Microelements in Radon Waters of The Zaeltsovsky field (The Southern Part of West Siberia)

D A Novikov1,2,a), T V Korneeva1

1Federal State Budgetary Scientific Institution Trofimuk Institute of Petroleum Geology and Geophysics of Siberian Branch of Russian Academy of Sciences, 630090, Novosibirsk, Koptug ave. 3
2Novosibirsk State University, Geological and Geophysical Department, 630090 Pirogov str. 1, Novosibirsk, Russia
a)Corresponding author:NovikovDA@ipgg.sbras.ru

Abstract. The results of the studies of the mechanisms of microelements accumulation in the radon waters of the Zaeltsovsky field (the southern part of West Siberia) are presented for the first time. The key role of the water-rock system in these processes is shown. The radon waters of calcium hydrocarbonate and calcium-sodium hydrocarbonate composition with total mineralization ranging from 322 up to 895 mg/dm³ (222Rn = 11-801 Bq/dm³) are prevailing in the field. Metal species such as Ag⁺, Ba²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Sr²⁺, Fe²⁺ are represented by free ions, and Be²⁺, Fe³⁺, Zr⁴⁺, Ti⁴⁺ by hydroxide complexes. Calculations reveal that the waters are saturated with carbonate (modifications CaCO₃ and CaMg(CO₃)₂, MnCO₃, FeCO₃, PbCO₃), silicate ((Fe²⁺,Fe³⁺)₂Si₃O₁₀(OH)₂), hydroxide (FeOOH and MnOOH) and oxide minerals (modification SiO₂, TiO₂, Mn²⁺Mn³⁺O₄). Radon waters are unsaturated with some compounds of zircon, zinc, barium, molybdenum, iron, copper, strontium: ZrO₂,Zn(OH)₂, BaCO₃, CaMoO₄, FeMoO₄, CuO, CuMoO₄, Cu₃(NiO)₂(II)₃, Fe(OH)₂, Cu(OH)₂, SrSO₄, SrCo₃, 3Mg₂SiO₄, 2H₂O etc. In some samples, the observed saturation of water is relatively rare phosphate minerals (Ca₁₀(PO₄)₆(OH)₂, Fe₃(PO₄)₂·8H₂O, MnHPO₄), chlorargyrite (AgCl) and lead molybdate (PbMoO₄). The concentrations of some elements (namely Sr, Pb, Zn, Mo, Be) in the radon waters of the Zaeltsovsky field are at the level of their concentrations in rocks.

1. Introduction
Radon waters have been under investigation for many decades [1-11]. The studies of the mechanisms responsible for the formation of the chemical composition of water are carried out; in particular, attention is paid to the microelemental composition. Novosibirsk is the only large city in Russia accommodating 12 proven deposits (regions) of radon waters for medical use at its territory and in the nearest neighborhood.

Prospecting works aimed at the search for radon waters were carried out within the years 1960-1980 by the hydrogeologists of the PGO Novosibirskgeologiya E.K. Verigo, N.K. Akmetzhanova, 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. The Zaeltsovsky field is situated in the central part of Novosibirsk and is confined to the water-abundant regions of the north-western contact zone of the large Novosibirsk massif of upper Paleozoic granitoids which break through more ancient rocks of the Inya series of upper Devonian – lower Carboniferous age. The Paleozoic formations are overlaid by loose Quaternary sediments up to 50 m thick. They emerge at the day surface in some places in the high-water bed of the
Ob river. Similar hydrogeological conditions characterize the marginal areas of the West Siberian artesian basin [12-14].

The studies rely on the results of the analyses of 97 water samples and more than 1000 rock samples. Seven types (according to S.A. Shchukarev) of radon waters are developed at the Zaeltsovsky field; calcium hydrocarbonate and calcium-sodium hydrocarbonate waters with the total mineralization of 322 to 895 mg/dm³ are prevailing (Fig.1) [15]. The presence of radon in ground water is natural. Its content is provided by the occurrence of scattered radioactive minerals in granites and granodiorites. Radon $^{222}$Rn content within the water-bearing zones of upper Devonian – lower Carboniferous hornstone and upper Paleozoic granites is 11 to 801 Bq/dm³.

![Piper diagram of the Zaeltsovsky.](image)

Radon waters exhibit an interesting spectrum of microelement distribution (Fig. 2). One can see that the microcomponent composition of radon waters is characterized by increased content of Sr (up to 4.7 mg/dm³), Mn (up to 1.3 mg/dm³), and Ba (up to 0.2 mg/dm³). At the deposit, the concentration of silica in water varies within the range 7 to 36 mg/dm³. With an increase in total mineralization, in addition to Si, Sr, Mn and Ba other elements are accumulated in solution. Their concentrations are (µg/dm³): Cu (up to 13), Ag (up to 14), Mo (up to 31), Ni (up to 9.7), Zr (up to 52), Ti (up to 197), Pb (up to 78), Zn (up to
235), Co (up to 1.0), Li (up to 40) etc. Increased U content up to 98 µg/dm³ is characteristic of waters of the zone of upper Devonian – lower Carboniferous hornstone, while waters from the water-bearing zone of upper Paleozoic granites contain uranium at a level of 0.32-2.6 µg/dm³. Similar uranium concentration is also characteristic of the water from the Shivelig - 1 spring at the Shivelig field of radon water in the Republic of Tuva [16].

One of the major factors determining the chemical composition of water is the lithological conditions, namely the geological structure of the catchment, the chemical composition of rocks, and the relations between their types. A.I. Perelman proposed to evaluate the aqueous migration relying on the coefficient determined as a ratio of element content in the mineral residue of water to its content in rocks. This coefficient depicts the intensity of migration in water, determined by the properties of an element, and the degree of element concentrating or dissemination in water. The calculated coefficients of water migration formed a decreasing sequence:

\[ \text{Mg}^{1429} > \text{Sr}^{92.2} > \text{Ti}^{135.16} > \text{P}^{10.38} > \text{Ba}^{11.39} > \text{Zn}^{2.64} > \text{Cr}^{1.23} > \text{Zr}^{0.96} > \text{U}^{0.86} > \text{Pb}^{0.53} > \text{Li}^{0.2} > \text{Co}^{0.03} > \text{Mo}^{0.01} > \text{Be}^{0.00004} > \text{Ag}^{0.000005}. \]

The spectra of component distribution in the rocks and in water exhibit differentiation between the elements according to the coefficients of migration in water. The concentrations of some elements in the radon waters of the Zaeltsovsky field, namely Sr, Pb, Zn Mo, Be, are at the level of the concentrations in rocks (Fig.2) [16].

![Figure 2. The spectra of microelement distribution in rocks and waters of the Zaeltsovsky field of radon waters. The distribution of microelements in the rocks of water-bearing horizons is: 1 - a Q_{IV}, 2 - a_3 Q_{III}, 3 - Q_{II}, IV kr1, 4 - P_{3nm}, 5 - D_{33-C_1}, 6 - D_{2r-C_1} + γP_{2-3}, 7 - γP_{2-3}, 8 - average, 9 - the average value of microelement content in radon waters.](image)

For the first time, in the present work using the Visual Minteq, WATEQ4f and HG-32 software packages, we considered the scale of accumulation and the forms of microelement migration in radon waters, as well as the degree of the saturation of waters in the Zaeltsovsky field with various mineral phases.

Thus, the hydrogeochemical conditions of radon waters are responsible for the forms in which the microelements are present. The results of the thermodynamic modeling demonstrated that the forms of
cation migration in radon waters are free ions (>90%) and hydrocarbonate complexes (<10%). Alkaline (K⁺, Na⁺, Li⁺) and alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) are present in the studied water entries in the form of monovalent (Me⁺) and divalent (Me²⁺) cations, respectively. Water saturation with oxygen causes rapid oxidation of Fe²⁺ into Fe³⁺, so the compounds of iron (III) are more frequent in aqueous solutions because these compounds are thermodynamically more stable. Fe³⁺ is characterized by the ability to form stable complex compounds with some inorganic anions, especially with OH⁻. For instance, the following hydro-oxide forms were identified in the studies of the major forms of Fe³⁺ migration: Fe(OH)²⁺, Fe(OH)³⁺, Fe(OH)₄⁻, (FeOH)₂⁺; the relations between these forms depend on pH and Eh of water, and on the total concentration of iron. Iron as Fe²⁺ migrates in the ion form, with the subordinate significance (1-7%) of sulfate complexes FeSO₄(aq). A similar behavior is demonstrated by manganese, which migrates in the ion form Mn²⁺ (65-90%), and in the form of carbonate and sulfate complexes MnCO₃(aq) (up to 4-23%) and MnSO₄(aq) (1-5%).

The forms in which some microelements migrate will be considered below. Molybdenum migrates mainly in the form of a negatively charged oxide complex MoO₄²⁻ (59-67%), in smaller fractions as the complexes MgMoO₄(aq) (14-22%) and CaMoO₄(aq) (12-20%). Barium belongs to the elements of the small range of migration in water; it migrates mainly in the form of Ba²⁺ ion (>90%), complex hydrocarbonate ion BaHCO₃ and sulfate ion BaSO₄(aq). Migration of a substantial fraction of beryllium (the element of the 1st group of danger) proceeds in the complex with hydroxide ion Be(OH)₂(aq), as revealed in the water-accommodating rocks of the zones of upper Devonian – lower Carboniferous hornstone (D₃-C₁) and upper Paleozoic granites (γPz). The forms of silver occurrence are represented by free ions Ag⁺ (39-65%), neutral aqua complexes AgCl(aq) (0-55%) and negatively charged complex AgCl₂⁻ (0.8-4.2%). The major forms of lead and copper presence in radon waters are carbonate complexes PbCO₃ (79.8%) and CuCO₃ (80-91%). Zinc forms are represented mainly by free Zn²⁺ ions, to a smaller extent by carbonate complexes ZnCO₃(aq) and hydrocarbonate complexes ZnHCO₃. The forms of uranium occurrence are represented mainly by the uranyl-carbonate complexes of calcium Ca₂UO₂(CO₃)₃(aq) (61-75%) and CaUO₂(CO₃)₂⁻ (25-36%).

The studied radon waters are saturated or nearly equilibrium to the series of carbonates (calcite, dolomite, siderite, rhodochrosite, magnesite) and silicate minerals (greenalite, sepiolite), the minerals containing heavy metals in the lattice (manganite, barite, rhodochrosite, rutyl, tenorite) and iron hydroxides (ferrihydrite, goethite and other amorphous compounds), that is, these minerals precipitate from waters and cannot be the source of iron in waters. Under these conditions, active dissolution is exhibited by silicate minerals, chrysotile Mg₃Si₂O₅(OH)₄, sepiolite Mg₄Si₆O₁₅(OH)₂·6H₂O, magnesite MgCO₃, strontianite SrCO₃, which are unstable under these conditions and act as the source of not only Mg but also Cu, Sr, Si, and other elements.

The features of the saturation of radon waters with respect to the minerals depending on their chemical composition were established. For example, HCO₃⁻-Ca waters are saturated with respect to calcite CaCO₃, ferrihydrite FeOOH, different modifications of SiO₂, greenalite (Fe²⁺, Fe³⁺)₂·3SiO₂(OH)₄, manganite MnOOH, rutile TiO₂, siderite FeCO₃. The equilibrium with aragonite CaCO₃, chaledony SiO₂, cristobalite, dolomite, rhodochrosite and faterite is observed. Waters are unsaturated with respect to ZrO₂, Zn(OH)₂, witherite BaCO₃, tenorite CuO, sepiolite Mg₄Si₆O₁₅(OH)₂·6H₂O, povellite CaMoO₄ and its modifications, pyrochroite Mn²⁺(OH)₂, nesquehonite MgCO₃·3H₂O, Na-jarosite NaFe₃(SO₄)₂(OH)₆, magnesite MgCO₃, ferrous molybdate FeMoO₄ and ferrous hydroxide Fe(OH)₂, epsomite MgSO₄·7H₂O, celestine SrSO₄, brusite Mg(OH)₂, hypsum CaSO₄·2H₂O and anhydrite CaSO₄. Waters of the HCO₃⁻-Ca- Νa composite are in equilibrium with respect to aragonite, barite BaSO₄, calcite CaCO₃, chlorargyrite AgCl, cerussite PbCO₃ and hydrocerrusite 2PbCO₃·Pb(OH)₂, chaledony, cristobalite, dolomite, siderite, faterite CaCO₃, ZnCO₃, and their deposition is probable in the case of the geochemical parameters of the medium (pH, Eh) change. The waters are saturated with ferrihydrite, greenalite, manganite, gausmannite, modifications of quartz, hydroxyapatite Ca₁₀(PO₄)₆(OH)₂, rhodochrosite MnCO₃ and rutile TiO₂. The features of the microelement composition of separate samples of radon waters cause the formation and possible precipitation of a suspension containing such mineral phases as vivianite Fe₃(PO₄)₂·8H₂O, and
manganese hydrophosphate MnHPO$_4$. However, radon waters are sharply unsaturated with respect to hydrozincite Zn$_5$(CO$_3$)$_2$(OH)$_6$.

Radon waters of the Zaeltsovskoe field are fissure, cold, with the 6-10 °C, occur at a depth of 50-200 m. The chemical composition of the waters (according to S.A. Shchukarev) is mainly calcium hydrocarbonate and calcium-sodium hydrocarbonate, with total mineralization 322-895 mg/dm$^3$. All the wells drilled through granites and near-contact hornstone were tested for $^{222}$Rn content in water. Its concentrations vary within a broad range from 11 to 801 Bq/dm$^3$, this means that these waters belong to low-radon and medium-radon with respect to $^{222}$Rn, mineral (according to the classification proposed by N.I. Tolstikhin). Radon concentration in water from the wells drilled through hornstone is 37-241 Bq/dm$^3$. The content of $^{238}$U and $^{226}$Ra does not exceed 0.098 mg/dm$^3$ and 1.9·10$^{-9}$ mg/dm$^3$, respectively.

The concentrations of some elements in the radon waters of the Zaeltsovsky field, namely Sr, Pb, Zn, Mo, Be are at the level of concentrations in rocks. The results of thermodynamic modeling showed that the forms of migration of the basic cations (K$^+$, Na$^+$, Li$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) in radon waters are free ions (>90%) and hydrocarbonate complexes (<10%). The forms of migration of Fe(III) are represented by Fe(OH)$_2^{+}$, (FeOH)$_2^{+}$, Fe(OH)$_3^{+}$, (Fe(OH)$_4$)$^-$, while Fe$^{2+}$ migrates in the ion form, with the subordinate significance (1-7%) of sulfate complexes FeSO$_4$(aq). Manganese exhibits a similar behavior migrating in the ion form Mn$^{2+}$ (65-90%), as well as in the form of carbonate and sulfate complexes MnCO$_3$(aq) (up to 4-23%) and MnSO$_4$(aq) (1-5%). The major forms of lead and copper existence in radon waters are carbonate complexes PbCO$_3$ (79,8%) and CuCO$_3$ (80-91%). Zinc forms are represented mainly by free ions Zn$^{2+}$, to a lower extent by carbonate ZnCO$_3$(aq) and hydrocarbonate complexes ZnHCO$_3$. The forms of uranium presence are represented mainly by uranyl-carbonate complexes of calcium Ca$_2$UO$_2$(CO$_3$)$_3$(aq) (61-75%) and CaUO$_2$(CO$_3$)$_3^{2-}$ (25-36%).

Acknowledgments
The studies were carried out with the financial support from the Russian Foundation for Basic Research and the Government of the Novosibirsk Region under the research project No. 17-45-540086-p a.

References
[1] Alonso H, Cruz-Fuentes T, Rubiano J G, González-Guerra J, Cabrera M C, Arnedo M A, Tejera A, Rodriguez-Gonzalez A, Pérez-Torrado F J, Martel P 2015 Radon in Groundwater of the Northeastern Gran Canaria Aquifer Water 7 pp 2575-2590
[2] Beitollahi M, Ghiassi-Nejad M, Esmaeli A, Dunker R 2007 Radiological studies in the hot spring region of Mahallat, central Iran Radiat Prot Dosim 123(4) pp 505-508
[3] Bertolo, Bigliotto C 2004 Radon concentration in waters of geothermal Euganean basin-Veneto, Italy Radiat Prot Dosim 111(4) pp 355-358
[4] Chaudhuri H, Nisith K D, Bhandari R K, Sen P, Sinh B 2010 Radon activity measurements around Bakreswar thermal springs Radiat Meas 45 pp 143-146
[5] Duenas C, Fernandez M C, Enraquez C, Carretero J, Liger E 1998 Natural radioactivity levels in Andalusian spas Water Res 32(8) pp 2271-2278
[6] Eross A, Madl-Szonyi J, Surbeck H, Horvath A, Goldscheider N, Csoma A E 2012 Radionuclides as natural tracers for the characterization of fluids in regional discharge areas, Buda Thermal Karst, Hungary J. Hydrol. 426-427 pp 124-137
[7] Hoehn E, von Gunten H R 1989 Radon in Groundwater: A Tool to Assess Infiltration From Surface Waters to Aquifers Water resources research 25(8) pp 1795-1803
[8] Kamenova-Totzeva R M, Kotova R M, Tenev J G, Totzev A V, Badulin V M 2015 Natural radioactivity content in Bulgarian drinking waters and consequent dose estimation Radiat Prot Dosimetry 164(3) pp 402-407
[9] Kies A, Hengesch O, Tosheva Z, Nawrot A P, Jania J 2015 Overview on radon measurements in Arctic glacier waters The Cryosphere Discuss 9 pp 2013-2052
[10] Santos T O, Bonotto D M 2014 222Rn, 226Ra and hydrochemistry in the Bauru Aquifer System, São José do Rio Preto (SP), Brazil Applied Radiation and Isotopes 86 pp 109-117
[11] Vinson D S, Vengosh A, Hirschfeld D, Dwyer G S 2009 Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina (USA) Chemical Geology 260 pp 159-171
[12] Novikov D A 2017 Hydrogeochemistry of the Arctic areas of Siberian petroleum basins Petroleum Exploration and Development 44 pp 780-88
[13] Novikov D A, Sukhorukova A F 2015 Hydrogeology of the northwestern margin of the West Siberian Artesian Basin Arabian Journal of Geosciences 8 pp 8703-8719
[14] Novikov D A 2018 Genetic classification of subsurface waters and brines of Arctic regions of Siberia IOP Conference Series: Earth and Environmental Science 193(1) 012049
[15] Sukhorukova A F, Novikov D A 2018 Hydrogeology of Zaeltsovsko-Mochishchensky manifestation of radon waters (Novosibirsk) XXII Meeting on Groundwaters of Siberia and the Far East with international participation 473-480
[16] Bulatov A A, Kopylova Yu G, Dzhabarova N K, Rychkova K M, Arakchaa K D, Khvashchevskaya A A, Guseva N V, Pashagin A V 2013 New information on the composition of radon waters (Shiveligskoye field) Resort base and natural health-improving areas of Tuva and adjacent regions 1 pp 154-161
[17] Korneeva T V, Novikov D A 2018 Mechanisms of accumulation of trace elements in the radon waters of the Zaeltsovskoye deposit (south of Western Siberia) XXII Meeting on Groundwaters of Siberia and the Far East with international participation pp 270-276