

# Crystal chemical characteristics and physical properties of ferrous minerals as the basis for the formation of functional materials

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**Abstract.** Crystal chemical characteristics and physical properties of ferrous minerals can be criteria for search and evaluation of mineral (natural) raw for the production of functional materials. Special attention will be given to new experimental methods of transformation of minerals at different methods of influence. As a probe to identify the relationship between the actual crystalline structure of the mineral and its technological properties we used the oxidation - reduction reactions of iron ore-forming minerals. We will show that the inexpensive and affordable methods of influence at ore and technological products result in the observed  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge transfer, which result in the increase of the conversion degree of the structure and change of magnetic properties of the substance.

## Introduction

Natural titanium and aluminum minerals are not only an important source of aluminum and titanium, but also raw for functional materials. Traditional deposits of aluminum and titanium ores are coming to the end, which is boosting the search for new sources and technologies to solve these tasks. This may be a non-traditional raw – poor, but affordable and common minerals, ores and rocks (or technogenic and industrial wastes), which require innovative technologies for utilization. The efficiency of the technologies depends on the mineralogical and geochemical studies of oxide ores and supergene modification products. In this article the authors focused on the problem of iron-titanium and iron-aluminum minerals. For example, the presence of non-magnetic ferrous oxides is a significant obstacle for technological processes in bauxites; and low-magnetic titanium minerals are often a cause of non-conditional concentrates [1-4]. The iron ions are involved in the redox environment of natural mineral formation. Our experiments have shown that Fe-minerals are good test objects to identify the relationship between the crystal-chemical characteristics and technological properties of minerals. During the technological processes the inexpensive and affordable methods of influence at ore and technological products result in the observed  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge transfer, which results in the increase of the conversion degree of the structure and change of magnetic properties of aluminum, titanium and iron concentrates [5-7]. A special attention should be paid to the mechanisms of natural and technogenic phase transformations at different methods of energy methods of influence (e.g. radiation-thermal) in minerals of rebellious ores and wastes to control concentrations of the valuable components in the technological processing schemes, production of new industrial products.



The aim of the work – the phase analysis of iron-titanium and iron-aluminum minerals and studies of methods of  $\text{Fe}^{2+}$  -  $\text{Fe}^{3+}$  charge transfer as the basis of innovative technologies of utilization of the observed ores.

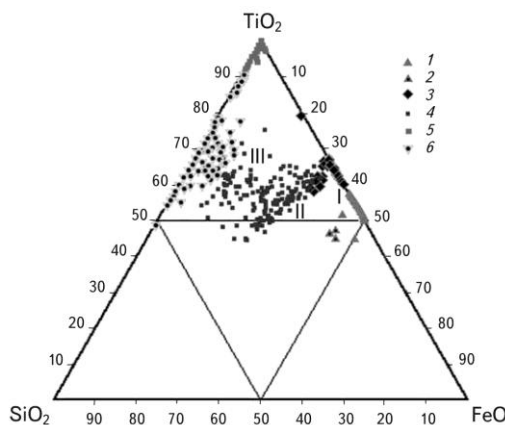
### 1. Objects and Experimental procedure

The objects of study are aluminum, titanium and iron ores associated with Devonian-Carboniferous tropical and subtropical lateritic weathering crusts and their redeposition products.

The analytics was done mainly by the equipment in the Institute of Geology of Komi Science Centre UB RAS: morphological features of the ore minerals and their composition were studied by a scanning electron microscope Jeol JSM-6480 LV. Other modern methods were also used, for example, X-ray fluorescence techniques (XRF), optical-mineralogical methods (stereomicroscope MBS-10, polarizing microscope POLAM L-311), etc.

### Results and discussion

Figure 1 represents a triangular diagram of  $\text{TiO}_2$  –  $\text{FeO}$  –  $\text{SiO}_2$  figurative points of titanium minerals from titanium concentrates of Pizhemscoe deposit presented in [6]. According to the authors' opinion, the first stage is associated with Fe-rutile transformation into pseudorutile, the second stage is associated with Fe-rutile transformation in pseudorutile, the third stage is associated with the transformation of pseudorutile into leucoxene. All steps of the transformation of ilmenite  $\text{FeO} \cdot \text{TiO}_2$  into leucoxene via intermediate phases:  $\text{Fe}_2\text{Ti}_4\text{O}_{11}$  (Fe-rutile),  $\text{Fe}_2\text{Ti}_5\text{O}_{13}$  (pseudorutile) and also leucoxene, hematite, Mn-siderite and rutile are recorded instrumentally and according to the authors' opinion they are formed within the same process described in [7]. Such a variety of iron-titanium minerals suggests that many natural processes occur with participation of iron ions. These minerals possess different physical and chemical properties, making difficult to obtain monomineral fractions of grains with similar magnetic or electrical properties. This reduces the efficiency of the separation of minerals.



**Figure 1.** Triangular diagram of  $\text{TiO}_2$  –  $\text{FeO}$  –  $\text{SiO}_2$  figurative points of titanium mineral from titanium concentrates of Pizhemscoe deposit [6]

About 10% leucoxene contain significant amounts of iron and possess magnetic properties. The magnetic susceptibility of ferrous leucoxene is variable, and its low-ferrous varieties are not removed during magnetic separation. Our experiments showed that  $\gamma$ -irradiation resulted in increasing magnetic susceptibility of the leucoxene at 4.5 times (Table 1). Thus, the magnetic characteristics can be easily changed for technological tasks.

**Table 1.** Influence of irradiation on the magnetic properties of leucoxene

Irradiation dose D, Mrad	Magnetic susceptibility, r.u.		
	High magnetic fraction	Medium magnetic fraction	Low magnetic fraction
0	1.80	1.0	0.14
1.85	1.80	1.1	0.13
2.85	3.42	1.4	0.14
3.75	7.62	1.0	0.10
4.75	17.70	4.1	0.10

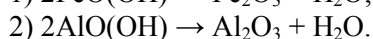
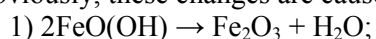
For example, in [4, 8] it was shown that leucoxene sandstone was represented by non-durable grains acicular rutile and anatase, which during sintering transformed into rutile, titanium magnetite and spinel, which crystals strengthened the glass phase and interporous partitions, durability and frost resistance of the ceramic batch. This is accompanied by intensification of redox reactions between organic and ferrous components that contribute to the  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  transformation.

We studied the selected from Vezhayu-Vorykvinskoe deposit samples of three most high-ferrous bauxite types with different ratios of mineral forms of iron: oxide, phyllosilicate and mixed oxyde-phyllosilicate. As is known, the ferrous silicate phase in the composition of exogenous rocks is treated as chamosite, i.e. 14 Å phyllosilicate with the chlorite structure (alternating layers of T-O-T or 2:1) and composition  $(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_5\text{Al}[(\text{Si}_3\text{Al})_4\text{O}_{10}](\text{OH})_8$ , or as septe-chamosite (berthierine) - 7 Å phyllosilicate with kaolinite structure (alternating layers of T-O or 1: 1) and composition  $(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})_{2-3}[(\text{Si}, \text{Al})_2\text{O}_5](\text{OH})_6$  [2, ]. The same mineral in the studied Timan bauxites, according to X-ray patterns, is 7 Å phyllosilicate, and therefore can be attributed to berthierine.

According to the lithochemical properties the studied types of ferrous bauxites are aluminum standard-superferrous superhydrolyzates. They are characterized by the highest content of iron within 20-35 %  $\text{Fe}_2\text{O}_3$ . By silicon module they correspond to rather high grade bauxites. The calculations of normative mineral composition show that all types of the ferrous bauxites are predominated by boehmite, which normative content is not lower than 60 mol %. The most important impurities are widely various ferrous minerals - berthierine, oxides, oxyhydroxides. It was determined that with increasing content of oxide and oxyhydroxide phases results in fast declining phyllosilicate proportion. Besides the recalculation of the chemical composition of the minerals identifies titanium oxides (this is confirmed by X-ray analysis) and X-ray amorphous siliceous substance.

Our studies showed that Timan ferrous bauxites by iron crystal chemistry can be divided into 1) oxide-oxyhydroxide with sharply dominant concentration of iron in the oxides and its distribution between the hematite, goethite and kaolinite in the ratio of about 1:0.1:0.3 (hematite-boehmite type) ; 2) oxide phyllosilicate-oxyhydroxide, in which iron is more inclined to hematite and berthierine in the ratio of 1:0.3:0.7 (hematite-berthierine-boehmite type); 3) phyllosilicate-oxyhydroxide with iron, almost entirely tied with berthierine (berthierine-boehmite type). The obtained data can be used to improve the processing technology of Timan bauxites and in particular, to minimize the aluminum loss within the structure of ferrous minerals.

An important obstacle for processing of bauxite is non-magnetic ferrous oxides - goethite-hydrogoethite and hematite-hydrohematite. Irradiation of ferrous non-magnetic materials with high-energy electrons result in the transformation of non-magnetic and low-magnetic minerals into ferromagnetic [ ]. The X-ray pattern of the sample, subjected to stepwise heating with quadruple 60 minutes exposure, lacks reflections from boehmite and goethite, but obviously amplifies reflections from hematite and adds reflections from quartz and  $\gamma\text{Al}_2\text{O}_3$  – spinels with defective structure. Obviously, these changes are caused by the thermal dissociation of goethite and boehmite:



The analysis showed that during such heating of the bauxite sample the proportion of the magnetic fraction was consistently reduced (coefficient of pair correlation of the share with temperature  $r = -0.86$ ). However, the gross value of the magnetic susceptibility was not changed [3]. This paradox can be explained by the fact that slightly larger magnetic susceptibility of hematite compared to goethite was enough to increase the yield of the magnetic fraction, but not enough for a substantial increase of gross magnetic susceptibility. It is clear that the presence of boehmite in radiation-thermal modification of bauxite is explained by incomplete dissociation of the latter due to insufficient heating of the sample at an appropriate temperature (500–600 °C). But the appearance of two ferromagnetic phases – maghemite and magnetite – should be attributed directly to the results of irradiation. The analysis showed that the formation of such phases significantly influenced the gross magnetic properties of the modified sample – volumetric and specific magnetic susceptibility were increased in comparison to the initial sample by 6–7 times. In accordance with this during the radiation-thermal processing of the sample the proportion of the magnetic fraction increased and, which consistency is confirmed by a strong direct correlation of the magnetic susceptibility with heating temperature ( $r = 0.71$ ).

### Conclusion

The paper presents the mineralogical and crystal chemical studies of ferrous minerals of titanium and aluminum ores from Timan. The specifics of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  distribution in the structural positions in oxides are discussed. It was shown that the inexpensive and affordable methods of influence at ore and technological products resulted in the observed  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  charge transfer, which resulted in the increase of the conversion degree of the structure and change of magnetic properties of the substance. The oxidation-reduction reactions of iron ore-forming minerals are a probe to identify the relationship between the actual crystalline structure of the mineral and its technological properties. Crystal chemical characteristics and physical properties of ferrous minerals can be criteria for search and evaluation of mineral (natural) raw for functional materials.

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