Mineralogy and crystal chemistry of iron in the Timan bauxite and products of their technological processing

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Abstract. Mineralogical and geochemical features of two series of samples of typical bauxites from two deposits of Middle Timan mining area (Vezhayu-Vorykva and Svetlinskoe) were studied. The phase composition of ferrous bauxites generally is boehmite, hematite, ultradisperse low-ordered goethite and berthierine. In a boehmite and kaolinite structural impurity of iron to 10%, and in the iron oxidehydroxides aluminum impurity is revealed. On iron content bauxites are subdivided into three mineral types for which quantitative data on valence states of ions of iron and proportions of their distribution last on nonequivalent structural positions in hematite, goethite and berthierine are obtained. Noble metals (Ag, Au, Ir, Rh, Pd) concentrating in bauxites are revealed for the first time. Obtained data can lead to decrease of power consumption during aluminum production and high quality ceramics, to provide production of valuable iron oxide, and also to minimize the ecological harm from accumulation of bauxite wastes.

1. Introduction
Russia is one of the world's largest aluminum producers, however it lacks own aluminous raw due to limitation of the explored reserves not exceeding 3 % from the world reserves. Besides a negative role is played by relatively poor quality of bauxites, in particular their iron content. It is obvious that in such conditions it is possible to meet the needs of Russian aluminum industry from domestic raw only by application of new processing technologies, which allow, first, to utilize ferrous varieties of bauxites stored in dumps, and secondly, to utilize natural raw more efficiently. The major precondition of success is the results of mineralogical-geochemical and crystallochemical studies of bauxite substance received by means of advanced analytical methods, and use of more effective technological methods. This has a special urgency in application to developing Timan bauxite province, where about 30 % of Russian reserves of aluminous raw are concentrated, which is characterized by heterogeneous composition and iron content.

2. Subjects and Methods
Objects of study are represented by two series of samples of typical bauxites from two most promising deposits of Middle Timan mining area - Vezhayu-Vorykva and Svetlinskoe. Corresponding bauxitea formation (bauxites, allites, aleurites and kaolinite-hydromicaceous clays) lies unconformably on Upper Riphean dolomitized limestones and argillaceous shales overlapped by sandstone-argillaceous and igneous-terigenous coastal-marine Devonian-Carboniferous sediments and Later Devonian platobasalts [1]. By its mineral composition the Middle Timan bauxites are traditionally subdivided on kaolinite-boehmite, chamosite-boehmite, hematite-boehmite, hematite-chamosite-boehmite types.
chemical composition they are subdivided on low-ferrous fire-resistant \((\text{Al}_2\text{O}_3 \, 56–75 \text{ wt %, } \text{Fe}_2\text{O}_3 \, 2–8 \text{ wt %})\) and ferrous \((\text{Al}_2\text{O}_3 \, 42–48 \text{ wt %, } \text{Fe}_2\text{O}_3 \, 12–36 \text{ wt %})\) varieties. As it is known at present in Russia and abroad bauxite raw is processed from contamination by chemical Bayer process. However this method is profitable only for relatively high-quality bauxites. But Timan bauxites along with oxide minerals of aluminum include oxide and silicate forms of mixed alumoferrous and ferrous-aluminum composition, which is difficult to enrich and process. Due to this reason brown bauxite varieties (Fig.1) with total \(\text{Fe}_2\text{O}_3\) content from 25 wt% are sorted out already in quarries, which leads to significant losses of not only aluminum, but also valuable small elements such as V, Ga, Li, some rare lantanoids. Our studies and experiments have shown that such losses can be minimized by the use of new processing methods.

Modern physical and physical-chemical methods were used: computerized reflective and transmission optical microscopy (POLAM P-312 and OLYMPUS BX51); analytical scanning electron microscopy (Jeol JSM-6400); X-ray fluorescent analysis (Horiba MESA-500W); ICPMS (Perkin Elmer ELAN 9000); thermal analysis (derivatograph Shimadzu DTG-60A/60AH); x-ray diffractometry (Shimadzu XRD-6000); IR-spectrometry (Fourier spectrometer Lumex FT-02 Intralum); 57Fe Moesbauer Spectroscopy (MS-1104Em); magnetometry; ferromagnetic and nuclear magnetic resonance; magnetic separation in weak magnetic field (less 0.5 T) at 0.01–0.4 A (SIM-1).

**Figure 1.** Change of color of Timan bauxites due to iron content from light low-ferrous variety toward brown highly ferrous variety

3. Experimental

Objects of study are bauxite samples with a wide variety of iron content collected from two main deposits of Middle Timan bauxite area – Vezhayu-Vorykva and Svetlinskoe. These samples represent two most enrichment-contrasting types of bauxites with considerable difference in chemical composition (wt%): 1) low-ferrous – SiO2 8–32, Al2O3 45–85, Fe2O3 2–18, silicon module \((\text{Al}_2\text{O}_3/\text{SiO}_2)\) 1.5–11; 2) ferrous – SiO2 4.5–38, Al2O3 25–63, Fe2O3 12–38, silicon module 1–13.

According to Yudovich’s lithochemical classification \([4]\) Timan bauxites vary from hypnormoferrous normal superhydrolysates (low-ferrous variety) to normosuperferrous normosuperhydrolysates (ferrous variety). Their composition contains 54 microelements including all 15 lantanoids. By their chemical and geochemical features these elements can be subdivided into 5 groups: 1) low charge lithophiles (alkaline, alkaline-earth, rare earth and rare elements) - Li, Rb, Be, Cs, Ba, Sr, Y, Ln, Mo, W, Sn,Tl; 2) multicharge lithophiles (elements-hydrolysates) - Ca, Ge, Sc, Zr, Hf, Nb, Ta, Th, U; 3) siderophilous and chalcophylous elements – Cr, Ni, Co, Cu, Zn, Cd; 4) noble metals – Ag, Pd, Pt, Rh, Ir; 5) semimetales and non-metals – Bi, Sb, As, Te, Se, B. The analysis showed that by relative content (normalized by the average composition of terrigenous sedimentary rocks in earth crust – Clark concentration) and distribution pattern the elements are subdivided into three groups (Fig.2): 1) excessive, i.e. concentrated in bauxites - Sc, Ga, Ge, Zr, Hf, Nb, W, Ln, U, Cd, Pb, Ag, Pd, Rh, Ir, Bi, Sb, As, Te, Se; 2) multidirected – Li, Be, Ba, Sr, Y, Cr, Cu, Ni, Co, Zn, Mo, Sn, Ta, Th, Tl, B; 3) deficit, i.e. decreasing at bauxite formation – Rb, Cs, Pt.

These data testify to that low charge lithophylous elements tend to decrease in bauxites, and multicharge elements-hydrolysates tend to accumulate, including metals, semimetales and nonmetals. Siderophylous and chalcophylous elements are characterized by intermediary geochemical features. It is obvious that such geochemical differentiation fully agrees with hypergene origin of the studied rocks. It should be considered that a number of noble metals is included in the group of excessive
elements forming the following succession of relative accumulation: Ir < Rh < Ag < Pd. This specifies
the necessity of more careful relation to bauxites as the source of not only aluminum, but some rare
highly valuable metals. It is also determined that ferrous variety of bauxites is characterized by higher
content of excessive microelements.

Phase composition of bauxites was determined by X-ray diffractometric, IR spectroscopic and
thermographic methods. The received patterns showed reflections from boehmite, kaolinite, 7 Å
septechamosite phase, hematite, crystal-imperfect goethite, rutile and andalusite. IR absorption
spectra well presented main lines of deformation and valency fluctuations of chemical bonds Al–O in
boehmite and septechamosite phase. Besides these spectra show lines conditioned by chemically
unbounded sorbed water (80–100°C) associated with X-ray amorphous phases, dehydration of
boehmite (500–600°C) and septechamosite phase (650–900°C). Some thermograms in area 300–
350°C represent endothermal peak corresponding to hydrogoethite dehydration.

As is known, the ferrous silicate phase in exogenic and hypergene rocks is treated either as
chamosite - 14 Å phyllosilicate with chlorite structure (three-layer package with T-O-T alternation) and
composition (Fe²⁺Fe³⁺,Al)₆[Si₂Al₄O₁₀](OH)₆, or as septechamosite - 7 Å phyllosilicate with
kaolinite structure (two-layer package with T-O alternation) and composition (Fe²⁺Fe³⁺,Mg)₂–
₃][(Si,Al)₂O₅](OH)₆. The latter mineral is determined as berthierine. Namely this mineral occurs in the
studied Timan bauxites

The mineral composition of Timan ferrous bauxites, estimated by the phase analysis, is
predominated by boehmite with its content above 60 mol%. This testifies to potentially high quality of
the raw. Admixtures to boehmite is berthierine (to 30–35 mol %), hematite (to 15–20 mol%), goethite
(to 6–7 mol %). Besides ferruginous substance is determined, which content can reach 10 mol% and it
seems to be amorphous by X-ray data. It is also determined that the growth of content of oxide and
oxidehydroxide phases in ferrous bauxites is accompanied by the rapid decrease of berthierine and
increase the disproportion between lithophylous (decreasing) and siderochalcophylous (increasing)
microelements.

The crystal-chemical features of ferrous bauxites were studied by Moessbauer spectroscopy. The
imaging was conducted in the range (−11 … +11)·10⁻³ m/s at normal conditions. The isomeric shift
was determined in relation to α-Fe. Time of spectra accumulation was from 16 to 180 hours in relation
to iron content in the samples. The conducted experiments resulted in two variants of multicomponent
spectra. The first variant – practically completely sextet – is characteristic for hematite-containing

Figure 2. Normalized concentrations of microelements in Timan bauxites on example of Svetlinskoe
deposit. Fill – assemblages of trends, lines – trends in ferrous bauxites
bauxites. The second variant – doublet – is characteristic of silicate-ferrous bauxites. The obtained data testify to that iron in Timan bauxites is not only present in various valency conditions, but also included in the structure of several crystal-chemically heterogeneous minerals – oxides, oxidehydroxides, silicates – distributing to non-equivalent structural positions in them as well.

The oxide phases in Timan bauxites are represented by hematite and ultradisperse (with sizes up to 20 nm and less) low-ordered goethite. In Moessbauer spectra these phases are corresponded by inherent line sextets with various values of ultrathin field intensity on iron nuclei (see Table 1). These values for hematite in all cases appeared lower than reference, which can be explained by the presence of aluminum admixture, which decreases the efficient value of ultrathin magnetic field intensity. The estimated concentration of aluminum admixture makes about 10 at% in hematite of Timan bauxites. The sextet components of goethite phase in spectra are partly relaxed due to ultradispersity of this phase.

Some varieties of ferrous bauxites contain the admixture of disperse x-ray-amorphous oxide alumoferrous and silicious substance. The size of particles, according to X-ray and synchrotron small-angle scattering methods, varies from 35–40 to 20–25 nm. The fluctuation of X-ray amorphous degree of this part of bauxite substance was estimated by the level of heat fluctuations.

### Table 1. Parameters of Moessbauer spectra of Timan ferrous bauxites

| Mineral type                          | QS, mm/s | IS, mm/s | H, kE     | S, %  | Fe position          | Fe$^{2+}$/Fe$^{3+}$ |
|---------------------------------------|----------|----------|-----------|-------|----------------------|---------------------|
| Hematite-boehmite                     | -0.21    | 0.37     | 500, 420–511 | 72.5  | Hematite -Al         | 0                   |
|                                       | -0.28    | 0.36     | 330, 200–380 | 7.8   | goethite -Al         |                     |
|                                       | 2.42     | 1.19     | 500, 410–511 | 2.8   | Fe$^{2+}$/VI, kaolinite | 0.16               |
|                                       | 0.84     | 0.34     | –         | 11.6  | Fe$^{2+}$/VI, kaolinite |                     |
|                                       | 0.47     | 0.37     | –         | 5.3   | Fe$^{3+}$/IV, kaolinite |                     |
| Hematite - berthierine-boehmite       | -0.21    | 0.37     | 500, 410–511 | 52.4  | Hematite -Al         | 0                   |
|                                       | -0.28    | 0.36     | 314, 200390 | 13.4  | goethite-Al          |                     |
|                                       | 2.64     | 1.13     | 500, 410–511 | 23.3  | Fe$^{2+}$/VI(M2), berthierine | 2.53               |
|                                       | 2.28     | 1.08     | –         | 12.2  | Fe$^{2+}$/VI(M1), berthierine |                     |
|                                       | 0.83     | 0.44     | –         | 7.0   | Fe$^{3+}$/VI, berthierine |                     |
|                                       | 0.5      | 0.31     | –         | 2.7   | Fe$^{3+}$/IV, berthierine |                     |
| Berthierine-boehmite                  | 2.654    | 1.124    | 500, 410–511 | 62.8  | Fe$^{2+}$/VI(M2), berthierine | 2.15               |
|                                       | 2.28     | 1.06     | –         | 5.5   | Fe$^{2+}$/VI(M1), berthierine |                     |
|                                       | 0.71     | 0.52     | –         | 12.2  | Fe$^{3+}$/VI, berthierine |                     |
|                                       | 0.57     | 0.34     | –         | 19.5  | Fe$^{3+}$/IV, berthierine |                     |

**Note.** QS – quadrupole splitting, IS – isomeric shift, HHF – effective value of ultrathin magnetic field intensity (average and variation range), S – area for relevant component

According to crystal-chemical features of iron distribution ferrous bauxites are subdivided into three mineral types. The first type – **hematite-boehmite** – iron bonds with Al-hematite at more than 70%, it is determined by goethite admixture at about 8%, about 20% of iron is related to the aluminosilicate phase, probably kaolinite. In kaolinite the main part of iron is in tervalent state (Fe$^{3+}$/Fe$^{2+} = 6.03$), occupying mainly octahedral and in lesser extent tetrahedral positions. Insignificant amount of iron is present in kaolinite lattice in bivalent state, also occupying octahedral positions. In the second type – **hematite-berthierine-boehmite** – more than 50% of iron is confined to hematite, about 13% relates to goethite, and about 34% is included to berthierine. In berthierine, as in other phyllosilicates with kaolinite structure type, Fe$^{2+}$ ions fill M1 and M2 octahedral positions characterized by trans and cis configurations of OH-group position. The occupation of M2 positions by these ions results in great deformations of lattice, therefore these positions are assigned by the most intense doublet with greater
 quadrupole splitting (QS). Accordingly doublet with smaller QS is related to Fe\textsuperscript{2+} ions in M1 positions. The doublets, related to Fe\textsuperscript{3+} ions in berthierine, are also assigned to different positions: with greater QS – top octahedral M2, and with smaller QS – to octahedral M1 or tetrahedral positions. In the studied case 68 % of iron in berthierine is represented by Fe\textsuperscript{2+} ions in M2 octahedral positions. Fe\textsuperscript{3+} part makes 28 %, and Fe\textsuperscript{3+}(IV)/Fe\textsuperscript{3+}(VI) ratio reaches 0.39. Total Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio in berthierine is 0.40. In the third type – berthierine-boehmite – practically all iron bonds with berthierine. The doublet Moessbauer spectrum for such bauxites contains only components corresponding to irono ions in phyllosilicate lattice. The parameters of doublets, corresponding to M1 and M2 positions, are very close to the parameters for berthierine in literature. Fe\textsuperscript{2+} part in octahedral M2 positions of berthierine in this case is 63%, Fe\textsuperscript{3+} ions – 32%, Fe\textsuperscript{3+}(IV)/Fe\textsuperscript{3+}(VI) ratio is estimated at 1.6. Total Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio reaches 0.46.

4. Modification of technological properties

The experiments with the bauxites revealed considerable increase of magnetic product yield in size class –315+250 μm after drying at 150 °C. This means that the considerable increase of efficiency of utilization of ferrous bauxite raw can be reached already by the change of surface state, in particular by decreasing degree of its hydroxylation. The experiments with red mud revealed that it is characterized by much greater (4-5 times) particle dispersity in comparison with ferrous bauxites. Particles of class –71 μm make 81% which are divided equally between classes –71+45 and –45 μm. The division of red mud into non-magnetic and magnetic fractions occurs in the conditions of weak magnetic field. Non-magnetic material dominates in red mud at the initial sample. At that magnetic fraction yield decreases with the decrease of particle size, however in –45 μm class this yield slightly increases due to increasing content of hematite and goethite. After two hours drying at 150 °C the trend of yield decrease is preserved and covers both size classes. After drying at 300 °C the magnetic product yield increases considerably and grows with decreasing particle size. Above data testify to that the efficiency of magnetic separation of initial ferrous bauxites and red mud is influenced by two factors: content of weak magnetic oxides and oxydehydroxides (favorable factor) and hydroxylation of particle surface (unfavorable factor). The influence of the last factor can be minimized by the way of drying geomaterials and their products to 150–300 °C. However this procedure only partly improves separation of aluminum raw without a real success. To achieve greater degree of separation of ferrous and aluminum components of the studied bauxites we, together with the colleagues from the Ukraine, conducted the pioneer program of magnetization experiments. During these experiments we achieved transformation of initially non-magnetic and low-magnetic oxides and oxihydroxides of iron into strong magnetic oxides [2, 3]. The experiments were conducted in water environment in the conditions of electromagnetic field in the presence of chemical catalyst with reduction characteristics. The physical essence of the transformation is in recharge of iron ions in the structure of relevant minerals. The objects of our studies were samples of high-ferrous bauxites of hematite-boehmite and hematite-berthierine-boehmite types, average mineral composition is within the range (mol%): boehmite 62.9–65.6; berthierine 0–12.6; hematite 17.4–11.9; goethite 6.3–6.5; rutile + anatase 2.6–3.4; X-ray amorphous phase 10.8–0. It was determined that at the microwave influence on ferrous bauxite the phase composition and magnetic characteristics were considerably changed. Low-magnetic oxides and oxihydroxides – hematite and goethite already at low temperature 95°C transit to strong magnetic state due to the transformation of these minerals into maghemite and magnetite. This is confirmed by X-ray diffraction analysis, which reveals that initial hematite is decreased (reflexes d/n = 2.702 and 2.518 Å), but instead a newly formed magnetite phase appeared (d/n = 2.969, 2.525, 2.096, 1.612 Å) in the modified samples. The degree of transformation directly depends on the conditions of magnetization. The magnetic characteristics of bauxites act accordingly with phase-crystal-chemical changes. In particular, the value of saturation magnetization increases at about an order in comparison to the initial stage (Fig.3).
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Figure 3. Dependence of magnetization degree (M) of typical sample of hematite-boehmite bauxite, conditioned by outer magnetic field (B). 1, 2 – magnetization curves for initial and modified samples accordingly

5. Conclusion
Results of the experiments convince that it is possible to considerably improve the technological features of ferrous bauxites by a certain influence, namely, to increase the efficiency of magnetic separation by directed phase-crystal-chemical transformation of ferrous minerals in bauxite composition. This transformation can be characterized by the following equations: 1) $12\text{FeO(OH)} \rightarrow 6\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{O} \uparrow \rightarrow 4\text{Fe}_3\text{O}_4 + \text{O}_2 \uparrow$; 2) $6\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{O}_2 \uparrow$. It is obvious that this transition is carried out gradually with intermediary phase of maghemite and can have various degrees of completion. Therefore to achieve maximal efficiency of separation it is necessary to vary the mode of magnetic separation. We consider the achieved result as the scientific precondition to development of a new method of bauxite separation without power-consuming chemical processing. This method can lead to decrease of power consumption during aluminum production and high quality ceramics, to provide production of valuable iron oxide, and also to minimize the ecological harm from accumulation of bauxite wastes.

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