Prospect of heat-treat of the reservoir for the active mechanism of oil recovery, due to the study of the geochemical composition of terrigenous rocks of the section of Karkali, South-East of Tatarstan

EI Fakhrutdinov¹, NG Nurgalieva¹, RA Mudarisova¹

¹Institute of Geology and Petroleum Technologies, Kazan Federal University, Kazan, Russia
E-mail: MKS-1989eduard@yandex.ru

Abstract. The present paper shows the thermal features of the treatment on the reservoir, geochemistry of sediments, and intensity of chemical weathering of terrigenous rocks of the Ufimian-Kazanian natural reservoir of the section of Karkali in the basin of the r. Sheshma and r. Inesh, to predict the efficiency forecast of the application of heat-treat at the object and decipher the genesis of sedimentary formations in the area. Changes in the main elements in rocks are represented in the variation diagram.

1. Key requirements
Karkali section, heat-treat, geochemistry, climate, oxides, Ufimian-Kazanian natural reservoir, South-east of Tatarstan.

Over the years, the geochemical method of the approach has been used to study sedimentary environments in the sedimentation basin. The geochemical method allows to divide and correlate the formation, without the biogenic component of sediment. This method is based on the study of the geochemical characteristics of the layers in the section.

A known quantity, that both carbonate and terrigenous sediments “remember” the s environment and hydrochemical features of the sedimentary basin in the form of content of “indicator elements”, such as Ca, Mn, Fe, Si, Cl, SO₃, Al, Ti, V, etc. That is, the turn in the sedimentation cycles is a change in the hydrochemical condition, which is reflected in the chemistry of rocks. And thus, the variation of chemical elements within each several of the lithotypes form a peculiar tool in the identification of geological boundaries, with the subsequent description of the sedimentary environments in consequence of the content analysis of the “indicators” elements of the paleodynamic condition.

2. Introduction
The sediments of the Permian system in the east of the Russian Plate are the objects and interests of many studies, since there a thought arises in the knowledge and understanding of the processes occurring in this geological time.

Basin of the Volga and Kama rivers is known as an unique stratigraphic and paleogeographic object formed in littoral, transition and continental environments. We considered the Kazanian stage (~ 272 - 266 million years) within the Late regional cycle [1]. The Late regional cycle can be characterized as a cycle of second order corresponding to the supercycle or sequence that began his formation
after the fifth global regressive phase of the Late Paleozoic [2]. Investigated Permian cycle acts as a foreland basin supercycle history from its opening until closing. Three megacycles corresponding to the Ufimian, Kazanian and Urzhumian+Severodvinskian + Vyatskian occurred inside this supercycle [1]. According to lithofacies zonation proposed in [3] the Kazanian rocks of Volga-Kama rivers area belong to the zone of carbonate marine and lagoon sediments. The most interesting Permian sections in the South-Eastern Tatarstan (Volga-Kama rivers region) are exposed in the upper reaches of the Sheshma River, near the villages of Shugurovo and Karkali.

3. Objects and research methods
The Karkali section is exposed in a quarry on the right slope of the r. Sheshma and Inesh near the villages of Shugurovo and Karkali.

The description of the section begins at the road-bed between the villages of Karkali and Shugurovo, there are concentrated outcrops of the sandy-clayey red formation of Ufimian rocks and the boundary between the Ufimian and Lower Kazanian sediments (outcrops II – beds 1-7). In outcrop III is concentrated thick series of clayey rocks of bed 8. Outcrop IV (fig. 1) is confined to the western part of the Karkali quarry (beds 8–12) along the right slope of the r.Inesh; outcrop V (beds 13-16), outcrop VII (beds 14-23), outcrop VI (beds 16-18), outcrop VIII (beds 16-18) is confined to the eastern part of the Karkali quarry, on the left slope of the r. Inesh (fig. 1). Outcrop I — the bottom of bed 1 (Ufimian sediments) — in the territory of the Shuguro Tar Plant [4].

Along the whole length section is represented by Ufimian, Lower Kazanian and Upper Kazanian sediments. Consisting of Ufimian sediments includes red sandy-clayey continental sediments. The boundary with Lower Kazanian sediments is accompanied with evidence of erosion. Lower Kazanian sediments are represented by marine facies. The bottom is mainly terrigenous with small layers of carbonate material and the top is carbonate-terrigenous. The carbonate material consists mainly of oolitic carbonates. Upper Kazanian substage consists of continental terrigenous sediments with alternation of siltstone and clayey sandstone [5,6].
Figure 1. Generalised geological map of the Sheshma river, Republic of Tatarstan. Legend: 1 – Quaternary and Neogene; 2 – Urzhumian; 3 – Upper Kazanian; 4 – Lower Kazanian; 5 – Ufimian (according to Nurgalieva, 2015).

4. Results and Discussions
For identification the geochemical data, all samples were studied on an X-ray fluorescence spectrometer. Knowing information about precipitation chemistry it is possible to decipher the genesis of sedimentary formations.

The content of rock-forming oxides and trace elements in the terrigenous rocks of the Ufimian and Kazanian ages was studied 116 samples. Such as clay samples -45, sandstone samples -71. Analysis for 43 elements (Si, Ti, Al, Fe, Mn, Ca, Mg, Na, K, P, Sr, S, Cl, V, Cr, Co, Ni, Cu, Zn, As, Br, Rb, Y, Zr, Nb, Cd, Mo, Sn, Sb, Te, Ta, Sm, Nd, Pb, Bi, Se, Cs, Pr, La, Ce, W, Ge, In) performed at the Kazan Federal University using an X-ray fluorescence spectrometer BRUKER S2 Ranger (Bruker, Germany). The obtained results and their mathematical treatment by package STATISTICA allowed to clarify the composition of sediments, as also to get some information about the conditions of sedimentation in the Ural-Biarmian time.

Clay rocks in the section of the Lower Kazanian substage in the basin of the r. Sheshma and r. Inesh were studied according to the data of the modular diagrams by Ya.E.Yudovich and M.P.Ketris: TM(titanium module)-TiO₂ (fig.2) и FM-NKM (femic module-normalized alkaline condition) (fig.3). They allow to classify clay rocks by mineral composition.
Figure 2. TM-TiO2 diagram for clay rocks in the basin of the r. Sheshma and r. Inesh. 1- kaolinitic clay, 1a- low modulus kaolinitic clay – products of catagenetic transformations of montmorillonite and kaolinite substrates, 2- hydromicaceous clay, 3- montmorillonite clay.

Figure 3. FM-NKM diagram for clay rocks in the basin of the r. Sheshma and r. Inesh. I- kaolinitic clay, II- montmorillonite clay with minor kaolinite and hydromica, III- clay rocks with a composition of chlorite and a small adulteration of Fe-hydromica IV- hydromicaceous clay, V- clay rocks with a composition of three components (chlorite, montmorillonite, hydromica).

According to the TM-TiO2 and FM-NKM, it can be interpreted that the clay rocks of the Lower Kazanian substage are hydromica in mineralogical composition. The maximum values of TM are typical for tideland, the minimum – for deep marine shelf [6].

For the classification of sandstones, F.J.Pettijohn with coordinates log(Na2O/K2O) – log(SiO2/Al2O3). A geochemical approach is used, depending on the prevalence of quartz, clay components and feldspar in sandstone. For immature sandstones characteristic log(SiO2/Al2O3) <1,3 и log(Na2O/K2O)>0 [7].


**Figure 4.** Diagram by Pettijohn for 1-2 beds (A-Ufimian) and 9-10 beds (B-Lower Kazanian) sandstones

The main sandstone samples of beds 1-2 and 9-10 are of lithic sandstones, in the composition of which mainly clay components enriched in $\text{Al}_2\text{O}_3$ and depleted alkalis. The samples №5, №8 - bed 1; №100, №101 - bed 10, contain micaceous and chlorite components. Ufimian sandstones multiple re-settle–accumulation occurred far from the provenance area, in them the most pronounced tendency to enrich quartz – mature sandstones. Lower Kazanian sandstones were exposed to significant effects of chemical weathering.

**Figure 5.** Diagram by A.G. Kossovskaya and M.I. Tuchkova with figurative points of sandstones of Middle Permian sediments

The upper corner in this diagram is either the composition of the rocks in the area of ablation, or the degree of maturity of the fragmentary material. The right corner of the classification triangle reflects the content of feldspars, and the left - the total melanocracy of rocks. The diagram separated four fields: I – quartz sandstone; II – oligomictic sandstone; III – polymictic sandstone; IV - volcaniclastic sandstone. Practically Ufimian sandstones are oligomictic; all Kamyshla sandstones are polymictic.

The most sandy rocks are formed from persilicic or average igneous rock or metamorphic formations in which is present. crystalline quartz.
According to the figurative expression of A.G. Kossovskaya and M.I. Tuchkova, sand-and-gravel clastic of abyssal basins and the greater of the mid-ocean ridges, formed by the rocks breaking of the mafics, gradually "melts" and gives rise to a wide range of authigenic minerals and paragenesis of such minerals.

The main triangular diagram is supplemented by two diagrams: AM - \([(\text{Al}_2\text{O}_3/\text{SiO}_2-\text{Fe}_2\text{O}_3+\text{FeO+MgO+TiO}_2+\text{MnO})] \) и AF - \([(\text{Al}_2\text{O}_3/\text{SiO}_2-(\text{CaO+Na}_2\text{O+K}_2\text{O})]\). The ratio \(\text{Al}_2\text{O}_3/\text{SiO}_2\) is there an indicator of the maturity of psammites, \(\text{CaO+Na}_2\text{O+K}_2\text{O}\) indicates the presence of feldspar, \(\text{Fe}_2\text{O}_3+\text{FeO+MgO+TiO}_2+\text{MnO}\) as well as in the main diagram, it reflects the degree of melanocracy. These diagrams show the composition fields of the main types of mafic [7,8].

Clay samples in the section in the basin of the r. Sheshma and r. Inesh on the triangular diagram \(\text{Al}_2\text{O}_3-\text{Na}_2\text{O-}\text{K}_2\text{O}\) as a result of increased chemical processes of hydrothermal alteration, controlled by warm and humid climatic conditions, lost in its composition alkali metals within closer to Al (fig.6). The upper corner Al in the diagram \(\text{Al}_2\text{O}_3-\text{Na}_2\text{O-}\text{K}_2\text{O}\) does not divide the clay sediments into chlorites, smectites or kaolinites. Samples in the upper parts of the triangular diagram indicate that the maximum loss of alkali metal elements occurred during the weathering process. During intense chemical weathering, elements such as K and other alkaline-earth elements may be identifiers indicating kaolinite as the only residual phase of intense weathering of rocks. In our case, all the samples directed towards the increased value of \(\text{Al}_2\text{O}_3\), which links the formation of hydromica with potassic feldspar (K-spar) [9].

5. Conclusions
For clays of the Upper Kazanian and Ufimian ages, generally characteristic the continental cold and moderately cold conditions of their formation. In their chemical composition, they carry only minor signs of weathering of the source rocks. These clays formed directly on rocks of provenance area or re-settle into freshwater bodies of water. The compositions of these clays are most similar in composition to igneous rocks, due to which they formed. While the Lower Kazanian clayey sediments in more cases formed in the marine and lagoon conditions. All the clayey sediments in the section in the basin of the r. Sheshma and r. Inesh formed under conditions of for the most part suppressed chemical weathering.
The sandstones in the basin of the r. Sheshma and r. Inesh with minor SiO2 content, on average, 63.77% (in the range of 55.7-76.04). The minimum content of quartz in sandstone in bed 9 (the beginning of the Kamyshta time). The maximum values are characteristic of Ufimian sandstones (beds 1,2). The concentration of TiO2 is on average 0.814% (in the range 0.386-1.29) — the maximum values in the sandstones of the Upper Kazanian age in bed 25 - minimum are concentrated in bed 10 in Kamyshta time, content of Al2O3 is about 8.05% (in the range of 5.76-10.23), Fe2O3 the average 6.31% (in the range of 3.68-17.9) and MgO is about 3.84% (in the range of 1.15-5.55). The minimum MgO values are characteristic of Ufimian sandstones, while the maximum values are mainly in the sandstones of the “Lingula” package at the beginning of the formation. Changes in the basic elements of geochemistry in the sandstones in the basin of the r. Sheshma and r. Inesh are presented in a variation diagram of a linear dependance SiO2 with TiO2, Al2O3, Fe2O3, MnO, CaO, MgO, Na2O, K2O [1,4,7].

The negative correlation of SiO2 with other basic elements is associated with a most with silicon dioxide being engrossed in quartz. In these samples, the concentration of TiO2 increases with Al2O3, which indicates that TiO2 is most likely, associated with phyllosilicates, particularly illites. Such compounds can form only in the presence of water [10].

Geochemical data, as well as lithochemical, allow in many cases a more accurate reconstruction of the facial and tectonic features of sediment accumulation. According to geochemical data, currently information can be obtained on the facies conditions of environment (depth area of sedimentation, mineralization, redox features of the bottom water, etc.)

References
[1] Nurgalieva N G et al 2016 The Lower Kazanian rocks as shallow marine facies (South-Eastern Tatarstan) on geochemistry (ARPN JEAS, vol 11 23) pp 13462-13471
[2] Ignatiev V I 1976 The formation of the Volga-Urals Anteclise in the Permian Period (Kazan: Kazan University Press) p 256
[3] Kotlyr G V et al 1984 Osnovnye cherty stratigrafi permskoy sistemy SSSR (Leningrad: The main features of the stratigraphy of the Permian system of the USSR) p 280
[4] Nurgalieva N G et al 2015 Type and reference sections of the Middle and Upper Permian of the Volga and Kama river regions Karkali section. Ufimian/Kazanian boundary and the Lower Kazanian in shallow marine facies (Kazan: Kazan University Press) pp 176-192.
[5] Fakhrutdinov E I et al 2015 The Lower Kazanian substage in the key section: Lithologies and Paleoenvironments based on the ESR data (Uchenye Zapiski Kazanskogo Universiteta. Seriya Estestvennye Nauki vol 157 3) pp 87-101
[6] Fakhrutdinov E I et al 2018 Features of the particle size distribution of the Ufimian-Lower Kazanian sediments of the section of Karkali (Academic science - problems and achievements XVII.: Proceedings of the Conference. North Charleston, USA) pp 5-9
[7] Yudovich Ya E et al 2000 Basics of lithochemistry (Saint Petersbourg.: Nauka) p 479
[8] Pettijohn F J et al 1972 Sand and Sandstone (Heidelberg: Springer)
[9] Kay Scheffler 2004 Reconstruction of sedimentary environment and climate conditions by multi-geochemical investigations of Late Palaeozoic glacial to postglacial sedimentary sequences from SW-Gondwana

[10] Dabard M P 1990 Lower Brioverian formations (Upper Proterozoic) of the Armorican Massif: Geodynamic evolution of source areas revealed by sandstone petrography and geochemistry (France: Sedimentary Geology vol 69 1-2) pp 45-58