Role of water-rock interactions in the formation of the composition of radon waters of the Zaeltsovsky field (the southern part of West Siberia)

D.A. Novikov¹,², a), F.F. Dultsev¹ and A.V. Chernykh¹

¹) Trofimuk Institute of Petroleum Geology and Geophysics of Siberian Branch of Russian Academy of Sciences, Koptugaave. 3, Novosibirsk, 630090, Russia
²) Novosibirsk State University, Department of Geology and Geophysics, Pirogova str. 1, Novosibirsk, 630090 Russia
a) Corresponding author: NovikovDA@ipgg.sbras.ru

Abstract. Results of thermodynamic calculations of the interactions of radon waters from the Zaeltsovsky field with the minerals of host rocks are presented for the first time. It was established that waters under study are supersaturated with respect to calcite and siderite, and to a smaller extent with respect to magnesite and dolomite. No saturation of radon waters with respect to primary aluminosilicate minerals (albite, anoritite, microcline, ferrosilite) is observed. The points are located in the fields of stability of clayey minerals (kaolinite, Ca- and Mg-montmorillonite, Fe-sepiolite), gibbsite and leptochlorite. In the evolution of the water-rock system, they correspond to the siallit type of interaction with rocks.

Key words: water-rock system, radon waters, equilibrium, hydrogeochemistry, Novosibirsk, Western Siberia.

1 Introduction

Radon waters in the world have been under investigation for many decades. The studies are aimed at the revelation of the processes involved in the formation of their chemical composition and the role of water-rock interactions. Novosibirsk and its surroundings form the only large urban agglomeration in Russia where 12 regions of radon waters are proved; the concentrations of $^{222}$Rn vary from 2 to 25220 Bq/L.

Prospecting work for radon waters was carried out during the years 1960-1980 by hydrogeologists of the Novosibirskgeologiya PGO: E.K. Verigo, N.K. Akhmenzhanova, B.L. Vrabiy, E.G. Kuksova, G.T. Kostenko, N.A. Plaksina, P.L. Makidon, L.N. Koss, V.A. Zhukovsky, I.P. Karpinsky and many others[1, 2]. The Zaeltsovsky field is situated in the central part of Novosibirsk (Figure 1) and is confined to water-abundant regions of the north-western contact zone of the large Novosibirsk massif of Upper Paleozoic granitoids which are here breaking through the older rocks of the Inskaya series related to Upper Devonian – Lower Carboniferous age. The Paleozoic formations are overlaid by loose quaternary sediments up to 50 m thick. They emerge onto the day surface in some sites in the floodland of the Ob [3, 4]. These hydrogeological conditions characterize the near edge zone of the entire West Siberian artesian basin [5-22].
Figure 1. Location of the region under investigation.
Legends: 1 – the Zaeltsovsky field, 2 – Novosibirsk city boundary, 3 – railroads; 4 – roads, 5 – city name.

2 Methods and materials
The present work is based on the results of exploration work over the Zaeltsovsky field of radon waters, represented by 97 water samples and more than 1000 samples of rocks. The methods and approaches to the solution of the problems formulated for the present work were determined by the new theoretical provisions developed in the Siberian hydrogeochemical school by Professor S.L. Shvartsev, which may be considered as pioneering in the depth of understanding the mechanisms of water-rock evolution. Within the present investigation, an attempt is made to approach the revelation of these mechanisms through the idea of a hydrogenous-mineral complex [23].

3 Results and discussion
It should be noted that the radon waters of Novosibirsk are investigated to a low extent, and any generalization of the available hydrogeochemical data is absent. Radon waters of the Zaeltsovsky-Mochishche zone are neutral and weakly alkaline (pH from 6.9 to 7.8), fresh with total mineralization varying from 322 to 895 mg/L. With respect to to radon content (according to the classification proposed by N.I. Tolstikhin), these waters relate to very weak to moderate with $^{222}$Rn content from 11 to 801 Bq/L. The concentrations of $^{238}$U and $^{226}$Ra do not exceed 0.098 mg/L and $1.9\cdot10^{-9}$ mg/L, respectively. Radon waters exhibit insignificant differences in chemical composition and the concentrations of main macro- and microelements. With respect to the chemical type (according to the classification proposed by S.A. Shchukarev), dominating waters are mainly calcium hydrocarbonate and calcium-sodium hydrocarbonate. The formulas of the chemical composition of calcium hydrocarbonate, calcium-sodium, calcium-magnesium-sodium and magnesium-calcium waters are presented below (in M.G. Kurlov’s formula, the concentration of $^{222}$Rn is given in $\text{nCu/L}$):

- $\text{Rn11.8M0.65} \quad \frac{\text{HCO}_3^{-90\text{Cl}^-55\text{SO}_4^{2-7}}}{{\text{Ca}^{2+68}}{{\text{(Na}^{+}+\text{K})^{19}}\text{Mg}^{2+13}}} \quad \text{pH}9.6T6.7 - 7.3 \quad (\text{well No. 36})$
- $\text{Rn18.5M0.79} \quad \frac{\text{HCO}_3^{-78\text{Cl}^-18\text{SO}_4^{2-4}}}{{\text{Ca}^{2+55}}{{\text{(Na}^{+}+\text{K})^{33}}\text{Mg}^{2+2}}} \quad \text{pH}7.2T6.9 - 7.5 \quad (\text{well No. 29})$
- $\text{Rn16.5M0.32} \quad \frac{\text{HCO}_3^{-79\text{Cl}^-9\text{SO}_4^{2-2}}}{{\text{Ca}^{2+41}}{{\text{(Na}^{+}+\text{K})^{30}}\text{Mg}^{2+30}}} \quad \text{pH}7.6T7.2 - 8.3 \quad (\text{well No. 20})$
- $\text{Rn7.1M0.80} \quad \frac{\text{HCO}_3^{-77\text{SO}_4^{2-5}}}{{\text{Mg}^{2+62}}{{\text{Ca}^{2+33}}}{{(\text{Na}^{+}+\text{K})^{5}}}} \quad \text{pH}7.2T6.9 - 7.0 \quad (\text{well No. 62})$

In the studied waters, the closest connection with total mineralization is observed for the sum of sodium and potassium, calcium, hydrocarbonate ion, sulfate ion and chloride ion, with the concentrations varying within the ranges 7-107, 28-160, 207-488, 3-126 and 4-100 mg/L. It was revealed that the concentration of hydrocarbonate ion starts to decrease for the total mineralization of
radon waters about 750-800 mg/L. This is accompanied by a regular increase in the concentrations of sulfate and chloride ions, and the change of the chemical type of water. The revealed features of the accumulation of the main salt-forming components more clearly manifest themselves in different chemical types of radon waters. For example, in calcium hydrocarbonate waters, the concentration of sodium is 7-56, calcium 79-159 mg/L, while in calcium-sodium waters these concentrations vary within the ranges 27-107 and 43-111 mg/L, respectively.

A comparative analysis of the geochemical features of radon waters of the Zaeltsovsky field and a number of fields of the Altay, Tuva, Italy and Tunisia [24-28] showed that each field has its own unique spectrum of the distribution of macro- and microcomponents. In addition to the chemical composition, radon waters vary in total mineralization from ultrafresh and fresh within the Zaeltsovsky-Mochishche zone in Novosibirsk, Belokurikhinskoe, Kamenskoe, Rakhmanovskoe fields in the Altay and Shiveligskoe in Tuva, to salty waters with total mineralization up to 19.9 g/L at the Ile de Jerba in Tunisia [28]. It was established that radon concentration is independent of the chemical nature of waters. To a substantially higher extent, radon concentration is controlled by water temperature, which is due to a decrease in gas solubility with an increase in temperature. The life-span of $^{222}\text{Rn}$ in the series of uranium and radium is 3.823 days, so radon migration at a distance longer than several ten meters from the emanation source is practically impossible, which also affects radon concentration in water. For this reason, $^{222}\text{Rn}$ is present in significant amounts both in ultrafresh, fresh waters, and in brackish, salt waters. So, radon concentration in water is not defined by the geochemical type of water and is connected first of all with the mineralogical composition (in the accessory and ore parts) of water-embedding rocks, the degree of rock disintegration and the presence of isotope decay products of the uranium-radium series (emanating collector).

Analysis of the thermodynamic diagrams with the plotted points of component activities depicting the composition of radon waters of the Zaeltsovsky field showed that almost all the studied water samples are supersaturated with respect to calcite and siderite, to a smaller extent with respect to magnesite and dolomite, and are able to precipitate them in the form of a secondary mineral phase. The equilibrium of radon waters with primary aluminosilicate minerals (albite, anortite, microcline, ferrosilite) is not achieved (Figure 2). In this situation, the points are located in the fields of stability of clayey minerals (kaolinite, Ca- and Mg-montmorillonite, Fe-sepiolite), gibbsite and leptomontmorillonite. In the evolution of the water-rock system, they correspond to the siallite type of interaction with the rocks (according to S.L. Shvartsev), which is understood as the united monosiallite (the formation of kaolinite and its analogs) and bisiallite (the formation of illite, montmorillonite and other three-layered minerals) types of weathering, which are associated with the aluminium-siliceous and siliceous-calcium (K, Mg, Na) water types [23].

For instance, in the system with calcium minerals (Figure 2.a) the points are equally located in the fields of stability of kaolinite and Ca-montmorillonite. It should be noted that the dissolution of primary aluminosilicates, in this case anortite, is accompanied by the precipitation of clayey minerals. In the system with magnesium minerals (Figure 2.b) all the studies water samples fit within the fields of stability of kaolinite and Mg-montmorillonite and at the boundary with gibbsite. In the system with sodium minerals, one can see (Figure 2.c) that the majority of points are located in the field of stability of kaolinite, and a minor part of point are within the field of stability of gibbsite. The decisive effect on the result of silicate hydrolysis is caused by the concentration of silicon compounds in water. Investigation of the equilibrium of waters with calcium-sodium minerals (at $\text{lg}[\text{H}_4\text{SiO}_4]=-3.5$) (Figure 2.d) demonstrated the close positions of points in the field of Ca-montmorillonite and an insignificant number of points in the field of kaolinite. In the system with iron-containing minerals (Figure 2.e), all the studied water samples are located in the fields of stability of Fe-sepiolite, at the boundary with gibbsite and kaolinite. Several points are at the boundary in the field of stability of leptomontmorillonite. The major controlling factors for the evolution of the water-rock system are pH of the medium and the concentrations of silica and aluminium in the solution.
Figure 2. The diagram of the equilibrium of calcium (a), magnesium (b), sodium (c), calcium-sodium (with $\lg[H_4SiO_4]= -3.5$) (d) and iron-containing (e) minerals at 25 °C with the data on the composition of radon waters of the Zaeltsovskoe field.

4 Conclusion

At the Zaeltsovsky field, fissure cold (6-10 °C) radon waters are developed in the water-bearing zones of Upper Devonian – Lower Carboniferous clay shale and hornstone, and Upper Paleozoic granites. With respect to the chemical composition, the waters are mainly calcium hydrocarbonate and calcium-sodium hydrocarbonate with total mineralization of 322-895 mg/L. With respect to $^{222}$Rn (11 – 801 Bq/L), the waters relate to weak and medium radon mineral waters. It was established that all the studied kinds of radon waters were supersaturated with respect to calcite and siderite, to a smaller extent with respect to magnesite and dolomite. Saturation of radon waters with respect to the primary aluminosilicate minerals (albite, anorthite, microcline, ferrosilite) is not observed. The points are located in the regions of stability of clayey minerals (kaolinite, Ca- and Mg-montmorillonite, Fe-sepiolite), gibbsite and leptochlorite. In the evolution of the water-rock system, they correspond to the siallite type of interaction with rocks (according to S.L. Shvartsev).
Acknowledgments
The research was carried out with the financial support from the Russian Foundation for Basic Research and the Government of the Novosibirsk Region within the framework of scientific project No. 19-45-540004.

References
[1] Verigo E K, Bykova V V and Gusev V K 1979 New data on geology and mineral resources of the West Siberia 14 47-51
[2] Gusev VK and Verigo EK 1984 Changes in the environment caused by the human activities pp 99-107
[3] Novikov D A, Sukhorukova A F and Korneeva T V 2018 Geod. and Tect. 9 1255-74
[4] Novikov D A and Korneeva T V 2019 J. Phys: Conf. Ser. 1172 012096
[5] Kruglikov N M 1964 Hydrogeology of the northwestern side of the West Siberian artesian basin (Leningrad: Nedra) p 166.
[6] Nudner VA 1970 Hydrogeology of the USSR. West Siberian Plain (Tyumen, Omsk, Novosibirsk and Tomsk Regions) (Moscow: Nedra) XVI p 368.
[7] Kruglikov N M, Nelyubin V V and Yakovlev O N 1985 Hydrogeology of the West Siberian oil and gas basin and features of the formation of hydrocarbon deposits (Leningrad: Nedra) p 279.
[8] Kartsev A A, Vagin S B and Matusевич V M 1986 Hydrogeology of oil and gas basins (Moscow: Nedra) p 224.
[9] Stavitskiy B P, Kurchikov A R, Kontorovich A E and Plavnik A G 2004 Geol. i geof. 45 826-32.
[10] Matusевич V M, Ryklov A V and Ushatinskii I N 2005 Geofluid systems and oil and gas problems of the West Siberian megabasin (Tyumen: TyumGNGU) p 225.
[11] Novikov D A 2018 Neft. Khoz. - Oil Ind. 4 16-21.
[12] Novikov D A 2018 IOP Conf. Ser.: Earth and Env. Sc. 193 012049.
[13] Novikov D A and Saraev M M 2017 Petr. Exp. and Dev. 44 737-44.
[14] Novikov D A 2017 Geod. and Tect. 8 881-901.
[15] Novikov D A 2017 Geod. and Tect. 8 881-901.
[16] Kokh A A and Novikov D A 2014 Wat. Res. 41 396-405.
[17] Novikov D A 2019 Lith. and Min. Res. 54 236-47.
[18] Novikov D A and Sukhorukova A F 2015 Arahl. J. Geos. 8 8703-19.
[19] Novikov D A and Shvartsev S L 2009 Russ. Geol. and Geoph. 50 873-83.
[20] Dultsev F F 2019 J. Phys: Conf. Ser. 1172 012081.
[21] Novikov D A 2019 E3S Web of Conf. 98 01037.
[22] Novikov D A, Vakulenko L G and Yan P A 2019 Russ. Geol. and Geoph. 60 662-674.
[23] Shvartsev S L 2007 Lithosphere 1 65-89
[24] Baryshnikov G Ya and Eliseev V A 2009 Bull. of the Alt. St. Un. 3 41-7
[25] Bulatov A A, Kopylova Yu G, Dzhabarova N K, Rychkova K M, Arakchaa K D, Khvaschevskaya A A, Guseva N V and Pashagin A V 2013 Resort base and natural health and recreation areas of Tuva and adjacent areas I 154-61
[26] Mineeva L A, Arakchaa KD and Kyzyl OM 2016 Bull. of the Irk. St. Un. Earth Sc. Ser. 17 115-34
[27] Allocca V et al 2018 J. of Geoch. Exp. 185 105-15
[28] Telahigue T, Agoufi B, Souid F and Kharroubi A 2018 J. of Env. Rad. 182 74-84