

## Geological-hydrogeochemical characteristics of a “silver spring” water source (the Lozovy ridge)

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**Abstract.** Geological and hydrogeological characteristics of the Lozovy ridge (Southern Primorye) are studied, as far as karst phenomena are widely distributed within its boundaries. Water-bearing rocks of the karst water source “Silver Spring” (“Serebryany Klyuch”), which is located near the bottom of the “Bear’s fang” (“Medvezhiy klyk”) cave, are investigated. It is found that karst rocks are presented by calcite (CaCO<sub>3</sub>), and an accessory mineral is barite (BaSO<sub>4</sub>). It is determined that among the trace elements forming the composition of carbonate water-bearing rocks the maximum concentrations are typical for Sr, Ba, Fe, Al, Zn, Mn, Cu, and Ni. Also, the chemical composition of the waters taken from the “Silver Spring” water source is studied. These waters are fresh, hydrocarbonate, calcium, and weakly alkaline. Among the elements of the spring, such elements as Sr, Ba, Fe, Al, Zn, Mn, Cu, and Ni have the maximum concentration. The other elements have concentrations less than 1 µg/l.

### 1. Introduction

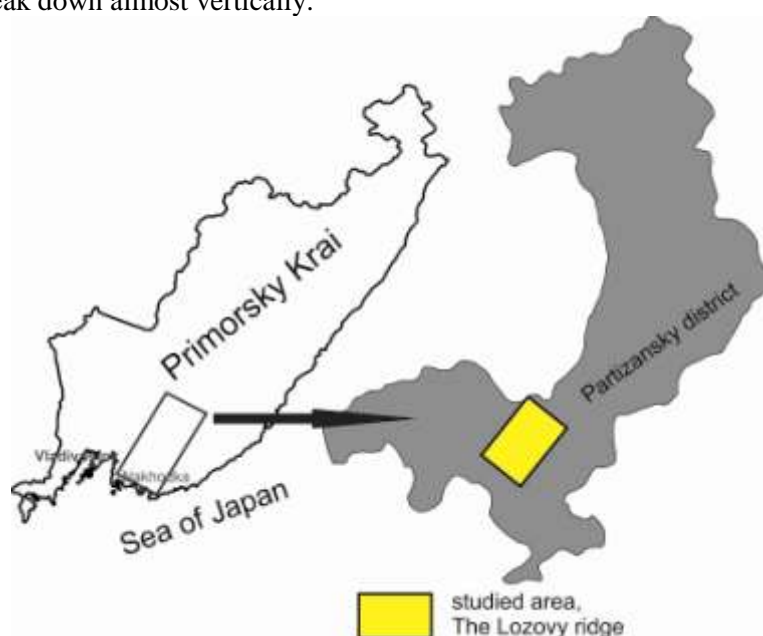
Karst phenomena are widely spread. Geologically, about one third of the Earth’s land has the conditions for karst development. However, karsts do not have uniform distribution. Thus, limestone karst forms karst areas in the Pyrenees, the Alps, and the Carpathians. The Alps are characterized by intensively developed karst within mountain ice highlands bordered with limestone. Karst develops well in the Ordovician and Silurian limestone on the southern slope of the Baltic crystalline shield: on Aland and Gottland islands. In Central Europe karst develops in the Paleozoic rocks and Mesozoic calcareous formations embracing the territory of the Krakov Jura, numerous karst areas of Czechoslovakia, and Czech karst [3, 4]. Karst development is typical for Balkan Peninsula: Kras (Karst) plateau, Slovenian highland, Istrian Peninsula, and the Dinaric Alps. In the Carpathians carbonate karst develops, mostly, in reef limestones. In the Crimea karst phenomena are spread in mountain and steppe areas. Karst is rather wide spread in the Urals, Southern Siberia, in spots of Central and Eastern Siberia, and in the Far East. Therefore, in Eastern Primorye karstland the carbon-Permian and high-Triassic rocks are karstified, as well as reef limestones. In addition, sodded and bare karst is distributed with swallow holes, craters, rock shelters, and caves. In Southern Primorye karstland reef limestones of the late-Permian age are karstified. Also, sodded and bare karst is spread with swallow holes, craters, sink holes, and pepino hills [3].



## 2. Research object

The research objects are the karst waters of the Lozovy ridge and water-bearing rocks. The materials obtained by the authors as a result of their field works, having been carried out in August, 2015, are used in the paper. In addition, the published materials of the other authors are cited [1,6]. Rapidly changing parameters, such as temperature, Eh, pH, electric conductivity, and hydrocarbonate-ion content have been determined during field investigations and *in situ* hydrochemical testing. Rock and water samples have been investigated in the Primorsky centre of local elemental and isotope analysis (the Far East Geological Institute, the Far Eastern Branch of the Russian Academy of Sciences).

The studied region is related to the Partizansky karst area of the Primorsky Territory (Figure1). The Lozovy ridge is the remnant massif formed by reef limestones, and it continues down to 7 km. The massif is stretched between the Partizanskaya and Novorudnaya rivers, northward of Nakhodka. It is bordered by low highly destroyed denudation watershed mountains. Alongside the distinguished geological features, the dominating role of the Partizanskaya river influences the territory hydrology. The massif slopes directed towards the Partizanskaya valley are flatter than the opposite stiff slopes of the ridge, which break down almost vertically.



**Figure1.** Sketch map of the studied area.

Karst in the southern part of the massif is mostly bare, and in the northern part it is partially sodded. Karst surface is presented by swallow holes, grooves, rock remnants, rock shelters, craters, pot holes. As to subsurface karst structures, a few tens of caves are known, including the deepest cave in the Primorsky Territory – “Solyanik”, as well as the caves called “Bliznets”, “Dalnyaya”, “Skvoznaya”, “Malaya”, “Mechta Speleologa”, “Medvezhiy Klyk”, etc.

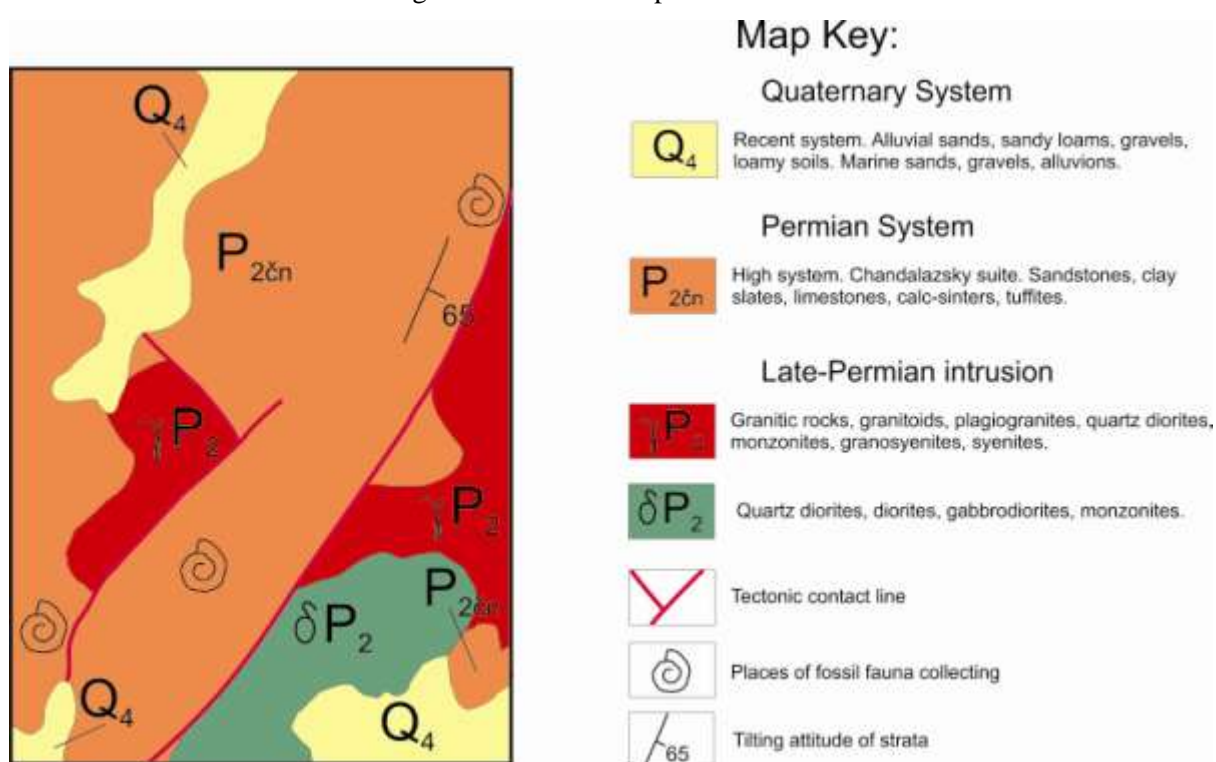
The geology of the Lozovy ridge is studied in details [2,6,10,11]. The high-Permian sediments are widely spread within the studied area. They are presented by marine, marginal-marine and continental formations (Figure 2).

The Sicinsky suite (P2sc) is formed by terrigenous, igneous-sedimentary and igneous rocks being in the equal ratio. The thickness of the suite is 280 meters in the northern part of the area, and it increases up to 630 meters in the Nakhodka region.

The Chandalazsky suite (P2cn) is spread as a broken band, and it extends from Trudny Peninsula to the Povorotnaya river basin. It overlies the Sicinsky suite. The suite is formed by limestones, aleurolite horizons (the first scores of meters), and bands of conglomerates, sandstones and aleurolites interbedding. On the whole, the suite composition does not change in the strike. The suite thickness is 385-570 m.

Alluvial sediments (aQ) build up an accumulative part of high terraces. They are presented by inequigranular sands with occasional fine pebble and clays with interbeds of loamy and sandy soils. The thickness of sediments reaches 50 m [1, 12].

Hydrogeologically, the territory of the Partizansky karst region including the Lozovy ridge refers to the southern part of Sikhote-Alin hydrogeological area. The area is characterized by low mountain relief and arterial drainage. The zone of active water exchange with the thickness of 300-500 m. occupies the upper fractured part of horizontal section: quaternary deposits, the upper section part of the Cenozoic intermountain area. Ground waters are formed, mostly, due to atmospheric precipitation infiltration and surface waters. Deep carbonate karst rock are present. Mainly, they are connected with a perched water subzone and the zones of alternating, horizontal, and, partially, siphon circulation. Solutional caves, karts channels, coves and caverns are attributed to this group. Quaternary deposits are the most water-abundant. Water-bearing strata and complexes of a fracture-karst-stratal type are associated with carbonate and terrigenous-carbonate deposits of the late Paleozoic.



**Figure 2.** The Partizansky region (The Primorsky Territory) geological map.

### 3. Results and discussion

One of the main conditions for karst development is permeability of karsting rocks determined by their porosity, fractures, and cavernosity. The authors have investigated the adjacent rocks and waters of the “Silver Spring” source (N43°0'49", E133°1'18") coming out near the bottom of the karst massif, close to the “Bear’s Fang” cave. The “Bear’s Fang” cave is located at the height of 430 m. above sea level on the narrow rocky ridge. Cave rocks are divided by fracture systems of various thickness and directions. The expansion of cave cavity has finished due to mountain massif destruction and its drainage area elimination. The “Silver Spring” discharge does not exceed 50 l/sec. The chemical composition of waters is shown in Table 1.

In basic physical and chemical properties, spring waters are fresh (mineralization – 243mg/l), weakly alkaline (pH 8,1), hydrocarbonate, and calcium ones. Ions of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  have strictly subordinate value in the salts composition. The concentration of organic carbon ( $\text{C}_{\text{org}}$ ) in waters reaches 1.6 mg/l, which makes only 4% of the total dissolved carbon.

Trace elements in karst waters do not determine the chemical type of water and its general mineralization; they are contained in insignificant quantities determined by the first mg,  $\mu\text{g}$ , and fractions of  $\mu\text{g}$  per 1 liter [7]. The trace elements are determined using the method of atom-emission spectrometry with inductively coupled plasma at the iCAP 6500Duo spectrometer (the analysts: Gorbach G.I., Tkalina E.A., Khurkalo N.V.). The trace elements composition of the “Silver Spring” waters is shown in Table 1. Only Ca is notable for its high concentration with regard to an average value for the waters of hypergenesis zones. It is worth saying that the “Silver Spring” karst waters are poor with trace elements, and only such elements as Sr, Ba, Fe, Al, Zn, Mn, Cu, and Ni have concentrations ranging from 6 to 46  $\mu\text{g/l}$ . Such elements as Li, Pb, As, Se, Rb, V, Cr, Ag, U, Cs, Co, Y, Cd, Ce, La, Sc, Nd, Ga, Tl, Gd, Pr, Dy, Sm, Er, Be, EuTb, Ho, Yb, Th, Tm, and Lu are characterized by decreased values (the concentration is less than 1  $\mu\text{g/l}$ ).

**Table 1.** Physical and chemical parameters of the “Silver Spring” karst waters

Components	Units	Karst waters	Average value for waters of hypergenesis zones [8]	Components	Units	Karst waters	Average value for waters of hypergenesis zones [8]
T	$^{\circ}\text{C}$	8	–	Cu		1.17	5.58
pH		8.1	6.9	Zn		6.18	41.4
Eh	mV	152	–	Ga		0.0083	0.37
TDS		243	469	As		0.40	1.46
$\text{Ca}^{2+}$		72.3	39.2	Se		0.321	0.72
$\text{Na}^{+}$		2.22	67.6	Rb		0.261	1.86
$\text{Mg}^{2+}$		1.23	18.2	Sr		46.0	183
$\text{K}^{+}$		0.54	5.15	Y		0.0281	–
Si		4.00	8.3	Ag		0.181	0.26
$\text{HCO}_3^{-}$	mg/l	156.10	187	Cd		0.0243	0.24
$\text{SO}_4^{2-}$		5.33	70.7	Cs		0.041	0.26
$\text{Cl}^{-}$		2.05	59.7	Ba		13.86	18.3
$\text{NO}_3^{-}$		1.34	2.4	La		0.0151	0.67
TC		40.50	–	Ce	$\mu\text{g/l}$	0.0186	–
IC		38.90	–	Pr		0.0028	–
TOC		1.60	8.29	Nd		0.0120	–
Li		0.84	13.0	Sm		0.0026	–
Be		0.0018	0.19	Eu		0.0017	–
Al		8.43	226	Gd		0.0032	–
Sc		0.0150	0.07	Dy		0.0027	–
V		0.252	1.34	Er		0.0019	–
Cr	$\mu\text{g/l}$	0.233	3.03	Yb		0.0015	–
Mn		1.40	54.5	Tl		0.0037	–
Fe		11.11	481	Pb		0.493	2.97
Co		0.0392	0.39	Th		0.0004	0.24
Ni		1.06	3.58	U		0.0799	1.31

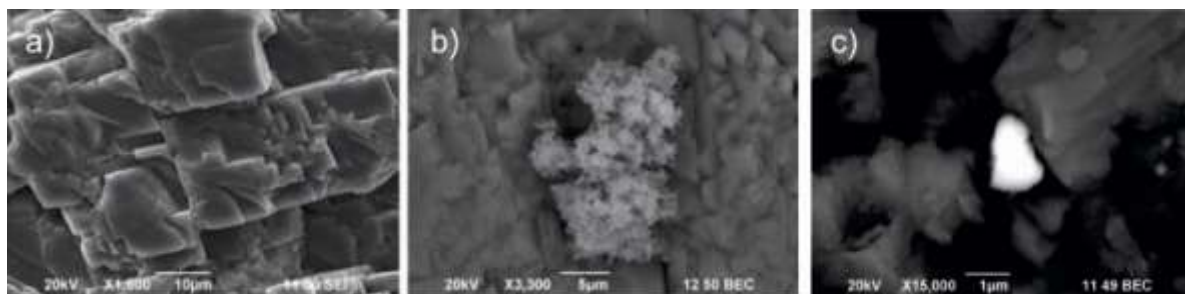
Note: «–» – no data; T – water temperature; TDS – total dissolved salts; TC- total carbon; IC – inorganic carbon; TOC – total organic carbon.

Strontium has good migration properties, and it is easily leached out of rocks. This fact is proved by one of the highest concentration values among the trace elements in the studied waters (46  $\mu\text{g/l}$ ). The content of strontium in waters is determined, mostly, by the time of water interaction with rocks. Barium has lower chemical activity than strontium, therefore, its content in ground waters is much lower (14  $\mu\text{g/l}$ ). According to the results of ICP-MS, total distribution of heavy metals in the “Silver Spring” karst waters has the following sequence:  $\text{Fe} > \text{Zn} > \text{Mn} > \text{Cu} > \text{Ni}$ , though their concentrations are small, and they range from 11 to 1  $\mu\text{g/l}$ , respectively.

To determine the sources of chemical elements in waters, the microelement composition of adjacent rocks has been studied. It is performed using the method of mass-spectrometry with inductively coupled plasma at the Agilent 7500 spectrometer (the analyst: Elovsky E.V.). The main elements of the studied rock are CaO– 54.9 wt.% и SiO<sub>2</sub>– 0.92 wt.%. Among the elements found in the composition of carbonate rocks, the maximum concentrations are typical for Sr (374 g/t), Cu (15.9 g/t), and Ba (18.6 g/t). Cr, Ni, Zr, La, Ce, Nd, Y, Sc, V, As, and Pb are characterized by the content ranging from 1.0 to 8 g/t. The minimum concentrations are found among Sn, Cs, Tb, Tm, Lu, Hf, and Ta.

Strontium should be set apart all the other trace elements, because its concentration is the highest one. It could be met in rocks of any lithologic composition. Mostly, it is found in the composition of carbonate rocks, either as an impurity element, or as calcium isomorphous substitutions in the structure of carbonate minerals' crystalline lattice (limestone and dolomite). Strontium is fully engaged in the processes of dissolution and leaching occurring under the influence of atmospheric and ground waters. Moreover, strontium may form separate minerals – strontianite (SrCO<sub>3</sub>) and celestine (SrSO<sub>4</sub>), though they have not been found on the investigated territory [9]. Strontium has not been observed in the sample studied by the electron microscope, either.

Petrographic research of rocks has been performed at a JeolJSM 6490LV scanning electron microscope with an INCAEnergy 350 add-on unit (the analyst: Bushkareva K.Yu.). Based on the sample analysis, it is possible to make the following conclusion: the karst rocks of the “Bear’s Fang” cave are presented by calcite (CaCO<sub>3</sub>) with a small part of magnesium (Figure 3, a). The obtained results are proved by the archival materials [2]. It is stated that the main rock components are CaO (55 wt.%) and MgO (0.5 wt. %). FeO (Figure 3, b), SiO<sub>2</sub>, TiO<sub>2</sub>, as well as single crystals of pyrite (FeS) and Au, have been identified as microinclusions. Barite (BaSO<sub>4</sub>)(Figure 3, c) is the most widespread accessory mineral. Also, the alloys of CuNi- and CuZn-types are met, which have, probably, a technogenic origin.



**Figure 3.** Photos of the Lozovy ridge carbonate rocks samples obtained using the JeolJSM 6490LV electron microscope: a) CaCO<sub>3</sub> morphology, b) FeO morphology, c) BaSO<sub>4</sub> microinclusions in carbonate.

#### 4. Conclusion

The analysis of the obtained material allows confirming the fact that the carbonate karst type is typical for the Lozovy ridge, where karsting rocks are the limestones of the Chandalazsky suite. Carbonate rocks contain Sr, Ba, and Ni in the high amount. Their mineral forms, except Sr, have been proved by the use of electron microscopy. Ground waters held in Paleozoic terrigenous-carbonate sediments form the complexes of a fracture-karst-stratal type. The spring waters are also characterized by the maximum concentrations of such elements as Sr, Ba, Fe, Al, Zn, Mn, Cu, and Ni, the sources of which are carbonate adjacent rocks. The obtained geochemical characteristics for the karst rocks of the “Spring Silver” water source demonstrate that water aggressiveness is insignificant in relation to carbonate rocks. The vertical down-flow water communications occur only on the slopes due to the significant vertical filtration gradient.

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