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HIGH-GRADE IRON ORES OF KMA AS A RAW MATERIAL FOR METALIZATION

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Abstract: Mineralogical composition of rich iron ores of KMA deposits is considered in the work, with the aim of potential obtaining high-quality iron ore products, as a raw material for metallization. It is noted, that rich iron ores of KMA have a complex geological and mineralogical structure. As a result of the research, it was found that the diversity of mineral types of high-grade iron ores of KMA deposits is due to the different mineral composition of parent materials, and the development of secondary processes (carbonation, chloritization). Significant heterogeneity of high-grade ores in composition, properties and quality is shown in the work.

Keywords: high-grade iron ore, chemical composition, martite, hematite, hydrohematite, goethite, hydrogoethite, carbonation, chloritization.

I. INTRODUCTION

The reserves of high-grade iron ores are amounted to billions of tons, and further development of Kursk Magnetic Anomaly should be oriented towards their extraction and processing. Rich iron ores can be a potential source of high-quality multi-purpose metallurgical raw materials, and with the development of production of metallized raw materials, the need for them will only increase. There is no production of high-quality raw materials for the metallization of hematite ores in Russia, but in the world practice (Australia, Brazil) industrial processing of such ores with different mineral composition is widespread.

Belgorod Iron Ore District is the world's largest basin of high-grade iron ores (up to a depth of 1200 m) with total reserves and estimated resources of 82 billion tons. Iron ores have an average iron content of more than 60% and have insignificant amount of harmful impurities (sulfur, phosphorus) and slag-forming oxides (mainly silicon dioxide). So, these deposits belong to the category of large

and unique [1-4]. Total balance reserves are estimated at 26.1 billion tons. Yakovlevskoe, Gostishchevskoe, Vislovskoe, Shemraevskoe deposits are explored. The ore reserves of Razumenskoe, Olimpiyskoe, Melikhovo-Shebekinskoe, Olkhovatskoe, Bolshetroitskoe deposits were preliminarily estimated according to the category C2. Several occurrences of rich iron ores were found, some of which were complex iron ore and bauxite ores (Table 1).
The high-grade iron ores from deposits of this district are presented by fairly uniform geological and mineralogical types. Depending on the presence and quantitative ratio of ore-forming minerals and secondary superimposed processes, the following types are mainly distinguished: martite and iron mica-martite; hydrohematite-martite and martite-hydrogoethite, goethite-hydrohematite and goethite; carbonated; redeposited [1 - 3, 5 - 7] (Table 2). The variety of mineral types is due to the different mineral composition of parent materials and the development of secondary processes (carbonation, chloritization).

Table 1: Characteristics of rich iron ore deposits

Field site	Reserves (by category), mln. t			Mass content of components and oxides,%				Stratification depth, m	The ratio of martite and iron mica-martite ores in total reserves *,%
	$B+C_1$	C_2	P_I	Fe_{tot}	SiO_2	Al_2O_3	LOI**		
Yakovlevskoe deposit									
Central	1621	-	-	60.58	4.95	2.13	4.89	525	60 (30)
Smorodinsky	-	1384	-	60.60	5.08	1.86	5.72	540	70 (30)
Gostishchevskoe deposit									
Kryukovsko-Gostishchevsky	2594	995	-	60.8	3.5	2.89	4.14	487	85 (50)
Khokhlovo-Dalneigumensky	-	7042	-	63.6	3.3	2.25	2.84	483	85 (50)
Luchkinsky	-	2046	-	61.4	3.9	2.61	4.50	454	60(30)
Vislovskoe deposit									
Vislovsky	1078	1929	147	60.39	4.15	1.84	6.41	577	43 (24)
Belgorodsky	-	571	369	61.70	3.65	2.63	5.01	669	72 (24)
Razumenskoe deposit									
	-	13684	1000	61.02	4.72	2.00	4.98	678	75 (30)
Olkhovatskoe deposit									
Malinovsky	-	2779	545	59.74	4.70	3.56	5.16	435	65 (8)
Bolshetroitskoe deposit									
	-	2150	-	62.41	3.08	1.27	4.44	440	78 (18)
Shemraevskoe deposit									
	419	618	390	63.59	3.88	1.51	2.64	445	93 (56)

*in brackets - including friable varieties; ** - loss on ignition

The ores are represented by two genetic types: eluvial (residual) and redeposited (sedimentary). Due to the fact, that lately the demand for low-grade iron ore has declined sharply, the issue of production of high-quality raw materials for the manufacturing of metallized products is highly relevant [8].

In this regard, high-grade iron ores may soon become a potential source of such raw materials:
- for the production of metallized raw materials (pellets, briquettes);
- for powder metallurgy;
- for ferrite and battery production;
- for weighting in the process of drilling of deep oil and gas wells, etc.

Table 2: Chemical composition of the main types of high grade iron ores.

Components and oxides	Content of the component in the mineralogical variety of deposits, %							
	Yakovlevskoe		Gostishchevskoe		Shemraevskoe		Vislovskoe	
	Martite and iron mica-martite ore	Hydrohematite-martite and martite-hydrohematite with goethite	Martite and iron mica-martite ore	Hydrohematite-martite and martite-hydrohematite with goethite	Martite and iron mica-martite ore	Hydrohematite-martite and martite-hydrohematite with goethite	Martite and iron mica-martite ore	Hydrohematite-martite and martite-hydrohematite with goethite
Fe_{tot}	63.19	59.4	64.47	54.51	65.11	59.39	64.12	59.56
$SiO_{2\ tot}$	4.35	5.66	2.68	5.42	2.54	4.89	3.0	4.86
Al_2O_3	1.25	3.94	1.93	6.2	0.98	2.94	1.42	2.39
S_{tot}	0.014	0.031	0.032	0.064	0.04	0.11	0.06	0.09
P	0.11	0.05	0.08	0.17	0.09	0.11	0.08	0.09
Loss on ignition	3.04	4.62	2.81	8.57	2.21	6.54	3.4	6.1

The first deposit, explored in the district, is Yakovlevskoe (1953). Its total reserves are estimated at 6 billion tons, according to categories B+C1+C2 [3]. At present, only there the mining and processing of ore are carried out on an industrial scale, with the production of a sinter product with an iron content of about 60.0%.

Among the high-grade iron ores of the Pre-Middle Visean weathering crust, four geological and industrial types were distinguished: Yakovlevsky, Shemraevsky, Stoilensky and Chernyansky, according to the amount of ores, their composition, extraction method, technological redistribution, physico-mechanical and metallurgical properties. The leading role among them belongs to the objects, composed of rich ores of Yakovlevsky and Shemraevsky type. Yakovlevsky type includes the main body of high-quality martite and iron mica-martite ores with low strength, which can be mined by open or underground methods. Shemraevsky type combines friable martite ores with iron content of 64.0 - 69.0%, which occur usually jointly or as a part of large deposits of Yakovlevsky type. Friable and semi-friable rich ores of Shemraevskoe deposit comprise Shemraevsky type, suitable for extraction by the method of hydraulic borehole mining. About 70,000 tons of ore with an iron content of 66.5 - 68.5% was mined at the Shemraevskoe deposit, using the method of hydraulic borehole mining.

II. OBJECTS AND METHODS OF RESEARCH

The object of this research is more than 300 composite geological and technological samples of natural high-grade iron ores, obtained from detailed exploration of the central part of Yakovlevskoe deposit. They cover all the areas of deposit and reflect the most representative textural, structural and mineralogical features of ores in this deposit.

The study of the composition and properties of the selected samples was carried out using optical microscopy, Moessbauer spectroscopy, high-temperature magnetometry, micro sounding, X-ray diffractometry. The determination of the micro hardness of minerals, magnetic and strength properties was carried out on the ground of their physical, physico-mechanical, and technological properties [3, 9, 10].

III. RESULTS AND DISCUSSIONS

The high-grade iron ores of Yakovlevskoe deposit, occurred under sedimentation mass at a depth of 600 m, are eluvial formations, connected with the creation of Pre-Paleozoic and Early Paleozoic lateritic weathering crust. The formation of ores was accompanied by the removal of alkali and alkaline earth elements and silica, with the simultaneous accumulation of oxides of iron and alumina, as well as the secondary processes of carbonation and chloritization. Several mineralogical types of ores have been defined at the deposit: martite and iron mica friable and semi-friable, martite- and hydrogoethite-hydrohematite, siderite-iron mica-martite, martite-iron mica chloritized, redeposited.

Among the parent materials, iron mica ores are the most developed. The rich martite-iron mica hematite ("blue") ores were formed on their ground. Silicate-magnetite ores are less developed. Based on them, high-grade martite-hydrohematite and hydrogoethite ores ("pigments") were formed. Due to the confinedness of rich iron ores to a certain type of metamorphic rocks, the ores inherit their textures.

Iron mica and martite-iron mica ores are characterized by a thin-banded composition, with a thickness of interlayers from fractions up to 1-2 mm, and have a typical bluish color. For the most part, the ores are friable and porous.

Martite-hydrohematite and hydrogoethite ores have a dark red, brick-brown color. The texture of ores is banded, uneven. Using X-ray diffractometry, it was found that the main ore-forming minerals are martite and hydrohematite. Hydrogoethite, clay matter, carbonates, chlorite, and quartz are present in the inclusions (Fig. 1).

Hydrogoethite ores are closely related to the martite-hydrohematite ores, forming among them interlayers, which are not stable in thickness.

The study of granulometric composition made it possible to conclude that the high-grade iron ores, such as the "blue" type, are classified as aleurites, which are characterized by a high content of coarse silt fraction up to 80%; the minimum content of this fraction is 39%.

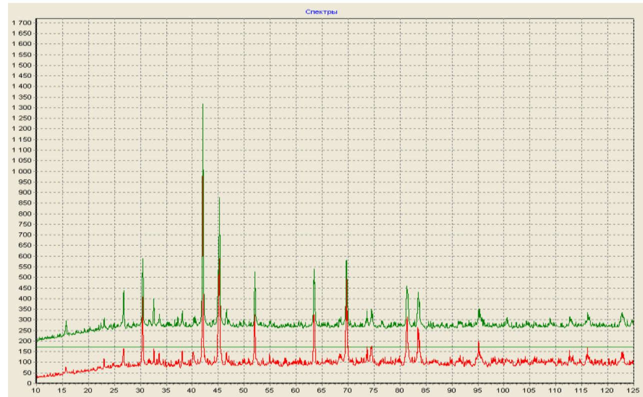


Fig. 1: X-ray patterns of martite-iron mica ore and hydrohematite-martite ore

In addition, there is an insignificant presence of a fine fraction of d <0.002 mm. "Pigments" can be attributed to consertal, pulverescent sands, where the content of the fine fraction can increase to 7% (clay sands), the coefficient of heterogeneity is on average 11, and in some cases 37–39.

Chemical characteristics of mineral types of ores are given in Table 3. Among the rare elements, germanium is of interest. Its content varies from 2 to 42 g/t, and is on average 9.1 g/t. The ores of the deposit sidewall are rich in germanium, where its content reaches 12 g/t.

According to their strength properties, the ores are subdivided into 5 classes, depending on the strength value under uniaxial compression (σun.com.): (Table 4):

- rocky, relatively strong σun.com.> 600kgf/cm2;
- rocky σun.com. = 300-600 kgf/cm2;
- semi-rocky σun.com. = 100-300 kgf/cm2;
- semi- friable σun.com. = 20-100 kgf/cm2;
- friable σun.com. = 0-20 kgf/cm2.

The share of friable and semi-friable ores in the deposits of the district varies from 36 to 60%, while at the Yakovlevskoe deposit, located in the central area, their share is amounted to 53.7%.

Depending on the degree of cementation by chlorite, iron mica-martite ores are presented by rocky, semi-rocky, semi-friable, and friable varieties.

Martite-hydrohematite and hydrogoethite ores are presented only by friable and semi-friable types, and carbonatized ores are represented only by rocky and semi-rocky varieties. The main difference between them is the content of total iron, iron oxide and crystallization water.

Iron mica-martite ores are characterized by a high content of total iron (66.24-68.26%), iron oxide (91.48-93.7%) and low content of crystallization water (0.41-1.2%). Martite-hydrohematite and martite-goethite ores have a lower content of total iron (53.33-62.25%), iron oxide (70.56-

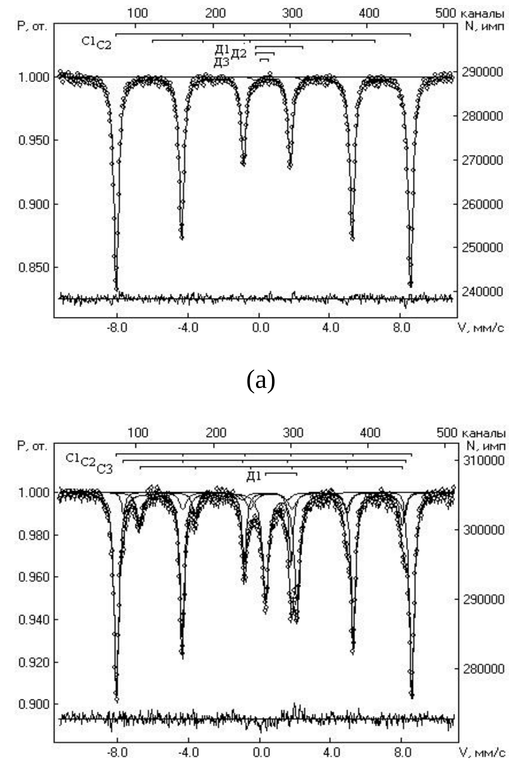
83.34%) and increased content of crystallization water (4.83-13.0%).

Table 3: Chemical characteristics of mineral types of ores.

Components and oxides	Content of oxides and components in mineral types, %					
	Friable martite- iron mica ore	Martite-hydrohematite ore	Hydrogoethite- hydrohematite ore	Siderite- iron mica-martite ore	Martite-iron mica ore chloritized	Redeposited
Fe_{tot}	67.57	62.74	58.43	57.35	65.9-63.3	56.36
Fe_2O_3	95.17	86.57	73.15	55.2	89.3-81.0	69.28
FeO	1.22	3.35	9.37	24.18	4.38-8.55	10.68
$SiO_{2\ tot}$	0.92	3.5	5.93	0.85	3.08-4.34	7.57
Al_2O_3	0.55	2.54	5.24	0.23	1.43-3.48	5.15
CaO	0.45	0.65	0.1	1.12	0.69-0.8	0.8
MgO	0.1	0.49	0.45	2.12	UQ	0.72
TiO_2	0.08	0.18	0.47	0.06	0.1	0.24
Loss on ignition	0.4	3.15	4.65	15.9	0.69-1.44	5.64
S_{tot}	0.03	0.02	0.01	0.27	0.18-0.04	0.06
P	0.02	0.06	0.06	0,03	0.06-0.01	0.06
Total	99.21	100.4	99.42	99.69	100.1	100.14
Share in the composition	59.5	26.2		10.0		3.3

Table 4: Qualitative characteristics of the main types of rich iron ores.

Ore types	Strength grade	$\Sigma_{un.com.}$, kgf/cm^2	Mass content of oxides, %		
			Fe_{tot}	SiO_2	Al_2O_3
Iron mica-martite	Rocky	300 - 600	57.0 -59.0	5.5 -10.0	1.5 -2.3
	Semi-rocky	100 - 300			
	Semi-friable	20 - 100	66.0 -68.5	0.8 -2.5	0.7 -0.8
	Friable	20			
Martite-hydrohematite	Semi-friable	20 - 100	59.0 -61.0	4.0 -5.5	2.1 -2.4
	Friable	20			
Hydrogoethite-hydrohematite («pigments»)	Cledgy, plastic	-	55.0 -58.0	5.0 -7.0	3.9 -4.3



(a)

(b)

Fig. 2: Mossbauer spectrum of iron mica-martite ore: (a) friable and semi-friable; (b) rocky and semi-rocky

Iron oxide in ores is mainly connected with martite and iron mica, less often with iron hydroxides, and that is confirmed by Mossbauer spectroscopy (Fig. 2). Iron oxide enters into the composition of chlorite, siderite, residual magnetite and pyrite. The content of silicon dioxide varies from 0.97 to 9.54%, and is connected with relict and veinlet quartz, chlorite and, to a lesser extent, with hydromicas and kaolinite.

The content of aluminum oxide varies from 0.55 to 2.74% and is closely related to the manifestation of chlorite and, in small quantities, with hydromicas, kaolinite, gibbsite and benite. The content of calcium oxide in ores ranges from 0.19 to 1.5% and is associated with the presence of calcite in them.

The increased content of crystallization water is due to the high content of hydrohematite, goethite, and hydrogoethite, and varies from 4.83 to 13.0%.

The main ore minerals, which form residual ores, are martite and hematite (iron mica), carbonates (siderite, calcite), magnetite (rarely). Moreover, there is a significant amount of hydrohematite, goethite and hydrogoethite. The content of martite in friable and semi-friable varieties of iron mica-martite ores is much higher, than in rocky and semi-rocky ores.

Quartz marshallitized and chlorite of the chamosite type are occurred in some types of ores. They are present in a subordinate amount. Metamorphogenic quartz, lepidocrocite, pyrite, marcasite, boehmite, gibbsite are sometimes observed as inclusions. Chalcopyrite and galena are occurred in the form of single grains.

Hematite (iron mica) is the most abundant mineral and the prominent representative of rich iron ores. The curves of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) of hematite showed that hematite α-Fe2O3 with Curie temperature of 675.8 °C was present in all selected fractions. Moreover, there was even higher temperature phase, probably iron (θ = 775 °C). It was also found the impact of martite with a Curie temperature of 578 °C (Fig. 3).

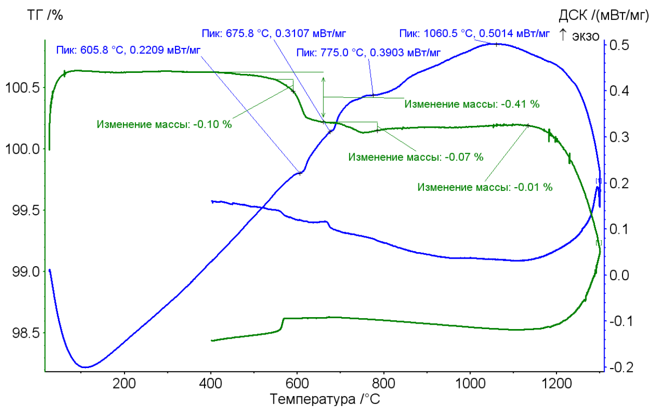
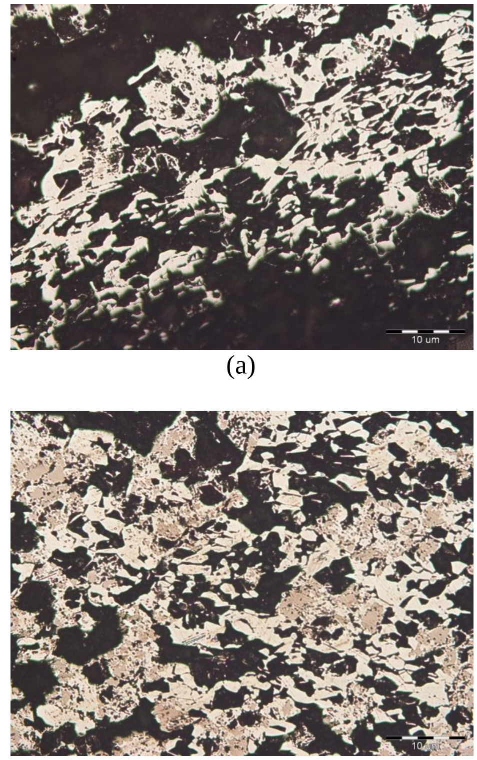


Fig. 3: The curves of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) (monomineral fraction of hematite)

ТГ/%	TGA/%
Пик…..°C,…..мВт/мг	Peak…..°C,…..mW/mg
ДСК/(мВт/мг)	DSC (mW/mg)
Экзо	Exo
Изменение массы	Change of mass
Температура /°C	Temperature / °C

Hematite occurs in the form of zonal-colloform formations (up to cryptocrystalline aggregates), and small grains of irregular, pseudo-scaly and thin flake form.

Its separate scales or complex looped formations comprise interlayers with uneven, often jagged edges. The colors of crystals and dense masses are from gray-steel to dull gray-black. Friable varieties have red-brown color, semi-metallic luster, and they are opaque. Hematite is found using X-ray diffraction method, by a number of reflexes. It is in close textural and structural combinations with martite. The content of iron in hematite varies from 66.6 to 69.9%, on average - 68.12%, in finely-dispersed - from 66.4 to 67.7%, on average - 66.9%.



(a)

(b)

Fig. 4: Acicular hematite in the mass of chlorite and ferruginous carbonates (a) and martite in the mass of relic magnetite (b). The light is reflected, magnification 500.

Three generations of hematite were identified (Fig. 4, a):

- the first is crystalline hematite, formed as pseudomorph, due to the replacement of primary mineral (martite), with preservation of its shape;
- the second is xenomorphic hematite or aggregates of xenomorphic and crystalline hematite, formed as pseudomorphs, due to the replacement of martite (magnetite);
- the third is acicular hematite, formed due to the processes of dissolution and redeposition of iron-containing minerals; it is the product of high-temperature hydrothermal activity.

Martite is the main mineral of rich ores, it is observed in the form of separate isometric grains, as well as in the form of polygonal aggregate intergrowths. It is a hematite pseudomorph of magnetite in the form of rhombic dodecahedral or octahedral crystals. Martite has a gray or gray-blue color. Light pink (reflected light) relics of magnetite are often observed in some grains of martite (Fig. 4, b). The relics of magnetite are represented by crystal and twin crystal planes. Typical replacement of magnetite by martite in crystallographic directions is observed. In turn, martite is often replaced by iron hydroxides with an obscure colloform structure. In some places, martite grains were hydrated, and as a result, earthy hydrohematite was formed. Hydration of martite grains most often begins with the edge parts of the grains, frames them, and also fills micro cracks and the gaps between them. The iron content in martite varies from 67.6 to 69.9%, averaging 69.0%.

Hydrohematite is a secondary ore-forming mineral, but in some places there are interlayers where it dominates. It is represented by a dispersive friable variety and gives the interlayers a brick-red color. Based on martite, it develops in the form of nests and rims, forming a corrosive structure. In some places, hydrohematite is a product of loosening of biotite, presented in small amounts. Hydrohematite occurs in all varieties, and it is one of the main minerals in the composition of hydrohematite-hydrogoethite ores.

Three generations of hydrohematite were defined:

- the first is hydrohematite, formed due to the cavity fillings of quartz leaching; it is of paramount importance in the process of formation of pigment and hematite-pigment ores;
- the second is hydrohematite, based on chlorite. Genetically, its formation can be confined to the parent shales (chlorite);
- the third is hydrohematite of counter-veins (along cracks). It is developed all over the place in the form of healing joints with the formation of thin layers (up to 1.0 cm). Hydrohematite formations are often observed on the planes of shales bedding and especially hematite interlayers with relict shale texture, in the form of shapeless spotted or vein-like formations.

In addition, there are red (burgundy), red-brown (brown) and brown-red iron hydroxides, having predominantly colloform structure of the fibrous or earthy mass of aggregates.

Both goethite and hydrogoethite are observed in the form of a friable, earthy ocher mass. In some places they are clay-like and have dark brown color. Mainly, they are the products of decomposition of iron-containing amphiboles and carbonates. They almost don’t occur in pure form, and have a transverse-fibrous structure. Goethite has gradual transitions to hydrogoethite and other hydroxides of iron that is reflected in dual diagnostic signs. According to [3, 6], the content of total iron varies from 63.89 to 68.83%, silicon dioxide - from 2.4 to 2.63%.

Magnetite occurs in the form of relict grains in martite and forms single grains. It is highly susceptible to martitization, and in rare cases it forms pseudomorphs, based on hematite (muschketowite - epigenetic magnetite). It is developed on the wide planes of the plates and flakes of hematite. Magnetite replaces martite grains, forming typical forms of substitution. The iron content in magnetite varies from 69.6 to 72.2%, averaging about 71.0%.

Iron sulphides are mainly represented by pyrite and, less frequently, by marcasite. Pyrite is distributed in the form of small scattered dissemination, small aggregates and cross-cutting veinlets.

Silicate minerals are represented mainly by chamosite-type chlorite and, in minor quantities, by hydromica, aluminum oxides and hydroxides. Chlorite is observed in the form of spots, nests, solid amorphous or cryptocrystalline masses, concentrated by layers. Chlorite is a cementing material, due to the filling of space between the ore grains and aggregates.

Aluminum oxides and hydroxides occur in small quantities in the form of friable formations and are most often confined to interlayers, composed mainly of iron hydroxides. They are predominately represented by kaolinite, gibbsite and benite.

Carbonates are mainly presented by siderite and calcite, and are found all over the place. Sideroplesite and dolomite are less widespread. Siderite often plays the role of one of the main ore-forming minerals. The aggregate state and strength of ores mainly depend on its quantity. It is the main cementing mineral in ores, it fills the pores and voids, forming veinlets and nesting clusters. Cementing mass of siderite is formed by grains of different size and shape, ranging in size from 0.01 to 0.40 mm. Siderite-cement is in close relation with martite and sometimes replaces it reactively. Siderite is crystalline, uneven-grained.

Calcite occurs more rarely than siderite. It forms layered and intersecting veins and nests in cracks and voids. It often forms sinter colloform formations.

Quartz is mainly relict mineral. It is usually marshallitized, and represented by grains with jagged edges, corroded by siderite and iron hydroxides. Moreover, there is coarse quartz in the form of intersecting veins of various thicknesses. Relic interlayers of quartz are friable mineral aggregates of their submicron grains (quartz - marshallit).

Three types of quartz were defined:

- the first is fine-grained (0.025 - 0.01 mm); it is usually contaminated with fine ore dust, is represented in small quantities in hematite ores;
- the second is medium-grained (up to 0.1 mm) recrystallized (often marshallitized), pure, filling the cavities and pores in hematite and berthierite-hematite ores;
- the third is veined.

IV. CONCLUSIONS

The high-grade iron ores of the region are typical hypergene products of the weathering crust of ferruginous quartzites. The diversity of their mineral types is due to the different mineral composition of parent materials and the development of secondary processes of carbonation and chloritization. The complex of research, aimed at study of material composition of rich iron ores, has shown that the region’s high-grade iron ores are a potential source of high-quality multi-purpose metallurgical raw materials.

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