Abstract

This paper offers the results obtained through a survey of $^{37}$Cl and $^{81}$Br stable isotopes in ground saline waters and brines in sedimentary and intrusive rocks of the Siberian Platform. Over 60 ground water samples collected in wells and springs have been analyzed. In addition, the chlorine and bromine isotope compositions in deep ground waters of the Siberian Platform have been compared with that of ground waters in crystalline rocks of the Canadian and Fennoscandian Shields, as well as in sedimentary sequences of the North China Plain. Preliminary results showing patterns of distribution and isotope compositions in ground brines of the Siberian Platform confirm the meteoric nature of the chloride Na brines, as well as formation of chloride Ca brines from evaporated paleo-seawater.

1. Introduction

The genesis and evolution of brines in platform sedimentary cover and basement highs is of prime interest in hydrogeochemical investigations recently complemented by comprehensive isotope studies. Cl and Br stable isotopes have been broadly utilized as useful tracers to constrain the origin of chloride ground waters or for investigating geochemical evolution of bittern connate waters in sedimentary basins. Studies of processes causing fractionation of halogen isotopes have revealed that Cl isotopes fractionate due to salt precipitation, evaporative concentration of brines, ion exchange and diffusion, the latter playing a significant role in bromine isotope fractionation.
This paper aims at describing the distribution of $^{37}$Cl and $^{81}$Br stable isotopes in chloride ground waters of the Siberian platform, to enlarge the databank on their isotope features and to assess the feasibility of using halogen isotopes as a critical tool for unraveling the water-rock evolution of the Siberian Platform since Early Cambrian time.

2. Sampling and analysis

Research on halogen isotopes in ground waters of the Siberian Platform was initiated in 2005 in collaboration with Canadian scientists from the Waterloo University. A total of 47 samples of Na-Ca chloride type waters with salinity varying from 38 to 626 g/l were analyzed for their Cl and Br isotopic compositions. Analyses were performed by Isotope Ratio Mass Spectrometry (IRMS) with an analytical precision of 0.1 ‰ for $^{37}$Cl and $^{81}$Br. In 2014, the analyses of the State Key Laboratory of Biogeology and Environmental Geology of the China University of Geosciences determined $\delta^{37}$Cl and $\delta^{81}$Br in 20 samples of Ca-Na chloride brines with salinity of 40-434 g/l. Water samples were collected through depth 244-3389 m. The analyses were performed using the GasBench II-IRMS by Thermo Finnigan MAT-253. The $^{37}$Cl and $^{81}$Br isotopes were measured with precision 0.07 and 0.06 ‰, accordingly. The results acquired in this study for the isotope features of ground waters collected in the sedimentary and intrusive rocks of the Siberian platform constitute the foundation of this article.

3. Geology and hydrogeology

The Siberian Platform, including the studied hydrogeological formations, occupies the area over 4 000 000 km$^2$, extending from the Laptev Sea in the North to the Baikal Lake in the South (Fig. 1). The geological-tectonic and hydrogeological features of the platform developed since the late Upper Cambrian due to trap and kimberlite magmatism, accumulation of halogen sequences in the southern part and carbonate ones on the northern termination and long-term erosion. Particular conditions of heat exchange led to formation of the unique cryolithozone in the north-eastern part of the craton, which thickness reaches over 1400 m. Groundwaters are found in the sedimentary cover down to depth of 2-3 km, they are saline to strongly saline brines of primarily chloride sodium or calcium (in places mixed) composition.

![Fig.1. Location of the Siberian Platform.](image)
4. Results and discussion

Figure 2A provides generalized data on the distribution of Cl isotopes in the geological section. The range of Cl isotopes in natural systems generally covers about 15 ‰: from –8 ‰ in pore waters of subduction zones, to +7 ‰ in volcanic gases. In ground waters of different regions the Cl isotope variations were established within the narrow range: viz. –2.5 to +2.5 ‰ (SMOC). In the ground saline waters of the Canadian and Fennoscandian Shields with salinity varying from 1.9 to 258 g/l the range is broader, going from –0.78 to +0.98 and –0.54 to +1.52 ‰, respectively.

The few data on δ⁸¹Br value in the ground waters of crystalline and sedimentary rocks are also depicted on the diagram (Fig. 2B). In ground saline waters of the North China Plain occurring in the largest oil-gas field of the Hebei province (composed of Mesozoic-Cenozoic sandstones and argillites) the δ⁸¹Br values are positive: going from +0.28 to +1.22 ‰ (SMOB). In the ground waters of the crystalline rocks within the shields they vary differently: in the Canadian Shield from +0.01 to +1.29 ‰, in the Fennoscandian Shield they are +0.26 to 2.04 ‰ and in the oil-gas field Oseberg (Norway) the values amount to +0.08 to +1.27 ‰ (SMOB).

Based on available data, we have defined ranges for δ³⁷Cl and δ⁸¹Br variations in ground waters of the Siberian Platform; these are –1.67 to +1.54 ‰ (SMOC) and –0.80 to +3.35 ‰ (SMOB), respectively. The δ³⁷Cl values are within the range (–2.5 to +2.5 ‰) reported for ground waters of different regions of the world. The range of δ⁸¹Br values in ground waters of the platform sediments is close to that in ground waters of the Williston sedimentary basin (the North America).

In chloride calcium brines the values of Cl and Br stable isotopes show greater variations (Fig. 2): δ³⁷Cl ranges from –1.67 to +1.26 ‰ (scatter 2.93 ‰), and δ⁸¹Br from –0.8 to +1.47 ‰ (scatter 2.27 ‰). Salinity of very
concentrated brines reaches 626 g/l, bromine content is 8.5 g/l and genetic coefficient Cl/Br amounts to 25-83. Chloride calcium brines are referred as the formation water. The chloride sodium brines are characterized by a smaller range of Cl isotope ratios and larger range for Br isotopes against calcium brines: $\delta^{37}$Cl varies from $-0.29$ to $+1.54$ ‰ (1.83 ‰), $\delta^{81}$Br varies from $-0.07$ to $+3.35$ ‰ (3.42 ‰). Salinity of these waters changes from 44 to 318 g/l, Br content is not high (on average 380 mg/l), and Cl/Br coefficient reaches 8000. These are typical leaching brines.

Variations of halogen isotopes in chloride calcium brines may indicate a common source of the elements supplied into ground waters and an equal impact of evolutionary geochemical processes (diffusion, ion filtration, etc.) of buried bittern connate waters. This observation is also confirmed by the positive correlation ($R^2=0.62$) between $\delta^{37}$Cl and $\delta^{81}$Br (Fig. 3). Enrichment of chloride sodium brines with heavy-Br isotopes proceeded through the process of chloride salt leaching and subsequent evaporative concentration of brines at the stage of their formation.

![Fig.3. $\delta^{37}$Cl vs. $\delta^{81}$Br in brines of the Siberian Platform (SMOW - Standard Mean Ocean Water).](image)

5. Conclusion

The $\delta^{37}$Cl and $\delta^{81}$Br values in ground waters of the Siberian Platform fall within the range currently documented for ground waters in different regions of the world. The range of $\delta^{37}$Cl values virtually coincides with that of Cl isotope in ground waters of crystalline shields and North China Plain. The $\delta^{81}$Br in ground waters of the platform in many cases turns out to negative, as in the sedimentary Williston basin (North America). This may indicate quite different ways of ground water evolution in the Siberian Platform and crystalline shields, on the one hand, and similar processes controlling the isotope composition of brines in sedimentation basin, on the other hand.

The application of stable halogen isotopes with the other hydrogeochemical parameters is useful for constraining ground saline water and brine origin. Preliminary results showing patterns of distribution and isotope compositions in ground brines of the Siberian Platform confirm the meteoric nature of the chloride Na brines, as well as formation of chloride Ca brines from evaporated paleo-seawater.
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