Hydrogeochemistry of the authigenic mineral-forming processes (a case study of Oxfordian deposits in the Ob-Irtysh interfluve)

D. A. Novikov¹ ² a), L.G.Vakulenko¹ ², P.A.Yan¹ ², F.F. Dultsev¹, A.V. Chernykh¹

¹Trofimuk Institute of Petroleum Geology and Geophysics of Siberian Branch of Russian Academy of Sciences, Koptuga ave. 3, Novosibirsk, 630090, Russia
²Novosibirsk State University, Department of Geology and Geophysics, Pirogova str. 1, Novosibirsk, 630090 Russia

a)Corresponding author: NovikovDA@ipgg.sbras.ru

Abstract: Results of the pioneering numerical physicochemical modeling of interactions in the water – rock system on the example of Oxfordian deposits in southern regions of the Ob-Irtysh interfluve (southeastern regions of Western Siberia) are presented. It has been established that, despite the groundwaters having low salinity (up to 46 g/dm³) of and their persistent interactions with rocks (during tens, or probably hundreds of millions of years), they practically have no equilibrium with primary (endogenous) minerals: albite, anortite, microcline. At the same time, groundwater is in equilibrium with micaceous minerals, Ca-, Na- and Mg-montmorillonites, kaolinite, Mg-chlorite. There is always a carbonate barrier in the way of groundwater attaining an equilibrium with primary aluminosilicate minerals. As a result of the detailed petrographic studies, the genetic series of authigenic minerals of the diagenetic and catagenetic phases were established in the studied silty-sandy rocks. Relict diagenetic minerals are represented by glauconite, pyrite, siderite, calcite of the first generation of precipitation, kaolinite, anatase and leucoxene. Catagenetic minerals are considerably dominated by calcite of the second and third generations of precipitation, quartz, kaolinite, whereas siderite, chlorite, albite, dolomite are developed in minor amounts. The results of petrographic studies have corroborated the thermodynamic calculations.

Key words: hydrogeochemistry, water-rock, authigenic minerals, horizon Yu₁, Verkh-Tarskoe oilfield, Western Siberia

1 Introduction

Identification of the nature and mechanisms of the diagenetic and catagenetic transformations of the submerging sediments is one of the biggest issues in the study of sedimentary basins, which has long been addressed to by purely lithological methods. However, the physicochemical processes involved in such transformations have thus been poorly understood, which is due to the composition of groundwater are largely ignored. The evolution of chemical composition of groundwaters is set in motion, once they enter the sedimentary basin and is closely connected with the enclosing rocks and dispersed organic matter (DOM). Each of the sedimentary rocks represent in themselves the totality of paragenetic association of mineral and (or) organic components and liquid-fluid phase. The "water – aluminosilicate minerals"
system is assigned to the most complex heterogeneous systems with interphase interactions. The interactions between aluminosilicates and water results in the formation of secondary products with the solubility lower than that of the initial products. This is critical, since it determines persistent unsaturation of water with respect to primary minerals, which can therefore be subjected to dissolution processes during all the time of their interaction with groundwater [1].

2 Results and discussion

Hydrogeological signatures. It is not by chance that this paper addresses this object of study, inasmuch as Oxfordian regional reservoir (Upper Jurassic aquifer complex) has been the best studied by geological and geophysical methods within Jurassic deposits and represents a major exploration target in southern parts of the Ob-Irtysk interfluve (Verkh-Tarsko, Igl’sko-Talovoe and other fields). Groundwaters in the Upper Jurassic aquifer complex described as brackish to weak brines with a total mineralization (TDS) value of 1.6 to 56.2 g/dm³ (hydrogeochemical background is 23-26 g/dm³) and are Cl-Na, Cl-HCO₃ Na and to a lesser extent Cl Na-Ca и Cl-HCO₃ Na-Ca in composition (according to S.A. Shchukarev’s classification). The pattern of TDS variations of groundwater in the area is mosaic, showing a decreasing trend in the southeastern direction. There is an explicable increase in major salt-forming components with an increase in groundwater salinity [2-5].

During the field work conducted at the Verkh-Tarsko and East-Tarsko oil fields (November 2018), it was established that the studied waters belong to sedimentation genetic type [6-12] and are characterized by Cl-Na composition with the TDS value varying from 28 to 46 g/dm³, averaging 35 g/dm³. Their pH value varies from 7.4 to 7.9 (average value: 7.6). The concentrations of Cl and Na (major macrocomponents) are from 14 to 23 g/dm³ and from 8.3 to 17 g/dm³, respectively. While minor elements are represented by Ca²⁺ (0.5 – 0.9 g/dm³), Mg²⁺ (0.1– 0.3 g/dm³), and HCO₃⁻ (0.3 – 0.7 g/dm³). The concentration SO₄²⁻ is almost zero in these waters, since they were subjected to desulfurization at early diagenetic (“silt”) stage. The levels of strontium (up to 1328 mg/dm³), barium (up to 358 mg/dm³), silicon (up to 56.0 mg/dm³), lithium (up to 7.1 mg/dm³) and manganese (up to 3.2 mg/dm³) are elevated in the micro-component composition of the studied waters. As total mineralization of the solution increases, heavy metals, besides silica, strontium, barium, trend to accumulate in higher concentrations (mg/dm³) as follows: copper (up to 0.06), zinc (up to 0.37), cadmium (up to 0.04), cobalt (up to 0.07), nickel (up to 0.01), molybdenum (up to 0.03), lead (up to 0.02), tin (up to 0.02). Waters in well № 507 are characterized by higher concentrations of chromium (up to 0.1 mg/dm³), while the background values do not exceed 0.01 mg/dm³. Among rare earth elements (REE), the most abundant appeared to be (in μg/dm³): lanthanum (up to 20.8), europium (up to 7.9), gadolinium (up to 1.8) and dysprosium (up to 0.57).

This paper is devoted to the study of chemical equilibrium of groundwater with minerals of the host rocks with the main focus on the Verkh-Tarsko oilfield. It has been found that, despite the low salinity of groundwaters (up to 46 g/dm³) and their long-term interaction with rocks (tens, and possibly hundreds of millions of years), the equilibrium between groundwaters and primary (endogenous) minerals (albite, anortite, microcline, etc.) is practically absent. At the same time, groundwaters are in equilibrium with micaceous minerals, Ca-, Na - and Mg-montmorillonite, kaolinite, Mg-chlorite. There is always a carbonate barrier that provides additional challenges to attaining an equilibrium of groundwater with primary aluminosilicate minerals. In our plots of the chemical composition of groundwater we used diagrams from the works of H. Helgeson, M. Ben Baccar, B. Fritz and others [13-16].

Authigenic mineral formation. The studied rocks of the Verkh-Tarsko field (2486-2902 m depth interval) represent a wider range of particle size distribution species: from coarse to medium-grained sandstone to coarse-grained siltstone. The clastic part is polymictic in composition and is largely dominated by quartz. The detailed microscopical examination of rocks revealed aggregates of
authigenic minerals formed at different stages of lithogenesis. These are commonly involved in the composition of cement. The established minerals are: diagenetic glauconite, pyrite, calcite of the first generation of precipitation, siderite, anatase, leucoxene; diagenetic-catagenetic the second generation calcite, chlorite, kaolinite; catagenetic siderite, quartz, feldspar, kaolinite, calcite, third generation dolomite. The bulk volume of authigenic mineral formation is associated with carbonate minerals, of which calcite is the most abundant (from first percentage points to 45-50%, locally up to 60%) and is documented in almost all the sections. The first of the established three generations of calcite precipitation involve thin microcrystalline calcite which is a relic of the sedimentation-early diagenetic micrite occurring rarely in clot and spots (Fig. 1 a). The second generation of calcite precipitation is represented by individual crystals and calcite aggregates of finely, fine-, rarely medium to fine-crystalline structure, forming the pore-filling, at times basal cement (Fig. 1 b). The third generation of calcite precipitation is described as poikilitic, fine to medium, sometimes medium to coarse and coarsely-crystalline (Fig. 1 c). It corrodes the fragments (including quartz regeneration rims), fully or partially substituting them, and forming thereby either pore-filling-basal or basal cement and is most remarkably manifest in the studied rocks. Siderite forms microcrystalline and pelitomorphic clot and spots, and increasingly concentrates in areas of plant detritus accumulation. In addition, during catagenesis pelitomorphic siderite develops on biotite and some lithoclasts (fragments of shales, silty-clay rocks, effusives).

Figure 1. Calcite of different generations in the sandstone cement: a: micro-fine-crystalline calcite (Ct) of the first generation, authigenic pyrite (Py); b: fine-crystalline calcite of the second generation; c: poikilitic coarse-crystalline calcite of the third generation. d: Dolomite (Di), finely-fine-crystalline, overprinting poikilitic calcite.
Dolomite is observed as single thin-crystalline (up to 0.05 mm), more rarely fine-crystalline (up to 0.1 mm) rhombohedrons and their aggregates, overprinting the fragments of feldspars, and develops in all types of cement, including poikilitic calcite (Fig. 1 d). Dolomite thus represents a mineral involved in the latest catagenetic processes. Its levels are usually minor: from a fraction % to 1-2, rarely up to 5-8%.

Kaolinite is the most widespread among authigenic aluminosilicate minerals. The forms of its precipitation, crystallite size, the degree of structural perfection differ significantly, which can probably be explained by the presence of several generations which formed during both diagenesis and catagenesis. The earliest generation of thin platelet (to 0.01 mm) kaolinite was observed in the areas of developed significantly hydromicaceous (kaolinite-hydromicaceous) material (Fig. 2 a). More frequently manifested interstitial kaolinite appears as agglomerates of fine - to coarse - platelet structure, sometimes vermiculite-like, spherolitic, or sheaflike in shape, whose formation was probably influenced by pore solutions (Fig. 1 2 b, c). Replacement of feldspar and muscovite platelets with kaolinite is observed mostly locally. Jurassic sandstones of Western Siberia occasionally yield authigenic chlorite replacing biotite, as well as albite, and forming regeneration rims around fragments of K- feldspars (Fig. 2 d).

Equilibrium in the water – rock system. Analysis of the thermodynamic diagrams with plotted
points of activity of groundwater constituents provided some interesting insights. At reservoir temperatures varying between 80 and 100°C, all the studied waters are supersaturated with respect to calcite and dolomite (Fig. 3 a, b), and are capable of precipitating them as a secondary mineral phase, which is clearly seen from the petrographic studies (Fig. 1). Given that the solubility of calcite tends to decrease with increasing temperature, the highest degree of water saturation with this mineral was observed in the most submerged horizons, which is exactly the case with dolomite (Fig. 3 b).

Figure 3. Diagrams showing the degree of water saturation with calcite (a) dolomite(b); and mineral stability in the systems Si-Al-Na (c); and Si-Al-Ca (d) – at 100 °C, with the superimposed data on the chemical composition of groundwater of Upper Jurassic deposits in southern regions of the Ob-Irtysh interfluve.

Waters from: 1 – Verkh-Tarskoe oilfield (the 2018 expedition works), 2 – central parts of the study area, 3 – southern and southeastern parts of the study area.
The water – aluminosilicates equilibrium system is multicomponent, whose saturation by individual elements can be understood only in its integrity. For all its complexity, incongruent dissolution stems primarily from the phenomena of hydrolysis. Thus, in the $\text{SiO}_2\text{Al}_2\text{O}_3\text{Na}_2\text{O}\text{CO}_2\text{H}_2\text{O}$ system (Fig. 3 c) the scatter of points of groundwater composition is fairly wide. The points are evenly distributed in the stability fields of paragonite, Na-montmorillonite and albite. The most likely directions of sodium aluminosilicates transformation will therefore involve the formation of kaolinite, montmorillonite and mica. In the $\text{SiO}_2\text{Al}_2\text{O}_3\text{CaO}\text{CO}_2\text{H}_2\text{O}$ system (Fig. 3 d), all the studied waters are located in the stability fields of clay minerals. The equilibrium is attained between $/g587/g602$-montmorillonite and kaolinite. Note that dissolution of primary aluminosilicates (anortite, in this case) is accompanied by precipitation of primary clay and micaceous minerals. In the $\text{SiO}_2\text{Al}_2\text{O}_3\text{K}_2\text{O}\text{CO}_2\text{H}_2\text{O}$ system, most points are located in the stability field of illite and microcline. Concentrations of silicon compounds in stratal waters exert a formative influence on the result of hydrolysis of silicates: $\text{H}_4\text{SiO}_4$ in lower concentrations favors the formation of illite, while higher concentrations – mica and microcline. Analysis of the equilibrium of stratal waters with magnesium minerals allowed plotting a dense, almost linear arrangement of points slanting towards the formation of Mg-montmorillonite and Mg-chlorite.

Several points are plotted in the stability fields of illite and albite. The example of the $\text{HCl-H}_2\text{O-}\text{Al}_2\text{O}_3\text{CO}_2\text{MgO-Na}_2\text{O-SiO}_2$ system thus shows that most points are plotted in the stability fields of Mg-chlorite and Mg-montmorillonite. Localization of individual points in the stability fields of low-temperature albite indicates that there is possibility of the secondary albitionization process, as the water – rock system evolution progresses further. There is a generally growing trend in the degree of water saturation with respect to relatively low-temperature albite, in parallel with increasing pH value and silica concentrations in the solution. As in the previous case, most points of the $\text{HCl-H}_2\text{O-}\text{Al}_2\text{O}_3\text{CO}_2\text{MgO-K}_2\text{O-SiO}_2$ system are located in the stability fields of Mg-chlorite and one point in the illite stability field.

The equilibrium compositions were established for waters that serve as the source for the formation of equilibrium mineral phases at definite pH of and silica concentrations. However, more detailed studies will be required to cover this issue at the level of our previous research conducted for the northern and arctic regions of Western Siberia [17-21].

The thermodynamic analysis generally showed that within Upper Jurassic deposits in southern regions of the Ob-Irtysh interfluve, the relationships within the water-rock system are fairly complex and exhibit equilibrium-disequilibrium character. Groundwaters are ubiquitously saturated with carbonate minerals. Alternatively, waters unsaturated with respect to primary aluminosilicate minerals provoke their continuous dissolution. The $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^{+}$, $\text{K}^{+}$, $\text{Al}_2\text{O}_3$, $\text{H}_4\text{SiO}_4$ ions that enter the solution become bound by secondary (authigenic) minerals, which appear stable at this stage of the system development and in equilibrium with groundwaters, limiting thereby the growth of cations in the solution. The results of petrographic studies have confirmed the modeling results.

Acknowledgments
The research financially supported by the Russian Foundation for Basic Research and the Government of Novosibirsk region within the framework of Scientific Projects No.18-45-540004 and No.19-45-540006.

References
[1] Shvartsev S L 1991 Geol. and Geoph. 12 16-50.
[2] Novikov D A, Ryzhkova S V, Dultsev F F, Chernykh A V, Ses K V, Efimtsev N A, Shokhin, A E 2018 Bull. of the Tomsk Pol. Un., Geo Ass. Eng. 329(12) 39-54 DOI: 10.18799/24131830/2018/12/19
[3] Novikov D A, Shvartsev S L 2009 Rus. Geol. and Geoph. 50(10) 873-83 DOI: 10.1016/j.rgg.2009.09.005
[4] Dultsev F F, Novikov D A 2017 Bull. of the Tomsk Pol. Un., Geo Ass. Eng. 328(11) 6-15
[5] Dultsev F F 2019 *Journal of Physics: Conference Series* **1172**(1) 012081 DOI: 10.1088/1742-6596/1172/1/012081

[6] Novikov D A 2018 *IOP Conf. Ser.: Earth and Env. Sc.* **193**(1) 012049 DOI: 10.1088/1755-1315/193/1/012049

[7] Shvartsev S L, Novikov D A 2004 *Geol. i Geof.* **45**(8) 1008-20

[8] Novikov D A, Lepokurov A V 2005 *Geol. Neft. i Gaz.* (Oil and gas Geol.) **5** 24-33

[9] Novikov D A, Sukhorukova A F 2015 *Arab. J. of Geosc.* **8**(10) 8703-19 DOI: 10.1007/s12517-015-1832-5

[10] Novikov D A 2017 *Petr. Expl. and Dev.* **44**(5) 780-8 DOI: 10.1016/S1876-3804(17)30088-5

[11] Koh A A, Novikov D A 2014 *Wat. Res.* **41**(4) 396-405 DOI: 10.1134/S0007807814040083

[12] Novikov D A 2017 *Geod. and Tect.* **8**(4) 881-901 DOI: 10.5800/GT-2017-8-4-0322

[13] Aagaard P, Helgeson H C 1982 *Am. J. Sci.* **282** 237-285

[14] Ben Bacar M, Fritz B 1993 *J. of sedim. Pet.* **63**(6) 1100-1109.

[15] Garrels R M 1984 *Clays Clay Min.* **32**(3) 161-166.

[16] Helgeson H C 1969 *Amer. J. Sci.* **267**(7) 729-804.

[17] Novikov D A 2016 *Oil and Gas Studies* **6** 19-25. DOI: 10.31660/0445-0108-2016-6-19-25

[18] Novikov D A 2018 *The Geo. Evol. of the Water-Rock Inter.* 140-144. DOI: 10.31554/978-5-7925-0536-0-2018-140-144

[19] Novikov D A, Vakulenko L G, Yan P A 2019 *Rus. Geol. and Geoph.* **60**(6) 662–74 DOI:10.15372/RGG2019041

[20] Novikov D A 2019 *E3S Web of Conferences* **98** 01037 DOI:10.1051/e3sconf/20199801037

[21] Novikov D A 2019 *Lith. and Min. Res.* **54**(3) 236-47. DOI: 10.1134/S0024490219030076