

## Hydrochemical characteristics of Lastochka Spa (Primorye, Far East of Russia)

N.A. Tchepkaia\*, G.A. Chelnokov, A.A. Karabtsov, I.A. Tarasenko

*Far East Geological Institute, Far East Branch of Russian Academy of Sciences, Vladivostok, Russia*

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### Abstract

This study presents new data on major, trace and REE element concentration of groundwaters in Lastochka spa located in the northern part of Primorye, Far East of Russia. The studied area is characterized by two types of groundwaters issued from a spring and wells: fresh waters with low mineralization (Total Dissolved Solids is up to 400 mg/l) and high pCO<sub>2</sub> waters with high mineralization (TDS is up to 4700 mg/l). New data and previous  $\delta^{13}\text{C}_{(\text{TIC})}$ , oxygen ( $\delta^{18}\text{O}$ ) and hydrogen ( $\delta^2\text{H}$ ) isotope data indicate that these waters result from meteoric water infiltration in the Sikhote–Alin mountain, circulating at shallow depths in sedimentary rocks. CO<sub>2</sub> in groundwater is of mantle origin.

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### 1. Introduction

The spa of Lastochka with high pCO<sub>2</sub> waters is well known in the Russian Circum-Pacific Region and widely used as a source of potable bottled water. This spa is located in the northern part of the Primorye region, in the southwestern part of Ussuri River catchment.

The investigation of Lastochka spa has been carried out over a period of 100 years. During this period, the detail geohydrological characterization of the region which allows to understand groundwater circulation paths was performed (Fomin et al., 1977; Chelnokov, 1978, 1997). The investigation of chemical composition of the liquid and gas phases was started in 1931 and goes on presently (Chudaeva et al., 1999; Chudaev,

2003; Tchepkaia et al., 2004). In spite of the huge amount of chemical analysis, the origin of this water and the role of pCO<sub>2</sub> and processes of water–rock interactions during water evolution are not solved yet. The aim of this study is to assess the impact of bedrock on groundwater chemical composition. We combine new chemical analyses with oxygen ( $\delta^{18}\text{O}$ ), hydrogen ( $\delta^2\text{H}$ ) and,  $\delta^{13}\text{C}_{(\text{TIC})}$  isotopic data of gas phases and mineralogical composition of the bedrock.

### 2. Material and methods

The rocks exposed in the investigated region range in age from the Triassic and Jurassic to the Quaternary (Fig. 1). The bedrock consists of Jurassic sandstones, siltstones and shales that dip 45–50° to the northwest. Numerous tectonic faults are spread across the study area. The fracture zone related to faults is about 50 m wide.

\* Corresponding author. Tel.: +7 4232318520; fax: +7 4232317847.  
E-mail address: [tchenat@mail.ru](mailto:tchenat@mail.ru) (N.A. Tchepkaia).

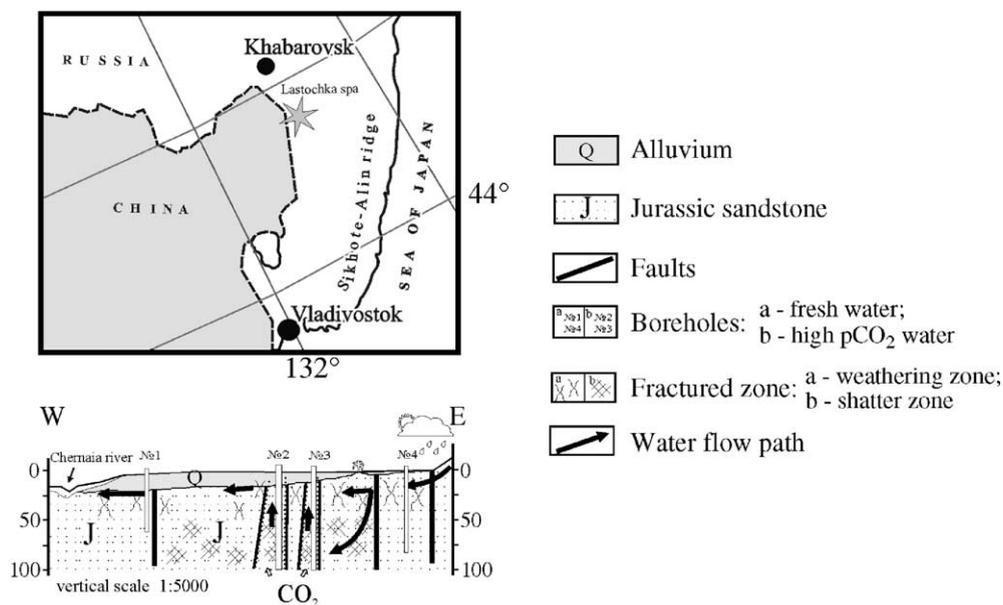


Fig. 1. Schematic hydrogeologic cross-section of the study area.

Groundwater circulation occurs in the upper fractured zone of sandstones and in the shatter zones. The bedrock is capped by Quaternary clays with a 3–28 m thickness. Clays are a protective screen from the migration of surface pollution and  $\text{CO}_2$  degassing. The water table is 3 m below land surface in the valley and about 20 m deep beneath the boreholes pumped. The ridge surrounding the study area is a recharge area and the Valley of Chernaia River is a discharge area. The influence of the fracture flow complicates the interpretation of the flow system in this area. Measurements of water discharge show a narrow seasonal variation. The flow values are 1.5–2 l/s for high  $\text{pCO}_2$  waters and 3–5 l/s for fresh waters. The bedrock, down to 100 m, of this spa was first investigated in detail using traditional petrographic and mineralogical methods. Samples of bedrock from a drilling core at 5 m interval were analyzed.

Groundwater samples were collected over a three year period, additionally some data from Chudaeva et al. (1999) have been analyzed. Collected samples from springs and wells were analyzed by ion chromatography to determine the major components concentration. Trace elements and REE concentrations in groundwater were determined at Tokyo University, Japan using ICP-MS (Agilent 4500). Analytical precision for the REEs, except for Ce and Pr, was better than 5% relative standard deviation (RSD). For Ce and Pr, the precision was of 9% and 18% (RSD), respectively. For trace elements the precision did not exceed 1% (RSD).

Index saturation of mineral phase and activities of the non-REE species in solution for each water sample were carried out using WATERQ4F (Ball and Nordstrom, 1991). Geochemical calculations are based on the total analytical concentration determined in laboratory and parameters measured in field. In all the samples modeled, the charge balance was better than  $\pm 5\%$ .

### 3. Mineralogy

The dominant mineral phases within the studied rocks are quartz, oligoclase, microcline and acidic feldspar. The sediment cement, which makes up to 10% of the rock volume, is mainly composed of quartz and hydromica. Zircon, sphene, leucoxene, anatase, tourmaline are accessory minerals. Locally, a very minor amount of organic and coaly material was observed in thin sections. From surface to a depth of 15 m, all primary rocks are strongly weathered. Dots and veins of limonite and Fe-oxides were observed in this zone. All aluminosilicate minerals are slightly altered to sericite. Sometimes, threads of sericite and muscovite (below 90 m) are recorded. The secondary carbonate minerals such as siderite and calcite were observed below the depth of 30 m. Cubes of pyrite are widespread below the depth of 65 m and their amount increases with depth. Most of the fractures are filled with white clays, kaolinite or smectite.

#### 4. Water geochemistry

Two types of groundwaters are distinguished in the study area: the first one is fresh waters with low mineralization (TDS varied from 200 to 400 mg/l, pH 7.3–7.5,  $\text{HCO}_3^-$  is about 305 mg/l) and the second one is high  $\text{pCO}_2$  waters (TDS varied from 3700 to 4700 mg/l, pH 5.8–6.4,  $\text{HCO}_3^-$  is about 3200 mg/l). Both types of waters are used as a source of potable bottled water and belong to the Na–Ca– $\text{HCO}_3$  type with comparatively low chloride content (Fig. 2).

Monitoring of the studied springs during a complete annual cycle has revealed that both types of groundwaters do not show any significant temporal variation in their chemical composition. Representative analyses of studied waters are shown in the Table 1. The content of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{HCO}_3^-$  is high in waters with high  $\text{pCO}_2$  while  $\text{SiO}_2$  content is higher in fresh waters. TDS and  $\text{Na}^+$  content in groundwaters depends on  $\text{HCO}_3^-$  contents. The content of trace elements in high  $\text{pCO}_2$  water is considerably higher than in fresh water from this area.

The main gas in the high  $\text{pCO}_2$  groundwaters is  $\text{CO}_2$ , which can reach 98% of the total amount of all gases. The  $\text{pCO}_2$ , calculated using the water analyses, is about 0.6 atm, while measured in the field; it could reach 2.6 atm. The  $\text{pCO}_2$  in fresh water is  $10^{-2}$  atm. According to Chudaev et al. (2001) the  $\delta^{13}\text{C}_{(\text{TIC})}$  values observed in the cold  $\text{pCO}_2$  groundwaters of the region range between  $-8.19$  and  $-4.19\%$ , indicating a deep-seated mantle origin for the major part of the carbon of  $\text{CO}_2$  in the studied waters. Thus, the high  $\text{CO}_2$  content in waters could be caused by migration of gas from mantle to the surface through faults. Additional  $\text{C}/^3\text{He}$  ratio data confirms this suggestion (Chudaev et al., 2001).

Table 1

Representative groundwaters and surface water chemical analyses (mg/l)

Parameter	Groundwater		Surface water (R. Chernaia)
	High $\text{pCO}_2$	Fresh	
TDS	4150	450	80
pH	6.74	7.6	6.7
Na	520	43.5	4.83
K	57.4	2.0	0.5
Ca	184.4	32.08	8.02
Mg	150	12.16	2.43
$\text{Fe}^{2+}$	0.52	0.10	0.20
$\text{Fe}^{3+}$	0.17	0.10	0.10
$\text{NH}_4$	0.6	0.2	0.2
Cl	4.3	2.8	3.55
$\text{SO}_4$	6.00	4.00	2.00
$\text{HCO}_3$	3200	305	48.8
$\text{SiO}_2$	38.74	53.00	7.69
Pb	0.005	0.005	0.005
Zn	0.054	0.007	0.012
Cu	0.015	0.019	0.036
As	0.34	0.01	0.01
F	0.08	0.12	0.04
Mn	0.28	0.05	0.30
Cr	0.004	0.004	0.004
Sr	6.26	0.50	0.50
Rb	0.171	–	–
Ba	3.28	–	–
Li	1.547	–	–

– not determined.

Oxygen ( $\delta^{18}\text{O}$ ) and hydrogen ( $\delta^2\text{H}$ ) isotopic data (Chudaeva et al., 1999) prove that meteoric water is the source of both types of waters. In the classical  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  diagram, all the  $\text{CO}_2$ -rich mineral waters in the Primorye region lie on or close to the world meteoric water line. Therefore, the dominant factor controlling the chemical composition of these waters is water–rock–gas interactions.

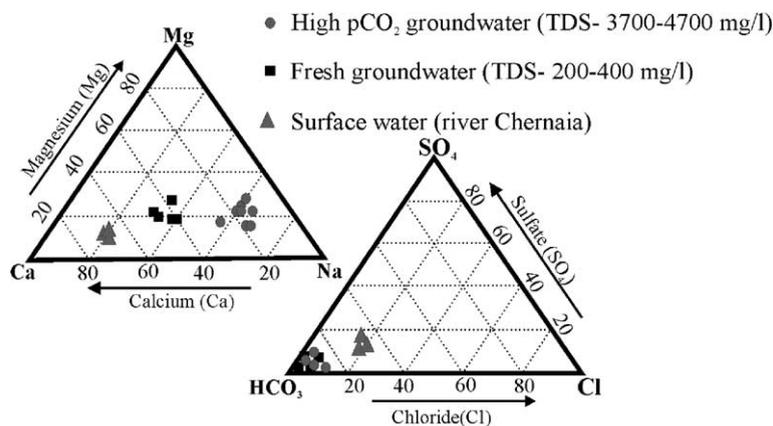


Fig. 2. Triangular diagrams showing the chemical compositions of the studied waters.

The thermodynamic data denote that both types of groundwater are in equilibrium with calcite, dolomite, quartz, chalcedony and supersaturated with kaolinite, mica, hematite and goethite. Moreover, fresh waters are slightly undersaturated with Ca-smectite and siderite. All waters are strongly undersaturated with pyrite and primary allumosilicates. Stability diagrams indicate that  $p\text{CO}_2$  water data are grouped within the stability field of kaolinite, while fresh water data lie at the kaolinite–Ca-smectite boundary or within the Ca-smectite stability field.

### 5. REE content in groundwater

Shale-normalized plots of several mineral and fresh groundwaters in the Sikhote–Alin region are presented in Fig. 3. The fresh waters and mineralized waters have different LREE content. This is probably due to preferential aqueous transport of HREE, which form stronger aqueous carbonate complexes than LREE. Previous studies indicate that in the presence of the carbonate ion, HREE are more strongly complexed than LREE (Cantrell and Byrne, 1987) and therefore LREE are

more easily sorbed on particles or colloids. For all studied samples, negative Ce anomalies are clearly observed. This is probably caused by the removal of Ce from the waters onto Fe or Mn-oxyhydroxides. The anomaly is especially prominent for the high mineralized Na– $\text{HCO}_3$  water type and only slightly negative for the Ca–Mg– $\text{HCO}_3$  water-type. Experimental data (Bau, 1999) indicate that adsorption of Ce onto iron oxyhydroxides is a relatively slow process so the variations in the magnitude of the Ce anomaly could result in the difference in residence time of circulation groundwater. All samples have positive Eu anomalies. According to Nelson et al. (2004), positive Eu anomalies could be associated to bedrock with high contents of Eu or to reduced groundwater with positive Eu anomalies. All studied waters circulate in the three different units of the bedrock, where plagioclase is the predominant mineral. Most of the Eu in the studied rocks is contained in plagioclase (Chudaev, 2003). Taking into consideration that plagioclase dissolves faster than other allumosilicates, it could explain the enrichment of Eu in groundwaters. In this case, it is not clear however, why there is no difference in Eu contents in groundwaters with var-

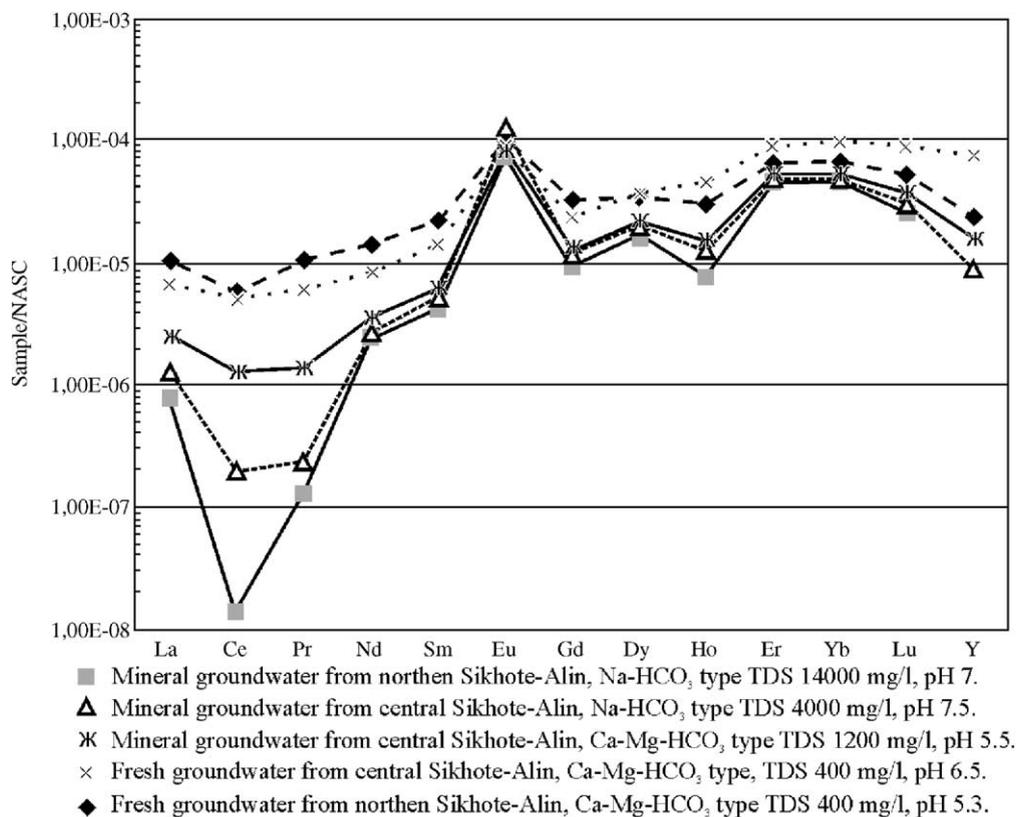


Fig. 3. NASC (North American Shale Composite)-normalized concentrations of REE in the groundwaters from Sikhote–Alin mountain system. NASC data were taken from Hannigan and Sholkovitch, 2001.

ious  $p\text{CO}_2$  values, since the  $p\text{CO}_2$  appears to affect the dissolution rate of plagioclase. The positive Eu anomaly in the high  $p\text{CO}_2$  water from Sikhote–Alin is probably caused by more reduced conditions where groundwaters evolved.

## 6. Conclusions

Our studies of the Lastochka spa groundwater hydrochemistry coupled with detailed investigation of a drilling core indicate that:

1. Both types of groundwaters (fresh and high  $p\text{CO}_2$ ) have the same origin: meteoric water. The chemical composition of groundwaters is controlled by interactions between meteoric waters, host rocks and gas.
2.  $\delta^{13}\text{C}_{(\text{TIC})}$  values indicate a deep-seated mantle origin for  $\text{CO}_2$ . The addition of  $\text{CO}_2$  to the groundwater locally leads a pH decrease and a drastic increase of TDS with  $\text{Na}^+$  content. The huge difference in trace element concentration in both waters is caused by more intensive weathering of primary minerals in presence of  $\text{CO}_2$  gas.
3. All high  $p\text{CO}_2$  groundwaters from Sikhote–Alin region are enriched in HREE compared to LREE, and this difference depends on  $p\text{CO}_2$ . A positive Eu anomaly is observed in all types of water from Sikhote–Alin mountain region and probably reflect the reducing conditions of the underground environment where groundwaters evolved.

## Acknowledgements

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