Mineral waters and sediments of the ferruginous spring Ulan-Bulak Urulyunguevsky (South-Eastern Transbaikalia, Russia)

L V Zamana
Institute of Natural Resources, Ecology and Cryology Siberian Branch of RAS, 16a, Nedorezova Street, Chita, 672014, Russian Federation
E-mail: l.v.zamana@mail.ru

Abstract. The data on the chemical composition and content of balneological components (Fe, H₂SiO₃, CO₂, S²⁻) for three water samples from the Ulan-Bulak acidic ferruginous spring are presented. For the first time, carbonic water was released in the composition of the spring waters, the origin of which is explained by the ingress of hydrocarbonate water into an acidic medium, followed by dissociation according to the HCO₃⁻ + H⁺ → H₂CO₃ → H₂O + CO₂ scheme. An acidic environment is formed as a result of oxidation of sulfide mineralization, presumably gold-bearing. From secondary minerals at the spring, modern sulfate minerals (gypsum, jarosite), hydromica (illite) were found, ocher sediments are widely developed. Given the uncertain nature of the formation of the spring waters, it is considered worthy of special studies, including an inspection of the presence of sulfide mineralization.

1. Introduction
The purpose of this article is to provide information on the detection of carbon dioxide and hydrogen sulfide mineral waters on a known ferruginous spring and on the composition of modern mineral sediments.

2. Object and methods
The ferruginous spring Ulan-Bulak Urulyunguevsky is located in the South-Eastern Transbaikalia on the left bank of the river Argun' in 20 km from settlement Priargunsk (figure 1). It is represented by several concentrated outlets and seeping in the sides of a weakly incised creek valley on the southeastern slope of the Nerchinsky ridge. The total length of the mineral water outlet is 600–700 m with the total maximum flow rate of the spring being about 1.0 l/s. The geographic coordinates of the spring are 50°30.637’ N lat., 118°55.094’ E, and the absolute elevation of the central part of the spring opening is about 630 m. The outlet of mineral water is confined to the zone of junction of the Middle Riphean metamorphic rocks with the Lower Cretaceous effusive-sedimentary deposits. The former are represented by metamorphosed effusive, quartz-mica, carbonaceous-argillaceous, quartz-graphite and greenstone shales, and the latter – by sandstones, siltstones, mudstones, conglomerates, andesite-basalts.
The components of the chemical composition of water were determined in the laboratory of the Institute of Natural Resources, Ecology and Cryology of the Siberian Branch of the Russian Academy of Sciences (Chita) using generally accepted methods. Carbon dioxide components were found by potentiometric titration, chlorine and fluorine – by potentiometry, sulfate ion – turbidimetrically in the form of BaSO₄, nitrogen compounds – by colorimetry. Cations and some metals, including iron, were determined at high concentrations by the atomic absorption method. In this case, samples passed through a blue ribbon paper filter were analyzed. In addition, samples filtered under pressure through a membrane filter with a pore diameter of 0.45 μm were analyzed by the ICP-MS method at the Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences (Irkutsk). The mineral composition of modern sediments was analyzed by XRD on the DRON-3 apparatus at the Institute of the Earth's Crust, SB RAS (Irkutsk).

3. Results and discussion

The Ulan-Bulak spring belongs to the so-called Gaisk type of acidic ferruginous waters [1], N.I. Tolstikhin distinguished from this spring an independent Ulan-Bulak type. In terms of anionic composition, such waters, like the spring water, are exclusively sulfate. The cationic composition according to the results of testing from 03.09.2016 (table 1) according to samples UB-16-1 and UB-16-3 is magnesium-calcium, according to sample UB-16-2 – magnesium-calcium-ferrous.

Iron in the spring water was found in concentrations of 225–1263 mg / L, which is higher in maximum value than in acidic drainage waters of ore deposits in Transbaikalia, in which the Fe content did not exceed 1009 mg / l.

In addition to iron, according to the content of metasilicic acid H₂SiO₃ (52.4–72.4 mg / L), the waters are also mineral, and according to the concentration of CO₂, calculated from the difference in total and free acidity, in some outputs the water is carbonic, while at the sampling site UB-16-2 slight emission gas was observed. A periodic release of gas in the main outlet in the form of a funnel with a diameter of up to
1.0 m was observed during sampling in June 2012 [2]. According to the standard adopted in Russia, water with free CO₂ content of more than 500 mg / L is classified as carbonic.

**Table 1. Physicochemical indicators of water samples from the Ulan-Bulak spring.**

| Indicator | UB-16-1 | UB-16-2 | UB-16-3 | Indicator | UB-16-1 | UB-16-2 | UB-16-3 |
|-----------|---------|---------|---------|-----------|---------|---------|---------|
| T, °C      | 15.1    | 7.6     | 15.5    | Si        | 24.8    | 26.0    | 18.8    |
| pH        | 3.17    | 3.79    | 3.08    | Al        | 13.0    | 15.1    | 80.3    |
| Eh, mV    | 488     | 216     | 517     | Mn        | 66.5    | 126.2   | 84.1    |
| CO₂, mg / L | 299   | 1707    | 638     | Fe        | 237.9   | 1263    | 225.5   |
| SO₄²⁻     | 3234    | 5767    | 3930    | Cu        | 0.30    | 0.09    | 0.37    |
| Cl⁻       | 4.9     | 2.1     | 8.2     | Zn        | 5.7     | 12.4    | 9.9     |
| F⁻        | 1.46    | 3.88    | 7.22    | Li, μg / L | 213    | 220    | 381    |
| NO₃⁻      | 2.22    | 0.89    | 1.77    | Be        | 4.9     | 27     | 29     |
| Ca²⁺      | 697.5   | 639.8   | 678.0   | Co        | 707     | 430    | 1206    |
| Mg²⁺      | 187.8   | 259.7   | 291.0   | Ni        | 1384    | 3420   | 3348    |
| Na⁺       | 112.4   | 59.2    | 65.1    | As        | 5.7     | 2.4    | 2.3     |
| K⁺        | 9.96    | 14.6    | 0.34    | Sr        | 3400    | 2121   | 1882    |
| NH₄⁺      | 1.45    | 0.55    | 0.59    | Ag        | 0.69    | 0.57   | 0.50    |
| Σ ions    | 4258    | 6748    | 4982    | РЗЭ      | 455     | 2208   | 3353    |

*Results of analyzes by ICP-MS method.*

The origin of CO₂ from carbonic waters is usually explained by mantle input, thermometamorphism of carbonate rocks, or biochemical decomposition of organic matter in sedimentary cover rocks. In particular, the participation of all three sources is recognized for the carbonic waters of the Greater Caucasus [3]. For carbonic waters of Southeastern Transbaikalia, the participation of the mantle component is excluded due to the geological and structural features of the territory [4]. In the case of the Ulan-Bulak spring, the origin of carbon dioxide may be special, associated with the neutralization of the acidity of the aquatic environment by a hydrocarbonate ion, followed by the dissociation of the resulting carbon dioxide according to the scheme HCO₃⁻ + H⁺ → H₂CO₃ → H₂O + CO₂ when the hydrocarbonate waters developed in the adjacent territory enter the acidity zone, which is formed as a result of the oxidation of sulfide minerals. In this case, due to the predominance of oxidative processes, the acidic environment is retained, and carbon dioxide components at pH <4.5 are in the form of CO₂. When solubility is exceeded, CO₂ passes into the gas phase.

Sample UB-16-3 found 290 mg / L S²⁻ (more than in the water of the Matsestra resort), which determines the water as "strong" hydrosulfuric. A faint smell of hydrogen sulfide was also felt in sample UB-16-1, in which the concentration of sulfide sulfur was 3.1 mg / L, which is lower than the balneological norm (10 mg / L) for hydrogen sulfide waters.

It is believed that acidic ferruginous high-metal waters are associated with the oxidation of sulfide deposits. In the materials of geological works, the presence of ore occurrences at the site of unloading of the source and the adjacent territory is not indicated. In terms of physicochemical parameters, including high concentrations of a number of metals, the spring waters are similar to the acidic waters of the gold deposits of Eastern Transbaikalia [5].

In addition to the high content of iron and the combination of different types of mineral waters in one place, the Ulan-Bulak spring is distinguished by abundant deposition of secondary mineral formations. The bottom of the valley, up to 80–100 m wide and 0.6–0.7 km long over the entire area of its outlet, is covered with brownish-yellow ocher deposits with a small content of shale gruss and quartz fragments up
to 30 cm in size with leached voids or ferruginous veins. On the fragments to a height of up to 2–3 cm in the zone of the capillary border, outgrowths of small crystals of mineral new formations of white color are formed, in more elevated places (up to 30–40 cm above the surface of ocher deposits), as a rule, deposits in the form of clusters of gray color, as shown determination by X-ray diffraction, are mainly gypsum.

X-ray phase analysis investigated 4 samples of modern mineral sediments. Three of them had the following phase composition: 1) hydromica (illite) \((K,H_3O)(Al,Mg,Fe)_2[(Al,Si)_{10}](OH)_2 \cdot H_2O\) – 35% ± 5, jarosite \(KFe_3(SO_4)_2(OH)_6\) – 20% ± 5, goethite \(FeOOH\) – 20% ± 5, quartz \(SiO_2\) – 15% ± 5; hematite, gypsum, feldspar, chlorite, mixed-layer minerals are also possible; 2) gypsum \(CaSO_4 \cdot 2H_2O\); 3) gypsum – 90% ± 5, jarosite – 8% ± 5, traces of quartz. The appearance of the deposits and the X-ray diffraction pattern of a gypsum sample are shown in Figure 2. Sulfate minerals are locally distributed and form thin surface accumulations, probably with the participation of water evaporation in their formation.

![Figure 2. Appearance of gypsum deposits and X-ray of its sample.](image)

The fourth sample, taken from ocher, is mainly represented by an X-ray amorphous phase (figure 3), which usually includes iron oxides and hydroxides (hematite, lepidocrocite, limonite, etc.). Of the
Impurities in it, according to the analysis, the presence of quartz, goethite, and jarosite is possible. Ocher makes up the bulk of hydrogenous deposits, their thickness exceeding 1 m.

4. Use of spring waters
The acidic ferruginous waters are used by the sanatorium-resort network on a singular basis. Known sanatorium Gai in the Orenburg region, where these waters are used externally for the treatment of the musculoskeletal and nervous systems diseases, as well as the skin and gynecological ones. In GOST R 54316–2020 [6] such waters are not included as drinking waters, therefore, they are not considered. However, in the seasonal sanatorium on the sour ferrous spring Azhyg-Sug in the Republic of Tuva, water is also consumed internally for the treatment of gastrointestinal diseases, and this water is also bottled [7]. At the Ulan-Bulak spring, the local population spontaneously treats the musculoskeletal system, nervous system, skin and gynecological diseases.
5. Conclusion
Thus, the Ulan-Bulak mineral spring is characterized not only by exceptionally high iron content, but also by the manifestation in one place of various types of mineral waters – ferroginous, carbonic and hydrogen sulfide. Based on the concept of the relationship of acidic ferruginous waters with sulfide mineralization and taking into account the presence of fragments of primary quartz in the composition of modern ocher sediments, one can expect the presence of gold-quartz formation mineralization in the area of its outcrop. Elucidation of the nature of the formation and the reasons for the high acidity of the Ulan-Bulak spring is of significant scientific interest and deserves special research, including an inspection of the site for the presence of gold mineralization.

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