

## Article

# The Problem of the Formation of Boehmite and Gibbsite in Bauxite-Bearing Lateritic Profiles

Vladimir Mamedov <sup>1,†</sup>, Natalia Boeva <sup>1,\*</sup> , Marina Makarova <sup>1</sup>, Elena Shipilova <sup>1</sup> and Philimon Melnikov <sup>1,2</sup>

<sup>1</sup> Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, 119017 Moscow, Russia; frolikovam@gmail.com (M.M.); lenusik.shipilva@rambler.ru (E.S.); filimon.mel@bk.ru (P.M.)

<sup>2</sup> Moscow Power Engineering Institute, National Research University, 111250 Moscow, Russia

\* Correspondence: boeva@igem.ru; Tel.: +7-(926)-203-97-61

† Died on 6 February 2022.

**Abstract:** The study of a large amount of factual material about the formation conditions of gibbsite or boehmite and their mutual transformations in lateritic bauxites allowed us to solve the problem of boehmite formation and its spatial and genetic relationship to gibbsite. The boehmite formation occurred only during the formation of sedimentary-lateritic bauxites from alluvial and lacustrine sediments that underwent bleaching and resilification at the stage of sediment flooding, as well as on bleached bedrock under sedimentary-lateritic bauxites. The most intense boehmite formation occurred at a depth of 20–30 m from the surface and was accompanied by an alumina input, which was realized here in the form of boehmite along with the gibbsite formation due to the hydrolytic decomposition of kaolinite and partially due to the input alumina. In the upper profiles, the recrystallization of bauxites occurs with the replacement of dissolving boehmite with gibbsite, with a decrease in the total  $\text{Al}_2\text{O}_3$  content and an increase in the amount of crystallization water. In classic lateritic bauxites, the boehmite content is highly insignificant; that is, its formation in them practically does not occur or is very much inhibited.

**Keywords:** lateritic bauxite; infiltration-metasomatic; sedimentary-lateritic; East Africa; Sangaredi Group; gibbsite; boehmite



**Citation:** Mamedov, V.; Boeva, N.; Makarova, M.; Shipilova, E.; Melnikov, P. The Problem of the Formation of Boehmite and Gibbsite in Bauxite-Bearing Lateritic Profiles. *Minerals* **2022**, *12*, 389. <https://doi.org/10.3390/min12030389>

Academic Editors: Maria Boni and Giovanni Mongelli

Received: 14 January 2022

Accepted: 18 March 2022

Published: 21 March 2022

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## 1. Introduction

Lateritic bauxite deposits are the main source of raw materials for aluminum production. These are residual deposits formed as a result of an intense chemical weathering of bedrock rich in aluminosilicates. The processing of bauxite by the Bayer method is largely determined by the nature of the bauxite. The rock-forming minerals in bauxites are gibbsite,  $\text{Al}(\text{OH})_3$ , and boehmite,  $\text{AlO}(\text{OH})$  [1]. The most reactive is gibbsite bauxite. The processing of boehmite bauxite requires a higher temperature and pressure [2]. Therefore, it is important to study the mineral composition of bauxite to optimize the operating modes of processing plants.

West Africa, in the territory of the Republic of Guinea and the Republics of Mali and Guinea-Bissau, contains the world's largest Fouta Djallon-Mandingo bauxite province (FDM) (Figure 1). Within this province, with an area of 111,000  $\text{km}^2$ , there are more than 1130 bauxite deposits and occurrences identified holding half of the world's resources of this natural raw material, important for the development of civilization. According to our estimates [3], over 92% of the 92 billion tons of the world's total bauxite resources are in the tropical zone of the Earth. Its name [3] derives from its geographical proximity to plateau-like mid-mountain massifs, i.e., the Fouta Djallon plateau in the west and the Mandingo Mountains in the east.



**Figure 1.** Overview map of the Republic of Guinea (the province of Fouta Djallon—Mandingo is red-outlined).

The formation of bauxite-bearing lateritic weathering profiles has occurred on various protoliths under various climatic and geomorphological conditions in specified provinces [4]. The study of the mineral composition of bauxite of various genetic and lithological types has allowed us to solve one of the most important problems of the formation of the main rock-forming minerals of bauxite—gibbsite and boehmite—and trace their spatial and genetic relationships.

Many researchers have tried to solve this problem over the past hundred years, relying on geological and mineralogical-petrographic methods of research and analysis, experimental data, mathematical modeling of physicochemical processes, and the use of data on climatic conditions [5–7].

Many believe that boehmite is formed due to the dehydration of gibbsite under the influence of elevated temperature due to the pressure of overlapping strata and the igneous intrusions, as well as metamorphisms [8]. Gibbsite is more common in a humid tropical climate, and boehmite is more common in a tropical climate with a long dry season. In addition, dehydrated minerals appear more often in the dry, upper parts of the profiles than in the lower, wetter parts close to the groundwater level. It is also well known that sedimentary bauxite deposits contain more gibbsite when they are porous and young but more boehmite and diasporite when they are old and compacted [8,9]. In an article by Y. Tardy and D. Nahon, the mechanisms of the formation of aluminum oxide and hydroxide and their distribution in various laterite media were discussed. They suggested that the two main factors of the distribution of minerals and bauxite might be the water activity and the temperature [10].

The influence of climate on the boehmite formation after gibbsite bauxites was noted by V. M. Sinitsyn, believing that the insolation is sufficient for this [11]. P. Didier and co-authors have believed that the boehmite or gibbsite formation is influenced by the humidity of the air in the weathering profile [12]. B. Balkay and G. Bardossy have noticed that,

in Guinea and Mali, the content of boehmite increases in more arid areas [13]. However, they did not say whether it was formed or preserved in these conditions.

Some researchers believe that boehmite is formed on the surface due to fires [14], and others believe it led to the formation of diasporite and corundum in Australia [15]. However, J. Lapparent and J. De. Les have indicated that boehmite is formed at the ground-water level [16]. The same conclusion was made by V. A. Bronevoy and co-authors [17]. W. D. Keller believe that boehmite is formed when gels age in the presence of humic acids [18].

Researchers have argued that boehmite forms under acidic conditions [19–21]. At pH 6.5–6.7, a narrow range in which the solubility of aluminum hydroxide is minimal, it precipitates as boehmite [22,23].

On the other hand, boehmite formation under more alkaline conditions has been recorded in some experiments [24]. Boehmite forms in weakly mineralized solutions with a low SiO<sub>2</sub> content [18]. Calculations by V. A. Bronevoy and co-authors have also shown a need for a low (less than 0.1 mg/L) SiO<sub>2</sub> concentration but a high aluminum concentration [17]. In 1926, a hypothesis was put forward by H. Harassovitz, according to which the primary mineral was gibbsite, and boehmite formed subsequently when the deposits were exposed to a high temperature and pressure [25].

At different times, boehmite formation has been recorded. In all cases, the study was carried out at an elevated temperature and pressure, at which the formation of boehmite was obvious [26–28].

All these viewpoints are based on unconfirmed facts and on experiments simulating various climatic, geologic, geomorphologic, and landscape–geochemical environments, which are difficult to compare. Much more reliable facts about the environments conducive to gibbsite or boehmite formation and their mutual transformations can be obtained by analyzing these problems within the Fouta Djallon—Mandingo bauxite province. This has been well studied for several decades. Within this province, prospecting, evaluation, and exploration work has been carried out in various areas, including a detailed exploration with large-scale mapping in hundreds of fields, routine year-round hydrological monitoring at a number of these fields, the year-round monitoring of the gas composition of underground intra-pore air, and a study of the hydrochemistry of hydrodynamically different waters in the weathering profile [29].

## 2. Geologic Setting

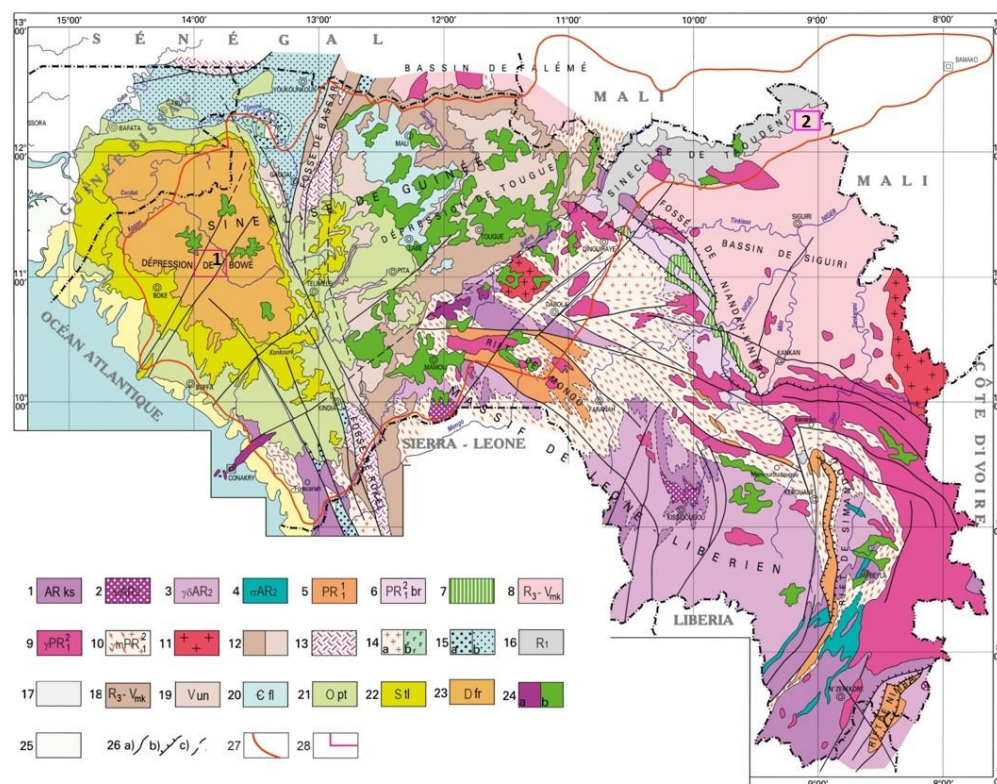
In regional geological terms, the territory of the FDM province is confined mainly to the platform cover of the Saharan Plate of the African Platform (Figure 2). In the central and western parts, these are terrigenous sedimentary rocks of the Guinean Syncline lying mainly subhorizontally. In the west, the Devonian, Silurian, and Ordovician sedimentary deposits form the Beauvais Syncline, and the Vendian and Riphean deposits form the Tuge Depression in the central part. In the east beyond the Baffing Valley, Vendian deposits of the southern marginal part of the Taudeni Syncline are developed and are also represented by terrigenous sedimentary rocks lying subhorizontally.

### 2.1. Parent Rock Geology

Parent rock geology is represented by the platform basement and the young polyfacial continental formations. Sixty to seventy percent of the parent rocks consists of sedimentary Paleozoic and Eocambrian–Vendian rocks of the platform cover of the South-Saharan Platform, among which significantly clay varieties (mudstones, siltstones, and fine-grained sandstones or aluminosilicate rocks) predominate, and 30–40% of the parent substrate in the province consists of sills and subordinate dikes of basic igneous rocks of the Mesozoic Trap Suite, which are widely intruded into the subjacent subhorizontal deposits of the platform cover. Dolerites and Konga diabases predominate, but gabbro-dolerites are much less common. The remains of the Middle Miocene continental deposits are located in this territory. Due to the wide spreading of lateritic weathering profiles, young continental



formations accumulated mainly due to the erosion and redeposition of weathering products in various (watered or dry) conditions (Figure 2). The greatest accumulation of alluvial and alluvial-lacustrine sediments occurred in the Middle Miocene during the last marine transgression, when vast areas of alluvial-lacustrine plains were formed and were towered over by the remnants and massifs of older topography [29]. To date, these Sangaredi Group deposits have been preserved only as pieces, with the largest body at the Sangaredi bauxite deposit (Figure 2) [30]. These sediments at the stage of flow flooding underwent a process of bleaching (removal of iron) that is important for subsequent lateritic bauxite formation, which was accompanied by resilification [29].



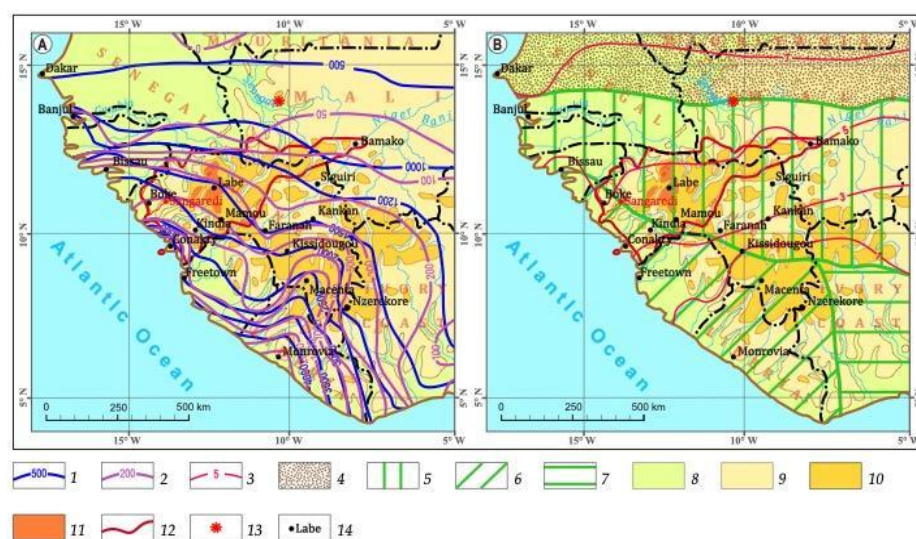
**Figure 2.** Tectonic framework of Guinea-Bissau and the western part of the Republic of Guinea with the province of Fouta Djallon-Mandingo outlined in red. The crystalline basement of the African platform. Crystalline foundation base. 1—gneisses and schists with quartzites and orthoamphibolites (Kasila, Dabola, Cambui, and Mani groups); 2—charnockites, enderbites, and anorthosites; 3—granitoids; 4—metanorites, amphibolites, metapyroxenites, and metahyperbasites; 5—the folded cover of the crystalline basement; sedimentary structures of the Early Proterozoic orogeny—metamorphosed terrigenous sediments with bodies of metagabbroids, metapyroxenites, and amphibolites (Tinikan Group, Mongo, and Timbo formations); 6—sedimentary structures of the late stage of the Early Proterozoic orogeny—terrigenous-volcanogenic formations (Birimian Group); 7—metasandstones, quartz-mica schists, and amphibolized mafic rocks; 8—sheared sandstones, phyllite-like shales, and phyllites (Birimian Group); 9—granitoids; 10—granite-gneisses and migmatites; 11—granites and aplites; 12—sandstones, siltstones, sericite-chlorite shales, and quartzites (Madina-Kouta and Oundou groups); 13—volcanic-sedimentary deposits (Pananpou, Koubia, and Bania formations); 14—intrusions of (a) acidic and (b) basic composition; 15—continental terrigenous deposits: (a) gravelstones and conglomerates with interlayers of siltstones and (b) arcose (Youkounkoun and Taban groups); 16—sediments (Segou Group and Dabatou Formation); 17—argillaceous-carbonate deposits (Bale Formation); 18—sandstones, siltstones, sericite-chlorite shales, and quartzites (Madina-Kouta Group); 19—siltstones and mudstones with interlayers of quartzite sandstones (Oundou Group); 20—marine terrigenous and terrigenous-carbonate deposits

(Faleme Group); 21—coarse quartz sandstones, gravelstones, and conglomerates (Pita Formation); 22—silty mudstones and mudstones with interlayers of fine-grained sandstones (Telemile Formation); 23—silty-mudstones, fine-grained sandstones, and mudstones (Faro Formation); Gondwana Platform Activation; 24—Mesozoic trap formation: (a) dunites, pyroxenites, gabbro-pyroxenites, and nepheline syenites, (b) dolerites, Konga diabbases, and gabbro dolerites; 25—Meso-Cenozoic Bissau depression; 26—faults: a—main faults; b—thrusts; c—supposed; 27—borders of the province of Fouta Djallon–Mandingo; 28—sampling areas: 1—Sangaredi Group, 2—regions of Western Guinea and Mali.

## 2.2. Climate/Weathering

The province is confined to a tropical monsoon climate zone. However, in different areas (Figure 3), many climatic parameters widely differ:

- The amount of precipitation varies from 3500–4000 mm/year in the southwest to less than 1000 mm/year in the extreme northeast.
- In the direction from the southwest to the northeast, the number of dry months increases from 3–4 to 6–7, and the amount of unevaporated moisture decreases from 600 to 100 mm/year.



**Figure 3.** Maps of (A) isohyets and isopleths of unevaporated moisture and (B) topoclimatic zones and dry period durations, West Africa, based on statistical data at [www.climatemps.com](http://www.climatemps.com), accessed on 1 March 2022. 1—iso-hyet with values in mm; 2—iso-pleth of unevaporated moisture with values in mm; 3—iso-pleth of the dry period ( $\leq 10$  mm/month) duration in months; 4–7—topoclimatic zones of 4—Sahel, 5—savanna and forest savanna, 6—monsoon climate, and 7—subequatorial and equatorial climate; 8–11 altitudes: 8—0–200 m, 9—200–400 m, 10—400–1000 m, and 11—1000–2400 m; 12—outline of the Fouta Djallon–Mandingo bauxite province; 13—Nyakolonesiraya bauxite deposit; 14—weather station and its label.

To the north and northeast of the province, topoclimatic zones change from forest savannas and wet savannas to dry savannas and Sahel-like climates.

In general, the landscape and climatic conditions vary from very humid to almost arid.

## 2.3. Genetic Classification of Bauxites

Depending on the protolith and the features of supergene processes in the tropical monsoon climate, there are three genetic classes of bauxites distinguishable in the Fouta Djallon–Mandingo Province [29], namely, classic lateritic in situ, sedimentary-lateritic, and infiltration-metasomatic.

Classic lateritic bauxites in situ were formed after the bedrock (Devonian silty mudstones and Mesozoic dolerites and Konga-diabbases) and are low-grade ( $\text{Al}_2\text{O}_3$  from 40 to

45 wt % according to the results of the calculation of deposits) with a relatively high iron content (<23 wt %). Gibbsite is dominant, and boehmite is subordinate. The lateritic bauxites show different textures: those formed after the Devonian sedimentary rocks are laminated, whereas those that are apodoleritic are conchoidal [29].

Sedimentary-lateritic bauxites formed after various lithofacies of the Sangaredi Group mainly have a boehmite content higher than that in the other ores. Among the sedimentary-lateritic bauxites with relict textures and structures of the original alluvial, proluvial-alluvial, and alluvial-lacustrine sediments of the Sangaredi Group, there are three lithological types: conglomerate and gravelstone-conglomerate bauxites, gravelstone bauxites, and gravelstone-sandstone bauxites. General differences consist in the texture and structure and in the size and composition of the detrital material. They form complex lenticular bodies and facies intercalation. In general, the Sangaredi Group stratification has a transgressive character, i.e., the coarser varieties (conglomerate and gravelstone-conglomerate) are more typical of the lower strata, whereas the finer varieties (gravelstone and gravelstone-sandstone) are of the lower strata.

Infiltration-metasomatic bauxites are related to the sedimentary-lateritic bauxites spatially and genetically. They are formed after bleached bedrock under the sediments of the Sangaredi Group [4]. They have a high-alumina composition ( $\text{Al}_2\text{O}_3$  is more than 50 wt %). They always contain boehmite; however, its content is lower than that in sedimentary-lateritic bauxites. The content of gibbsite in the infiltration-metasomatic bauxites is always greater than that of boehmite. Strictly speaking, all bauxites including those of the classic lateritic in situ class are infiltration-metasomatic, because the alumina input is also recorded in them, but to a much lesser extent than in classical infiltration-metasomatic bauxites formed under sedimentary-lateritic bauxites.

Textural and structural features of the protolithic have been completely obliterated in the infiltration-metasomatic bauxites. Therefore, it is possible to distinguish them as a separate genetic class. The bauxite acquires either the geliform aphanitic (cryptocrystalline) texture or the microolitic and oolitic texture. Lithological types are also distinguished: geliform aphanitic, geliform oolitic, and microolitic bauxites.

### 3. Sampling and Analytical Methods

#### 3.1. Sampling

Samples were taken in the territory of the province in the east (West Bamako, Falesa, Kenyeba, East Bamako, and Bafoulabe deposits) and in the west where there were bauxite deposits of the Sangaredi Group identified. The vast majority of them are located on the left bank of the Kogon River and in the Kogon-Tomine interfluvial area at the Sangaredi, Silidara, Bidikoum, N'dangara, Boundou-Waade, Koobi, Wouassou, Parawi, Thiapikoure, Bourou-sud, and Tiewere deposits (Figure 2).

To study the climatic factor of boehmite formation, bauxite samples, which were taken in 1982 to determine the industrial and economic prospect of “white bauxite” when sampling at deposits in the areas of Eastern and Western Bamako, were analyzed.

In total, 3265 bauxite samples of various lithological and genetic classes were analyzed. They characterized meter-long intervals of auger holes drilled during geological exploration on a 300 m × 300 m grid. The samples were combined by lithological type, the depth of occurrence from the surface, and the degree of lateritization. Previously published materials were also used for a complete analysis of the rocks of the area.

#### 3.2. Analytical Methods

The mineralogical composition of bauxites and their gibbsite and boehmite concentrations were determined by the combination of three methods of analysis: X-ray fluorescence, X-ray powder diffraction, and thermal analysis. Scanning electron microscopy with an EMP prefix was also used to identify minerals.

Whole-rock samples were crushed to 200 mesh size fractions using an agate mill.



The chemical composition of bauxites was analyzed by the XRF method using the model AxiosAX “RANalytical” (Netherlands, 2012; [www.panalytical.com](http://www.panalytical.com), accessed on 1 March 2022) X-ray fluorescence spectrometer. The spectrometer is equipped with a 4 kW X-ray tube with an Rh anode. The maximum voltage on the tube is 60 kV, and the maximum anode current is 160 mA. When calibrating the spectrometer industry and state, standard samples of the chemical composition of rocks and mineral raw materials were used. Standard samples of the US Geological Survey (USGS) were used as control samples. Dried at 110 °C, samples were prepared for measurements in the spectrometer as follows. The analysis of the main components was performed according to the NSAM VIMS 439-RS method for chemical research. According to this method, glassy discs were melted from the sample material by induction heating of calcined sample material with lithium borates at a temperature of 1200 °C. The calcined sample material was obtained after determining the losses during calcination at a temperature of 1000 °C (NSAM VIMS 118-X methodology). To perform the analysis of trace elements, tableted preparations were made by cold pressing the dry substance of the sample with the addition of a plastic filler. Thus, the presented table of analysis results combines the data obtained by measuring fused and pressed preparations and data on loss during calcination. The total content of iron and sulfur regardless of the actual valence state is presented in the form of total Fe<sub>2</sub>O<sub>3</sub> and SO<sub>3</sub>, respectively, which is a feature of the applied analysis method.

X-ray powder diffraction was performed by an Ultima-IV diffractometer manufactured by Rigaku (Japan, 2019; <https://japan.rigaku.com/en/products/xrd/ultima>, accessed on 1 March 2022). CuK $\alpha$ <sub>1</sub> radiation with the following operating conditions: a 40 kV voltage, a 80 mA beam current, a graphite monochromator, continuous scanning, a 8°/min scanning speed, a 1° slit DS = SS, an 18 °C ambient temperature, and a 30% humidity.

Simultaneous thermal analysis (STA) was performed by a STA 449 F1 Jupiter “Netzsch” device (Germany, 2009; <https://analyzing-testing.netzsch.com/ru/pribery-resheniya/sinhronnyj-termicheskij-analiz-termogravimetriya-i-dsk/sta-449-f1-jupiter>, accessed on 1 March 2022). The recording was carried out at speed of 10°/min in an air atmosphere in crucibles with closed lids at a temperature of 1050 °C. The weight of the suspension was ~40 mg.

Electron microscopic studies were carried out using Cambridge CamScan 4 (Cambridge, England) scanning microscope (SEM) with an energy dispersive spectrum LINK-860 (EDS).

## 4. Results

Contents of gibbsite and boehmite in bauxites can be estimated by compiling methods of data of X-ray fluorescence, X-ray diffraction, and thermal analysis.

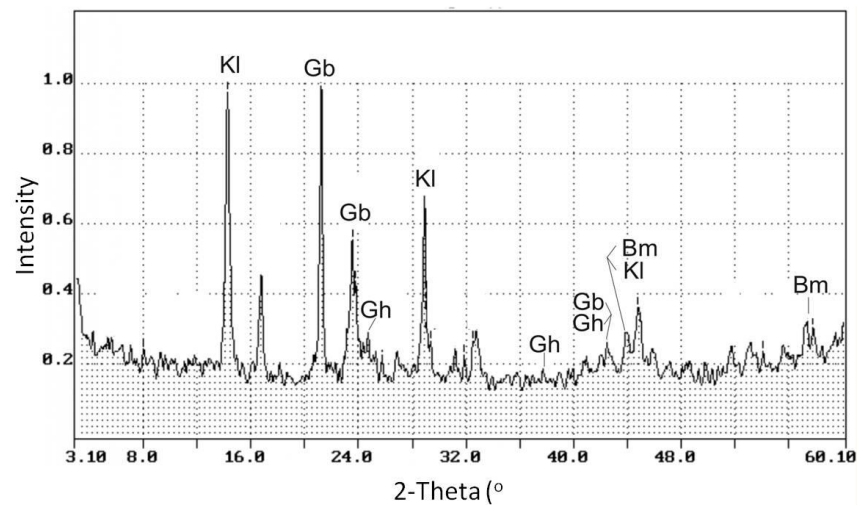
### 4.1. X-ray Powder Diffraction

The analysis showed that the major mineral components in all samples are boehmite, gibbsite, goethite, and kaolinite (a representative X-ray diffractogram is shown in Figure 4). Gibbsite (Gb) is typically well crystallized and shows characteristic reflections, the most important and best defined of which are the 4.83 and 4.37 Å peaks; the boehmite (Bm) reflection peaks occur at 2.34 and 1.84 Å.

### 4.2. Simultaneous Thermal Analysis

When gibbsite is heated in the temperature range of 240–450 °C, the endothermic effect associated with the release of the main mass of combined water of gibbsite is recorded in the graphs of differential scanning calorimetry (DSC). At the same time, some boehmite forms as an intermediate product. Dehydration and decomposition of boehmite occurs at a temperature of 45–600 °C. This is seen as the endothermic effect in this temperature range of the DSC graph. The exothermic effect in the temperature range of 950–1200 °C is related to the phase transition of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) (Figure 5a). It is known that gibbsite contains 34.6% H<sub>2</sub>O. If the TG graphs determine the mass loss during heating

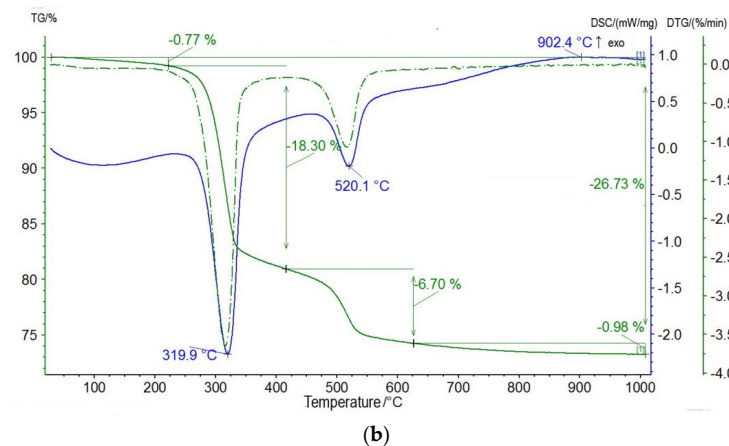
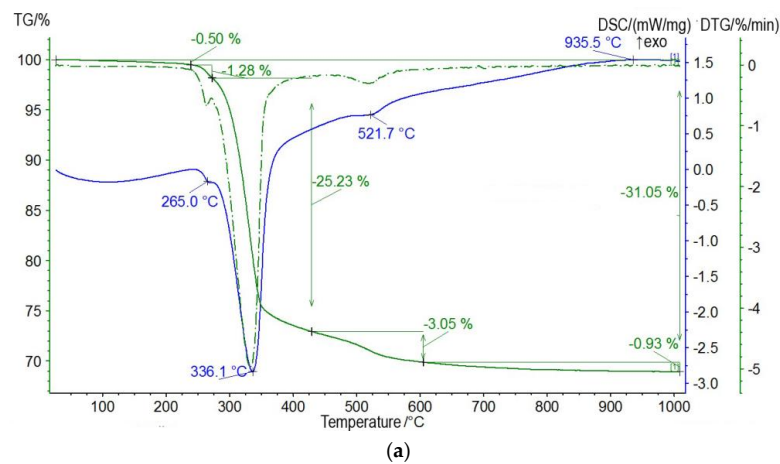
in the interval of its dehydration, then it is possible to calculate the gibbsite content in the rock by the following formula:



**Figure 4.** XPD parent of bauxite: Kl—kaolinite, Gb—gibbsite, Bm—boehmite, and Gh—goethite.

$$C_g = 2.89 \times C_w \quad (1)$$

where  $C_w$  is the weight loss during gibbsite dehydration (in %), and  $C_g$  is the gibbsite content in the sample (in %).



**Figure 5.** Thermal curves: (a) gibbsite; (b) gibbsite and boehmite.



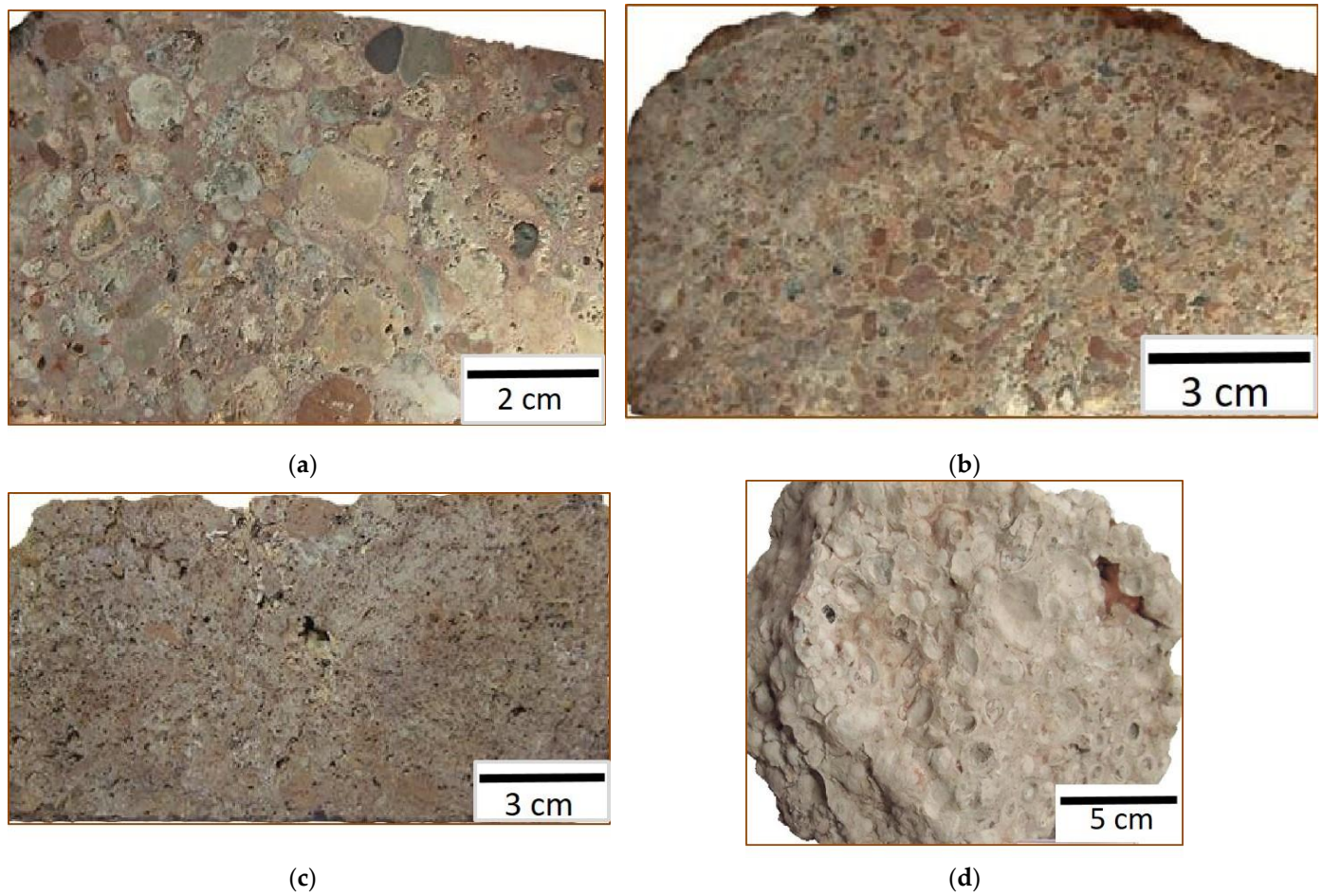
Boehmite is identified in the DSC charts in the temperature range of 500–650 °C. Therefore, 15% of the combined water is released (Figure 5b). The boehmite content in the rock was calculated by the same method as was used to determine gibbsite content.

#### 4.3. X-ray Fluorescence

Table 1 shows data on the average chemical composition of bauxites of various lithological types of the Sangaredi Group with consideration of their depth of occurrence (Figure 6). The composition of the sedimentary facies of the Sangaredi Group with consideration of the intensity of lateritic weathering is shown in Table 2. The chemical composition of the bauxite in the west of the province (the left bank of the Kogon River and the Kogon-Tomine interfluvium) and the bauxite in the east of the province (Eastern and Western Bamako) is shown in Table 3.

**Table 1.** The average chemical composition of bauxites of the Sangaredi District of various lithological types with consideration of their depth of occurrence.

Sampling Interval	Count of Samples	SiO <sub>2</sub> , wt %	Al <sub>2</sub> O <sub>3</sub> , wt %	Al <sub>2</sub> O <sub>3</sub> mono, wt %	Fe <sub>2</sub> O <sub>3</sub> , wt %	TiO <sub>2</sub> , wt %	LOI, wt %
Bauxites after sedimentary clays (geliform and oolitic)							
0–5 m	173	1.06	57.74	1.47	7.75	2.69	30.01
5–10 m	186	0.87	59.93	3.87	5.30	2.67	30.48
10–20 m	176	1.11	63.87	16.72	2.51	4.40	27.37
20–30 m	81	0.80	63.49	17.67	2.89	5.13	26.94
over 30 m	11	1.23	61.07	4.72	3.37	3.99	29.60
Psammite bauxites							
0–5 m	229	0.75	58.62	3.31	5.91	4.23	29.73
5–10 m	208	0.76	60.65	5.64	4.16	3.85	29.84
10–20 m	258	0.89	62.75	11.16	2.89	3.69	29.03
20–30 m	106	0.96	60.70	11.12	4.04	5.52	28.04
over 30 m	19	1.72	57.67	12.06	8.22	6.47	25.17
Gravelstone bauxites							
0–5 m	239	0.83	59.27	3.06	5.89	3.23	30.03
5–10 m	207	0.87	61.00	3.12	3.25	3.03	31.10
10–20 m	216	0.87	62.42	7.06	2.49	3.16	30.31
20–30 m	79	0.74	62.14	14.11	4.31	4.64	27.43
over 30 m	12	2.71	56.18	6.28	10.34	4.67	25.35
Conglomerate bauxites							
0–5 m	39	0.81	62.62	8.10	3.10	2.80	29.92
5–10 m	73	0.60	63.49	10.53	2.03	3.37	29.76
10–20 m	283	0.68	64.11	14.17	2.25	3.50	28.71
20–30 m	194	0.68	64.90	18.25	2.65	3.48	27.54
over 30 m	27	1.60	64.43	16.40	3.34	3.11	26.77



**Figure 6.** Photos sedimentary-lateritic bauxites: (a) conglomerate bauxites, (b) gravelstone bauxites, (c) sandstone-like bauxites, and (d) oolitic bauxites.

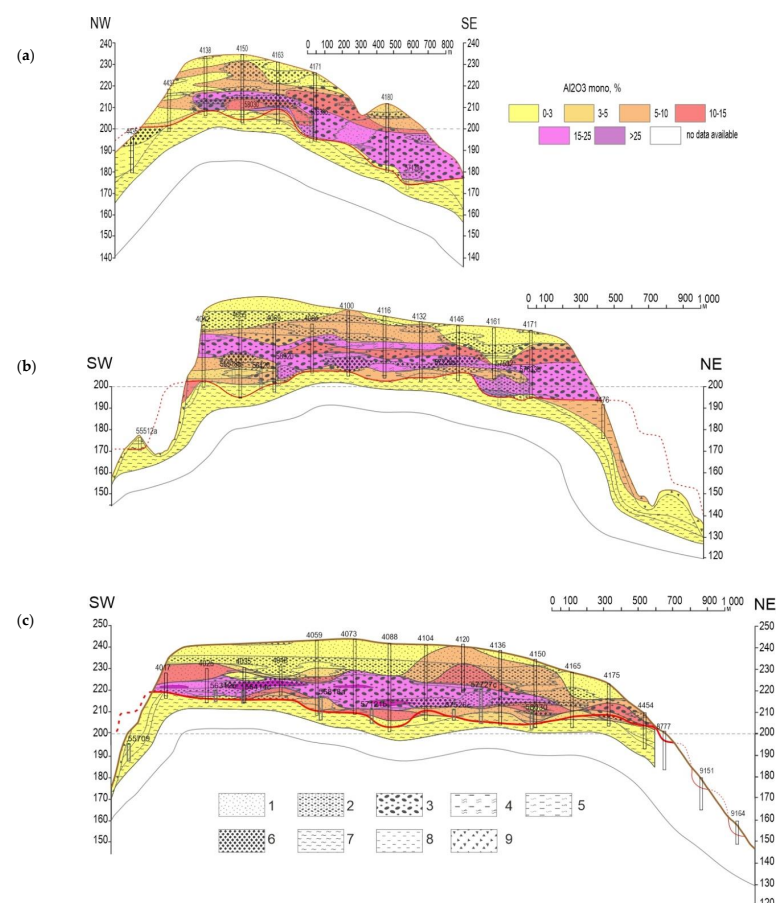
**Table 2.** The composition of sedimentary-lateritic formations of the Sangaredi Group with consideration of their lithological facies and intensity of lateritic weathering. Note: input/output values are calculated in relation to subjacent rocks of the weathering profile that are less lateritized.

Intensity of Lateritization		After Sedimentary Clays				After Psammite Sediments				After Gravel Sediments				After Gravel and Gravel-Pebble Sediments							
Value	Count of Samples	Content				Count of Samples	Content				Count of Samples	Content				Count of Samples	Content				
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3mono</sub>	Fe <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3mono</sub>	Fe <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3mono</sub>	Fe <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3mono</sub>	Fe <sub>2</sub> O <sub>3</sub>	
SiO <sub>2</sub> < 2	wt %	69	1	58	1	8	168	1	59	4	5	208	1	60	3	4	48	1	63	10	2
	kg/m <sup>3</sup>		20	1062	27	143		16	1169	79	108		14	1080	56	78		12	1229	196	43
	input/output, kg/m <sup>3</sup>		–37	108	–250	62		–41	164	–116	1		–46	86	–145	–16		–54	111	–145	–39
2 < SiO <sub>2</sub> < 5	wt %	7	4	59	17	5	16	3	58	11	6	18	4	59	12	6	11	4	61	19	5
	kg/m <sup>3</sup>		61	1014	294	86		57	1005	195	107		61	994	200	94		67	1117	341	82
	input/output, kg/m <sup>3</sup>		–49	121	196	14		–56	22	–2	–7		–64	–10	–10	–58		–80	28	–11	–12
5 < SiO <sub>2</sub> <10	wt %	10	7	55	6	4	14	6	56	11	7	23	7	57	15	6	12	8	59	19	5
	kg/m <sup>3</sup>		109	892	98	72		113	983	197	115		124	1004	259	101		147	1089	352	94
	input/output, kg/m <sup>3</sup>		–102	83	–25	36		–77	137	–29	37		–70	38	–1	19		–73	169	110	16
10 < SiO <sub>2</sub> < 15	wt %	6	14	54	8	2	4	12	54	14	5	5	11	56	15	5	3	13	54	14	5
	kg/m <sup>3</sup>		211	809	122	35		190	846	225	78		194	966	260	82		220	920	242	78
	input/output, kg/m <sup>3</sup>		–47	5	5	–20		–83	41	135	24		–78	115	58	3		–99	–8	51	22
15 < SiO <sub>2</sub> < 20	wt %	9	17	52	8	4	11	17	51	6	3	5	17	53	13	5	3	18	52	11	3
	kg/m <sup>3</sup>		257	804	117	55		272	805	90	54		272	851	202	79		319	928	191	56
	input/output, kg/m <sup>3</sup>		–373	245	113	31		–351	215	57	–3		–376	299	199	0		–377	330	188	5
Sediments least altered by lateritization	wt %	1	44	39	0	2	1	41	39	2	4	1	42	36	0	5	1	44	37	0	3
	kg/m <sup>3</sup>		631	559	4	24		624	590	33	56		648	552	3	79		697	598	3	52

**Table 3.** Data on the first meter of geliform bauxite the Middle-Late Miocene regions of Western Guinea and Mali.

Region	Count of Samples	Content, wt %				
		Variation	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> Mono	Fe <sub>2</sub> O <sub>3</sub>
Western Guinea	22	from	0.5	46.7	4.1	8.4
		to	1.5	59.5	16.3	28.3
		average	1.2	52	8.2	17.1
Mali (West Bamako, Falesa, Kenyeba)	9	from	0.5	54.36	15.1	1.96
		to	4.47	69.31	50.7	18.28
		average	1.17	63.45	27.86	5.82
Mali (East Bamako, Bafoulabe)	11	from	0.43	63.29	24.1	2.0
		to	1.07	70.7	62.0	6.05
		average	0.73	67.46	45.82	3.25

Based on the data of X-ray phase thermal and chemical analysis, the content of boehmite in the weathering crust profile was calculated (Figure 7, Tables 1–3).



**Figure 7.** Distribution of aluminum monohydrate (Al<sub>2</sub>O<sub>3</sub> mono) at the Sangaredi bauxite deposit. Lithology: 1—psammite sediments and bauxites; 2—gravellite sediments and bauxites; 3—conglomerate sediments and bauxites; 4—geliform bauxites; 5—gelified bauxites; 6—oolitic bauxites; 7—clayey sediments and bauxites; 8—classical bauxites and ferruginous laterites; 9—deluvium. (a) the northeastern part of the deposit; (b,c) the central part of the deposit, the distance between the profiles is 300 m.



## 5. Discussion

If we adhere to a dialectically based approach to the development of weathering profiles as a system that is destroyed from above and built up from below, it is quite clear that, as the planation develops, infiltration-metasomatic bauxites can become exposed on the surface.

### 5.1. Distribution of Boehmite in Bauxite-Bearing Lateritic Profiles Depending on the Genetic Type of Bauxite

In lateritic bauxites without remnants of infiltration-metasomatic bauxites, which are widely preserved in the bauxite deposits of the province, the amount of aluminum monohydrate rarely exceeds 1.5–2 wt %. This is due not only to boehmite but also to goethite. It is important that the average thickness of bauxite ores (with an  $\text{Al}_2\text{O}_3$  content >40 wt %) according to the calculation of bauxite resources at hundreds of deposits is mainly from 5 to 8 m, rarely up to 9–10 m. Consequently, the bauxite horizon is located close to the surface in a zone intensely influenced by the decomposition products of plant litter, roots, and active biota [31].

As mentioned above, sedimentary-lateritic bauxites are preserved as pieces and have the highest content of boehmite. It is important to trace the boehmite content of bauxites upsection. Only occurrences of sedimentary-lateritic bauxites show a high thickness, 5–7 times higher than that of the occurrences of classic lateritic bauxites. Such thick bauxite occurrences (up to 25–45 m) have been preserved only at the Sangaredi deposit. Among the sedimentary-lateritic bauxites, there are conglomerate bauxites, gravelstone bauxites, sandstone-like bauxites, and pelitomorphic and clayey bauxites, as well as oolitic bauxites formed after layers of sedimentary clays and after the sandy–clayey cement of gravelstone and conglomerate bauxites with the formation of larger pisolites (Figure 6).

As an example, we show three profiles of the Sangaredi deposit (Figure 7), which, along with its lithology, show the distribution of aluminum monohydrate ( $\text{Al}_2\text{O}_3$  mono), i.e., boehmite. There is a clear pattern in the boehmite distribution; namely, its abundance is maximum at the lower and middle depths (from 20 to 30 m from the surface) and minimum in the upper 10–12 m parts of the section (Table 1).

In the upper parts of the profiles (15–10 m from the surface and above), the active recrystallization of bauxite occurs with the replacement of dissolving boehmite with gibbsite, with a decrease in the total  $\text{Al}_2\text{O}_3$  content, and with an increase in the amount of crystallization water. This process is typical of the western regions of the province with a humid climate, rich vegetation, and active biota. In the east where the climate is more arid, much more boehmite has been preserved in the Late Miocene bauxites.

The most intense boehmite formation occurred at depths of 20–30 m from the surface. It was accompanied by an active input of alumina, which was deposited in the form of boehmite along with the formation of gibbsite due to the hydrolytic decomposition of kaolinite and partially from the input alumina.

It is important to note that the boundaries between zones of different  $\text{Al}_2\text{O}_{3\text{mono}}$  concentrations cross the lithological boundaries. Maximum boehmite concentrations reaching almost 50 wt % in individual samples (on average, the content is about 17 wt %) constantly coincide only with the oolitic bauxites.

The conclusion that the  $\text{Al}_2\text{O}_{3\text{mono}}$  content depends more on the depth of the bauxite position rather than on the bauxite lithology is confirmed by Table 1, which shows data on the average chemical composition of bauxites of various lithological types with details on their depth. The results are generally obvious. For almost all lithological types, the maximum values of  $\text{Al}_2\text{O}_{3\text{mono}}$  (boehmite) are analyzed in bauxite samples from depths of 20–30 m. In most of them, at the top near the surface, the monohydrate content sharply decreases to less than 4–5 wt %. The excess of these values is due to the fact that the bauxite depth from the surface is lower on the slopes, since the upper parts of the sedimentary-lateritic bauxites on these slopes are degraded by young erosion.

During the exploration of deep horizons of the Sangaredi deposit in depressions in the floor of the Sangaredi Group, deposits of the Sangaredi Group of various facies were found almost unaltered by lateritization or very weakly lateritized, bleached, and resilified.

We note that the content of  $\text{Al}_2\text{O}_{3\text{mono}}$  is very low in the protolith after its epigenetic alteration (bleaching and resilification). It is mostly less than 0.5 wt % and only reaches 2.17 wt % for sandstones. The decrease in silica content occurs together with the hydrolytic decomposition of kaolinite and an increase in the total alumina content; that is, its input begins with the release of alumina. Of the total  $\text{Al}_2\text{O}_3$  input,  $\text{Al}_2\text{O}_{3\text{mono}}$  accounts for an average of 50 wt %. It can be concluded that, with an increase in the content of gibbsite in the parent sedimentary rock, the boehmite formation intensifies. This is observed in the lowest part of the section, where the silica content is still very high—about 16 wt %.

The maximum input of aluminum monohydrate occurs above the groundwater level, when the amount of silica falls below 5 wt % at a relatively large depth. The increase in total alumina is due only to the input of  $\text{Al}_2\text{O}_{3\text{mono}}$ ; that is, all of the input alumina was deposited in the form of boehmite.

For psammite, gravelstone, and conglomerate bauxites, the area of the most intense absolute accumulation of  $\text{Al}_2\text{O}_{3\text{mono}}$  drops. This can be attributed to their higher water permeability compared to the bauxitization of sedimentary clays (Tables 1 and 2).

The maximum amount of aluminum monohydrate is found in profiles of infiltration-metasomatic bauxites at greater depths than the sedimentary-lateritic bauxites. Further down, its content decreases, and the gelification degree decreases with the transition to bauxites close to laterite in situ. Isovolumetric analysis shows that, in intensively gelified (geliform) bauxites (aphanitic or oolitic), the alumina input is highly significant (greater than the amount of initial alumina in the bedrock). According to the geological position of such profiles, it is quite obvious that the alumina input occurred from the overlying sedimentary-lateritic bauxites.

### 5.2. Geomorphologic and Climatic Factors of the Formation of Essentially Boehmite Bauxites

A new look at the geomorphology of the region allowed us to trace the Middle-Late Miocene topography to the regions of Western and Eastern Bamako. In the west of the province, the climate is wetter, whereas it is drier in the east. It is important to note that boehmite-rich geliform bauxites in the west of the province, in the areas of the Left Bank of the Kogon River and the Kogon-Tomine interfluvium on the surface of the bovals, as a rule are characterized by a lower content of boehmite than in the east of the province.

Table 3 summarizes the data on the first meter of geliform bauxite in more than 20 sections in the west of the province. They show that the boehmite content, although it varies from 4 to 16 on average, yields a relatively small value—8.2 wt %.

All samples taken in the east of the province were typical geliform (less often with oolites) white, pinkish, or fawn bauxite. The total alumina exceeded 60 wt %. At the same time, the share of boehmite did not decrease below 28 wt %. Mainly ferruginous laterites with an  $\text{Al}_2\text{O}_3$  content of 24.9–32.48 wt %,  $\text{Fe}_2\text{O}_3$  content from 33.2 to 42.63 wt %, and  $\text{SiO}_2$  content from 13.2 to 14 wt % are developed between bauxite blocks and fragments at the deposits in Eastern Bamako. This indicates the degradation of lateritic bauxite formation processes in this area. At the same time, the modern climate here is moderately humid with a significant excess of evaporation compared to the non-evaporated moisture.

The Siberian laterites on the Chadobetsky Uplift also have a sedimentary-lateritic genesis, and the gibbsite crystals have retained their original chemical and mineral composition and perfect surfaces for tens of millions of years [31]. In addition, this gibbsite does not transform into aluminum monohydrate (boehmite or diasporite). This fact is important in solving controversial issues about the thermodynamic stability of alumina hydrates under the conditions of the Earth's surface [32–34].

It is difficult to agree with V.M. Sinitsyn that only insolation can lead to a heating of the upper lateritic profile that is so serious that the formation of boehmite will occur [13]. Didier and colleagues more logically hold that the formation of gibbsite occurs there at

higher humidity [14]. This coincides with our observations in various parts of the province. When the humidity of the climate is higher, the humidity of the air increases as a whole. However, the decreasing humidity of the air alone cannot explain the boehmite formation at the deep horizons of the lateritic profile and in the Sangaredi deposit, particularly in the humidification zone above the vertical fluctuation zone of the ground water table where the conditions are moist. It is unlikely that this is simply due to the depth of occurrence in the classic lateritic profiles of the Eastern Ghats. For example, at the Panchpatmali bauxite deposit, gibbsite bauxites at depths of more than 20–30 and even 40 m are not significantly replaced by boehmite ores.

### 5.3. pH Factor in the Formation of Boehmite

The study of pore solutions showed that their pH ranges from 4 to 6.5 (4.7 on average) [29], and the concentration of aluminum increases by an order of magnitude or more (up to 1.78 mg/L) even in dilute versions. In case of the initially permeable low-iron sedimentary layer of the Sangaredi Group, organic acids mainly form aluminum-organic compounds, the concentration of which increases with depth. In the humidification zone, when faced with oxygen-containing moisture, the aluminum chelates are destroyed in fine-porous sedimentary clays and the clayey-sandy (silty) rocks of interlayers and cement in gravelstone and conglomerate bauxites, and the supersaturation of solutions and mass deposition of aluminum oxide occurs. Alumogel is probably formed first and later crystallizes as fine-grained boehmite. The periodic concentration of CO<sub>2</sub> and partly CO in the underground atmosphere plays a positive role in the concentration of aluminum in the zone above the groundwater table. In parallel with the formation of boehmite, the hydrolytic decomposition of kaolinite and hydromicas and the formation of gibbsite occur here. The formation of carbonic acid confirms the slightly acidic geochemical environment, despite the removal of alkaline components from clays.

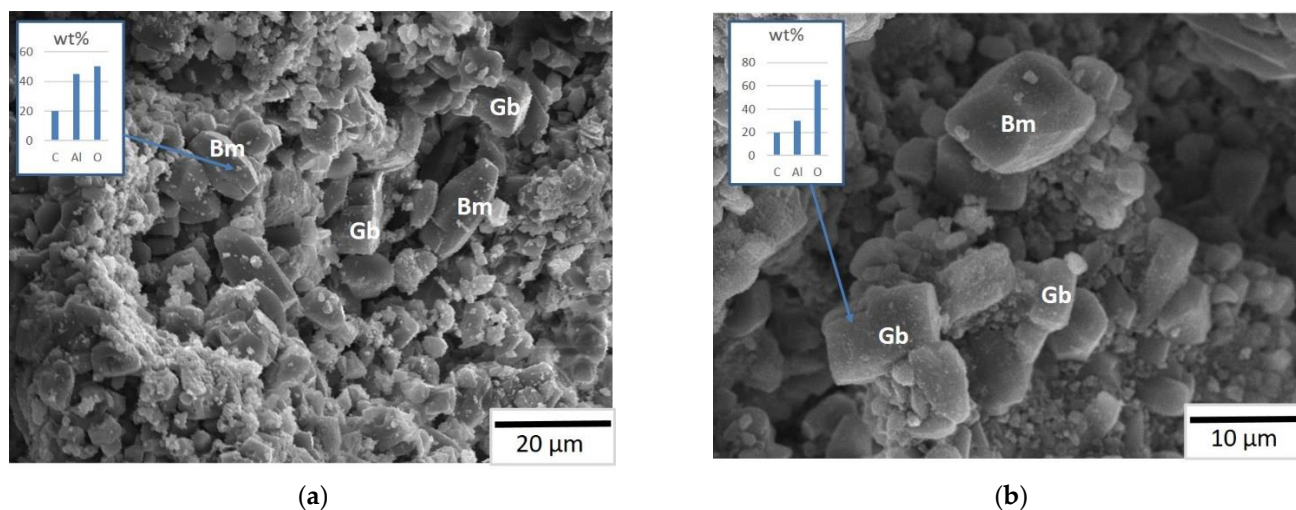
J. Lapparan and later W. Keller importantly stated that boehmite is formed during the aging (apparently crystallization) of gels in the presence of humic acids [16,18]. When microscopically studying bauxites with a high content of boehmite, geliform cryptocrystalline structures with a high relief are widely noted. Gelification during the formation of infiltration-metasomatic bauxites with an increased content of boehmite is confirmation of this.

We can agree with the researchers that the boehmite formation in lateritic profiles occurs under acidic conditions. The fact that this happens in the pH range of 6.5–6.7 was considered by P. Souza-Santos [23] and M. Gastyusha [22]. Under these conditions, due to the low solubility of aluminum hydroxides, boehmite is formed from supersaturated solutions, which is clearly visible in the SEM image (Figure 8). Cryptocrystalline boehmite was formed directly from the solution, and barrel-shaped crystals were formed due to the loss of water by gibbsite.

### 5.4. High Aluminum Concentration as a Factor of Bauxite Formation

A high aluminum concentration is necessary for boehmite formation according to the calculations of [21]. A low SiO<sub>2</sub> content is also needed (less than 0.1 mg/L), which is not confirmed by our actual data. The alumina in input occurs in rock with a high content of kaolinite, which continues to decompose hydrolytically, significantly increasing the SiO<sub>2</sub> content. The change in these solutions leads to the silica output.

The experimental results indicating that boehmite is formed in solutions with weak aluminum mineralization and a low SiO<sub>2</sub> content are not confirmed by the actual data.



**Figure 8.** SEM images gibbsite (Gb) and boehmite (Bm): (a) barrel-shaped crystals boehmite; (b) large well-crystallized boehmite.

#### 5.5. Fire as a Factor of Boehmite Formation

The impact of fires on the boehmite formation in the upper part of the weathering profile in the province is highly insignificant. A small amount of this mineral (1–3%) was determined by diffractometric analysis in some samples of the soil-vegetable horizon lying on the boehmite-free laterites. In Western Australia, frequent fires of eucalyptus forests could lead to the formation of boehmite, diaspore, and even corundum in soil pisoliths [15]. It should be borne in mind, however, that the climate in the area of Darling Range bauxite deposits is much less humid than that in the west of the province under consideration.

### 6. Conclusions

- (1) Gibbsite is formed in all classical in situ bauxites in the west of the FDM province. The thickness of the laterite covers is no more than 10–15 m. This is the zone of the formation and existence of exclusively gibbsite bauxites.
- (2) The genetic type favorable to the formation of boehmite bauxites is precisely sedimentary-lateritic bauxites. Boehmite formation occurs during the lateritization and resilification of bleached, aqueous continental sediments and of bleached bedrock under these sediments at depths of more than 20–25 m, mainly due to the redistribution (input from above) of aluminum.
- (3) Planation causes more deep horizons of sedimentary-lateritic bauxites to become exposed on the surface. In a humid climate, with more intense drainage and the direct influence of organic debris and microorganisms, boehmite becomes unstable. It begins to dissolve and is replaced by gibbsite, which is more stable under these conditions. During gibbsite formation, excess aluminum is redistributed, enriching pore solutions and contributing to their saturation with aluminum during depositions from solutions at any depth.
- (4) The concentration of aluminum increases by an order of magnitude or more (up to 1.78 mg/L) under acidic conditions. The concentration of organic acids associated with the vital activity of organisms also increases with depth. At the depth of oxygen-containing groundwater, alumichelate are decomposed, and the supersaturation of solutions and the mass deposition of aluminum oxide occur.
- (5) In the northeast part of the province, the current topoclimatic conditions are changing significantly. The rainfall is decreasing by more than two times compared with the Eastern Bamako region, the air humidity is decreasing, and the average annual temperature is increasing. However, the main factor of boehmite formation is apparently the decrease in unevaporated moisture to 100 mm/year. The profile wash is sharply decreasing. The intensity of the effect of the decomposition and alteration products of



organic matter and the intensity of bacterial activity on lateritic covers is also expected to decrease.

- (6) The combination of these factors ensures the preservation of boehmite bauxites formed by the end of the Late Miocene or during the Pliocene-Early Pleistocene.

**Author Contributions:** Conceptualization, V.M.; methodology, N.B.; software, P.M.; formal analysis, M.M. and E.S.; investigation, all authors.; writing—original draft preparation, N.B.; writing—review and editing, N.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** The study work was supported by a state task IGM RAS (topic no. 121041500220-0), and the analytical studies were conducted at the Center for Collective Use IGM ANALITIKA.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors are grateful to E.A. Zhegallo and L.V. Zaytseva for their work on SEM.

**Conflicts of Interest:** The authors declare no conflict of interest.

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