XXXVIII
IAH Congress

Groundwater Quality Sustainability
Krakow, 12–17 September 2010

Extended Abstracts

Editors:
Andrzej Zuber
Jarosław Kania
Ewa Kmiecik

University of Silesia Press 2010

abstract id: **342**

topic: **4**
Mineral and thermal water

4.2
Origin of mineral and thermal waters

title: **Geochemistry and origin of mineral geoundwater from Fadeevskoe spa (Far East of Russia)**

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keywords: mineral groundwater, high pCO_2, CO_2 origin

INTRODUCTION

The Fadeevskoe spa is located in south part of Russian Far East, in Primorye region, in the upper reaches of the Klyuch Ivanov Creek. Yushakin was first to study this spa in 1968, in the subsequent years, nobody purposefully studied this deposit, and its further research was continued again only during works on the regional assessment of the mineral water resources. The intense drilling conducted in 1999–2001 allowed us to determine the geological and hydrogeological conditions of the deposit and to study the composition of the waters, gases, and host rocks. Four boreholes were drilled in the deposit area with core sampling from certain intervals. The deposit was studied to a depth of 100 m.

The performed studies of the underground waters, host rocks, and gas components of the Fadeevskoe deposit made it possible to determine the physico-chemical conditions of the formation and subsequent evolution of the mineral waters during their interaction with host rocks, to assess the circulation period of mineral waters, and to establish the genesis of carbon dioxide in the waters of the deposit localized in the watershed part of the Sikhote Alin Range.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The Fadeevskoe deposit of high pCO_2 groundwater is located in the Samarka Terrane (Fig. 1) extending in the northeastern direction from the southern coast of the Primorye region to the lower reaches of the Amur River in the form of a band up to 100 km wide. The surrounding bedrock is composed of Jurassic stratified and chaotic terrigenous sediments enclosing abundant allochthonous sheets, blocks, and fragments originating from the Late Paleozoic and Early Mesozoic oceanic crust.

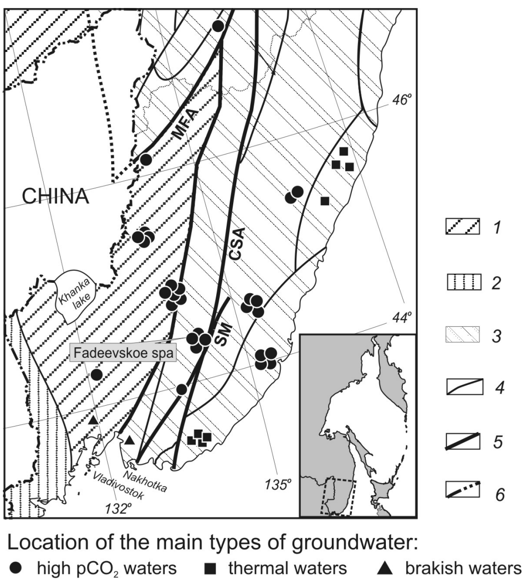

Figure 1. Tectonic scheme of the southern Russian Far East and the main types of groundwater location. 1 — Early Paleozoic superterrane; 2 — Late Paleozoic terrane; 3 — collage of Cretaceous terranes; 4 — boundaries of terranes; 5 — major faults: CSA — Central Sikhote Alin; MFA — Mishan-Fushun-Alchan; Sm — Samarka; 6 — state boundary of the Russian Federation.

The deposit is confined to the dense network of differently oriented fractures. The most significant among them is a system of near latitudinal fractures represented by thick subvertical brecciation zones best traceable along the river valleys, including the Klyuch Ivanov Creek. The system of feathering faults of northwestern strike is subordinate. The deposit is located in the Sikhote Alin hydrogeological massif and comprises two widespread aquifers: the aquifer of Quaternary fluvial sediments (aQ) and the aquifer zone of volcano_sedimentary sequences of the Upper Jurassic–Lower Cretaceous Samarka Formation (J_3–K_{1sm}).

The aquifer of Quaternary fluvial sediments (aQ) up to 3.5 m thick is ubiquitously distributed in the Klyuch Ivanov Creek valley, where it extends in the form of a relatively narrow band along its channel, being the uppermost one in the section. Its occurrence depth changes through the distribution area from zero (swamped areas) to 1.5–2.0 m. The water enclosing.

sediments are represented by sands, gravel, and boulders. The aquifer contains largely fresh waters with low mineralization and takes a limited part in the formation of carbonated mineral waters.

The aquifer of the Upper Jurassic–Lower Cretaceous Samarka Formation originates from zones of exo and endogenic fracturing. The waters from the exogenic fracturing are ubiquitously distributed in the undivided volcanosedimentary sequences of the Samarka Formation (J_3–K_{1sm}). The host rocks are represented by fractured siliceous varieties, sandstones, siltstones, and rhyolites. The zone of intense fracturing is developed up to a depth of 30 m. The aquifer is the uppermost one in the section of valley slopes and watershed areas and the second one from the surface under the water_bearing fluvial sediments of the creek. Below 30 m, the underground waters of the Samarka Formation are related to zones of endogenic fracturing. The waters are fresh with their mineralization being as low as 0.2–0.5 g/l, carbonated, ferruginous, and siliceous in composition. They were recovered by boreholes in tectonic fracturing zones in the depth interval of 30–100 m in local areas of intense water exchange that receive gas through fractures. The discharge of mineral waters to the surface is determined by the elevated pressure of the accompanying gas and is observable in the upper reaches of the Klyuch Ivanov Creek. The yield of the natural spring of mineral waters under undisturbed conditions is 0.15 l/s.

GEOCHEMISTRY OF WATERS

Surface waters. The Klyuch Ivanov Creek is the main surface water course of the area. Its drainage area is only 20 km^2. The creek is an intermittent channel, being characterized by a temporary flow; it dries up in the summer and becomes frozen over in the winter. The water consumption in the usual period is 10–15 l/s, and it manyfold increases during floods. The module of the surface runoff is 2–3 l/s from a square kilometer. The creek waters are hydrocarbonate with a mixed cation composition (Fig. 2). Among the cations, calcium, sodium, and magnesium are dominant. The chemical composition of the waters in the creek inherits to a certain extent that of the atmospheric precipitation. The water is characterized by low TDS (up to 240 mg/l) and pH (5.5–6.8). The analysis of seasonal variations in the composition of surface waters shows that their maximal TDS and concentrations of hydrocarbonate ion, Ca, and Na are observed in the spring (in March) during the period of the commencing of the snow cover thawing. This period is also marked by a decrease in the pH value from 6.8 to 5.5 and lowered Mg, sulfate ion, and chlorine ion contents.

Fresh groundwater. The fresh groundwater is confined to weathering, brecciation, and fracturing zones in the volcano-sedimentary rocks constituting the upper part of the Samarka Formation and is distributed through the entire study area. This type of groundwater are head waters and hydrocarbonate sodium and calcic in their composition with an elevated content of silica (Fig. 2). The waters are characterized by low TDS (up to 0.1–0.2 g/l), which is explained by the intense water exchange.

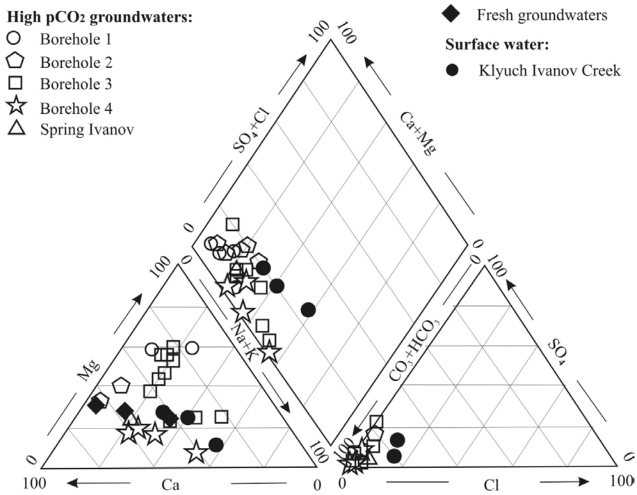

Figure 2. Piper diagram illustrated connection between the main ions in waters from Fadeevskoe spa.

High pCO_2 groundwaters. For the study of the hydrochemical section and the distribution of high pCO_2 groundwaters through the deposit, they were sampled with a step of 25–40 m. The chemical analysis of the high pCO_2 groundwaters shows that they are characterized by relatively low TDS in comparison with the other high pCO_2 groundwaters of the Primorye region (0.2–0.5 g/l). At the same time, they demonstrate relatively high concentrations of free CO_2, which is variable both through the section and laterally. Among the four boreholes that recovered high pCO_2 groundwaters in this spa, the minimal CO_2 content is recorded in Borehole 4, where it does not exceed 80 mg/l; the maximal CO_2 content (up to 2253 mg/l) is registered in the depth interval of 30–60 m in Borehole 1.

By their anion composition, the waters from all four boreholes are hydrocarbonate with different HCO_3^- contents. The highest content of HCO_3^- (1162 mg/l) was established in the sample taken in February of 2000 from Borehole 1 and the lowest one (189 mg/l) was recorded in the sample obtained in March of 2001 from Borehole 2. By the concentrations of the main cations, the mineral waters in the boreholes significantly differ from each other as well. The highest Na^+ concentration is observed in the waters of Borehole 4, while the concentrations of this element in the spring are almost three times lower. The highest (up to 168 mg/l) and lowest (up to 16 mg/l) Ca^{2+} contents are recorded in the waters from boreholes 4 and 1, respectively. The Mg^{2+} concentrations are also highly variable in the different boreholes with the highest (up to 66.8 mg/l) and lowest (7.3 mg/l) values being registered in the waters from Borehole 1 and the spring, respectively. By their geochemical type, the high pCO_2 groundwaters of the spa in the examined boreholes are also different. The Mg–Ca-HCO_3^- type of groundwater was found in boreholes 1–3, while borehole 4 yielded Ca–Na-HCO_3^- type of groundwater. The mineral waters from the spring belong to the Ca–Mg-HCO_3^- type.

The comparison of the concentrations of the hydrocarbonate ions with that of the sodium and calcium ions shows that the enrichment of the mineral waters with these elements almost directly depends on the content in the waters (Fig. 3), which is, in turn, proportional to the partial CO_2 pressure in the system. Precisely the influx of CO_2 into high pCO_2 groundwaters is responsible for the proceeding reaction: $H_2O + CO_2 \leftrightarrow H^+ + HCO_3^-$.

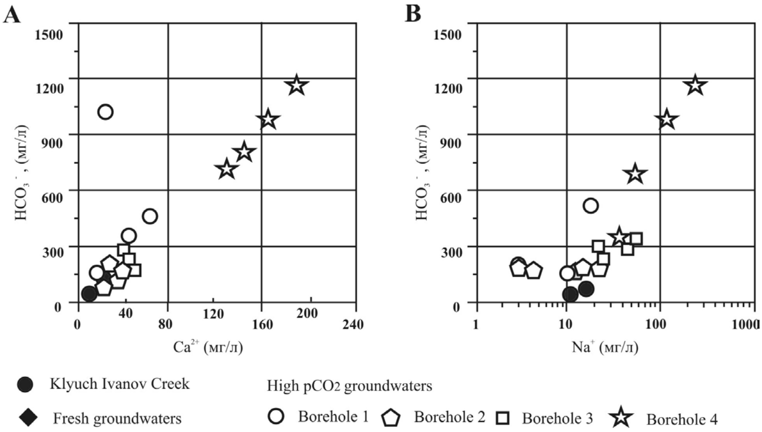

Figure 3. Correlation between HCO_3^- and Ca^{2+} (A) and HCO_3^- and Na^+ in waters from Fadeevskoe spa.

This type of groundwaters is ferruginous. Similar to the other components, the concentrations of Fe_{total} are highly variable through the area. The maximal (up to 45.56 mg/l) and minimal concentrations of Fe_{total} are recorded in the waters from boreholes 3 and 4, respectively. It is established that the waters from boreholes 1 and 2 are characterized by a positive correlation between the concentrations of ferrous iron and chlorine ion in the waters. A particular feature of the chemical composition of the high pCO_2 groundwaters is the high SiO_2 concentrations (17–69 mg/l), which is untypical of the mineral waters from the other manifestations in the Primorye region. The elevated silica content in the waters was presumably determined by its relatively rapid leaching from the rock cement. The high pCO_2 groundwaters are characterized by extremely low contents of the minor elements (Cu, Zn, Mn, Al, and others). This property is most likely explained by the high water exchange rate, i.e., the short term interaction in the water–rock system.

For establishing the correlation between the contents of the major components, as well as the pH and the TDS, we carried out the statistical processing of the chemical analysis. The results shows that the waters from Borehole 1 are characterized by positive correlations between the Fe^{2+} and Cl^-, HCO_3^- and Cl^-, Na^+ and HCO_3^-, and Fe^{2+} and HCO_3^- contents, as well as between TDS and the concentrations of Cl^-, Fe^{2+}, and HCO_3^-. For the mineral waters from Borehole 2, positive correlations with high correlation coefficients (>0.87) are recorded between the Mg and Na ions, the sulfate and sodium ions, the sulfate and Mg ions, the ferrous Fe and Cl, the Si and hydrocarbonate ion, TDS and hydrocarbonate ion content, and TDS and Si content. Negative correlations with high correlation coefficients are observed for the ions of Na and Cl, Mg and Cl, and Fe and Mg; the sulfate and Cl; the sulfate and ferrous Fe; and the CO_2 and pH. The groundwaters from Borehole 3 show a different correlation pattern between the components. The only positive correlation (with a moderate correlation coefficient of 0.7) is noted between the concentrations of hydrocarbonate and sodium ions. Also noteworthy is the negative correlation between the concentrations of Cl ions and the CO_2. Between the remaining components of the underground mineral waters, no significant correlations are recorded. The proportions of the components in the groundwaters from Borehole 4 are similar to their relations in the water from Borehole 1: positive correlations with relatively high correlation coefficients (>0.83) between the HCO_3^- and TDS, the HCO_3^- and Na^+, the Na^+ and CO_2, and the Fe^{2+} and Cl^-; a negative correlation between the pH and CO_2. Some of the compositional features of the groundwaters from Borehole 4 are determined by the stable correlations between the concentrations of the Mg ions and TDS ($r = 0.97$), the concentrations of the Fe^{2+} and Cl^- ($r = 0.96$), and the concentrations of the Fe^{2+} and CO_2 ($r = 0.99$).

The distinct positive correlations observable for some of the components in the high pCO_2 groundwaters from the boreholes in question allow the inference that their TDS (at least in three of the four boreholes (1, 2, 4)) directly depends on the content of HCO_3^- and is practically indifferent to the concentrations of the cations in the waters. This fact confirms the above assumption that the high pCO_2 groundwaters from the Fadeevskoe spa are characterized by very rapid circulation, which prevents their sufficient saturation with salt components during the interaction in the water–rock system. This assumption is also supported by the geological and hydrogeological structure of the deposit. The distribution of the high pCO_2 groundwaters is consistent with the formation of the fresh groundwater in this area. The high pCO_2 groundwaters waters replace partly fresh groundwaters to form a flow in common. They are characterized by the same movement direction, consumption, and main sources of resource formation, except for the chemical and gas compositions.

The hydrogen and oxygen isotope ratios first obtained for the aqueous phase of the mineral waters from the Fadeevskoe deposit are well consistent with similar data on other deposits of the Primorye region and characterize them as being of the atmospheric infiltration type.

Gas phase. Table 1 presents data on the chemical and isotopic composition of the freely released gas. The high pCO_2 groundwater contain 0.5 to 1.6 g/l of dissolved CO_2 gas. The waters in the central part of the studied area exhibit elevated pressure on account of the spontaneous gas release. The partial pressure of the CO_2 calculated for the mineral and fresh underground waters is 0.7 and 0.1 bar, respectively. The free gas is represented by carbon dioxide and nitrogen with an insignificant methane and oxygen admixture. The nitrogen is of atmospheric origin, while the insignificant hydrocarbon concentrations may be explained by the transformation of organic matter in the section. The carbon isotope composition ($\delta^{13}C$, ‰) indicates that the carbon dioxide is of deep mantle origin. The $\delta^{18}O$ value in the CO_2 is also lighter as compared with that in the water, which indicates their different geneses and short-term interaction in the rock–gas system.

Table 1. Composition of the escaped gas from the Fadeevskoe spa.

Sampling data	CO_2,%	O_2-Ar, %	N_2, %	CH_4, %	$\delta^{13}C$,‰	$\delta^{18}O(CO_2)$,‰
03.08.2001	98.84	0.17	0.99	0.0001	—	—
26.02.2008	97.10	0.28	2.59	0.0027	–9.9	–23

CONCLUSIONS

So, the geochemical study of bedrocks, underground and surface waters, and associated gases in the Fadeevskoe deposit of carbonated waters (Sikhote Alin, Primorye region) revealed that the chemical composition of these waters is formed in the zone of active water exchange in the limited area of the discharge zone. The high pCO_2 mineral groundwater has s short residence period. Calculations of the saturation indices show that the mineral waters are undersaturated with carbonates and aluminosilicates. The main factors that influence the water mineralization are the excess carbon dioxide in water and the circulation time.

International Association of Hydrogeologists

AGH University of Science and Technology

2-vol. set + CD
ISSN 0208-6336
ISBN 978-83-226-1979-0