Geochemistry of strontium in fresh underground waters of the Sredneobskoy basin (Tomsk region, Russia)

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Abstract. In the central part of Western Siberia a study of the chemical composition of fresh underground waters in the upper 600 m of the Sredneobskoy artesian basin was carried out. It was shown that underground waters generally contain high concentrations of strontium. The minimum concentrations of Sr are typical for Neogene-Quaternary sediments (600 μg/L), maximum values in the waters of the Upper Cretaceous sediments (more than 1300 μg/L). The study of strontium accumulation mechanisms in drinking underground waters is undoubtedly an important issue, as strontium is a biologically active element. Especially dangerous is the consumption of underground waters with a calcium-strontium ratio less than 100, that is the hydrogeochemical precondition for Urov endemic (Kashin-Beck disease). According to the calcium/strontium ratios data waters of the Neogene-Quaternary and Paleogene sediments selected in the south-western part of the Tomsk region are unsuitable for drinking water supply. Underground waters are shown to be in equilibrium with Al and Fe hydroxides; Ca, Mg, Fe carbonates; and clay minerals, including ferruginous. Increased strontium content in aquifers is determined not only by the chemical composition of the water-bearing rocks, but also increasing resident time of water rock interaction.

1 Introduction

Groundwater is the main source of drinking water supply in the Tomsk region. Groundwater of this region is rather effectively protected from surface contamination by low permeability argillaceous deposits. However, the water quality in its natural condition does not correspond the sanitary regulations and standards (SanR&S) 2.1.4.1074-01 «Drinking Water. Hygienic Requirements to Water Quality in Centralized Drinking Water Supply Systems. Quality Control». In areas with intensive human activity, groundwater is polluted. Natural factors also affect the quality of drinking water. The Tomsk region is located in the southeast part of the Sredneobsky artesian basin which is characterized by huge resources of underground waters. Using these waters are complicated because they have the high concentrations of iron [1] reaching several tens mg/L. Besides, groundwater

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is characterized by the high content of Sr – biologically active element, which has an impact on people's health. In this regard, it is important to study the prevalence and conditions of strontium accumulation in the groundwater of the active water exchange zone used for drinking water supply of the Tomsk region.

2 Objects and methods

The object of research is fresh groundwater in the south-eastern part of the Sredneobskoy artesian basin. The study area is wetland, composed of Neogene–Quaternary deposits up to 350 m in thickness. The upper part of those deposits in the major portion of the territory is represented by peat layers up to 8 m in thickness. The Neogene–Quaternary deposits are underlain Paleogene deposits (sand and clay) 200–400 m in thickness, overlying Upper Cretaceous deposits up to 600 m in thickness. Two aquifer systems exist in the Tomsk region: Eocene–Quaternary and Eocene–Upper Cretaceous, separated in the territory by Eocene clay. Each aquifer is divided into several levels, the most important of which are the Neogene-Quaternary, Paleogene, and Cretaceous. All aquifers, except for the first, are confined. The maximal thickness of the upper hydrodynamic zone reaches 800 m [2].

In this article has used data collected by the author in annual field trips since 2009. Overall, the authors studied 58 groundwater samples from different wells which use as table waters (fig. 1). At each point of the hydrogeochemical sampling «in situ» was determined the environmental parameters such as Eh, pH, T°C.

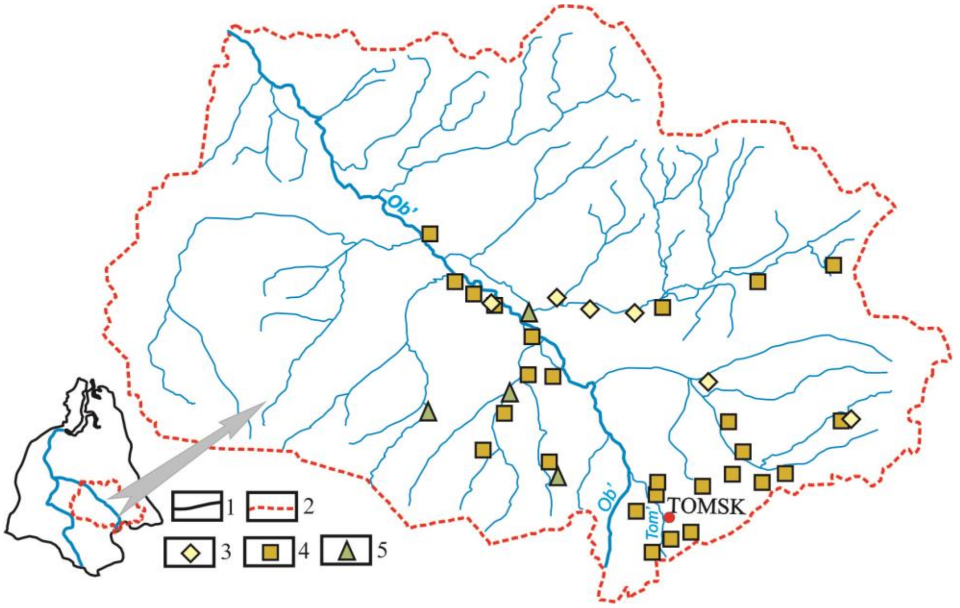

Fig. 1. Scheme of groundwater sampling: 1 – border of the West-Siberian artesian basin; 2 – border of Tomsk region; locations of groundwater sampling points (3) – Neogene-Quaternary, (4) – Paleogene, (5) – Upper cretaceous sediments.

3 Results and discussion

The main chemical composition of drinking groundwater is described in detail in previous works by the author [1, 3], therefore, this article contains averaged data on the chemical composition (tabl. 1). Sampling depth is from 4 to 740 m.

The change in the chemical composition of the groundwater of the artesian basin is subject to general hydrogeochemical patterns and vertical zonality. The groundwater of Neogene-Quaternary sediments is fresh, bicarbonate calcium or calcium-magnesium, weakly acid or neutral (pH 6.3–7.3). The waters of Paleogene sediments are most widely used for drinking water supply are fresh also (TDS up to 0.8 g/L), bicarbonate calcium, sometimes magnesium-calcium, and characterized by slightly higher pH values (6.8–8.1). Deeper waters of the Upper Cretaceous sediments are studied insufficiently, they are fresh or salty (TDS from 0.8 to 2.4 g/L), with the increased alkalinity (pH up to 8.3). There is a change in the chemical composition of water from calcium bicarbonate to sodium (soda) bicarbonate and sodium chloride.

Table 1. Chemical composition of groundwater: minimum-maximum (average), mg/L.

Indicator	Waters of Neogene-Quaternary sediments	Waters of Palaeogene sediments	Waters of Upper Cretaceous sediments
Depth, m	10-30 (21)	40-180 (93)	130-740 (307)
pH	6.3-7.3 (6.8)	6.8-8.1 (6.9)	6.5-8.3 (7.2)
TDS	130-1000 (400)	200-800 (560)	800-2400 (1300)
HCO_3^-	98.1-430.8 (220.5)	146.4-554.6 (410.2)	359.3-817.0 (548.7)
SO_4^{2-}	1.0-2.1 (1.7)	0.1-14.0 (2.7)	0.1-11.2 (3.3)
Cl^-	1.8-11.9 (6.5)	0.5-94.0 (10.8)	1.7-514.7 (88.2)
Ca^{2+}	52.9-82.0 (67.9)	34.0-168.0 (100.6)	2.0-147.0 (78.9)
Mg^{2+}	7.5-10.9 (8.9)	3.6-31.7 (17.4)	0.9-40.2 (21.3)
Na^+	7.5-9.0 (8.2)	5.0-68.0 (15.5)	43.0-900.0 (254.2)
Fe_{tot}	2.0-24.6 (8.5)	0.2-25.4 (5.7)	0.1-9.5 (3.1)
Sr^{2+}	0.1-0.6 (0.3)	0.6-0.9 (0.5)	0.5-1.3 (0.9)
Ca/Sr	49-280 (107)	28-300 (131)	38-233 (103)
Number of samples	11	42	5

Note: TDS – total dissolved solids

Among the trace elements in the studied ground waters, strontium (Sr) has a high content relative to the waters of the hypergenesis zone [4]. Its average content in the earth's crust is 350 ppm [5]. Among sedimentary rocks this element mainly accumulates in carbonates ($6.1*10^{-2}$ %), its content is slightly lower in clay ($3*10^{-2}$ %) and in sandstones – $2*10^{-2}$ %. There are over twenty Sr-bearing minerals in nature. Main of them are strontianite ($SrCO_3$) and celestine ($SrSO_4$). The first mineral has a strontium oxide content of 70.2 %, and the second – 56.4 %. However, pure strontium-containing minerals are not observed in the study area. It is probably present as isomorphic impurities in minerals of clays and sandstones.

Strontium is characterized by high migration ability [6] and can easily be leached from rocks, that is also confirmed by one of the highest concentrations among trace elements in the studied groundwater. The content of strontium increases while concentrating solution and its alkalinity increasing. Its minimum content is typical for Neogene-Quaternary sediments (600 μg/L). Below the Paleogene sediment strontium concentrations in waters increase to 980 μg/L. The maximum values of Sr are reaching in the waters of the Upper Cretaceous sediments (more than 1300 μg/L), selected on the territory of Bakcharsky iron ore deposit.

These sediments are presented by glauconitic rocks, iron ores, sandstones, siltstones and clays. It is known, that glauconites are active natural sorbents, so that they are able to accumulate elements during sedimentation process (in situ). In the work of M.A. Rudmin describes mineral inclusions in glauconites of Bakcharskoe deposit among which, in rare cases, mineral phases of strontium (baritoselestin and complex oxides) are revealed [7]. There is no strict direct relationship between strontium concentration and pH values of

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groundwater as in deeper Cretaceous waters at pH> 8 there is a sharp decrease in its concentrations, which is associated with the process of deposition of a number of trace elements, including strontium, and the formation of secondary carbonate and clay minerals. However, there is a linear relationship of strontium content on TDS (fig. 2a), calcium content (fig. 2b) and bicarbonate-ion (fig. 2c).

The study of strontium accumulation mechanisms in drinking groundwater is undoubtedly an important issue, as strontium is a biologically active element. Getting into the human body strontium replaces calcium in bone tissue, leading to the deformation of the skeletal system. Especially dangerous is the consumption of groundwater with a calcium-strontium ratio less than 100, that is the hydrogeochemical precondition for Urov endemic (Kashin-Beck disease) [8]. According to the strontium/calcium (Sr/Ca) ratios data water of the Neogene-Quaternary and Paleogene sediments selected in the south-western part of the Tomsk region are unsuitable as table water.

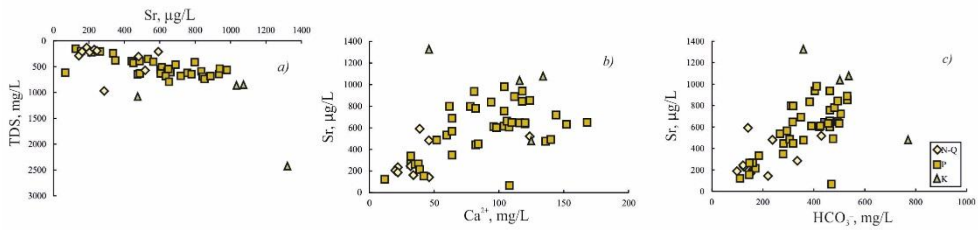

Fig. 2. The relationship between the content of strontium and TDS (a), calcium content (b) and hydrocarbonate-ion (c) in groundwater.

Strontium is a weak complexing compound with low stability constants for the most common anions of groundwater [6]. Calculations carried out using the Hydrogeo software package [9] based on the method of equilibrium constant have shown, that the main form of strontium migration in fresh and low-mineralized waters is the simple cation Sr^{2+}(more than 90%). However, in the presence of the CO_3^{2-} anion, there is an increase of the strontium binding into associates $(SrHCO_3)^+$, $SrCO_3^0$, $SrSO_4^0$. According to S.R. Krainov [6] the latter forms can be important only in low-mineralized (TDS more than 1 g/L) carbonate waters with a pH higher than 8.5. But even in such waters, the significance of these forms is not high and within the study area does not exceed 10%.

Based on earlier thermodynamic calculations of the equilibrium state of waters with various carbonate and aluminosilicate minerals, it was established that all groundwater is not in equilibrium with the primary minerals of water-bearing rocks: feldspars, muscovite, biotite, epidote and many others. At the same time, the studied waters are in equilibrium with various montmorillonites, illite, kaolinite and other clays, as well as calcite, siderite [1]. Thus, as water is saturated regarding clay and carbonate minerals, strontium deposits from solution as an isomorphic impurity of these minerals.

4 Conclusion

The underground waters of active water exchange zone in the Sredneobskoy artesian basin are characterized by a high content of strontium relative of the waters of zone hypergenesis. In the distribution of strontium in waters, a clear link is established between TDS of groundwater and the strontium content. Strontium content increases with depth, reaching maximum values in the waters of the Upper Cretaceous aquifer, where maximum values of total dissolved solids are observed. Based on thermodynamic calculations of the equilibrium state of waters with various carbonate and aluminosilicate minerals, it is established that all groundwater is not in equilibrium with the primary minerals of water-bearing rocks (feldspars, muscovite, biotite, hornblende, etc.). At the same time, waters are in equilibrium with various clay minerals (montmorillonite, illite, kaolinite) and carbonate (calcite, siderite) minerals, with which strontium partially precipitates as an isomorphic impurity. Thus, increased strontium content in aquifers is determined not only by the chemical composition of the water-bearing rocks, but also increasing resident time of water rock interaction. The study of strontium accumulation mechanisms in drinking underground waters is undoubtedly an important issue, as strontium is a biologically active element. Especially dangerous is the consumption of underground waters with a calcium-strontium ratio less than 100, that is the hydrogeochemical precondition for Urov endemic (Kashin-Beck disease). According to the calcium/strontium ratios data waters of the Neogene-Quaternary and Paleogene sediments selected in the south-western part of the Tomsk region are unsuitable for drinking water supply.

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References

1. I.S. Ivanova, O.E. Lepokurova, O.S. Pokrovsky, S.L. Shvartsev, *Procedia earth and planetary science*, 7, 385-388 (2013)
2. *Hydrogeology of the USSR. Volume XVI: West Siberian Plain,* (Nedra, Moscow, 1970)
3. I.S. Ivanova, O.E. Lepokurova, Tomsk State University Journal, **398**, 224-232 (2015)
4. S.L. Shvartsev, Geochemistry international, **46**, 13, 1285-1398 (2008)
5. S.R. Taylor, S.M. McLennan, *The Continental Crust: its Composition and Evolution.* (Blackwel Blackwell Scientific, Oxford, 1985)
6. S.R. Kraynov, V.M. Shvets, *Geochemistry of groundwater potable purposes*, (Nedra, Moscow, 1987)
7. M.A. Rudmin, A.K. Mazurov, I.V. Reva, Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering, **327**, 5, 54-64 (2016)
8. E.V. Polyakova, A.I. Malov, Arctic Environmental Research, 1, 39-46 (2005)
9. M.B. Bukaty, Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering, **305**, 6, 348-365 (2002)