of the profile under the soil layer, lateritic bauxites are affected by chemically active rainwater penetrating through the living foliage of the vegetation cover, soil, mortmass, and root system. Bauxite is subjected to powerful mechanical, biological, biochemical and biogeochemical processing. An amorphous mass is formed, saturated with biota, from which biofilms of various compositions are formed [1].

Biofilms are an aggregate of microbial cells, other particles, water and extracellular polymeric organic matter [1]. They form on any wet surface in the weathered rock strata, in cracks, pores, and caverns, penetrate deep after the filtered water, and are fixed at the top of the profile by evapotranspiration. Biofilms are especially abundant in the zone of biopedoturbation, where swarming organisms, supplying bauxite, are the most active biochemical substances [3].

In recent years, the products of biota's impact on mineral matter have been intensively studied [1,4,5]. Using electron microscopes, unique photographs of biogenic minerals—hematite, goethite, and gibbsite—have been obtained, indicating the huge role of biomechanical, biological, and biochemical processes [6,7]. The genus Bacillus was revealed in some lateritic bauxites in present tropic regions [8]. Biomineral interactions and their role in mineral formation are among the most important issues in mineralogy in the 21st century. Organic matter of plant and/or bacterial origin in the Earth's crust under supergenesis has two functions: destructive, contributing to the destruction and dissolution of the original minerals, and creative, due to the inclusion of mineralized organic residues in the supergenic new formation [9]. Our task is to study the evolution of mineral formation in the process of bauxite formation. The study of the products of natural biomineralization processes is important for understanding the conditions of their formation as well as for choosing the most rational method of bauxite enrichment. A detailed study of the morphology and composition of biofilms and minerals containing the rare and rare-earth elements present in bauxite ores will help technologists develop a scheme for the associated extraction of these elements during bauxite enrichment. The complex and varied nature of REE-bearing minerals in bauxite provides multiple targets for bioleaching, and although the majority of recoverable REE can be leached by organic and inorganic acids, there is the potential for enhanced recovery by bioleaching [10–12].

2. Short Geological Setting

At the Chadobets uplift on the Siberian Platform, lateritic bauxites crown a zonal weathering crust profile thickness of about 600 m. The uplift is a brachy-anticlinal fold, with two domes composed of Precambrian shales and a complex of alkaline ultrabasic rocks, including kimberlite pipes and carbonatites. On all these rocks, covering dozens of petrographic varieties, a lateritic weathering crust was formed in the Cretaceous-Paleogene. In the erosional depressions on the surface of the northern dome is the Central Deposit, composed of sedimentary bean-like fragments bauxite. The Central Deposit is located 120 km north-east of the Boguchany pier district center on the Angara River (Figure 1). The rubble contains pseudomorphic laterites throughout the bedrock. The lateritic bauxites over quartz-muscovite-feldspar schists are composed of gibbsite and contain up to 62% Al_2O_3. The lower zones are disintegrated parent rocks, passing upwards into clay zones composed of allophane, hydromica, montmorillonite, halloysite and kaolinite [10]. Supergene rocks preserve the relict textural and structural features of the parent rocks. Fragments of laterites on carbonatites are composed of Fe-Mn-ocher, with abundant nests of powdery supergenic monazite with a lantonoid content of up to 14.4%. Their denudation products were mixed in erosional depressions as sedimentary bauxites, with an average TiO_2 content of 9.5% and TR_2O_3 up to 4% [10]. This explains the increased content of rare and rare-earth elements in biofilms, which are powerful sorbents [4]. Supergenic rocks preserve relict textural and structural features of the parent rocks well.

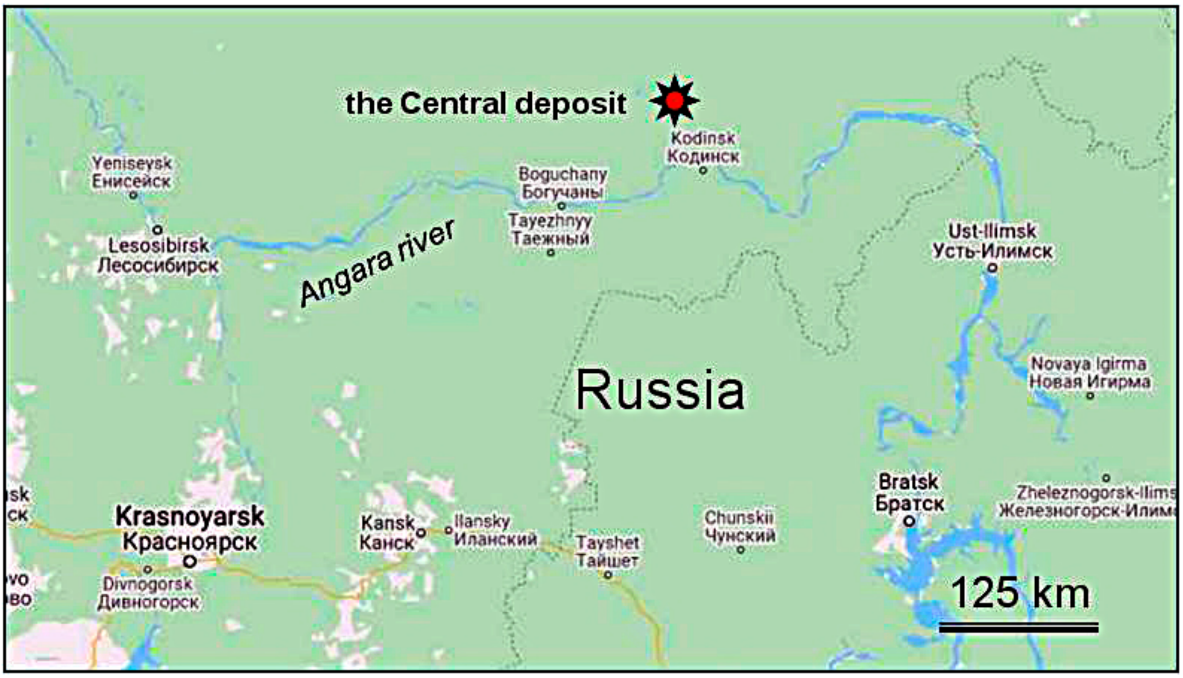


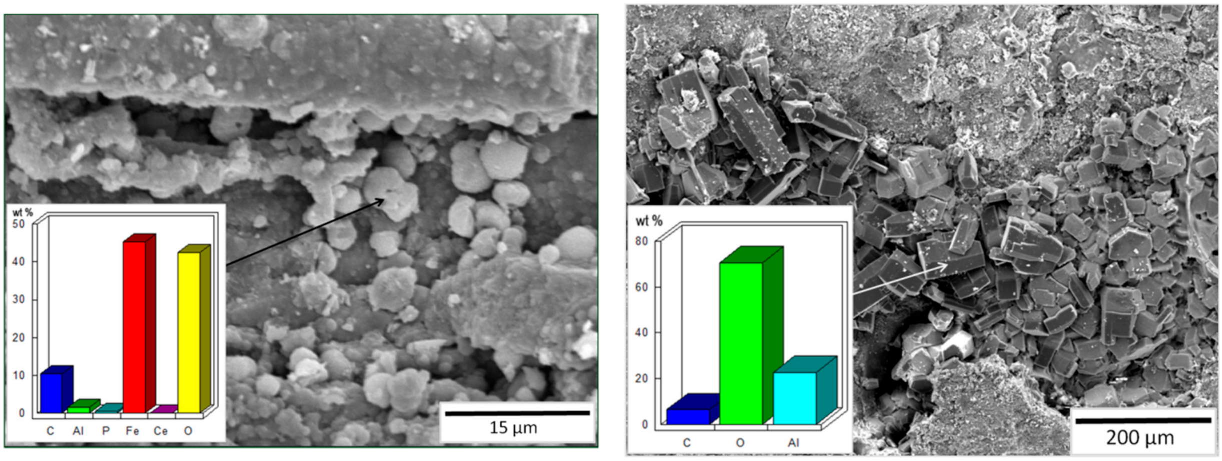
Figure 1. The location of the Central Deposit [13].

3. Materials and Methods

The main morphological and structural peculiarities were studied using scanning electron microscope (SEM) CamScan-4 (Cambridge, Britain), TESCAN VEGA IIXMU (Tescan, Czech), and transmitting (TEM) JEM 2100 (JEOL, Japan) microscopes. Microanalysis with TEM was performed using a device for X-ray energy-dispersive analysis: X-Max (Oxford Instruments, UK). More than 200 samples were studied. Bauxite samples were taken from different parts of the profile (depth 1–8.5 m) of the Central deposit. Biofilms were studied by electron microscope, and minerals were identified by morphological features formed by biofilms. With the help of EMF, their composition was determined; more than 1000 measurements were made. The chemical composition of individual minerals was constant within the margin of error (less than 5%). The preparations for TEM for the study were prepared from aqueous suspensions obtained by short-term ultrasound treatment, followed by evaporation of suspension droplets on the supporting film. Electron diffraction patterns and images were obtained from gibbsite particles oriented with the (001) plane parallel to the substrate.

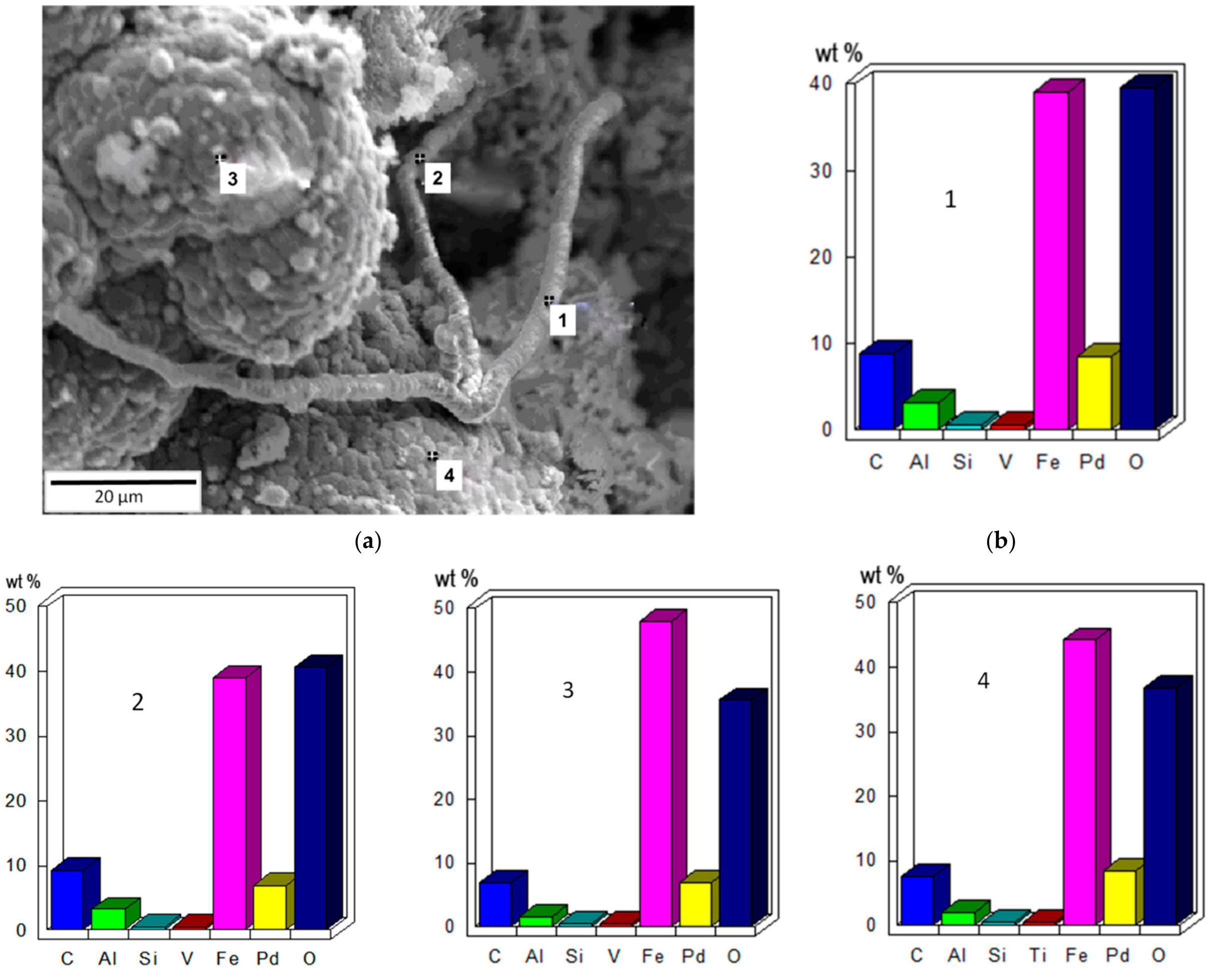
4. Results and Discussion

Laterites are the products of the complex cumulative effects of a variety of physical, chemical and biochemical forces. At the same time, the role of flora cannot be discounted. Both fauna and flora, as well as surrounding microorganisms and their common metabolites, produce not only mechanical but also biogeochemical destruction. It is known that the roots of living vegetation are always surrounded by microorganisms [14]. This symbiosis is captured in the petrification of goethite and hematite by plant residues and the accompanying abundant bacteria (Figure 2a). Under SEM, we were able to establish a variety of forms of gibbsite in phytomorphosis. Most of the roots are replaced by dense gibbsite, but their caverns contain druses of gibbsite crystals, probably formed by bacterial colonies (Figure 2b). Root hairs are completely replaced by gibbsite crystals. The fossilization of plant roots is shown in Figure 3a. Goethite was formed, covered by a biofilm composed of Al, Si, V, Ti, Pd (Figure 3b–e).



(**a**) (**b**)

Figure 2. SEM images: goethite biomorphosis by wood and bacteria (**a**), druses of gibbsite crystals in mineralized plant roots (**b**).

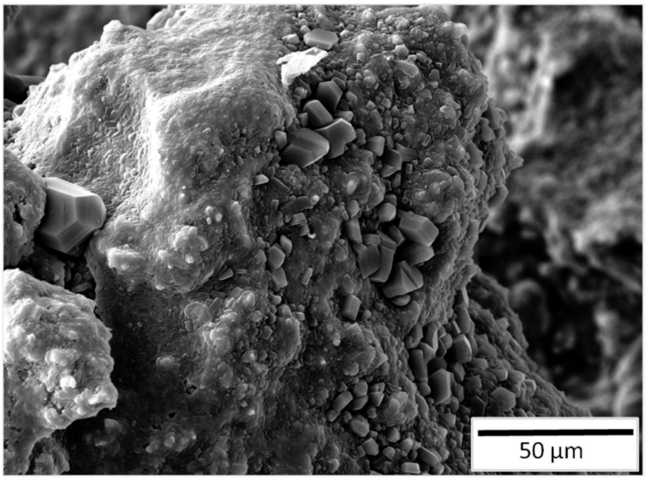


(**a**) (**b**)

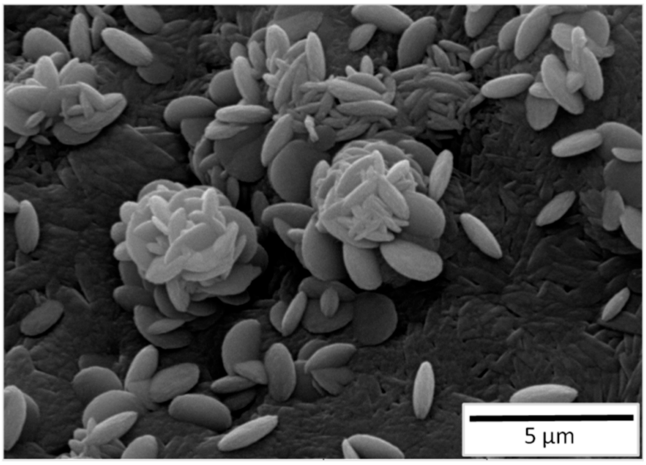
(**c**) (**d**) (**e**)

Figure 3. SEM image: goethite biomorphosis by wood and bacteria (**a**), energy-dispersive detector (EDS)microprobe data (wt.%) of biofilms (**b**–**e**).

In lateritic bauxites of the paleotropics on the Siberian Platform, gibbsite biomorphoses are widespread. Biofilms appear whenever the rock is moistened and are especially abundant during monsoon seasons. The chemical composition of the films is diverse and depends on the mineral composition of the area in general, the composition of the mineral to be covered by the film in particular, and on the changing composition of the filtered water. The films cover relicts of undissolved parent minerals and supergenic minerals. We found single-layer monomineral films—gibbsite (Figure 4a) and hematite (Figure 4b)—and bimineral films—gibbsite (Figure 5a) and gibbsite-hematite (Figure 5b).

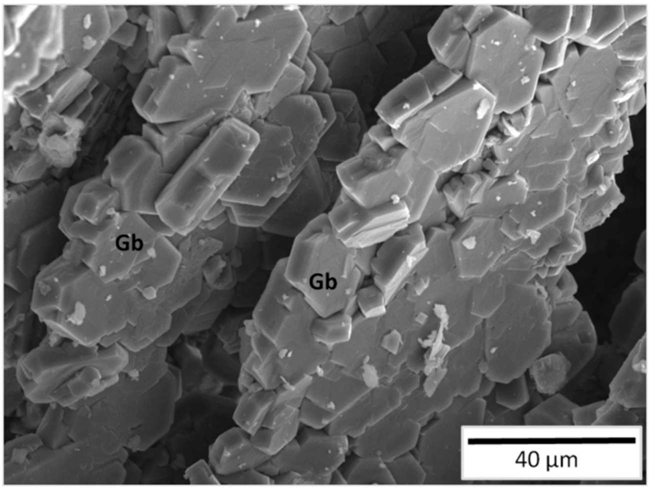


(**a**)

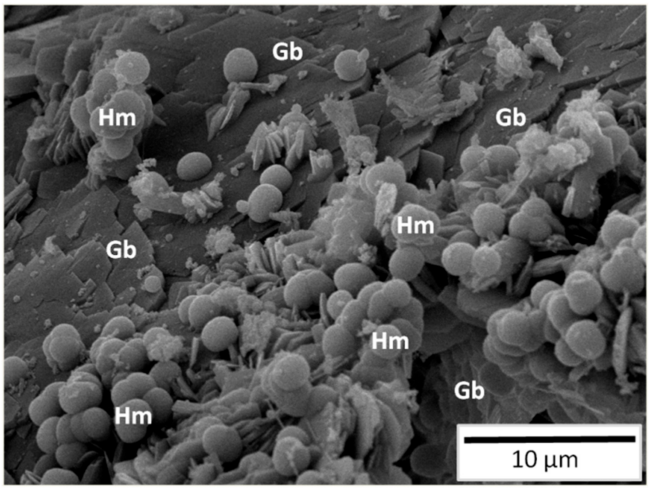


(**b**)

Figure 4. SEM images: single-layer monomineral biofilms: gibbsite (**a**) and hematite (**b**).



(**a**)



(**b**)

Figure 5. SEM images: gibbsite crystal bimineral film (**a**), gibbsite and hematite crystals (**b**). Gb: gibbsite, Hm: hematite.

At the time of their formation, biofilms have a smooth, shiny surface (Figure 4a). When they dry, they are covered by a network of cracks, recrystallize (well-crystallized) and become colonized by microorganisms, which quickly mineralize. According to EDS data, the chemical composition of the films (wt.%) is high in CO_2 (76.46), Al_2O_3 (18.44) and FeO (4.70). The gibbsite formed from it consists of CO_2 (26.29) and Al_2O_3 (73.71). Crystallization occurs gradually, and within the film single hexagonal plates appear; then, their number increases, and they form twin aggregates by (100) and (110). Short-column hexagonal prisms by (001) appear on the film surface (Figure 6a). Two crystallomorphological varieties of gibbsite are formed in the passages of digestive organisms: columnar forms on the products of the digestive tract and tabular forms of crystals on the walls. Complete crystallization ends in the formation of dense brushes of gibbsite crystals (Figure 6b). Films with Al-Fe composition crystallize sequentially: first gibbsite, then hematite (Figure 6c). The latter is in the form of biomorphosis by bacteria. Figure 6d shows a cross-section of the multilayer gibbsite film. The biomineral films are gradually transformed into crypto-, micro- and clear-crystalline gibbsite secretions.

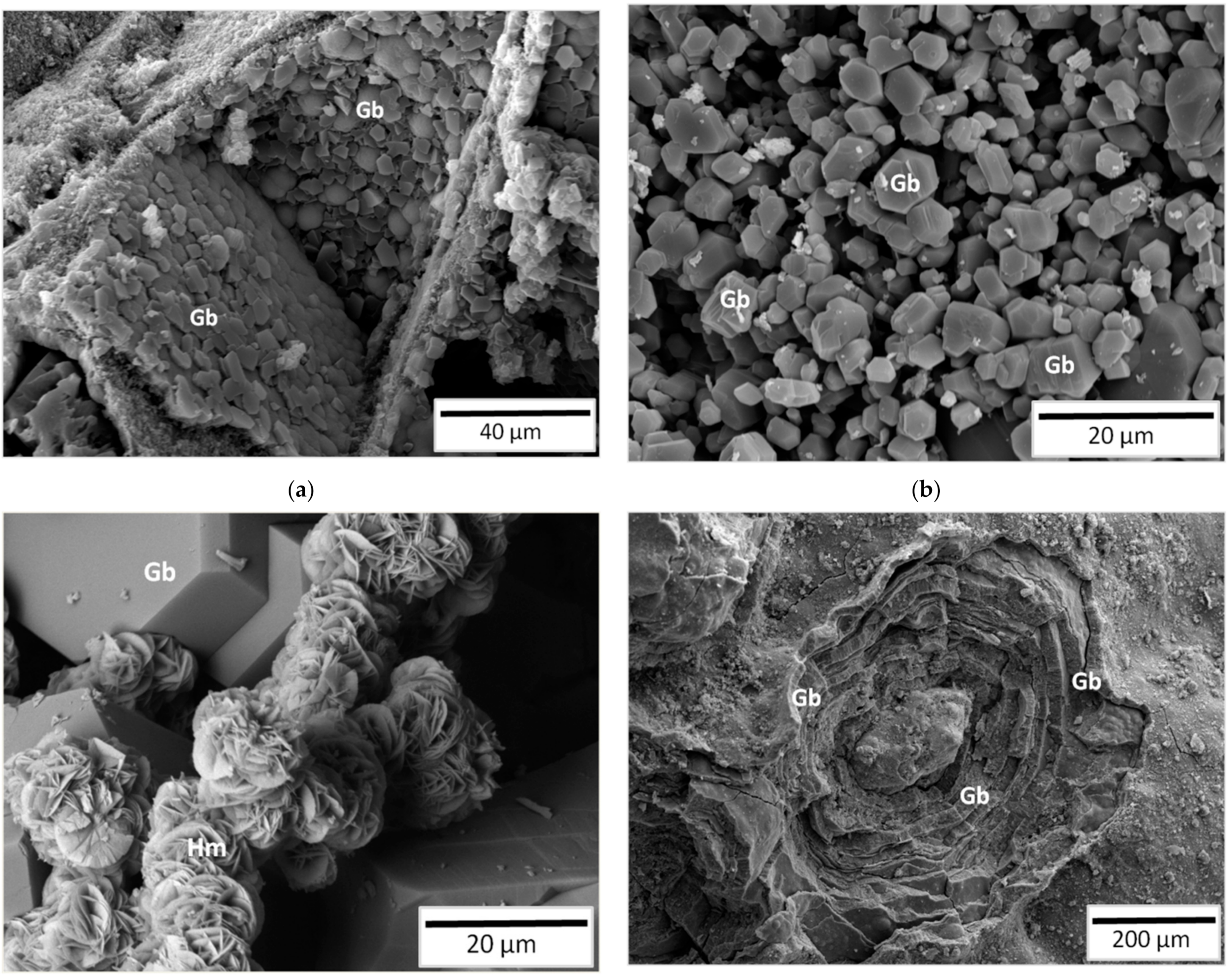
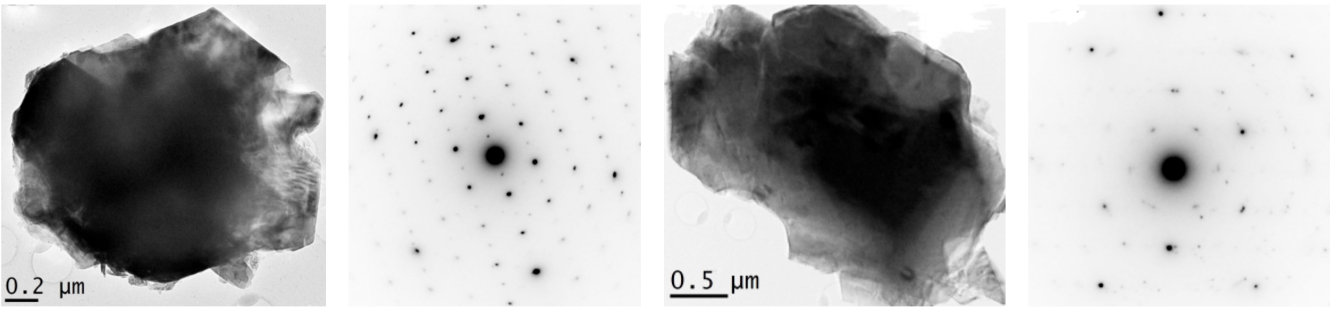


Figure 6. SEM images: short columnar gibbsite crystals (**a**), brushed crystalline gibbsite (**b**), gibbsite and hematite (**c**), section of multilayer gibbsite film (**d**). Gb: gibbsite, Hm: hematite.

The gibbsite was studied with a transmission microscope. Two types of diffraction patterns were obtained for single crystal gibbsite particles: type I (Figure 7a) and type II (Figure 7b). Type I composition is Al and $Al_{0.93}$ $Si_{0.05}$, and type II is $Al_{0.94}$ $Si_{0.05}$. In the patterns of the first type, relatively weak reflexes *hk*0 with $h + k = 2n + 1$ corresponding to a monoclinic structure (spatial group $P2_1/n$) were observed, while in the patterns of the second type, these reflexes caused by monoclinic distortion of perfect trigonal gibbsite structure were absent, with reflexes *hk*0 with $h + k = 2n$ more blurred in comparison than these reflexes in electronograms of the first type [3]. The appearance in some electronograms of the first type of *h*00 reflexes with 0*k*0 odd values of h or k indices forbidden by the spatial group $P2_1/n$ is likely connected with a local symmetry breaking of gibbsite crystals. In the patterns from textured gibbsite polycrystals, the *hk*0 reflexes with $h + k = 2n + 1$ were not observed [3,15–17]. A common feature of gibbsite is an irregular, often smooth shape of particles up to 2 microns in size. Only for gibbsite representing plant root phytomorphs, were particles showing hexagonal shaped fragments observed.



(**a**) (**b**)

Figure 7. TEM images: gibbsite for biofilms type I (**a**), gibbsite by biomorphosis type II (**b**).

Siberian laterites retain their original chemical and mineral composition and perfect gibbsite crystal surfaces for tens of millions of years [10]. In addition, this gibbsite does not convert to aluminum monohydrates boehmite or diaspore, a fact of extreme importance in solving the debate on the thermodynamic stability of alumina hydrates in the Earth's surface [15–17].

Tubular halloysite crystals formed from the biofilm are arranged radially, with the array in its plane and also perpendicular to the rock surface in the form of dense grouped brushes (Figure 8). The local pits contain randomly oriented crystals. The entire surface of Al-Si films and halloysite clusters is covered with red hematite biofilms. Regressive halloysite develops not only along the biofilms but also replaces the kaolinite at a depth of about 75 m. The replacement of alumina minerals by allophane and halloysite during climate change is widespread in nature and concerns even diaspore and corundum in Mongolia [10] and kaolinite in Central Africa [18]. In Siberia, drastic climate change began after the emergence in recent times of the highest mountain systems, such as the Himalayas and others [19].

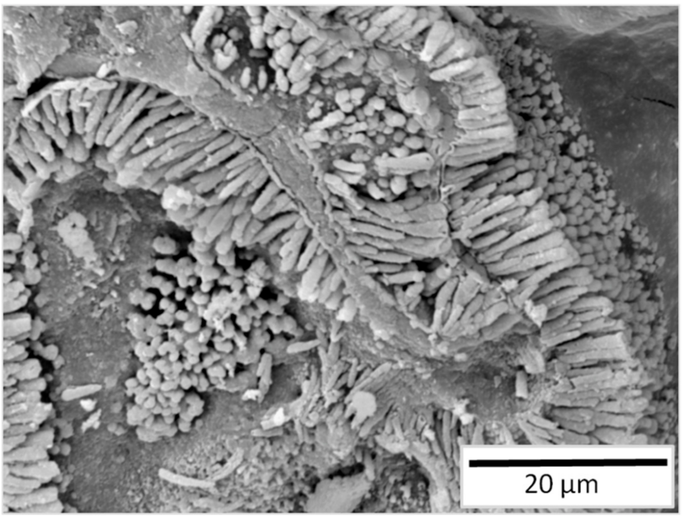
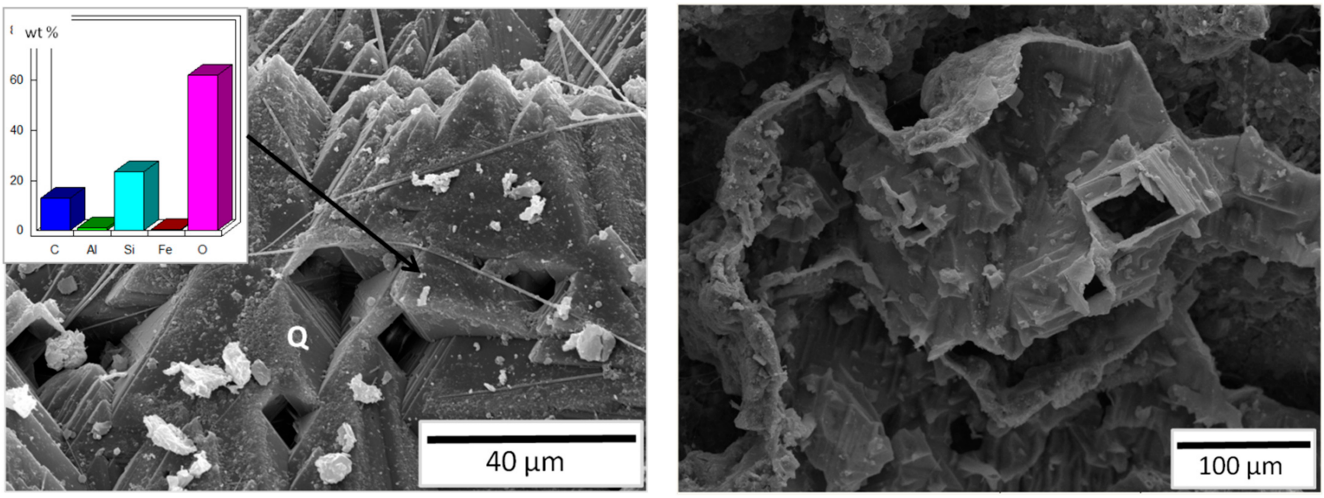


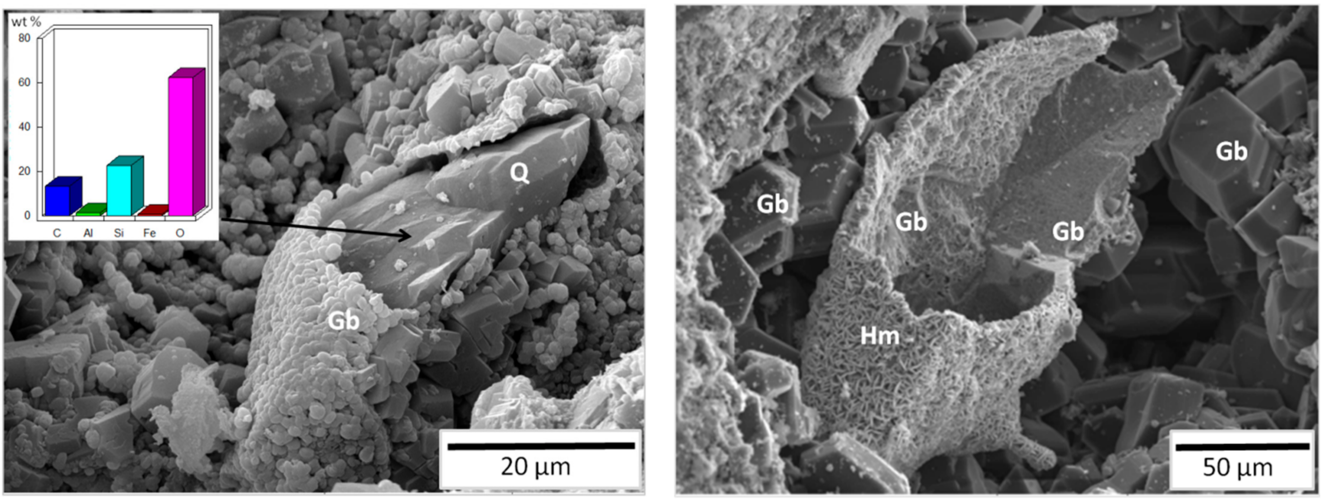
Figure 8. SEM image: biofilm and tubular crystals of halloysite.

Figure 9a shows a view of the parent quartz grain and defects in its crystal structure—tetragonal reflective pyramids. Biofilms have been found to develop most preferentially around crystalline quartz grains. The films completely cover its grains and, after drying, retain negative impressions with imprints of all its surface features (Figure 9b). They are biochemically active on quartz (Figure 10a), dissolving it; its volume decreases, and the film peels off and settles, turning into a shell of dense brush gibbsite. New biofilms and brushes of gibbsite emerge on the remaining relics until the quartz dissolves completely (Figure 10b). Biofilms are associated with quartz due to its piezoelectric properties [20].



(a) (b)

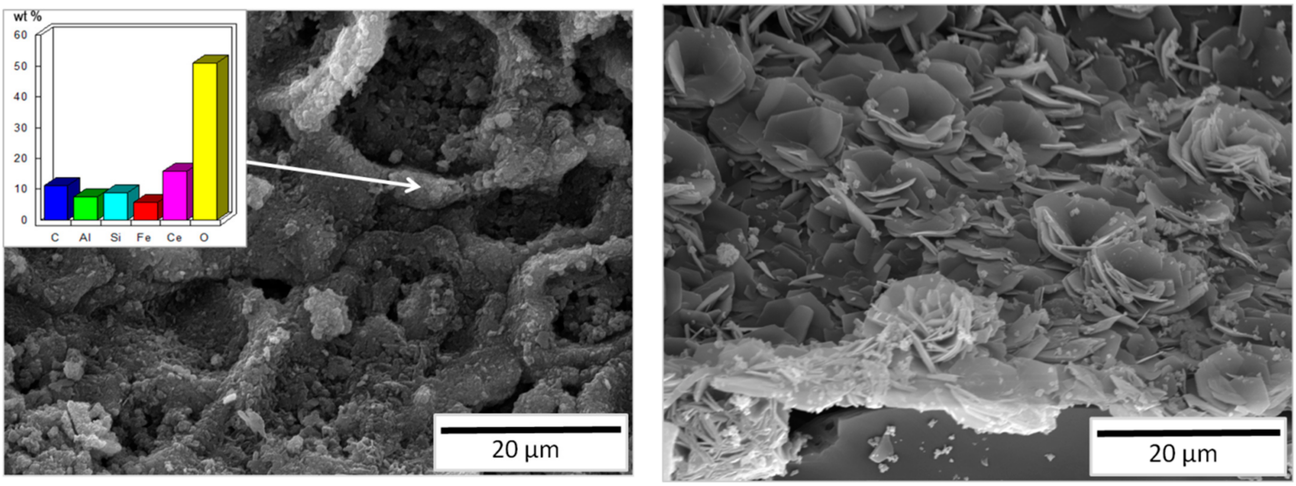
Figure 9. SEM images: the quartz surface of biofilm (**a**), negative casts of biofilms on the quartz surface (**b**). Q: quartz.



(a) (b)

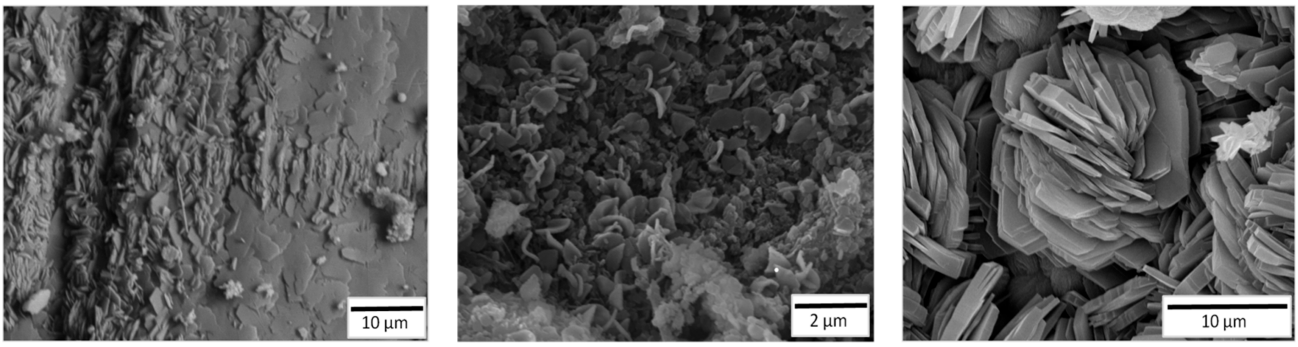
Figure 10. SEM images: relic of quartz grain surrounded by a brush of biogenic gibbsite (**a**), part of the biofilm around dissolved quartz grains: inside, brush of gibbsite crystals; outside: brush of hematite biomorphs (**b**). Gb: gibbsite, Hm: hematite, Q: quartz.

We followed the evolution of biofilms into kaolinite. The original films have a smooth surface that cracks when drying and ageing, with film fragments curling first around the edges and then all over the surface. Fe and Ce are present in the biofilms (Figure 11a). The film structure is reflected in the shape of the resulting kaolinite, including vermicular kaolinite (Figure 11b). Many examples show consonant occurrence of pseudohexagonal plates of kaolinite inside biofilm and on its surface. At the same time, next to them there are ridges of plates oriented perpendicularly to films (Figure 12a). In some films, kaolinite plates are oriented randomly (Figure 12b); in others, the ordering reaches fantastic degrees, expressed in mass formation of “stone flowers” from kaolinite (Figure 12c).



(**a**) (**b**)

Figure 11. SEM images: Si-Al biomineral film (**a**), vermicular kaolinite over biomineral film (**b**).



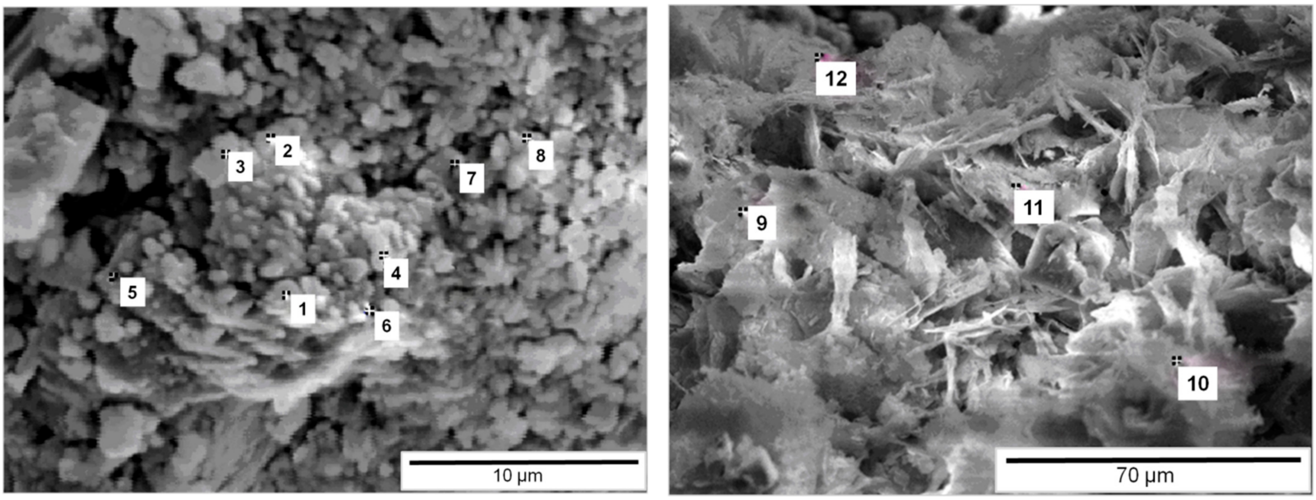
(**a**) (**b**) (**c**)

Figure 12. SEM images: hexagonal plates of kaolinite on Si-Al biofilm (**a**), haphazardly oriented kaolinite (**b**), and kaolinite roses on Si-Al biofilm (**c**).

As a result of the lateritization process under conditions of abundant water exchange and mass development of biota, biofilms consisting of C, Al, Si, Ti, Fe, La, Ce, Nd and Ba are formed. Clusters of spherical bodies containing, among others, rare-earth elements are formed along the films (Figure 13a, Table 1). Nd, La, Ba and Ce are present in biofilms, represented by differently oriented thin plates (Figure 13b, Table 1).

Table 1. EDS microprobe data (wt.%) of biofilms shown in Figure 10.

Spectrum	C	Al	Si	Ti	Fe	Ce	Nd	La	Ba	O	Total
1	11.96	6.05	5.51	0.23	9.16	17.75	-	-	-	49.34	100.00
2	15.33	7.28	7.97	0.42	4.32	5.76	3.2	-	-	55.71	100.00
3	19.13	4.49	2.21	0.61	10.35	2.02	-	-	-	61.19	100.00
4	12.89	8.26	9.57	3.51	4.72	4.06	-	-	-	56.99	100.00
5	16.69	10.94	1.46	0.56	10.04	1.04	-	-	-	59.27	100.00
6	11.12	11.26	12.76	0.43	5.60	2.36	-	-	-	56.47	100.00
7	9.23	11.86	13.99	0.00	2.84	8.70	-	-	-	53.38	100.00
8	12.07	11.16	12.87	0.00	3.10	2.69	-	-	-	58.10	100.00
9	15.27	7.49	5.41	1.45	1.65	9.43	3.03	5.98	1.46	48.82	100.00
10	16.13	8.46	6.05	1.19	1.52	8.84	2.54	4.88	-	50.38	100.00
11	16.33	9.28	6.36	0.25		10.03	3.25	4.96	-	49.54	100.00
12	9.72	3.11	7.19	3.73	4.55	15.06	4.19	9.27	2.39	40.80	100.00



(**a**) (**b**)

Figure 13. SEM image (1–12 spectrum): biofilm with spherical secretions (**a**), and plate-shaped biofilm (**b**).

5. Conclusions

Electron microscopic study of minerals of bauxite-bearing lateritic profiles of Siberia allowed us to establish that all processes of destruction of parent rocks and formation of supergenic minerals occur in close interaction with living and dead organic matter. The entire thickness of the weathering crust is affected by the organic world, especially its upper part in the 0–1 m interval, where the influence of flora, macrofauna and microfauna and their total mortmass is most evident.

Phytomorphoses of goethite and gibbsite caused by mineralization in tropical conditions of wood deposits, roots, biofilms and bacteria under conditions of bauxite formation were recorded by electron microscope.

Abundant biomineral films of various genesis and composition were established: Al, Fe, Al-Fe, Al-Si and Al-Fe-Si. The evolution of biofilms from amorphous to crystallized, and subsequently turning into druses crystals of gibbsite, hematite, halloisite and kaolinite were traced. Mono- and multilayer films were identified. Multilayer films arise because of the variable humid tropical climate, due to the alternation of dry and wet seasons.

For gibbsite, represented by phytomorphoses on plant roots, particles with the manifestation of fragments of hexagonal shape were observed using TEM.

According to biogenic gibbsite, the pattern of stepwise dissolution of quartz was restored.

Sorption of rare and rare-earth elements by biofilms was established. The mineral composition of the films is influenced by microlocal conditions: the accumulation of chemical elements, including rare and rare earths, with capillary water in dry seasons. Biomineralization products have microscopic dimensions, but they have universal and global significance for all weathering rocks and associated bauxite deposits.

Thus, the peculiarities of biomineral films, including their crystallization, as established herein, confirm their indispensable participation in the processes of bauxite formation.

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