Sodium groundwater in SE Western Siberia

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Abstract. The paper describes the updated results in the study of the formation conditions of sodium water within SE Western Siberia. The authors identified a classification of the types of sodium water, location conditions and chemical composition.

1. Introduction
Sodium groundwater are widely found throughout the Earth upper crust. The existence and formation of these groundwater is still the issue of the day. The investigation of specific formation conditions of sodium groundwater in nature, isotope studies and calculations of fossil water-secondary aluminosilicate equilibrium system deduces the possible identification of the sodium accumulation sources and mechanisms. In this case, the most significant sodium groundwater occurrences are being described. This, in its turn, embraces the SE region of Western Siberia. This choice is based on the following factors (1) sodium water is extensive and diverse in this region and (2) influence of the complete water-rock (aluminosilicate)-gas (methane, carbon dioxide) – organic matter (coal, swamp) system on formation of water composition can be found in this region, if anywhere.

2. Investigation background
Most specialists from different countries associated the formation of sodium water with ion exchange. This recognized fact has been confirmed in numerous publications [1–5]. This proves the fact that the importance of aluminosilicate rocks in the formation of sodium water remains out of view of hydrogeologists, geochemists and geologists, which, in its turn hampers the further development of geochemistry. S.L. Shvartsev [6, 7] proposes to decipher the genesis of sodium water on the basis of the existing concept: water-rock interaction. This concept embraces the experimental data results from different European and American laboratories investigating such aspects as mineral dissolution in various geochemical environments under different temperatures; physico-chemical modeling of different hydrogeochemical processes; and calculations of water-rock system equilibrium [8–18]. However, the most significant aspect of this concept is that it involves the data results of numerous geological and hydrogeological observations. S.L. Shvartsev proved that sodium formation is the natural consequence of water-aluminosilicate interaction and is attributed to a specific evolution phase of this system if water is carbonate saturated. This interaction could be as a result of the equilibrium-nonequilibrium behavior within the system itself: water is not always in equilibrium relative to endogenous minerals which are consequently dissolved and, this provides the continuous evolution of
the water composition; however, in this case, water is in equilibrium to a definite set of secondary minerals.

3. Regional distribution and specific features of chemical, gaseous and isotope composition of sodium groundwater

Distribution conditions (Figure 1) and specific composition characteristics of sodium water (Table 1) are discussed below; each region – Western Siberia artesian and Kuznetsk artesian basins are described separately.

Figure 1. General map and cross-sections[19, 20]: 1 – civil division boundary; 2 – investigated area; 3 – cross section line; 4 – distribution area of natrium hydrocarbonate (sodium) water; 5 – regional confining layer; 6 – stratigraphic boundaries; 7 – wells; 8 – faults.

Hydrogeologically, S-E region of Western Siberia artesian basin is disclosed. There is no Cretaceous- Paleogene water confining layer, (figure 1, cross-sections AB) as a result the influence of filtration water was not distinctly observed. The boundary of fresh water can be found at 1.5km. Sodium water can be widely found in Cretaceous continental sedimentary rocks (sandstones and aleurolites). Groundwater intake is from Altai-Sayan Mountain bordering, where sodium water can also be found in subsurface conditions within intrusive rock fractures (mainly granites and granodiorites). In the Chulim basin sodium water can be found at a depth from several tens to hundreds of meters (up to 2 m). Maximum distribution area of above-mentioned water is confined to the artesian basin slope, gradually declining in the NW direction, i.e. in Mid Ob basin.

Unique sodium water can be found in Cretaceous sediments, Illekian suite within Chulim basin at a depth of 600-1300m. The uniqueness of sodium water is that it is rather fresh (salinity: 0.25–0.6 gr/liter), however, strongly alkaline (pH 9.1–10.3). Such alkaline water can be found in many regions of the world as it is associated with magmatic rocks. In this case, such water prevails in Lower Cretaceous continental sedimentary rocks and aleurolites (K1il). Water produced from Chulim wells
(1266–1277 m) is therapeutic-table water with high silica content ($H_4SiO_4$ up to 50 mgr/liter) [21] and is labelled as “Omega” (first mineral water produced in Tomsk Oblast).

Table 1. Chemical composition of some sodium water types in SE Western Siberia (numerator-allowable concentration; denominator- average, dash- no data), mgr / liter.

| Parameters | Sodium water in Kuznetsk basin; moderate water exchange | Sodium water in Kuznetsk basin; moderate water exchange in lower zone area | Tersian acidulous water [23] | Borisovian nitrate-methane minerals [24] | Fresh alkalines in Chulim basin [21] | Kolpashev mineral water; well 2
|-----------|---------------------------------------------------------|-------------------------------------------------|----------------------------|---------------------------------|---------------------------------|-----------------------|
| Host rocks | Permo-Carbonifeous carbonaceous-terrigenous sediments | Cretaceous argilloarenaceous sediments          |                           |                                 |                                 |                       |
| Sampling depth, m. | 30–1197 | 190–1495 | 370 | 575 | 1266–1277 | 744–760 |
| pH | 8.2 | 7.2–10.0 | 6.4–6.9 | 8.2 | 9.1–10.3 | 7.9 |
| $\Sigma$ ions | 436–4627 | 1499–25139 | 4054–5809 | 2875 | 261–404 | 815–1111 |
| Oxidability | 0.2–7.1 | 0.5–19.2 | 10 | 1.1–1.6 | – | |
| $HCO_3^-$ | 258–3289 | 630–15494 | 3002–5809 | 2013 | 73–209 | 370–568 |
| $CO_3^{2-}$ (CO$_2$) | 0.3–742.8 | 8.4–1285 | (1656–3060) | 54 | 19–82 | – |
| Cl$^-$ | 863 | 6110 | 3953 | 2013 | 73–209 | 370–568 |
| $SO_4^{2-}$ | 0.2–596 | 0.2–75 | 0.5–14 | 1.3 | 2.0–20.4 | 0–2.5 |
| $Ca^{2+}$ | 1.0–165 | 0.2–60.5 | 235–307 | 2 | 0.4–5 | 6–8 |
| Na$^+$ | 34 | 18 | 235–307 | 2 | 0.4–5 | 6–8 |
| Mg$^{2+}$ | 44–1200 | 426–7230 | 732–1054 | 862 | 85–99 | 236–380 |
| K$^+$ | 317 | 2976 | 50–119 | 0.6 | 0.1–2 | 0–2.4 |
| SiO$_2$ | 90 | 35 | 94 | 1 | 13 | 7 |

Sodium water distribution thickness in Mid-Ob basin is much less and could extend to full pinching out in regional occurrence areas of Cretaceous-Paleogene water confining layer. B In Kolpashev region in well 2 (Figure 1, cross-section AB) sodium mineral water was found in Cretaceous sediments of Pokursk suite at the depth of 744–760 m. Low-mineralized water (up to 1.1 gr/liter), weak alkaline (pH 7.9) with high chloride concentration [11]. This water is used as drinking therapeutic-table water “Siberian Resort.”
Sodium water is significantly developed in Kuznetsk artesian basin under forest-steppe conditions, even at near subsurface conditions. Comparably to above-described basin, the sodium water distribution thickness is continuous throughout the cross-section (figure 1, cross-sections CD) and is 2000 m. [22]. This water is usually found at the depth of 100–200 m and is confined to the zone of moderate water exchange in Permian carbonaceous-terrigenous sediments. Mineralization ranges from 0.4 to 5 gr/liter; pH from 7.2 to 9.8, sometimes high chloride and sulphate concentration; in gas-predominately methane. Some are used as mineral water. For example, Borisovskysya therapeutic-table water includes nitrate-methane concentration, analogous to North Caucasian water “Essentuki”, due to its similar medical treatment properties [24].

Unique sodium water with quite high salinity (up to 25 gr/liter) was discovered in Nariksko-Ostashkin area, Ernakovsk in 2012–2014. This water was assigned to the lower part of the moderate water exchange zone. Besides the significant mineralization values, this water embraces has heavy isotope composition of water-dissolved carbon (to +30.3‰), which, in its turn, requires further detailed investigation (Table 2). Investigation by positive δ13С in СО2 appeared only in 2000s, i.e. only recently. Such anomaly values δ13С are rare: predominately in pore water of lake and marine bottom sediments (up to 34,9‰), which, in its turn, coordinates with geochemical reduction conditions (China, Argentina, USA) [25], cold mud volcano methane waters [26] and in coal layers (up to 22%) within the production areas of shale gas and coal-bed methane (USA, Australia) [27–28].

Table 2. Carbon isotope concentration in water dissolved gases and hydrocarbonates from Nariksk-Ostashkinsk area.

| № samples | δ13СCH4, ‰ | δ13ССО2, ‰ | δ13СDIC, ‰ | (δ13ССО2 – δ13СDIC) |
|-----------|-----------|-----------|-----------|------------------|
| 1         | -67.3     | 13.7      | 25.1      | 11.4             |
| 2         | -44.3     | 17.1      | 24.6      | 7.5              |
| 3         | -51.2     | 13.3      | 21.5      | 8.2              |
| 4         | -46.9     | 18.0      | 26.4      | 8.4              |
| 5         | -45.9     | -3.2      | 4.4       | 7.6              |
| 6         | -43.3     | 6.7       | 14.0      | 7.3              |
| 7         | -46.0     | 22.3      | 30.3      | 8.0              |
| 8         | -53.1     | 14.6      | 23.7      | 9.1              |
| 9         | -53.0     | 19.6      | 28.9      | 9.3              |
| 10        | -49.15    | 12.6      | 21.2      | 8.6              |
| 11        | -46.7     | 12.7      | 21.4      | 8.7              |

It should be noted that all scientists agree that heavy positive CO2 isotope is biogenic and is always related to alkaline sodium water. Based on the above-discussed facts, the following conclusion was made—groundwater enrichment mechanism by heavy isotopes 13С is associated with the sodium water formation mechanism. This could be a separate research topic.

It should be stated that in this region at conditions of significant methane gas distribution carbon dioxide gases can be found in the lower zones (Figure 1, cross-sections CD); especially, in the conjunction zone of Kuznetsk depression with Kuznetsk Altai Tersinsk carbonate mineral water fields are confined to the regional fault. Uniqueness of Tersinsk field is that it can not be attributed to recent volcanism occurrences as the youngest igneous rocks in Kuznetsk are only Triassic ones. This sodium carbonate water is cold (T at head = 12–13 ºС), salinity plus total mineralization 2.0–5.5 gr/liter, slightly acidic (pH 6.2 – 7.0). Comparative analysis of Tersinsk carbonate water composition to Kuznetsk sodium water in the zone of moderate water exchange (which is well-developed throughout the whole area) shows that genetically they are close in proximity. Moreover, obtained value δ13CHCO3- of carbonated water differs from sodium water in this region. In the, isotope-light carbon dominates which explains the biogenic genesis of CO2 in HCO3- composition. In Tersinsk field mineral water- “heavy” value δ13С (HCO3-) indicates metamorphic genesis, whereas source of CO2 are carbonates buried deep in the earth crust. Thus, carbonated water is sodium water
(one and the same thing). In this case, the composition significantly changes due to CO\textsubscript{2} ingress from the deepest zones of the earth crust through tectonic dislocations [23].

4. Conclusion
In conclusion, sodium water is widely distributed in SE Western Siberia: from ultradispersed (0.2 gr/liter) to saline (25 gr/liter); from weakly carbonate (pH 6.2) to strongly alkaline (10.3), with carbon dissolution anomaly (+30.3‰) and ultralight (-30.3‰), high and low organic matter concentrations. The gaseous composition is also rather diverse: nitrate, carbon dioxide, methane which are widely distributed in Mesozoic sediments on artesian water slope and Paleozoic sediments in Kuznetsk intermountain basin at a depth ranging from 100-200 to 2000 m.

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References
[1] Matthess G, Frimmel F H, Hursch P, Schulz H D and Usdowski E 1992 Progress in hydrogeochemistry (Berlin: Springer-Verlag)
[2] Kimura K 1992 Ground Water Hydr 32 (1) 5–16
[3] Appelo C A J and Postma D 1994 Geochemistry, groundwater and pollution (Rotterdam: A.A. Balkema)
[4] Parkhurst D L, Christenson S and Breit G N 1996 U.S. Geol. Surv. Water-Supply Pap 101
[5] Kim K, Yun S-T 2005 Geochemical Journal 39 273–284
[6] Shvartsev S L 2008 Geochemistry International 46 (13) 1285–398
[7] Shvartsev S L, Ryzenko B N, Alekseev V A, Dutova E M, Kondrat’eva I and Lepokurova O E 2007 Geological Evolution and Self-Organization of the Water-Rock System 2
[8] Lasaga A C 1984 J. Geophys. Res 89 (B6) 4009–25
[9] Helgeson H C, Murphpy W M, and Aagaard P 1984 Geochim. Cosmochim. Acta 48 2405–32
[10] Murphy W M and Helgeson H C 1987 Geochim. Cosmochim. Acta 51 3137–53
[11] Murphy W M and Helgeson H C 1989 Am. J. Sci. 289 17–101
[12] Casey W H & Ludwig C 1995 Mineralogical Society of America (Washington: A. F. White and S. L. Brantley) pp 87–118
[13] Brantley S L and Chen Y 1995 Mineralogical Society of America (Washington: A. F. White and S. L. Brantley) pp 119–172
[14] Nagy K. L. 1995 Mineralogical Society of America (Washington: A. F. White and S. L. Brantley) pp 173–233
[15] Dove P M and Czank C A 1995 Geochim. Cosmochim. Acta 59 1907–15
[16] Rubie D C, Thompson A B 1985 Advances in Physical Geogemistry 4 (New York: Springer-Verlag) 26–79
[17] Kerrick D M, Lasaga A C, Raeburn S P 1991 Mineralogical Society of America (Washington: A. F. White and S. L. Brantley) pp 583–671
[18] Sverdrup H 1990 The Kinetics of Base Cation Release Due to Chemical Weathering (Lund, Sweden: Lund University Press)
[19] Hydrogeology of the USSR 1972 18 479 [in Russian]
[20] Rogov G M and Popov V K1985 Gidrogeologija i katagenez porod Kuzbassa (Tomsk: Publishing house of Tomsk State University) p 191
[21] Shvartsev S L and Lepokurova O E 2014 Doklady Earth ScienceGidrogeologija i katagenez porod Kuzbassas 459 (1) 1464–1469
[22] Shvartsev S L, Khryukin V T, Donrocheva E V, Kuzevanov K I, Rasskazov N M, Popova T S, Lepokurova O E and Shvachko E V 2006 Russian Geology and Geophysics 47 7 881–891
[23] Kopylova Y G, Lepokurova O E, Tokarenko O G and Shvartsev S L 2011 Doklady Earth
Sciences 436 (2) 284–289

[24] Lepokurova O E, Tokarento O G and Kopilova Yu G 2007 Geohimija Borisovskih mineral'nyh vod Materialy nauchnoj konferencii Sovremennye problemy geohimii 103–105

[25] Zhu Z, Chen J and Zeng Y 2013 Quaternary Int. 286 85–93

[26] Lavrushin V Y, Polyak B G and Pokrovskii B G 2009 Lithology and Mineral Resources 2 171

[27] Colding S, Boreham C J and Esterle J S 2013 Int. J. of Coal Geology 120 24–40

[28] Sharma S and Frost C D 2008 Ground water 46 (2) 329–334