The geochemistry of water and gas phases from high pCO2 sparkling springs within the northern Sikhote-Alin ridge region (Russian Far East)

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Abstract. Two types of cold CO_2 rich groundwaters are located within the northern part of the Sikhote-Alin ridge: the first type is a Ca–Mg–HCO_3 water with low TDS content (≤ 1.7 g/l) and high concentrations of Fe^{2+}, Mn^{2+}, Ba^{2+}, and SiO_2, whilst the second type is a Na–HCO_3 water with a high TDS content (≈ 14 g/l) and elevated concentrations of Li^+, B_{tot}, Sr^{2+}, Br^-, and I^-. A notable feature of these waters is a predominance of CO_2 in the gas phase (up to 99 vol. %) and low contents of other gases (CH_4, N_2, O_2, etc.). The origins of both water types can be identified on the basis of water (δD, $\delta^{18}O$) and gas ($\delta^{13}C$, $^3He/^4He$, $^4He/^{20}Ne$) isotopic compositions considered in the context of the geology and hydrology of the region.

1 Introduction

Currently, there are almost 70 cold springs exhibiting elevated pCO_2 within the southern part of the Russian Far East, mainly localized near the faults of the Sikhote-Alin mountain system. The main feature of these groundwaters is a strong prevalence of CO_2 in the gas phase (96–99 vol.%) and only minor contents of other gases (CH_4, N_2, O_2, etc.). The most phenomenal and popular sparkling groundwaters in the northern part of the Sikhote-Alin territory are in the Mukhen spa which is located at about 100 km from Khabarovsk (Fig.1). The chemical composition of the Mukhen spa water is unique because of two different types of cold CO_2-rich groundwaters circulating in the same area [1, 2]. This study was undertaken to identify the source of water and gas phases of the Mukhen spa.

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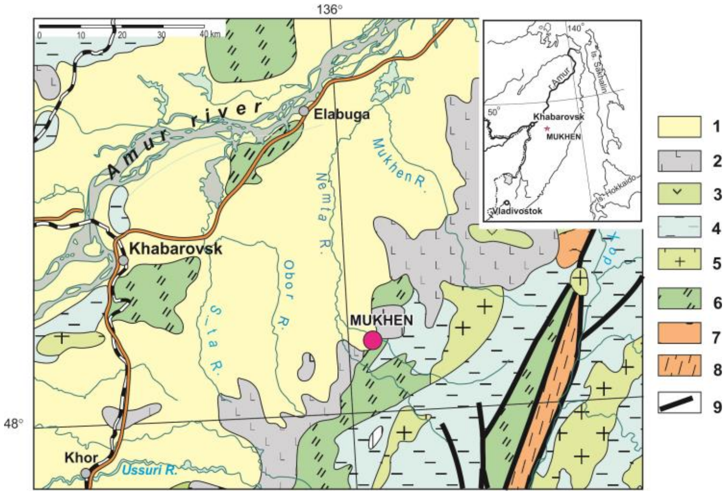

Fig. 1. Location and geology of the Mukhen spa area. 1 - (1) Quaternary alluvial sediments; (2) Pliocene–Quaternary basalts; (3) Early Cretaceous andesites; (4) Lower Cretaceous terrigenous deposits; (5) Early Cretaceous granites; (6) Jurassic volcanogenic–cherty–terrigenous deposits; (7) Triassic volcanogenic-terrigenous sediments; (8) Triassic gneiss; (9) faults.

2 Geology

The Mukhen spa is located on the border of the Middle Amur sedimentary basin, which is part of a complex geologic structure, and the large Sikhote-Alin mountain-folded system (Fig.1). The geological structure of the region is formed by Mesozoic basement, Oligocene–Miocene sedimentary and volcanic rocks, Pliocene–Lower Quaternary flood basalts, and Quaternary alluvium [1, 2]. The Mesozoic rocks are represented by the terrigenous sediments of the basement which are intruded by dikes of granodiorite, granite-porphyry, and layers of siltstones and sandstones. The Oligocene–Miocene rocks are 30–400 m thick and are composed of sands, gravel debris, and pebble. The large plate-like Oligocene–Miocene age dolerite and basalt bodies of 50 m thickness are overlain by bedrock. The study area contains many a fault zones, the largest being the Punchi fault zone which is approximately 150-200 m. Numerous gas seeps along these faults [3] extend from the western boundary of the region to the Mukhen River catchment beneath the volcanic and sedimentary rocks.

3 Sampling and analytical methods

The sparkling CO_2-rich groundwaters and their gas phases were sampled between 2000-2017. Measurements of water temperature, pH, Eh, alkalinity, and conductivity were performed directly in the field. Filtration through membranes with a pore size of 0.45 μm, was used to renove particulates. Major cations and anions were analyzed by ion chromatography, with trace element and REE concentrations determined by ICP–MS analysis at the Far East Geological Institute. Unfiltered water samples for H- and O-isotope analysis collected into glass tubes for later measurement of D/H and $^{18}O/^{16}O$ ratios (‰ SMOW) using a Finnigan MAT253 gas-source mass spectrometer. Analytical precision was ±0.8‰ for δ^2H and ±0.2‰ for $\delta^{18}O$.

Gas compositions were analyzed by gas chromatography and the C-isotope compositions (‰ PDB) determined by mass spectrometry. The precision of the $\delta^{13}C$. analysis is 0.25‰. A portion of the noble gas analysis was conducted by a static noble gas mass spectrometer (Micromass MM5400) at the Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology. The analytical error including reproducibility is ~3% [4].

4 Water and gas compositions

4.1 Water

Two groundwaters of different chemical composition are present in the Punchi catchment area: a Ca-Mg-HCO_3 type and a Na-HCO_3 type. The Ca-Mg-HCO_3 type is shallow water located at 100m depth, whereas the Na-HCO_3 type is a deeper water present below 200 m. The shallow water type typically has low TDS contents (< 1.7 g/L), pH 4.9 to 5.8, and a Ca/Mg molar ratio of about 0.94. The Na-HCO_3 groundwater type circulates below the Ca-Mg-HCO_3 water and is characterized by a narrow pH range of 7.2 to 7.5 and very high TDS contents of up to 14 g/L. The chemical composition data for both types of groundwater monitored over about a decade indicates stable concentrations of almost all components in the Na-HCO_3 water, excluding B_{tot} and Sr^{2+}. The Na–HCO_3 groundwater type haa elevated concentration of Cl^- (109–120 mg/l), B_{tot} (50–60 mg/l), Li^+ (up to 3.5 mg/l), Sr^{2+} (up to 0.3 mg/l), Br^- (0.15 mg/l) and I^- (about 0.04 mg/l). By contrast, the Ca-Mg-HCO_3 groundwater type has high levels of SiO_2 (80 mg/l), Fe_{tot} (up to 13 mg/l), Mn_{tot} (up to 0.6 mg/l) and Ba^{2+} (up to 0.2 mg/l). Both groundwater types exhibit positive correlations between K^+ and Li^+, Ca^{2+} and Mg^{2+}, SiO_2 and Fe_{tot}, and K^+ and Ca^{2+}. It is possible that these constituents enter both CO_2-rich groundwaters during the water-bedrock-gas interactions. The CO_2 intake in the groundwater system shifts the pH toward lower values (5.3 to 7.0), thus producing more aggressive solutions and, therefore, more intense weathering of the host rocks. In all samples studied, the REE concentration increases progressively with atomic number from La to Lu. Commonly, the unfiltered water samples have higher REE concentrations than filtered samples, as well as larger variations in the HREEs. Clear negative Ce anomalies ($Ce/Ce^* = -0.74$) are observed in the filtered samples, whilst surface and unfiltered samples are characterized by minor negative Ce anomalies ($Ce/Ce^* = -0.21$). Positive Eu anomalies are observed for all water and host rock samples studied. The REE concentrations and the shale-normalized REE patterns for both types of groundwater are similar and closely resemble the REE signature of the bedrock.

4.2 The gas phase

The chemical composition of dissolved and free gases for the two boreholes examined are almost identical, the predominant component is CO_2 gas (99.3 to 99.7 vol. %). Other gases are of minor proportion, with their total concentration <0.7% vol. The chemical composition of gas from the Mukhen spa is strikingly similar to that of gases from other CO_2-bearing spas (Table 1). However, the gas proportion in the two aquifers is different The groundwater from the upper aquifer has a gas-water ratio of about 3, whereas the groundwater of the lower aquifer demonstrates a high total gas saturation (~6.5 L/s) and the gas-water ratio varies in the range 32–50. The partial pressure of CO_2 in the groundwaters is 0.24 bar in the Ca-Mg-HCO_3 type and 0.47 bar in Na-HCO_3 type. The chemical compositions of the gas phase at selected spas are presented in Table 1.

Table 1. Chemical and isotope compositions of gases in sparkling springs of the Sikhote-Alin area.

Spa	pCO_2, bar	Content, vol.%				$\delta^{13}C_{PDB}$, ‰		$^3He/^4He$ (Ra)	$^4He/^{20}Ne$
		CO_2	N_2	O_2	other	free	dis.		
Mukhen[1]	0.24	99.5	0.04	0.09	0.04	-4.4	-4.6	5.34	4.03
Mukhen[2]	0.47	99.6	0.03	0.07	0.04	-3.5	-4.2	3.56	0.67
Shmakovka [3]*	1.7	96.4	1.26	0.07	2.27	-3.4	-4.19	4.06	1.12
Gornovodnoe*	0.74	94.7	5.05	0.05	0.05	-6.9	-10.8	6.52	19.2
Nijnie Lujki*	1.3	96.7	0.23	0.09	2.98	-5.2	-5.58	4.60	7.82

Notice: 1- Ca-Mg-HCO_3 type; 2 - Na-HCO_3 type; 3 – Medvejiy spring; *- data taken from [5]

5 Isotope data

5.1 Water

Measured δD and $\delta^{18}O$ values of Ca-Mg-HCO_3 groundwaters are similar to H- and O-isotopic compositions of surface water across the region and fall very close to the Global Meteoric Water Line (GMWL) on a δD-$\delta^{18}O$ plot (Fig.2). These compositions are similar to other CO_2 rich groundwaters within the region. Enriched in D but depleted in ^{18}O, the isotopic composition of the Na-HCO_3 groundwater type is unique and distinctly different from that of other high-pCO_2 waters. We suggest that the unusual isotope composition of the Na-HCO_3 groundwater might be caused by the high pressure of the CO_2 gas in the system during the infiltration of meteoric waters via overlying sediments.

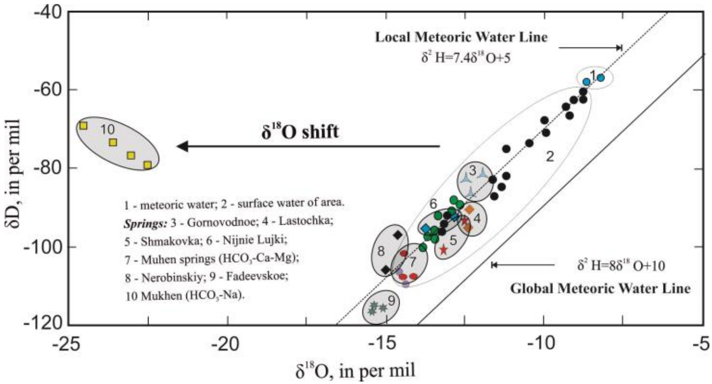

Fig. 2. Plot of $\delta^{18}O$ and δD for natural waters in the study area.

5.2 The gas phase

The source of CO_2 gas in CO_2-bearing cold spa waters in the Russian orient is still debatable. Therefore, we have investigated the genesis of $CO_{2gas\text{-}free}$ based upon $CO_2/^3He$ and $^4He/^{20}Ne$ ratios plus H-, He-, C-, and O- isotopic compositions [6, 7]. Our data indicate that $\delta^{13}C$ values for both dissolved and free gases are similar in the two boreholes studied, ranging from only –4.6 to –3.5‰ (Table 1). The comparison of $\delta^{13}C$ values for the gas phase in the Mukhen spa correlates with those in the high-pCO_2 spas in adjacent areas [5]. Measured $^3He/^4He$ ratios range from $2.85x10^{-8}$ to $9.21x10^{-8}$, which again is similar to previous determinations for other spas of the region [5]. Ratios of $^4He/^{20}Ne$ vary from 0.63

to 4.03 (Table 1). The positive correlation observed between $^3He/^4He$ and $^4He/^{20}Ne$ ratios indicates that noble gases in the spa waters are variable mixtures of deep-seated (mantle) and crustal components. It is possible that fluid derived from the mantle wedge (particularly CO_2) penetrated into the groundwaters, such that the original volatiles become contaminated with atmospheric and crustal components during the migration process. The geological setting of the area suggests that numerous regional faults could act as channels for the upward movement of deep-seated gas, with the local faults present across the region providing possible pathways for CO_2 movement to the surface. The minor (accessory) gases, such as N_2 and O_2, have an atmospheric character, and their concentrations vary due to technogenic factors (e.g. spa exploitation).

6 Conclusions

Chemical and isotope data for CO_2 rich groundwaters within the northern part of the Sikhote-Alin ridge, considered in the context of the regional geological and hydrological setting, allows us to conclude:

1. Both sparkling high pCO_2 groundwaters are meteoric waters, and their geochemical composition originates from water–rock–CO_2 interaction. The chemical composition of the Ca-Mg-HCO_3 type groundwater is due to the intense interaction of meteoric waters with bedrock. The Na-HCO_3 type groundwater formed during a long circulation of meteoric waters to deep crustal levels, where interaction occurred with shale, sandstone, and granite bedrock.
2. The main factor controlling the formation of the Mukhen spa water is the strong input of CO_2 along deep-seated faults in the subsurface aquifers. The isotopic data ($\delta^{13}C_{gas}$, $^3He/^4He$, $CO_2/^3He$) suggest that the CO_2 in two boreholes at the spa has a common deep-seated (probably mantle) source.
3. The negative $\delta^{18}O$ shift observed in the Na-HCO_3 type groundwater is a consequence of CO_2–H_2O isotope exchange at large CO_{2gas}/water ratios.

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