

Structural-chemical features and morphology of glauconites in sedimentary iron ore of Bakchar prospect (Western Siberia)

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Abstract. The research embraces the investigation results of glauconites in Bakchar iron ore occurrences to evaluate the potential diversified commercial application of this mineral. The following lab methods were used to analyze the morphology, chemical composition and structure of glauconites: granulometric analysis, optical microscopy, electron microscopy, X-ray fluorescence analysis, atomic arc-emission analysis and infrared spectroscopy. Glauconite was classified according to morphology and grain color and chemical composition and some specific characteristics were also determined (relative content of absorbed water, random distribution of smectite flakes within the grain structures). The research results showed that pistacho-green glauconite grains are less subjected to alteration than greenish-yellow grains due to the content of potassium, iron, absorbed water and organic impurities.

1. Introduction

Glauconite is iron potassium phyllosilicate nonstoichiometric mineral, $K_{<1}(Fe^{3+}, Fe^{2+}, Al, Mg)_{2-3}[Si_3(Si, Al)O_{10}][OH]_2 \cdot nH_2O$, prevailing in sedimentary rocks [1, 9, 14]. Due to its unique properties (molecular sorption, ion-exchange properties, thermal resistance, radiation stability, apparent coloring oxides, etc.), it is a diversified industrial application mineral [2-4] and a prospective geological (paleoclimatic, facies, etc.) information source [5, 7, 8, 12]. Its structure-texture properties and chemical composition determine the potential application of glauconite. Named in 1828 by Christian Keferstein, glauconite has attracted the attention of many geologists [5, 8, 12]. With the development of research and technology new and new domains of this mineral have been established: industrial application [1-4, 6] and mineral-indicator for sedimentation environments [5, 8, 11]. Recently, the processing behavior of this mineral (from the deposits in Central, Southern, North-western and Ural Federal Districts) has been investigated in details [4]. The following potential glauconite areas and provinces were determined: Central, Baltic, Volga, southern Pre-Ural, trans-Ural [3-4]. Notwithstanding the significant contribution of the following geologists E.F. Levchenko, M.L. Levchenko, N.G. Patik-Kara, L.P. Tigunov [1-4, 6, 7, 11], even, today, there is no information of the glauconite potential within the Siberian and Far Eastern territories.

This research is focused on the investigation of the glauconite structural-morphological properties and chemical composition in Upper Cretaceous sediments from Bakchar iron ore occurrences. The



practical aspect of this research involves not only the possible extraction of glauconite as a by-product free-milling concentrate during the development of sedimentary iron ore in Tomsk Oblast, but also the introduction of this glauconite concentrate into different enterprise domains (agriculture, petroleum industries, etc.). Bakchar ore mineralization is located in the S-E Western Siberia iron ore basin (figure 1), 200 km north-westward from Tomsk. Ferrous iron sediments include sediments of coastal-marine facies – gritstone, oolitic ores, sandstone, aleurolite and clays. Iron ores are oolites of goethite-hydrogeothite and / or chlorite-hydrogeothite composition and confined to three horizons: Narim, Kolpashev and Bakchar [9-10]. There are three types of native iron ores within the ore mineralization itself: loose hydrogeothite, weak and medium-cemented hydrogeothite-chlorite, closely cemented siderite-hydrogeothite [9-10]. Glauconite is predominate in weak and medium-cemented hydrogeothite-chlorite ores and has the granulometric size from 0.5 to 0.1 mm. Visually, optical testing showed that the glauconite content is 15-20%. Bakchar iron ore formation embraces layers of glauconite sandstones and sands which are interbedded between iron-ore lenses and layers. Based on the research results, glauconites in iron ore deposits can be evaluated in terms of extracted sovereign concentrations under conditions of iron-ore enrichment.



Figure 1. Map of Western-Siberia iron-ore basin [10]: 1 – Cretaceous-Paleogene extent sea area; 2 – extent coastal-marine iron-ore sediment zone; 3 – area of significant iron ore clusters (deposits).

2. Factual material and research methods

Factual material includes weakly cemented hydrogeothite – chlorite ore chip samples [10] of well cores from the depth of 180...220 meters. The following laboratory methods were used: granulometric analysis (“wet screening” method), optical microscopy, electron microscopy (TESCAN VEGA 3 SBU), X-ray fluorescence analysis (HORIBA XGT-7200), atomic arc-emission analysis (DEMO PRODIGY DC), infrared spectroscopy (Shimadzu IR Prestige-21). Glauconite monofractions of granulometric size from 0.5 to 0.1 mm were selected for binocular microscopy investigation.

3. Research results and discussion

Based on grain morphology the following types of glauconite were identified: isometrically rounded (globular, nodular) (figure 2a), elongated gobular (figure 2b), clustered (figure 2c), biomorphic

(figure 2d), composite aggregates (figure 2e). The grain surfaces are rough-pit with traces of erosion (cracks, vugs) and rarely, smooth and lustrous. If increasing in volume, the internal glauconite structure changes to composite-layered randomly scattered smectite-illite plates and flakes (figure 2f) with micron eosizes (up to 2 micron). According to color, the grains were divided into two basic categories: pistachio-green and greenish yellow. However, they are also bluish-green, practically black, yellow with slightly greenish tint, as well as other color tints, which, in its turn, reflect the chemical composition variability due to the post-sedimentation changes of original glauconite assemblages.

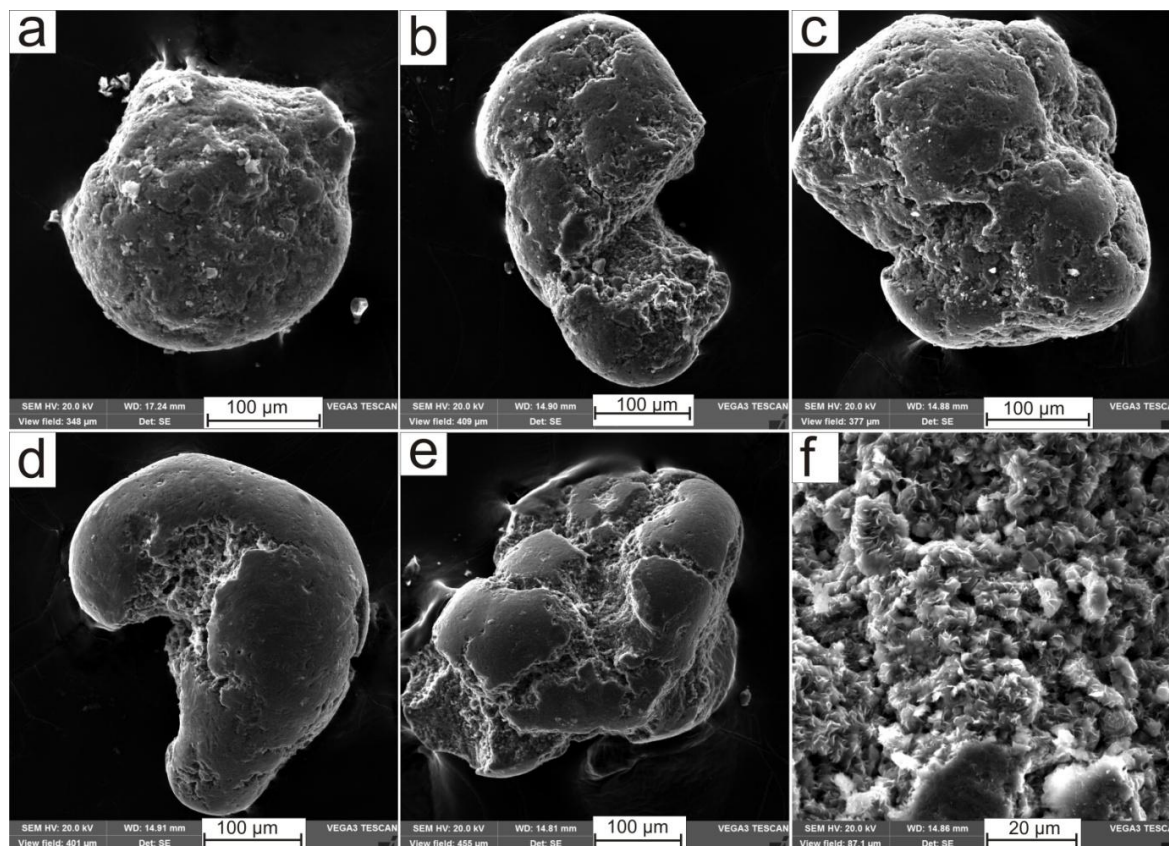


Figure 2. Morphology and internal structure of glauconite grains in Bakchar ore occurrences (electron micrograph): a –isometrically rounded; b – elongated gobular; c – clustered; d – biomorphic; e – composite aggregate; f – internal grain structure.

The microscopic investigations of glauconite surfaces and corroded vugs (cavities, cracks) revealed the following mineral impregnations (figure 3): framboid pyrite assemblages; kularite and spherulite aggregates, presumably bromin-carnallite; nickel-chrome mineral (redingtonite) adhesion. Pyrite is a framboid aggregate of up to 10 micron in size, which is cubic and /or octahedral microcrystal assemblages of up to 1 micron in size. In some cases, kularite can be found on the glauconite surfaces as microspherulite assemblages of up to 5...6 microns in size. According to the shape and chemical composition such kularite is found in hydrogeothite oolites of Bakchar ore occurrences [9]. Bromin mineral grains, comparable to bromin-carnallite ($KMg(Cl,Br)_3 \cdot 6H_2O$) in composition, are commonly found in glauconite (according to the data from www.mindat.org). These minerals (bromin-carnallite) are variform aggregates from 4...5 microns in size. Unidentified chromic mineral is found as a mineral adhesion of up to 0.5 micron thickness contouring micro- smectite flakes. Ni, Cr, Fe predominance indicates the fact that this mineral could be redingtonite, having the formula $(Fe^{2+}, Mg, Ni)(Cr, Al)_2(SO_4)_4 \cdot 22H_2O$ (according to the data from www.mindat.org).

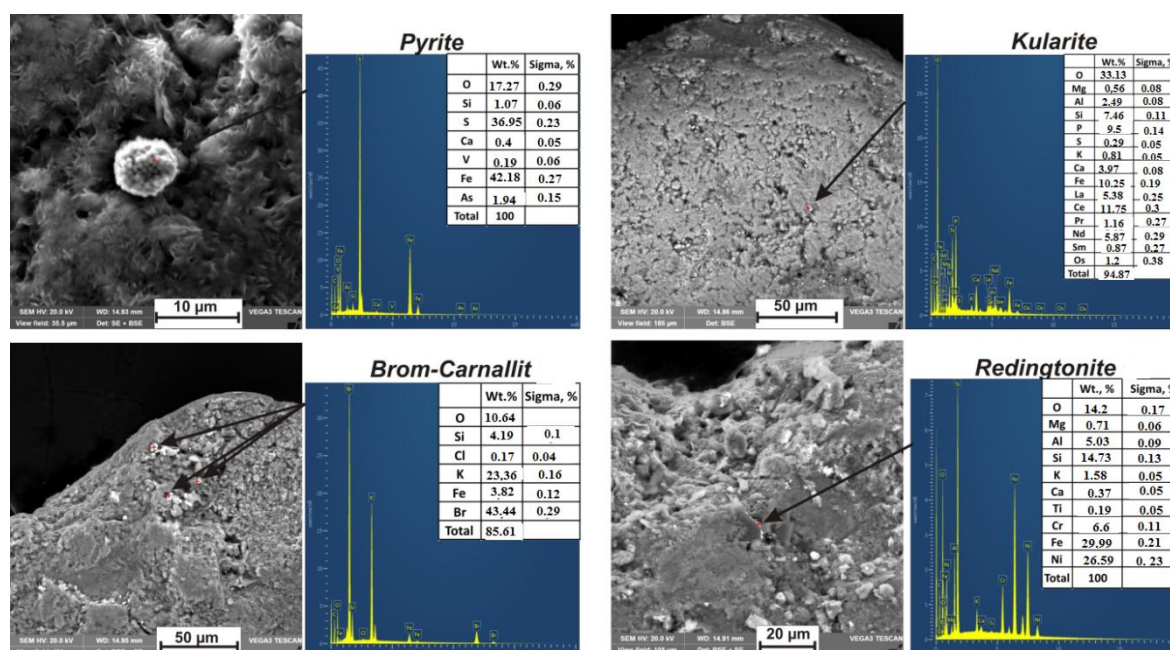


Figure 3. Electron micrographs and characteristic spectrum of mineral microphenocrysts on the glauconite grain surface.

It should be noted that the above-mentioned facts could be considered only as preliminary data, requiring further detailed investigation based on the electron microscopy analysis. Based on the X-ray fluorescence analysis the following chemical composition was defined and described in table 1. Based on these results the following conclusions can be stated: yellow and yellowish brown glauconite has a low K_2O content (up to 5.5%) and SiO_2 content (up to 39%) and a rather high $Fe_2O_{3(total)}$ content (up to 48%). The pistachio-green color of grains could be significant as a result of oxidation of the first, i.e. K_2O . The amount of impurity elements is an indicator of prevailing good glauconite sorptivity. Impurity elements precipitate in the mineral (glauconite) itself from the sedimentation environments as a consequence of its specific (random, composite-layered) inner structure. The impurity elements include Ti, V, P, Cr, Zn, Mn, As, Ni. Phosphate content varies from 0.13 to 2.04 %, while its average content is 0.42...0.83 %. Phosphate is a practical impurity for agriculture.

It is problematic to determine the absorption maximum of this or that bond in the mineral samples based on the infra-red spectrum, as the most statistically reliable absorption characteristic values, as a rule, are comparable to the equivalent bonds in reference samples. As glauconite is a mineral with alternative chemical composition, it could be also problematic to select a reliable reference infra-red spectrum. In addition, the reaction with environment bonds could possibly induce alterations of the characteristic absorption frequency itself, which, in its turn, become limiting. For example, V.I. Vigdorovich [11] described the fact that the Si-O bond in crystalline quartz is characterized by two stretching bands-1179 and 1109 cm^{-1} , whereas, these bands in glauconites cannot be observed as single absorption maximums due to the fact that they could overlap PO_4 absorption maximums resulting in infrared absorption (950...1100 cm^{-1}).

Infrared spectrum (figure 4) of investigated glauconites showed stretching bands of 1570 and 1380 cm^{-1} . Stretching bands of 1625...1660 cm^{-1} reflect the inner structure of the glauconites shatter micro-smectite plates and flakes. Stretching bands of 3200...3600 cm^{-1} are related to absorbed water variations and complicated by intensive ferric stretching bands, the frequency of which is 3530 cm^{-1} . Stretching band of 3600 cm^{-1} indicates a low Al^{3+} content in octahedral glauconite layers. Organic impurities show absorption maximum frequency of 2349, 667, 2850...2950 cm^{-1} .

Table 1. Average chemical composition of glauconite in iron ores of Bakchar ore occurrences.

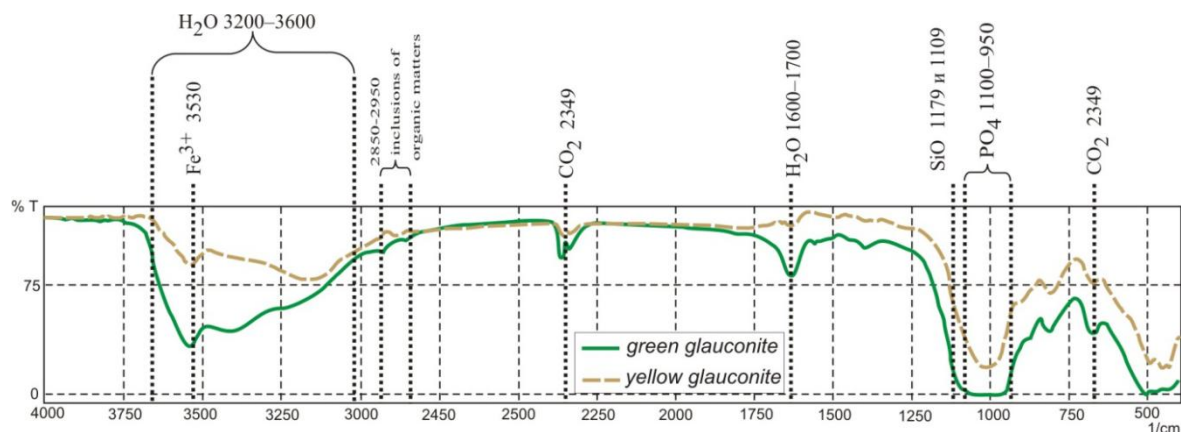
Grain color	Size, mm	Major elements, %					
		MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃
1	0.5.....0.2	2.7	9.2	46.4	4.5	1.0	37.6
1	0.5.....0.2	2.0	9.6	52.9	5.3	1.3	29.0
2	0.2.....0.1	1.9	8.3	37.4	3.3	0.8	48.5
2	0.2.....0.1	1.6	7.7	39.5	3.9	1.0	46.0

Grain color	Size, mm	Major elements, % (+ content more than 0.01%)							
		Ti	V	Cr	P	Zn	Mn	As	Ni
1	0.5.....0.2	0.33	0.15	0.10	0.42	0.03	0.11	0.11	0.34
1	0.5.....0.2	0.69	0.11	0.27	0.83	0.03	0.15	-	-
2	0.2.....0.1	0.35	0.26	0.72	0.76	0.16	0.15	0.10	-
2	0.2.....0.1	0.28	0.24	0.13	0.67	0.08	0.13	0.10	-

Note *Color of glauconite grains: 1 – pistachio-green, 2 – greenish-yellow

The results in the table are based on X-ray fluorescence analysis data including 250 glauconite grains.

Analyst – M.A. Rudmin

**Figure 4.** Infra-red spectrum of glauconite in iron ores of Bakchar ore occurrences.

Green-colored glauconite grains comparable to greenish-yellow ones predominately show intensive absorption peaks within the frequency intervals, which, in its turn, is associated with water absorption and organic impurities. This fact could be explained by the insignificant diagenetic alteration of green glauconites comparable to the greenish-yellow ones, as well as the specific chemical composition of green glauconites (content of K₂O, Fe₂O₃, SiO₂).

4. Conclusion

The research results are the following: 1) according to color and morphology different glauconite grains were defined; chemical composition of glauconite was described and the content of basic impurity elements were identified; 3) structural features of glauconites were described based on the

infrared spectrum; 4) micro-impregnations on the glauconite grain surface were determined and described, including bromin-carnallite and redingtonite.

Preliminary mineralogic-engineering investigation results of the glauconites in Mezozoic-Cenozoic sediments (Tomsk Oblast) were described. Thus, it could be stated that glauconite (in Tomsk Oblast) is a valuable industrial mineral with similar properties to the glauconites in Tambov and Cheljabinsk Oblasts [3-4]. It should be noted that a positive evaluation of the existing engineering properties of glauconites could further the mining efficiency of iron ores in Bakchar ore occurrences.

Acknowledgements

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