Vol. 44 Supp. SCIENCE IN CHINA (Series E) August 2001

Strontium hydrogeochemistry of thermal groundwaters from Baikal and Xinzhou

WANG Yanxin (王焰新)[1], SHEN Zhaoli (沈照理)[2]
& Shpeyzer Grigorii Moisevich[3]

1. Department of Hydrogeology and Environmental Engineering, China University of Geosciences, Wuhan 430074, China;
2. Department of Water Resource and Environmental Engineering, China University of Geosciences, Beijing 100083, China;
3. Laboratory of Hydrochemistry and Ecology Studies, Irkutsk State University, Irkutsk, 664033 Russia

Correspondence should be addressed to WANG Yanxin (email: yx.wang@cug.edu.cn)

Received December 12, 2000

Abstract This paper reports our work on the strontium hydrogeochemistry of thermal groundwaters in the Baikal Rift System (BRS) in Russia and Mongolia and the Xinzhou basin of the Shanxi Rift System (SRS) in northern China. Though similar in geological background, groundwaters from the BRS and the Xinzhou basin have different strontium isotope compositions. Both the strontium contents and the $^{87}Sr/^{86}Sr$ ratios of thermal water samples from Xinzhou are higher than those of most samples from Baikal. The major reason is the difference in hostrock geochemistry. The hostrocks of the Xinzhou waters are Archaean metamorphic rocks, while those of the Baikal waters except the Kejielikov spring are Proterozoic or younger rocks. In the study areas, cold groundwaters usually show lower $^{87}Sr/^{86}Sr$ ratio due to shorter water-rock interaction history and lower equilibration degree. Strontium hydrogeochemistry often provides important information about mixing processes. Ca/Sr ratio can be used as an important hydrogeochemical parameter. Case studies at Xinzhou show that thermal waters with lowest Ca/Sr ratios are most weakly affected by mixing with shallow groundwaters, as supported by our hydrochemical and sulfur isotope studies.

Keywords: strontium isotope, groundwater, hydrogeology, water-rock interactions, Baikal, Shanxi.

1 Introduction

In recent years, a lot of work has been done on strontium hydrogeochemistry, both as indicators of groundwater genesis and hydrogeochemical processes, and as constraints on flow and transport simulation models[1—4].

This paper reports part of our work on the hydrogeochemistry of thermal groundwaters in the Baikal Rift System (BRS) in Russia and Mongolia and the Xinzhou basin of the Shanxi Rift System (SRS) in northern China. Both systems are located on the east Asia continent and similar to each other in geological, geochemical and geophysical features[5]. The SRS is composed of three tectonic zones: the central NNE-orientated shear zone and the two extensional zones at both ends. The largest basins from north to south are the Datong, Xinzhou, Taiyuan, Linfeng, Houma, and Yuncheng basin. The BRS is also composed of three tectonic zones: the central Baikal Lake basin, and the two depression areas on the northeast and southwest. The largest basins from north to south are the upper Angara, Muyakan, upper Muiy, Muiy, Char, Tokkin, Tunkin basin in Russia and the Darhat and Hubsugul basins in Mongolia. Volcanism occurred in both systems from Eocene or Oligocene to Quaternary period. Most of the volcanic rocks are alkaline basalt.

There are two basic hydrogeologic units in the SRS and the BRS. One is hydrogeologic massif where groundwater occurs either in fissures-fractures of pre-Cretaceous metamorphic rocks or igneous rocks or in karst pores of Ordovician or Carboniferous-Permian carbonates (in Shanxi). The other is hydrogeologic basin where groundwater is found in porous media of Quaternary sediments.

2 Strontium isotope composition and water-rock interaction

Strontium geochemistry of thermal waters from Baikal has been studied by Plusnin et al.[1] and Pampura et al.[6]. In this study, 20 samples of surface water, groundwater and meteoric water were collected from Baikal and Xinzhou for strontium isotope and hydrochemical studies. The strontium isotope compositions were determined at the Geochemistry Institute of the Siberian Branch of Russian Academy of Sciences using mass spectrograph, and the hydrochemical compositions were analyzed at China University of Geosciences using ion chromatograph and ICP-MS. Labile water quality parameters including pH, temperature and dissolved oxygen were in-situ tested. $BaCl_2$ was in-situ added to water samples and $BaSO_4$ precipitate was then obtained by filtrating the samples. Sulfur isotope compositions were measured at the Ore Geology Institute of Chinese Geological Science Academy.

Though similar in geological background, groundwaters from the BRS and Xinzhou basin have different strontium isotope compositions (Table 1). Both the strontium contents and the $^{87}Sr/^{86}Sr$ ratios of thermal water samples from Xinzhou (Nos.14—18) are higher than those of most samples from Baikal. The major reason is the difference in hostrock geochemistry. The hostrocks of the Xinzhou waters are Archaean metamorphic rocks, while those of the Baikal waters except the Kejielikov spring are Proterozoic or younger rocks. The radioisotope ^{87}Sr is more enriched in older rocks. The hostrock of the Kejielikov spring is Archaean granite, which explains why it has the highest $^{87}Sr/^{86}Sr$ value among the Baikal water. The Wanshui and Baisha cold springs (Nos.20—21) have the lowest $^{87}Sr/^{86}Sr$ values among the Xinzhou waters. A shorter water-rock interaction history and a lower degree of strontium isotope equilibrium between groundwater and hostrock are the major reasons for the low $^{87}Sr/^{86}Sr$ values of the two springs.

For thermal groundwaters, the degree of overall strontium isotopic equilibrium between groundwater and hostrock can be calculated according to Elderfield et al.[7]:

$$\text{equilibration} = [(^{87}Sr/^{86}Sr)_{\text{altered rock}} - (^{87}Sr/^{86}Sr)_{\text{fresh rock}}]/[(^{87}Sr/^{86}Sr)_{\text{water}} - (^{87}Sr/^{86}Sr)_{\text{fresh rock}}] \times 100$$

The average $^{87}Sr/^{86}Sr$ value for the Baikal thermal waters is 0.7076. The $^{87}Sr/^{86}Sr$ value of the unaltered granite sampled from a 312 m deep borehole at the North Muiysk tunnel of the BRS is 0.7063 and that of altered rock around the thermal spring outcropping inside the same tunnel is

0.7071. The equilibration degree is calculated to be 61%, implying that the thermal water is not equilibrated with the hostrock. This conclusion is consistent with that from our geothermometer studies[5].

Table 1 Temperature, strontium contents and strontium isotope compositions of groundwater samples from the BRS (Nos.1—13) and Xinzhou (Nos.14—20)

No.	Sample name & type	T/℃	Sr/mg • L^{-1}	^{87}Sr/^{86}Sr
1	Muyakan, spring	57	0.25	0.71001
2	Upper-Zaimkin, spring	27	0.26	0.71247
3	Bushang, spring	48.5	0.13	0.71065
4	Shulinkin, spring	67.5	1.00	0.71088
5	Harkus, spring	46	NA[a]	0.70950
6	Baontov, spring	53	0.01	0.71001
7	Kejielikov, spring	62	0.07	0.72899
8	Arlin, spring	72	0.14	0.71067
9	Shieyiuy, spring	51	0.05	0.71058
10	Daphshin, spring	45	0.40	0.70882
11	Zmein, spring	45	0.07	0.70663
12	Gushishin, spring	72	0.85	0.70992
13	Goriaqin, spring	49	0.40	0.70707
14	Shangtangtou, well	49	1.14	0.73597
15	Wangdongbao, well	57	2.59	0.74260
16	Qichun, well	63	0.28	0.73917
17	Dunchun, well #1	44	0.91	0.74763
18	Dunchun, well #2	39.5	0.64	0.74644
19	Dunchun, well #3	24.5	0.46	NA
20	Wanshui, spring	8.5	0.14	0.71594
21	Baisha, spring	11	0.16	0.71459

a) Not analyzed.

As shown in Figure 1, the strontium isotope compositions of the thermal groundwaters from northern part of the BRS (except the Kejielikov spring) decrease from northeast to southwest. The waters with lowest ^{87}Sr/^{86}Sr values are located at the central part of the BRS where neotectonic activity and geothermal gradient are greatest. The R/R_a value (R is the ^{3}He/^{4}He value of water sample, and R_a that of air) of these waters are commonly high, up to 7.85[5]. Therefore it can be postulated that the deep faults developed at the central part provide the pathways for the upward migration of mantle-originated fluid with a higher ^{3}He/^{4}He ratio and a lower ^{87}Sr/^{86}Sr ratio.

3 Strontium hydrogeochemistry and mixing processes

Mixing phenomenon, one of the most important hydrogeological processes controlling groundwater properties, should be recognized and well studied before and during long-term and large-scale exploitation of thermal groundwater resource, since mixing of different types of waters results in inaccurate determination of water ages, flow patterns, and hydrodynamic parameters calculated from pumping test data, and leads to poor management decisions[8]. Mixing processes commonly occur in the genesis of thermal groundwaters. Strontium hydrogeochemistry often

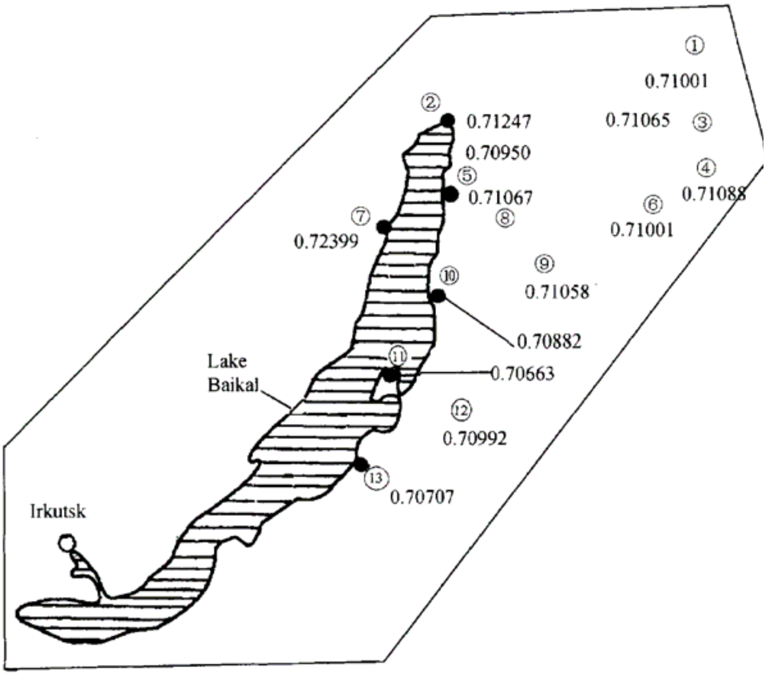

Fig. 1. The ^{87}Sr/^{86}Sr values of thermal groundwaters in northern and central part of the Baikal Rift System. It can be seen that the values decrease from northeast to southwest. The thermal waters with lowest ^{87}Sr/^{86}Sr values are distributed around the eastern bank of the Baikal Lake where the tectonic activity and heat flow are the greatest. The sample numbers and locations of the thermal waters are the same as in Table 1.

provides valuable information about the processes.

The geochemical behavior of strontium is similar to that of calcium. Ca/Sr ratio is therefore often used as an important hydrogeochemical parameter. A case study was done at Xinzhou. Since sodium is commonly the predominant cation of thermal waters that are formed in Archaean metamorphic rocks in Xinzhou and calcium the predominant cation of shallow cold groundwater, thermal waters with lowest Ca/Sr ratios are most weakly affected by mixing with shallow groundwaters. As can be seen from Fig. 2, the thermal waters from Xinzhou have lower Ca/Sr ratios than cold waters. Samples No.15 and No.16, with higher water temperatures (57 and 63℃ respectively) and sodium concentrations (80 and 90 milliequivalent percent) than the rest of thermal waters from Xinzhou, are therefore most weakly affected by mixing with cold shallow groundwaters. This explains why the two samples are located at the left corner of

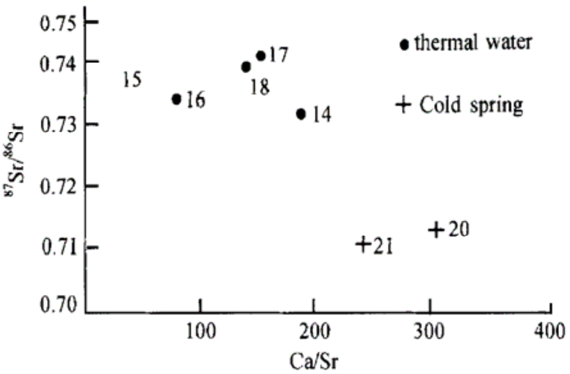

Fig. 2. The Ca/Sr - ^{87}Sr/^{86}Sr plot of groundwaters from Xinzhou.

the $^{87}Sr/^{86}Sr$-Ca/Sr plot. The two samples at the right side of the plot are the Wanshui and Baisha cold springs. The thermal waters (No.14, 17 and 18) appearing at the middle of the plot are more or less affected by mixing processes.

Hydrochemistry and sulfur isotope compositions of groundwaters from Xinzhou provide additional information about mixing processes. On Piper's diagram, thermal water from Xinzhou and the two cold springs appear on two sides (Fig.3). The four samples at the center of the diamond shape were collected from water-supply wells at Duncun, indicating the influence of ther mal waters from depth on their hydrochemistry. One important hydrochemical features of the thermal waters from Xinzhou that were weakly affected by mixing processes is that they are in reduced state and therefore have high concentrations of hydrogen sulfide. For instance, the H_2S

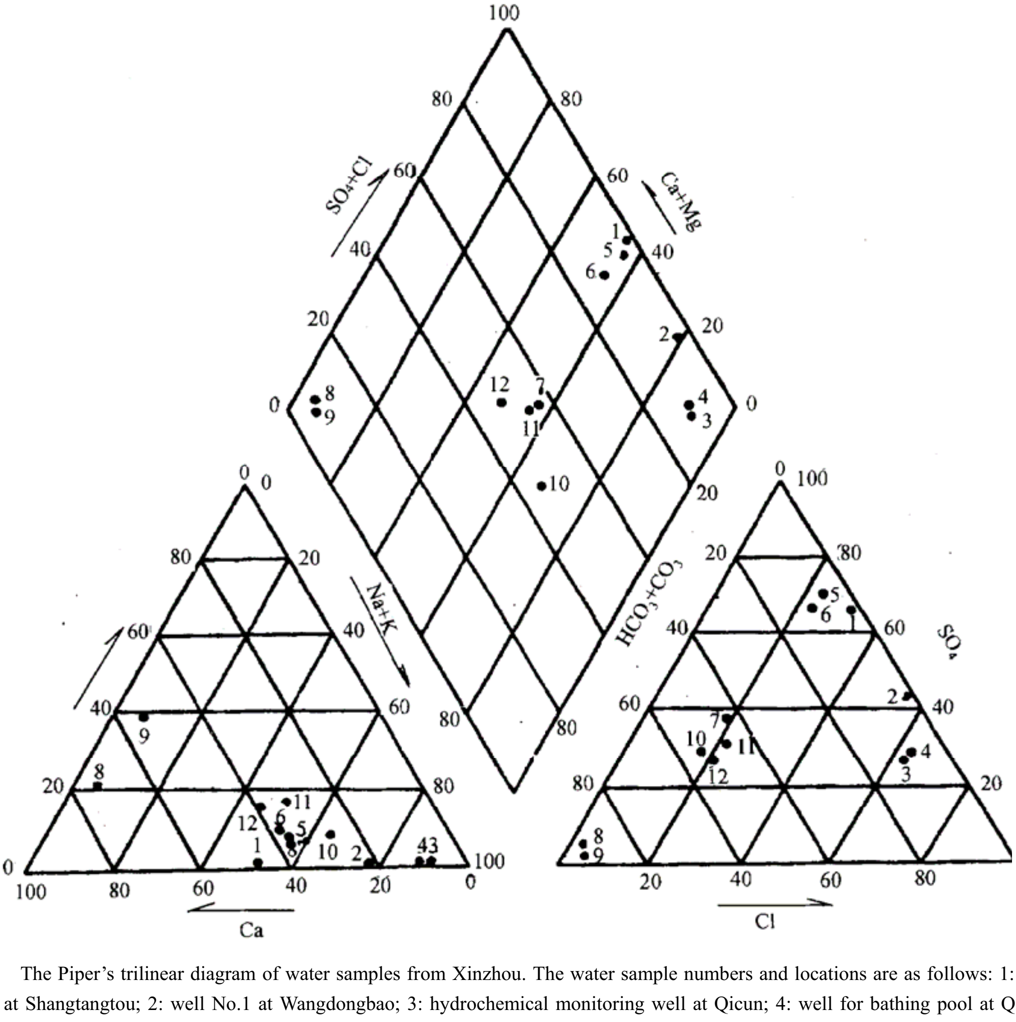

Fig. 3. The Piper's trilinear diagram of water samples from Xinzhou. The water sample numbers and locations are as follows: 1: well No.19 at Shangtangtou; 2: well No.1 at Wangdongbao; 3: hydrochemical monitoring well at Qicun; 4: well for bathing pool at Qicun; 5: well # 1 at Duncun; 6: well #2 at Duncun; 7: well #3 at Duncun; 8: the Wanshui spring; 9: the Baisha spring; 10—12: irrigation wells G1,G4 and G7 at Duncun. The correspondence of the water samples to those in Table 1 are: No.1, 2, 3-No.14, 15, 16; No.5, 6, 7, 8, 9-No. 17, 18, 19, 20, 21.

content in the Qicun deep borehole (sample 16 in Table 1) is 9.9 mg/L. Correspondingly, these waters should have a lower sulfate concentration and a lower $\delta^{34}S$ value. From Fig. 4, it is clear that there are two groups of thermal waters: one is sample 15 and 16, and the other sample 14 and 17. The samples 15 and 16 with highest temperatures among the Xinzhou waters are from boreholes that were better installed to prevent from mixing with cold shallow groundwaters. Besides, all available hydrochemical data in Xinzhou show that the SO_4/Cl values of cold shallow groundwaters are greater than 1.0. Therefore, if plotted on Fig. 4, they should be located above samples 15 and 16, as are the cases for samples 14, 17 and 19.

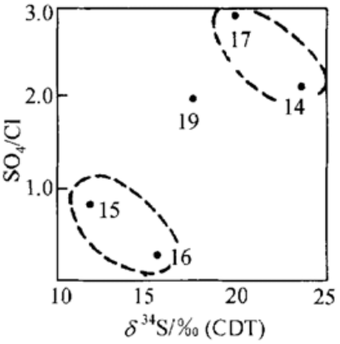

Fig. 4. The SO_4/Cl-$\delta^{34}S$ plot of water samples from Xinzhou. The water sample numbers and locations are the same as in Table 1.

4 Conclusions

Strontium hydrogeochemistry provides important information about the genesis and dynamics of thermal groundwaters from the study areas.

(1) Though similar in geological background, groundwaters from the BRS and Xinzhou basin have different strontium isotope compositions. Both the strontium contents and the $^{87}Sr/^{86}Sr$ ratios of thermal water samples from Xinzhou are higher than those of most samples from Baikal. The major reason is the difference in hostrock geochemistry.

(2) Ca/Sr and $^{87}Sr/^{86}Sr$ ratios, in combination with hydrochemical data, help discern mixing processes in the genesis of thermal waters.

Acknowledgements The research work was financially supported by the National Natural Science Foundation of China (Grant No. 49832005), Ministry of Science and Technology of China (Grant No. 95-pre-39) and The Higher Education Ministry of Russia.

References

1. Plusnin G. C., Genesis of hydrothermal fluids of the Baikal Rift Zone using isotopic data, (in Russian with English abstract), Geochemistry, 1978, 9: 481—487.
2. Chaudhuri, S., Clauer, N., Strontium isotope compositions and potassium and rubidium contents of formation waters in sedimentary basins: Clues to the origin of the solutes, Geochimica et Cosmochimica Acta, 1993, 57: 429—437.
3. Lyons, W. B., The use of strontium isotopes in determining groundwater mixing and brine fingering in a playa spring zone, Lake Terrell, Australia, Journal of Hydrology, 1995, 167: 225—239.
4. Johnson, T. M., DePaolo, D. J., Rapid exchange effects in isotope ratios in groundwater systems, Water Resources Research, 1997, 33: 187—195.
5. Pampura, V. D., Sandimirova, G. P., Geochemistry and strontium isotope composition in hydrothermal systems, Novosiberiask: Nauka(in Russian), 1991.
6. Elderfield, H., Greaves, M., Strontium isotope geochemistry of Icelandic geothermal systems and implications for seawater chemistry. Geochimica et Cosmochimica Acta, 1981, 45: 2201-—2212.
7. Wang, Y., Shpeyzer, G. M., Hydrogeochemistry of mineral waters from rift systems on the east Asia continent: case studies in Shanxi and Baikal (in Chinese with English abstract), China Environmental Science Press, 2000.
8. Mazor, E., Drever, J. I., Finley J., et al., Hydrochemical implications of groundwater mixing: an example from the southern Laramie Basin, Wyomin,. Water Resources Research, 1993, 29: 193—205.