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GEOCHEMISTRY

Isotopes of Sulfide and Sulfate Sulfur in Nitrogen Hot Springs of the Bauntov Group (Baikal Rift System)

L. V. Zamana[a], Sh. A. Askarov[a], S. V. Borzenko[a], O. V. Chudaev[b], and I. V. Bragin[b]

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The issue of sulfur sources is one of the most debatable in the problem of the formation of modern nitrogen hot springs of the Baikal Rift Zone (BRZ). In addition to the popular point of view on the origin of the chemical components of hot springs by the interaction in the water–rock system, there are concepts according to which sulfur, as well as fluorine, are introduced by deep (subcrustal) fluids [1, 2, and others]. The only evidence for this are the statements that the high sulfate concentrations in hot springs cannot be provided by the host rocks, which are mainly represented by acid crystalline varieties, especially granitoids. We established the concentration of isotopes of dissolved sulfide and sulfate sulfur in hot springs of the BRZ for the first time. This allows us to interpret the nature of sulfides and sulfates in this type of hot spring formed without spatial and genetic links to modern volcanism on factual evidence.

With few exceptions, nitrogen hot springs of the BRZ have a sodium cation composition, but significantly differ by anions. They are mainly represented by hydrocarbonate, sulfate, and intermediate hydrocarbonate–sulfate and sulfate–hydrocarbonate compositions. As a rule, hot springs are alkaline with a pH of up to 10.3 and a mineralization of up to 0.5 g/l; in sulfate hot springs it may reach 1.0 g/l ore more [3]. They often contain hydrogen sulfide, but its concentrations are low (up to 33 mg/l) [4]. The concentration of sulfate ions reaches 900 mg/l. Radiolithical oxidation of sulfide sulfur of host rocks is considered as one possible mechanism of the formation of high SO_4^{2-} concentrations [5]. The physicochemical characteristics of nitrogen hot springs presented in this paper were obtained using known analytical techniques. The sulfate-ion was determined turbidimetrically as barium sulfate; pH and Eh values were measured by the potentiometrical method directly on the sources. Hydrogen sulfide (in our case, hydrosulfide) and native sulfur after its transition to the sulfide form were measured by [6], with a photometric (microconcentrations) or iodometric (macroconcentrations) end. Precipitates for the isotopic analysis of sulfide sulfur were obtained by deposition with cadmium acetate; sulfate sulfur, with barium chloride. Because of the low hydrogen sulfide concentration, we did not manage to obtain an amount of precipitate sufficient for analysis for two of the five sampled hot springs; only sulfate sulfur was analyzed for them. Isotopic measurements were performed on a Finnigan-MAT 252 apparatus in the Analytical Center of the Far East Geological Institute, Far East Division, Russian Academy of Sciences. The isotopic composition was calculated on the basis of the meteoritic standard.

Recent studies of the isotopic composition of sulfate sulfur for eight hot springs of the Barguzin Baikal area demonstrated positive $\delta^{34}S$ in the range of 13.4–29.5‰ [7]. The authors explained the heavy sulfur composition by dissolving of endogenous sulfates (anhydrite, celestine, barite, thenardite, and others), which, in their opinion, were deposited during the volcanic activity at the early stages of rift formation.

However, the geological data supporting the presence of sulfate mineralization, which is more likely related to Cenozoic volcanism, are absent. The Vitim volcanic plateau, which, in the opinion of the authors of [7], provides evidence for such a possibility, is located near the rift zone, outside the arched uplift, where rift valleys were subsequently formed [8]. It is not only separated by the Ikat Ridge from feeding areas of hot springs of the Baikal region, but is related to another drainage basin as well. The considered hot springs of the Barguzin River basin are localized in the central part of the rift zone being completely amagmatic, as was concluded by N.A. Logachev. "Basaltic and doleritic dykes in the Archean Sharyzhalgai block on the southern Baikal end, as well as the dyke of

[a] *Institute of Natural Resources, Ecology, and Cryology, Siberian Branch, Russian Academy of Sciences, Chita*
[b] *Far East Geological Institute, Far East Division, Russian Academy of Sciences, Vladivostok*
e-mail: l.v.zamana@mail.ru

Isotopic composition of sulfide and sulfate sulfur in hot springs of the Bauntov group

Hot spring	Sample	T, °C	pH	Eh, mV	S^{2-}, mg/l	$\delta^{34}S^{2-}$, ‰	S^{6+}, mg/l	$\delta^{34}S^{6+}$, ‰
Tochin	AT-09-2	56.1	8.77	−226	7.8	2.4	8.7	25.2
Bauntov	AT-09-3	52.0	8.93	−198	7.6	2.6	8.3	36.2
Mogoi	AT-09-4	83.7	8.85	−230	12.8	1.2	10.6	18.5
Busan	AT-09-5	55.2	8.68	−197	1.08	–	6.7	23.3
Shurindin	AT-09-6-2	67.0	8.88	0	0.03	–	57.0	14.5

glassy biotite augitite on the Ushkan'i Islands, that is everything known about young magmatism there" [8, p. 115]. The same conclusion is supported by the recent interpretation of geophysical data on the Baikal basin [9].

The data on sulfate sulfur isotopes in nitrogen hot springs of Tianshan were interpreted in a different way. The concentration of $\delta^{34}S$ there (eight sources) ranged from +6 to +17.4‰ at an average value for granites of +3.2‰ in comparison with the meteoritic standard [10]. The heavy sulfur composition in these hot springs was explained by fractionation in the course of bacterial sulfate reduction; as this takes place, the wide diversity of $\delta^{34}S$ values, in the opinion of the author of [11], depends on the degree of sulfate reduction. Such reduction results in the appearance of hydrogen sulfide in hot springs and increase of the concentration of hydrocarbonate- (carbonate-) ions forming as a result of accompanying microbiological oxidation of organic carbon with simultaneous decrease of the sulfate concentration. Sulfide sulfur becomes lighter, and sulfate sulfur becomes heavier in the course of fractionation.

The definite influence of sulfate reduction in enrichment of sulfate sulfur in a heavy isotope is evident from the data on hot springs of the Baikal area considered above. The lighter composition is established in sulfate hot springs, namely Gargin and Gusikhin (13.6 and 14.8‰, respectively), in which signs of sulfate reduction were not registered, whereas the concentration of ^{34}S in hot springs of the sulfate–hydrocarbonate or hydrocarbonate–sulfate composition typical for hydrogen sulfide hot springs increases.

The data obtained for hot springs of the Bauntov group (table) located in the Vitim River Basin (Lena River drainage system) on the eastern flange of the central part of the BRZ and including the most high-temperature hot spring similar to that described in [7]. They provide evidence for the enrichment of sulfate sulfur in heavy isotopes as well. Its maximal concentration exceeds not only the values for sulfate of the oceanic water (20.1 ± 0.8‰) and modern evaporates (24.3‰), but the known upper limit of the range for acid rocks (26.7‰ at a lower limit of −13.4‰) as well being second only to sulfates of salt plugs (up to 62‰ in single samples; all values are from [12]).

Sulfide sulfur of the studied hot springs is significantly depleted in heavy isotopes in comparison with sulfates, which is possible only with their bacterial reduction. In a deep source of sulfide sulfur, sulfates formed by its oxidation should have the same isotopic composition, because in this case there is no isotopic fractionation [12]. In addition, chemical oxidation of sulfide sulfur under reduced environments at high Eh values (table) is practically impossible, although bacterial oxidation in near-surface conditions occurs in the studied hot springs to a small extent. This is evident from the presence of native sulfur in them found in the Mogoi (0.147–0.224 mg/l) and Bauntov (0.072 mg/l) hot springs; it is formed only by oxidation of sulfide sulfur. Chemical and especially bacterial sulfur oxidation is sharply strengthened to the end that results in decrease in the hydrogen sulfide concentration and abundant development of bacterial communities in the hot springs including sulfur-oxidizing species.

The isotopic characteristics of various forms of sulfur in hot springs of the volcanic areas significantly differ from nitrogen hot springs of the BRZ. Deep (magmatic) sulfur has a lighter isotopic composition. Practically the same isotopic compositions of sulfide sulfur (in metal sulfides) and hydrogen sulfide sulfur (in gases) from −6.1 to +3.0‰ were established in hot springs of the Uzon Caldera (Kamchatka). As a whole, they are close to the meteoritic composition that is consistent with the concepts on a deep subcrustal sulfur source [13]. In hot springs of the fumarole fields of the Mendeleev Volcano (Kunashir), the $\delta^{34}S$ value for sulfates is ~−3.2‰; in the Golovnin Volcano caldera this value ranges from 1.9 to 2.5‰ [14], and in native sulfur it varies from 0.0 to +3.2‰ [15]. Sulfate enrichment in heavy isotopes up to 22.1‰ in the Stolbovskii hot spring (Kunashir) and up to 22.5‰ in hot springs of the Uzon caldera is registered only when sulfates were inherited from sea deposits. When H_2S coming from magmatic chambers with a concentration of 15 vol % in the gaseous phase is oxidized, hot springs of volcanic areas become acid; this is not observed in hydrogen sulfide hot springs of the BRZ.

Thus, our data, as well as those presented in [7], provide definite evidence for crustal rock sulfur sources in nitrogen hot springs of the BRZ. The established variations of the isotopic composition of sulfate sulfur in hot springs are most likely explained not only by various intensities of sulfate reduction in them, but also by the different isotopic composition of sulfur in water-bearing acid crystalline rocks with the ^{34}S range reaching 40‰.

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