Water-Rock Interaction – Birkle & Torres-Alvarado (eds)

Geochemistry of the thermal waters of the Far East Russia and Siberia

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ABSTRACT: New geochemical data are reported on the low temperature thermal waters in Siberia and the Far East Russia. The studied alkaline waters belong to the HCO_3–Na type with significant trace element variations. The oxygen and hydrogen isotopic data of thermal waters suggest their meteoric origin. Dissolved gas is mainly nitrogen of atmospheric origin. The chemical composition of these results from water–rock interaction and strongly depends strongly on residence time and water/rock.

1 INTRODUCTION

The alkaline thermal groundwater of areas where absent recent volcanic activities are typically confined to fault zones, which facilitate penetration of infiltration waters in the high temperature horizons of the Earth. Examples of such water in Siberia and the Far East Russia are found in Belokuriha (Altay ridge), Baikal rift, Primorye (Sikhote-Alin ridge) and the Okhotsk region (Fig. 1).

The formation of thermal waters, especially in the Russian Far East, has not been studied very thoroughly. The available geochemical database on thermal waters is out of date, and contains only the major ions and some specific ions assumed to have medical effects (B, Br, and others). The first reliable trace element data on the Primorye thermal springs are reported by (Chudaeva et al. 1995) and those for the Okhotsk region reported by (Bragin et al. 2007 and Chudaev et al. 2008). However, the data are fragmentary and do not allow detailed interpretation of the regional geochemical characteristics for the formation of this type of thermal waters. In this paper, we report new geochemical data, obtained in 2006–2007 on the alkaline thermal waters of the Belokuriha springs, Baikal rift (North Baikal, Angarskii, Zipa-Bauntovskii springs) the Okhotsk region (Kuldyr, Annenskii, Tumninskii, Turma, and Lazarevskii springs) and the Primorye region (Chistovodnoe and Amgu springs).

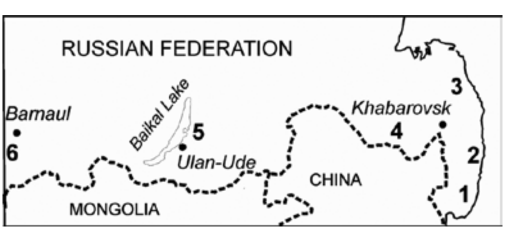

Figure 1. Location of studied hot springs. *Primorye region:* 1-Chistovodnoe, 2- Amgu. Okhotsk region: 3-Annenskii, Tumninskii, Turma & Lazarevskii; 4-Kuldur; Baikal rift: 5- North Baikal, Angarskii, Zipa-Bauntovskii; Al-tay region: 6-Belokuriha

2 METHODS

The unstable water parameters such as the pH, Eh, SEC (electroconductivity), DO (dissolved oxygen), and bicarbonate were measured *in situ*. The major cations and trace elements were analyzed using ICP-AES and ICP-MS on Thermo scientific iCAP 6000 and Agilent 7500c devices. The anion concentrations were measured using a LC-10 Avp (Shimadzu) liquid ion chromatograph. The oxygen and hydrogen isotopes were determined using a Finnigan-MAT 252 mass spectrometer. All these analyses were carried out at the Far East Geological Institute. The tritium concentrations were determined by liquid–scintillation counting using a Quantulus 1220 low-noise [alfa]–[beta] spectrometer at the Center of Isotope Research (VSEGEI). The computer modeling and calculation of the equilibrium reactions were done using the SOLMINEQ software package (Kharaka et al. 1988).

3 RESULTS AND DISCUSSION

The geological and hydrogeological characteristics of the nitric thermal waters of the Okhotsk and Primorye regions were reported in (Kiryukhin & Reznikov 1962, Bogatkov & Kulakov 1966, Chudaeva et al. 1999, Chudaev 2003, Chudaev et al. 2008). Most of the studied springs are located in the granite and/or their contact zones. The age of the granite intrusions varies widely (PR-K). The location of the intrusions are tectonically controlled and the waters penetrates along the fractures and faults. Maximum depth of water circulation is about 400 m. Measured temperature of the waters on the surface <100°C, and TDS is less than 500 mg/L.

3.1 *Major ions*

The studied thermal waters are characterized by pH >9 with Na as the predominant cation (Fig. 2). The concentration of sodium in this type of water as rule increases with increasing temperature of the water. According to the data of Ryzhenko et al. (1999, 2000), HCO_3–Na waters are formed in the granite/water system at the initial stages with high water/rock ratio. The sodium concentration in the studied thermal waters varies within 19–153 mg/L. The lowest contents were found in the Promorye region and the highest ones in Baikal rift springs.

It is lower than in the main European springs of this type and several times lower than in the similar water of the Republic of Korean (Michard 1990, Yum 1995). According to the thermodynamic calculations, sodium mainly occurs in the ionic form, and is an order of magnitude lower in the complexes of $NaCO_3^-$-$NaSO_4^{2-}$ than ionic. The potassium contents show no significant variations (1.2–0.33 mg/L) and practically do not differ from those in the water of shallow circulation. The thermal waters also have calcium contents within 2.0–5.4 mg/L. It is close to calcium variations in the thermal waters of the granite massifs of Europe and corresponds to the similar springs in Korea (Michard 1990, Yum 1995). Magnesium occurs in small amount in the alkaline thermal waters containing less than 0.03 mg/L. Similar thermal waters of Europe and Korea also have a low Mg content. The silica content in the thermal waters is 14.8–72 mg/L. The minimum concentration was found in Primorye, maximum in the Baikal rift. The contents of Si depends on the temperature water. High content of Si in Baikal rift (72 mg/L) corresponds to the highest calculated (quartz geothermometer) water temperature (116°C). The concentration (14.8 mg/L) of Si in Primorye is low as compared to the water temperature (60.8°C). Bicarbonate content in studied springs varies in widely range from 63.4 mg/L in Primorye to 207 mg/L (Baikal rift). The thermal waters contain low and weakly variable Cl contents, which correspond to those in surface waters: 1.4–23 mg/L. Sulfate ion behaves as a mobile complex. No saturation in calcium sulfate (gypsum or anhydrite) is attained in the alkaline waters. Its lowest contents were found in the springs of the Chistovodnoe springs (5.7 mg/l), and the highest contents, in the Belokuriha waters (22.6 mg/l). The TDS is mainly Composed of by sodium and bicarbonate, and partly, by silicon, whose content depends on the water temperatures.

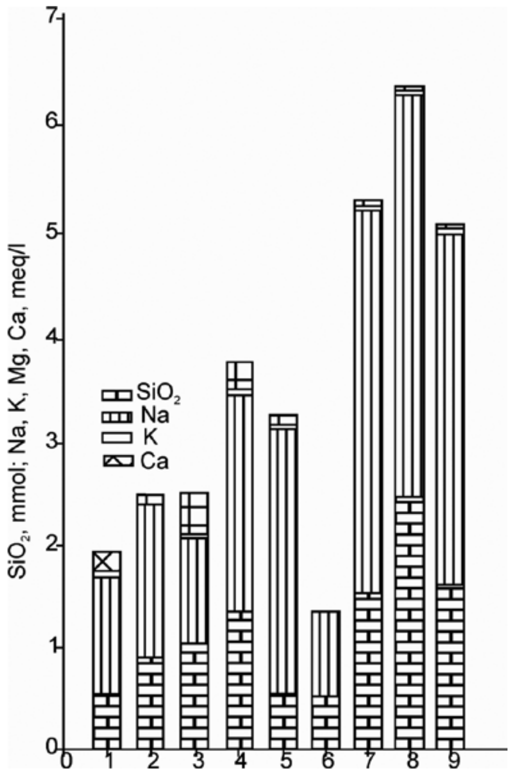

Figure 2. Proportion of the major cations and SiO_2 in thermal waters. 1–Chistovodnoe, 2–Amgu, 3–Tumninskii, 4–Annenskii, 5–Turma, 6–Lazarevskii, 7–Kuldur, 8–North Baikal region (Angarskii, Zipa-Bauntovskii), 9–Belokurikha.

3.2 *Trace elements*

Trace elements are subdivided into three main groups: siderophile, chalcophile, and lithophile. Rare earth elements (REE) will be described separately due to their particular geochemical features, though they belong to lithophile elements. Among the obtained trace element data (>50 elements), we deal with only the elements that emphasize the geochemical features of each of the selected water groups. Among the siderophile elements of most interest are iron, manganese, molybdenum, cobalt, and nickel. The thermal waters have a low Fe content within 0.013–0.005 mg/L, which somewhat increases only in the surrounding cold ground waters reaching 0.04 mg/L. The manganese concentration in the thermal waters, as that of iron, is extremely low, mainly below 0.1 μg/L. All the waters have high molybdenum contents, which are the highest in the Belokuriha springs (68.7 μg/L) and the lowest (6.2 μg/L) in the Annenskii springs. As is known, the molybdenum content in an alkaline environment is significantly higher than that in an acid environment. Cobalt varies within the limits 0.005–0.009 μg/L. The highest content was found in the Annenskii springs and the lowest, in the Chistovodnoe springs. The fresh river waters of the surrounding springs have an order of magnitude higher Co content. The nickel content increases northward from 0.033 μg/L in the Chistovodnoe springs to 0.43 μg/L in the Annenskii springs. The surrounding fresh waters contain 0.1–0.2 μg/L nickel. Among the chalcophile elements, we will consider copper and arsenic. The copper content in the studied thermal waters is low. In Belokuriha springs is about 8 μg/L; Baikal rift −1.2 μg/L. Lowest contents is 0.09 μg/L in Chistovodnoe springs. The lowest arsenic content was obtained in the Turma and Lazarevskii springs (2.41 μg/L) and the highest content, in the Kuldur springs (86.02 μg/L). Among the lithophile elements, we will consider Al, F, Li, The Al content in the studied waters varies within 3.6–19.5 μg/L. The highest contents were found in the Annenskii springs (19.5 μg/L). and the lowest contents, in the Chistovodnoe springs (3.6 μg/L). These values are insignificantly higher than those in the fresh waters. The F content in the studied thermal waters is within 0.8–24.7 mg/L with the lowest contents found in the Tumninskii springs (0.8 mg/L) and Amgu (0.9 mg/L) and the highest contents, in the Baikal rift. The Li content varies within 6.26–270 μg/L. The highest content was obtained in the waters of the Kuldur and the lowest content, in the Annenskii springs. The alkaline waters typically have low REE contents often within the detection limit of ICP-MS. An Agilent 7500s ICP MS equipped with a nebulaser allowed the direct determination of the REE contents in the studied thermal waters. Figure 3 demonstrates the REE patterns for springs of Primorye normalized to the North American Shale Composite.

The REE level in the thermal waters is close to that in the atmospheric precipitation (Chudaev 2003). All the studied waters show some HREE enrichment and Eu anomaly. Eu is supplied in the thermal waters from plagioclase during its interaction with the water.

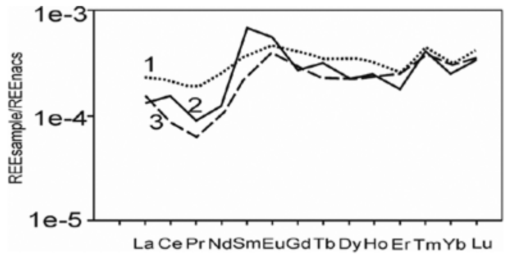

Figure 3. REE distribution pattern in studied springs of Primorye. 1–Amgu, 2–Chistovodnoe, 3–Tumninskii.

3.3 *Gas composition*

No significant deep supply of volatile components along the faults is observed at the discharge sites of the thermal waters. The absence of the influence of juvenile gases is confirmed by the low He isotopic ratio $^3He/^4He$ (0.1–0.24)*10^{-6} for the thermal waters of the Chistovodnoe (Bogolyubov et al. 1984). Data of Chudaev et al. (2008) indicate that the dissolved gases of the thermal waters of Primorye, as other thermal gases of the Far East, are dominated by nitrogen (up to 99%). The gas component presumably had an atmospheric origin.

3.4 *Isotope composition*

The oxygen and hydrogen isotopic compositions signify the meteoric origin of the water component in springs (Fig. 4).

The $^{87}Sr/^{86}Sr$ ratios are about 0.70638 in the Chistovodnoe group of thermal waters and 0.71027 in the fresh ground waters of this area. This ratio in the thermal springs of the Amgu group is within 0.70458–0.70483. In our opinion, the difference in the Sr isotopic ratios between the northern and southern groups of the thermal waters of Primorye is caused by the different water exchange rate. In particular, the tritium data on all the studied thermal waters showed that the tritium activity is less than the MDC, i.e., <0.97 Bq/l. This may indicate an older age than 50 years. Our data indicate that the cations in the atmospheric precipitation of the Far East Russia are dominated by sodium, whereas the ground waters have a mixed cation composition (Chudaev 2003). This can be explained by the fact that the HCO_3–Cl–Na rain water in the zone of the groundwater formation accumulates mainly calcium and carbonate ions owing to the decomposition of the soil organics, which leads to the formation of HCO_3–Ca–Na–Mg fresh ground waters. Further subsidence and heating of the waters is accompanied by the predominant accumulation of sodium via mainly plagioclase (albite) decomposition. This results in the formation of HCO_3–Na water. The results of Ryzhenko et al. (1999) of the modeling of the granite–water system showed that,

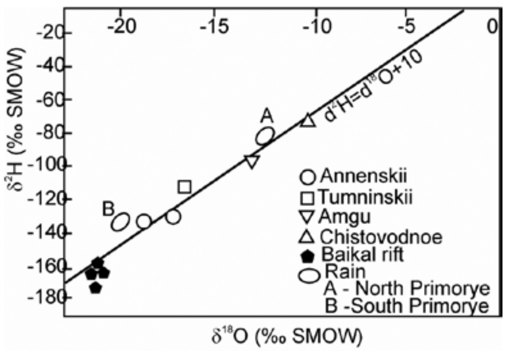

Figure 4. Variations of hydrogen and oxygen isotopes in thermal waters and atmospheric precipitation. The Craig (1961) world meteoric line is shown for comparison.

at the initial stage of the interaction (the water/rock ratio >> 1), weakly mineralized HCO_3–Na waters are formed. According to the calculations of Ryzhenko, the liquid phase in the water–granite system at a temperature >25°C has an alkaline reaction. The thermodynamic calculations showed that the studied thermal waters are supersaturated with respect to clay minerals (smectite, illite, and kaolinite), the group of low-temperature zeolites and albite. The calculation temperatures were close to 61°C in the Chistovodnoe springs, 81°C in the Amgu, 86°C in the Tumninskii, and 99°C in the Annenskii, 103°C in Kuldur and Belokuriha springs, 116°C in Baikal rift.

4 CONCLUSIONS

1. The considered thermal waters studied are low-salinity waters of the HCO_3–Na type. The level of most of the elements is lower than in similar waters of Europe and Korea. The content and behavior of the chemical elements in the waters is controlled by the water exchange rate and the formation of secondary equilibrium minerals.
2. The first obtained REE data showed their low contents close to those in the atmospheric precipitation. The REE distribution patterns indicate that their main source in the water were from plagioclases. The low salinity of the waters and the REE distribution pattern manifest to the rapid water circulation in the rock sequence.
3. The oxygen and hydrogen isotopic data indicate that the main water component is of meteoric origin.

ACKNOWLEDGMENTS

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