Sedimentary-diagenetic ore formation in the Jurassic system terrigenous deposits of the Tatarstan Republic

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Abstract. Authigenic ore mineralization of the Jurassic terrigenous complexes rocks, widespread in the Tatarstan, is considered. It has been established that the ore minerals associations’ composition is determined by geochemical conditions of mineral formation environment. In rocks of oxide geochemical facies (sandstones, siltstones), iron, manganese and titanium oxides predominate. Pyrite framboids and copper-nickel intermetallide compounds predominate in rocks of neutral geochemical facies (green clays). The rocks of anoxic geochemical facies (black clay, oil shale) contain only pyrite framboids. The main factor determining the authigenic ore minerals associations composition is redox potential of environment.

1. Introduction

Sedimentary ore formation is one of the least studied areas in ore geology. At the same time, while attention is being paid to mineral stratiform deposits and less to primary sedimentary ore minerals scattered in rocks. Although many experts in this field do not deny leading role of such processes, which is primary source, in deposits formation [1, 2]. Given this, a study of accessory ore minerals composition and distribution features in the Jurassic system terrigenous deposits of the Tatarstan territory was conducted.

According to V.V. Mitta [3] works the Jurassic sediments in the Tatarstan west are represented by terrigenous complex of the Bajocian, Bathonian, Callovian, and Oxfordian-Kimmeridgian stages, which unconformable lying on erosional surface of the Permian deposits. In the Jurassic sections of the Middle Volga region, greenish-gray and black clays with interlayers of siltstones, sandstones and oil shales prevail [4]. Throughout all geological history of territory under consideration, the rocks did not experience deep diving, remaining at diagenesis stage. Thus, possibility of studying primary ore mineralization of sedimentary deposits acquired during lithification of silty marine sediments has remained.
2. Objects and methodology

The main method for ore minerals studying was a MerlinCarlZeiss field-emission scanning electron microscope, combined with a BrukerAXS energy dispersion spectrometer. The resolution of the spectrometer is 129 eV. The measurement accuracy is 0.1-1%.

Rocks reflecting variations of the Russian Paleosea geochemical facies: sandstones, siltstones, clays and oil shales were chosen as objects of study. Shallow water sandstones and siltstones with undulation ripples marks represented deposits of an oxide geochemical facies, greenish gray clays represented neutral geochemical facies, black clays and oil shales represented an anoxic geochemical facies.

2.1. Sandstones

Sandstones form layers of insignificant thickness (up to 1.0 m) in the Bajocian stage deposits. The rocks are light gray, dense, fine-grained, with a well-defined wavy-layered texture, in stage roof bear traces of undulation ripples. According to optical microscopic studies, sandstones are 85% composed of clastic quartz grains, feldspars, flakes of muscovite and chlorite, and 15% composed of basal type calcite cement. The rocks porosity is weak 3-5%. Accessory minerals are represented by rounded grains of clastic zircon and authigenic ore newly formed structure.

Electron microscopic studies showed that iron oxides with manganese impurity and manganese oxides in sandstones are ore minerals. Iron oxides by chemical elements weight ratio can be attributed to magnetite with formula MnFe$_2$O$_4$. They form flattened tabular crystals up to 10.0 microns long, 6.0 microns wide, and 2.5 microns thick (figure 1). On the most developed face surfaces vicinal growth forms and numerous open fossae are noted. The octahedral forms of magnetite up to 2.5 microns in size are less common. Manganese oxides by elements weight ratio are similar to pyrolusite (MnO$_2$) in composition. They occur in the form of spherical aggregates with a well-defined internal concentric zonal structure. Each growth zone is composed of multiple dense needle crystals.

![Magnetite with manganese impurity](image1.png)

![Magnetite with manganese impurity](image2.png)

**Figure 1.** Photo of accessory ore minerals in sandstones of the Jurassic sedimentary complex.
2.2. Siltstones

Siltstones form layers up to 1.5 m thick in sediments of the Callovian and the Oxfordian-Kimmeridgian stages. According to composition of clastic component they are similar to sandstones of the Bajocian stage. The difference lies in clastic grains size, the predominance of contact-pore type carbonate-clay cement and presence of higher porosity to 10-15%. According to electron microscopic data, iron-titanium associations of ore accessory minerals prevail in siltstones. Both compounds with elements weight ratio close to magnetite and compounds with elements weight ratio close to rutile (TiO$_2$) are present. Iron-titanium mineralization is associated with rock pore space, their aggregates 8.0-15.0 microns in size grow on quartz and feldspar grains. The forms of excretion are represented by various ovaloids, strobilaceous stalactite like aggregates, tapering to center of siltstones pores (figure 2). The aggregates surfaces are characterized by imbricated structure.

**Figure 2.** Photo of accessory ore minerals in siltstone of the Jurassic sedimentary complex.
2.3. Claystone

Green clays are composed of axially oriented clay flakes of illite-montmorillonite composition with an impurity of chlorite and illite. The clastic components, represented by coccolithophora residues, quartz and feldspars grains, do not exceed 20%. Ore minerals are represented by framboids aggregates of pyrite and copper-nickel intermetallide compounds (figure 3). Pyrite framboids up to 4 microns in size form local aggregation. All of them are composed of smaller octahedral crystals that are in close contact with each other. Intermetallide compounds form flattened aggregates up to 25.0 microns in size with relatively smooth surface. Their orientation in clay mass according with rock lamination.

![Pyrite framboids](image1.png) ![Copper-nickel intermetallide](image2.png)

*Figure 3. Photo of accessory ore minerals in green clays of the Jurassic sedimentary complex.*

Black clays and oil shales are mostly composed of clay minerals (illite-montmorillonite, chlorite, illite), the content of clastic quartz and feldspars grains, muscovite and chlorite flakes does not exceed 25%. The rocks are characterized by dense composition, mineral grains are in close contact with each other, the structure is argillaceous, and the texture is horizontally layered. A characteristic feature of anoxic geochemical facies rocks is presence of organic matter, which is from 5.0 to 20.0% [5, 6]. Ore mineralization is represented by pyrite aggregates, content of which reaches 4.0% of rock mass. In black clays, pyrite is mainly represented by framboids up to 5.0 microns in size. Framboids, growing together, form small-length lenses; sometimes they are present in the form of single aggregates in clay mass. Agreggative intergrown pieces consisting of densely packed, relatively large octahedral pyrite crystals are rare. In oil shales, pyrite is represented by flattened aggregates with an uneven lumpy surface up to 4.0 microns in size. All aggregates are oriented according to lamination and fissility of sedimentary rocks. Some of them are replaced by authigenic gypsum.
Thus, in the Jurassic sedimentary complex sediments, there is clear differentiation of ore minerals according to geochemical zones of the Central Russian Paleosea. Near the coastline, in sandstones, iron-manganese compounds precipitated; below, in siltstones accumulation region, iron-titanium compounds; in transitional geochemical zone, where green clays were formed, copper-nickel intermetallic compounds and frambooidal pyrites were jointly formed; and in deepest, anoxic zone, where black clays and oil shales formed, iron sulfides.

3. Discussion

As can be seen from identified associations of ore accessory minerals, their distribution is subject to geochemical conditions of mineral formation environment. Given this, a thermodynamic simulation was carried out in sandstones. Among authigenic ore formations, jacobsite (MnFe₂O₄) and pyrolyusite (MnO₂) are found. The formation of jacobsite from components contained in sea water can be represented by reaction:

$$2Fe(OH)_3 + Mn^{2+} + 0.5O_2 = MnFe_2O_4 + 3H_2O \quad \Delta r G = -289.11 \text{ kJ/mol} \quad (1)$$

The magnitude of the Gibbs energy change of this reaction under standard PT (pressure-temperature) conditions is $\Delta r G = -289.11 \text{ kJ/mol}$. Its negative value indicates that it proceeds self-arbitrary, i.e. from left to right with jacobsite formation. The presence of oxygen small amount in initial components of this reaction indicates that the jacobsite formation requires weakly oxidizing environment, which, apparently, is easily achieved during diagenesis of sandy sediments in shallow sea, i.e. in coastal marine conditions. The question may arise why magnetite (FeFe₂O₄) does not form under these environmental conditions? The answer to this question is the following reaction:

$$3Fe(OH)_3 + e^- = FeFe_2O_4 + 4H_2O + OH^- \quad \Delta r Go = -152.84 \text{ kJ/mol} \quad (2)$$

The magnitude of the Gibbs energy change of this reaction is $\Delta r G = -152.84 \text{ kJ/mol}$, i.e. it can self-arbitrary flow from left to right with magnetite formation. However, for this it is necessary to restore
one of the three Fe$^{3+}$ in the Fe(OH)$_3$ molecule to divalent Fe$^{2+}$, which is necessary for magnetite formation, and reducing conditions are necessary for this. The calculated value of the redox potential $E_h$ of reaction (2) is -1.58 V, i.e. she is negative and not small. This means that for magnetite formation by reaction (2), a moderately reducing environment is needed, which, apparently, was not achieved during diagenesis of sandy sediments. The calculation of the $E_h$ value was performed according to the formula:

$$E_h = \Delta rG/n * F$$

where $n$ is the number of electrons participating in reaction (2), $F$ is the Faraday constant.

The formation of pyrolusite during sandy sediments diagenesis can be represented by the reaction:

$$Mn^{2+} + O_2 = 2MnO_2 + 2e^- \quad \Delta rG = -237.98 \text{kJ/mol}$$

(3)

The magnitude of the Gibbs energy change of this reaction under standard PT (pressure-temperature) conditions is $\Delta rG = -237.98 \text{kJ/mol}$. Since it is negative, reaction (3) can proceed self-arbitrary from left to right with pyrolusite formation. However, this requires moderately oxidizing environment, as evidenced by the reaction potential (3) $E_h = +1.23 \text{V}$, which, apparently, is achieved by sandy sediments diagenesis in some parts of the environment. Where it is achieved, pyrolusite is formed and no jacobsite. And in areas of weakly reducing environment pyrolusite is not formed, but jacobsite is formed. Therefore, pyrolyusite and jacobsite in the analyzed samples of sandstones are not found together.

In siltstones, among authigenic ore formations, magnetite with impurity of titanium and rutile is noted. The formation of magnetite can be expressed by above reaction (2), the reaction of which requires a moderately reducing environment ($E_h = -1.58 \text{V}$). The formation of rutile in siltstones can be represented by the reaction:

$$TiO^{2+} + 0.5O_2 = TiO_2 \quad \Delta rG = -258.27 \text{kJ/mol}$$

(4)

The change in the Gibbs energy of reaction (4) is $\Delta rG = -258.27 \text{kJ/mol}$; this reaction proceeds self-arbitrary, but this requires a weakly oxidizing environment ($E_h > 0$), as evidenced by presence of oxygen in initial components of reaction (4). It turns out that for magnetite formation requires a reducing environment, and rutile formation requires a weakly oxidizing environment. Apparently, this is why magnetite and rutile in siltstone do not occur together (side by side). They are noted in different areas with different values of $E_h$. In areas with a reducing environment, rutile does not form, but magnetite forms here, which incorporates Ti impurity. In areas with an oxidizing environment, on contrary, magnetite does not form, but rutile forms. The question arises, if an oxidizing environment is needed for rutile formation, then why it does not form during sandy rocks diagenesis? The answer lies in the fact that Ti is transported to marine basins mainly in form of organo-metallic compounds and titanyl ions occluded by clay minerals and vegetative detritus. The latter precipitate, accumulate in clay and silty sediments. In clay sediments enriched with organic matter (OM), the diagenesis environment is always reducing ($E_h < 0$) and therefore rutile does not form here, but in siltstones in areas with low OM content, the diagenesis environment can become weakly oxidizing ($E_h > 0$) and rutile can be formed by the reaction (4).

The question may arise: if magnetite formation requires a reducing environment of diagenesis, then why is it not found in black and even green shales? The answer lies in the fact that clay sediment diagenesis environment is highly reducing, therefore, all the iron goes into divalent form and magnetite cannot form, since 2/3 of iron should be in the form of Fe$^3^+$ ions in its composition.
In green clays, there are noted native copper with impurity of Ni (8-20%) and framboids of pyrite. The formation of native copper can be expressed by the reaction:

\[ \text{Cu}^{2+} + 2e^- = \text{Cu (metal)} \]  

(5)

The magnitude of the Gibbs energy change of this reaction is \( \Delta rG = -65.55 \text{ kJ/mol} \) and shows that it proceeds self-arbitrary, but requires weakly reducing diagenesis environment, since the value \( \text{Eh} = -0.34 \text{ V} \). These conditions are easily achieved, since clay sediments are usually enriched not only in Cu, Ni, but also in organic matter, which, when rotted, consumes oxygen to form \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and diagenesis environment becomes reducing. In areas of moderate OM content, the diagenesis environment becomes weakly reducing and native copper formed. The reaction of native nickel formation of proceeds similarly:

\[ \text{Ni}^{2+} + 2e^- = \text{Ni (metal)} \Delta rG = +45.6 \text{ kJ/mol}; \text{Eh} = -0.24V \]  

(6)

However, unlike native copper, it cannot flow self-arbitrary, because the value \( \Delta rG \) of this reaction (6) is positive. Therefore, native nickel in association with native copper is not found in green shale, but Ni can be replaced isomorphically with Cu atoms in native copper, since atomic radius of Cu (0.128 nm) and Ni (0.124 nm) are very close to each other. Therefore, in the studied samples of green shales, native copper contains impurity of nickel in amount of 8-20%.

For pyrite framboids formation in green, black clays and in oil shales, \( \text{S}^{2-} \) ions are necessary, which are formed in diagenesis by reduction of \( \text{S}^{6+} \) ions from sulfate of \( \text{SO}_4^{2-} \) ion of sea water due to organic matter rotting of sediment. The simplest reaction of this process is the following:

\[ 2\text{CH}_2\text{O} + \text{SO}_4^{2-} + \text{H}_2 + 8e^- = \text{H}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O} \Delta rG = -332.22 \text{ kJ/mol}; \text{Eh} = -0.43V \]  

(7)

It flows self-arbitrary from left to right, because \( \Delta rG \) is negative. In this case, a reducing environment is created (\( \text{Eh} <0 \)). Further, hydrogen sulfide, reacting with \( \text{Fe(OH)}_3 \) molecules of sea water in OM rotting areas of diagenesis zone, produces pyrite by the reaction:

\[ 2\text{H}_2\text{S} + \text{Fe(OH)}_3 + e^- = \text{FeS}_2 + 3\text{H}_2\text{O} + 0.5\text{H}_2 \Delta rG = -149.83 \text{ kJ/mol}; \text{Eh} = -1.55V \]  

(8)

In black clays and oil shales, pyrite framboids formation can be explained by same reactions (7-8).

4. Conclusion

Thus, taking into account the foregoing, we can draw the following conclusion. In rocks of terrigenous complexes of the Jurassic system, widespread in the Tatarstan territory, sedimentary authigenic ore mineralization is widely manifested. The composition of ore minerals associations is determined by geochemical conditions of mineral formation environment. In rocks of oxide geochemical facies (sandstones, siltstones), oxides of iron, manganese and titanium predominate. Pyrite framboids and copper-nickel intermetallides predominate in rocks of neutral geochemical facies (green clays). In rocks of anoxic geochemical facies (black clay, oil shale), only pyrite framboids are present. The main factor determining composition of authigenic ore minerals geochemical facies associations is redox potential of the environment.

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