SHORT COMMUNICATIONS =

New Isotope-Hydrogeochemical Data on the Bang Spring (Kuang Binh Province, Central Vietnam)

D. A. Novikov*^a***,** *b***, *, Phan Thi Kim Van***^c* **, Doan Van Tuyen***^c* **, Do Thi Thu***^c* **, and Tran Viet Hoan***^d*

aTrofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch, Russian Academy of Sciences, pr. Koptyuga 3, Novosibirsk, 630090 Russia

b Novosibirsk State University, ul. Pirogova 1, Novosibirsk, 630090 Russia

c Institute of Geological Sciences, Vietnam Academy of Sciences and Technology, Chua Lang 84, Dong Da, Hanoi, Vietnam

dNational Center for Planning and Study of Water Resources, Vu Huan Ti 93/95, Sai Don Vord, Long Bien, Hanoi, Vietnam

** e-mail: NovikovDA@ipgg.sbras.ru*

Received July 2, 2018; revised September 25, 2018; accepted October 10, 2018

Abstract—New isotope hydrogeochemical data on two types of thermal water from the Bang spring (Kuang Binh province, central Vietnam) are reported in the work. The first type includes $HCO₃-Cl-Na-Mg$ water with extremely low mineralization (44–87 mg/dm³) and pH variations from weakly acidic to weakly alkaline values (5.71–7.84). The second type includes $HCO₃$ –Na water with mineralization up to 256–659 mg/dm³ and pH 8.03 to 8.51. The studied types differ significantly in temperature: 24.3–34.5°C in the first type and $62.1-97.1^{\circ}$ C in the second type. The analysis of the distribution of oxygen (δ^{18} O) and hydrogen (δ D) isotopes carried out for the first time confirms different genetic nature of these hydrogeochemical water types. The first type has an atmospheric genesis $(\delta^{18}O = -7.3... - 6.2\%$ and $\delta D = -51.4... - 39.3\%$, while the second type restricted to the Kien Giang–Bang intersection zone has a deeper source $(\delta^{18}O = -1.6....-1.3\%$ and $\delta \hat{D} = -22.2...-21.4\%$, The tritium (³H) data also point to different circulation times of these waters. The formation time of the $\text{HCO}_3-\text{Cl}-\text{Na}-\text{Mg}$ waters does not exceed 50 years (${}^{3}\text{H} = 4.3-11.1 \text{ TE}$), while that of $HCO₃–Na$ water may reach more than 1000 years (³H = 0.5 TE).

Keywords: thermal waters, hydrogeochemistry, genesis, tritium, oxygen-18, Bang spring, central Vietnam **DOI:** 10.1134/S0016702919060077

INTRODUCTION

The study of Vietnam thermal waters has begun in 1980s. Results of studies of tectonic regime, geological and hydrogeological structure, and hydrogeochemistry of main geothermal fields are given in works by H. Amaguchi, G.R. Anderson, D. Bui, G.D. Kao, N.N. Kat, A.V. Kristensen, Ya. Dezi, T.V. Doan, K. Drog, A.D. Duchkov, R. Gilbuen, S.H. Harder, A. Kawamura, Y. Kenig, F. Larsen, N. Nakagava, V.K. Nghiep, and many others.

In Central Vietnam, low- and high-thermal springs have vent temperature from 25 to 99 °C. The springs mainly have hydrocarbonate, hydrocarbonate–chloride, and chloride–sodium compositions with the total mineralization varying from 0.05 to 10.05 g/dm³. Most of the thermal waters are characterized by salinity no more than 1 g/dm^3 , which can be related to the fact that their composition is formed within non-stratified units of hydrogeological massifs in the area of wide distribution of intrusive rocks resistant to weathering. Water circulates through aquifers of exogenic fracture and fault zones (Novikov et al., 2018).

This work reports the results of isotope-hydrogeochemical studies of 2014–2016 field seasons at the hydrothermal springs of the Bang (Lo Voi) deposits, one of the most important geothermal areas of the Kuang Binh province, Central Vietnam (Fig. 1). The first mainly descriptive study and hydrogeochemical sampling was carried out by Vo Kong Nghiep in 1998 and is characterized by two samples of high-thermal springs 1 and 2 (Fig. 1) (Nghiep, 1998). Unfortunately, only major component composition and silica content were studied in sampled solutions.

METHOD

In 2014–2016, we first carried out the detailed hydrogeochemical and isotope study of thermal springs of the Bang deposit. Complete chemical analysis, including trace elements, was carried out for 27 samples, and isotope composition was determined for 6 samples. The samples for the cation and anion analysis were filtered through a cellulose filter $(0.45 \,\mu\text{m})$ in sampling locality to remove the suspended matter and were collected in polyethylene bottles. For reliable determination of steady components

Fig. 1. Scheme of thermal springs of the Bang (Lo Voy) spring. Water points: (*1*) wells, (*2*) springs; (*3*) faults; (*4*) horizontals showing the area topography.

in the solution in sampling locality, the samples were conserved in situ (the samples were acidified with nitric acid for the cation analysis, and were not, for anion analysis). Then, they were delivered to the laboratory for subsequent measurements.

Stable isotopes were determined at the Analytical Center of the Geological Institute of the Vietnam Academy of Sciences and Technologies. Samples were prepared for isotope analysis by conventional technique of high-temperature water pyrolysis on carbon. The $18O/16O$ and D/H ratios were determined in water samples using high-temperature TC/EA converter connected with a MAT-253 mass spectrometer operating in a continuous He flow mode. The isotope ratios were measured relative to the laboratory standard calibrated against VSMOW, SLAP, and GISP international standards. The ${}^{18}O/{}^{16}O$ ratio relative to SMOW (seawater standard) was used for comparative estimates. Tritium was measured using β-counting on a QUANTULUS-1220 low-background liquid scintillation spectrometer with preliminary electrolytical enrichment.

Unstable parameters (pH, temperature, $HCO₃$) were determined in water in situ using field hydrogeochemical laboratory. Obtained results of analytical studies are given in Tables 1, 2, and 3.

northwest to the southeast. Magmatic processes were widespread in the studied area in the neotectonic time. Pliocene–Pleistocene basalts are abundant to the northwest of the Bang deposit. The section is subdivided into two hydrogeological stages. The low stage is represented by the Archean–Proterozoic crystalline basement, while the upper stage is represented by sedimentary cover made up of the Upper Ordovician– Lower Silurian water-bearing rocks (intercalation of clays, sandstones, and silts of the Longdai Formation), and Quaternary eluvium and alluvial deposits.

RESULTS AND DISCUSSION The Bang thermal springs are confined to the intersection zone of the large Kien Giang and Bang faults. The former extends from the north southward along the eponymous river, while the latter is traced from the

Thermal vents occur on the coast of the small Kien Giang River, with intense discharge and fumarole activity (Fig. 2). The total discharge of high-thermal waters with temperature $75-97^{\circ}$ C is more than 40 L/s. The vents produces travertines (up to $1.0-1.5$ m across) (Fig. 2a). It was established that the vent temperature widely varies from 30 to 100°С. Water with temperature more than 60°С is discharged in the Kien Giang–Bang faults intersection zone (water points 1– 10). Two shallow wells were drilled at the deposit:

730

GEOCHEMISTRY INTERNATIONAL Vol. 57 No. 6 2019

NOVIKOV et al.

Point no.	Μ, mg/dm ³	$T, {}^{\circ}C$	Mn	Zn	F^-	\mathbf{I}^-	Pb	As	C _d
			mg/dm ³				μ g/dm ³		
	530	96.29	0.007	0.002	4.10	0.20	0.03	1.25	0.137
2	659	97.12	0.003	0.021			3.06	3.86	0.189
3	650	93.85	0.001	0.003			1.82	2.50	0.134
4	660	90.07	0.005	0.002			2.15	1.35	0.137
5	654	84.13	0.041	0.002			0.04	2.02	0.135
6	647	86.41	0.009	0.007			2.43	2.15	0.152
7	648	85.32	0.005	0.023			2.08	1.05	0.356
8	335	68.43	0.001	0.096			1.63	1.25	0.171
14	518	28.20	0.182	0.074			3.11	1.65	0.180

Table 2. Trace element composition of thermal waters of the Bang (Lo Voy) deposit

(1) 40 m deep (water point 13) in June, 2013, and (2) 200 m deep (water point 14) in November, 2014. Results of geothermal studies showed that the larger the distance from the Kien Giang and Bang fault intersection, the lower the geothermal parameters of the section. In particular, the formational temperature of 34.5°С was recorded in the first well at a depth of 40 m, and reaches greater values of 86.3°С/100 m and 17.2°С/100 m, respectively in the latter well. In general, the geothermal gradients for large negative tectonic elements of Southeastern Asia, which are made

up of the Paleogene–Neogene rocks, often reach 5.5– 7.5°С/100 m (Utkin et al., 1986). For instance, at depths from 2500 to 4000 m in the Hanoi trough, the temperature of formational waters varies within 125– 180°С (Duchkov et al., 1992; Wysocka, 2009) and could reach 230°С at depths of 5000 m according to calculations (Skorduli et al., 1983).

The values of the total mineralization of the studied springs vary from 44 to 659 mg/dm^3 . The waters sharply differ in their chemical composition and con-

Fig. 2. Discharge of hydrothermal vents of the Bang spring along the coasts of the Kien Giang River (photo by Tran Viet Hoang, 2016).

tent of major and trace elements depending on spring temperature. The Piper diagram (Fig. 3) shows the ratios of main components in thermal waters, with literature data on seawater composition shown for comparison. Seawaters referred to as waters of World Ocean have the following composition $(mg/dm³)$: $Ca^{2+}-400$; $Mg^{2+}-1350$; $Na^{+} + K^{+}-11080$; Cl⁻ 19300; SO_4^{2-} -2700; HCO_3^- -160; Br⁻-65; I⁻-0.06; NH⁺₄-0.5; SiO₂-6; B⁺-4.6. Two main hydrogeochemical thermal groups were distinguished (according to S.A. Shchukarev). The first group is characterized by the vent temperature of 24.3–34.5°С, hydrocarbonate–chloride sodium–magnesium composition with the total mineralization of $44-87$ mg/dm³, and pH value from weakly acid to weakly alkaline (5.71–7.84). The second group differs in temperature of 62.1–97.1°С, hydrocarbonate–sodium composition, mineralization of 256–659 mg/dm³, and pH value from 8.03 to 8.51. Obtained results are well consistent with previously obtained data by Vo Kong Nghiep.

Established peculiarities in the accumulation of main salt-forming components are best expressed in different chemical types of thermal waters.

In particular, in the high-temperature hydrocarbonate sodium waters, the total mineralization shows the strongest correlation with sodium, potassium, and hydrocarbonate ion, concentrations of which vary within $132-165$, $12-14$, and $295-423$ mg/dm³, respectively. Among trace components, mineralization yields the strongest correlation with sulfur and silica contents of $4-12$ and $41-61$ mg/dm³, respectively, with regression correlation reaching 0.84–0.89. The proportions of cations and anions in the thermal waters with temperature below 35°С show that the cations are dominated by sodium, while magnesium is second in abundance. Anions are dominated by hydrocarbonate ion, concentration of which varies from 20 to 41 mg/dm^3 and chloride with $4-11 \text{ mg/dm}^3$. The results of chemical analyses of seasonal sampling in May and December show that proportions of major

Fig. 3. Piper diagram showing the composition of thermal waters of the Bang spring. Chemical types of waters after S. A. Shchukarev: (1) $\text{HCO}_3-\text{Cl}-\text{Na}-\text{Mg}$; (2) HCO_3-Na ; (3) $\text{HCO}_3-\text{Mg}-\text{Na}$; (4) seawater.

ions in thermal waters (springs 1–10, Fig. 1, Table 1) remain stable.

Silica contents increase with temperature increase, as mentioned previously (Plyusnin et al., 2013) during study of thermal waters of the Baikal rift zone. At the Bang deposit, water with temperature below 35°С contains $6-32$ mg/dm³ silica, while high-temperature waters (temperature above 80°С) contain 51– 61 mg/dm^3 silica. With the growth of total mineralization and water temperature, the solution, in addition to sulfur and silica, also accumulates ammonium (up

to 1.27 mg/dm³), lead (up to 3.11 μ g/dm³), manganese (up to $0.182 \,\mu g/dm^3$), zinc (up to $0.096 \,\mu g/dm^3$), arsenic (up to $3.86 \mu g/dm^3$), and cadmium (up to $0.356 \,\mu\text{g/dm}^3$) (Table 2). The highest Fe (total) enrichment is observed in springs with the total mineralization below 400 mg/dm³ (up to 1.86 mg/dm³); the high-thermal waters are characterized by trace Fe concentrations (below 0.001 mg/dm³). It should be noted that the highest lead and manganese contents are observed in hydrothermal springs sampled at a depth of 200 m in well no. 14. They are also character-

Fig. 4. Oxygen–Hydrogen isotope relations in the hydrothermal vents of the Bang deposit and Central Vietnam. Thermal waters of Central Vietnam (Novikov et al., 2018): (*1*) continent, (*2*) coastal areas; (*3*) hydrothermal vents of the Bang spring.

ized by the highest NO_2^- up to 0.038 and NO_3^- up to 0.95 mg/dm^3 , respectively.

As mentioned above, the isotope compositions of oxygen ($δ$ ¹⁸O), hydrogen ($δD$), and tritium ($³H$) were measured for the first time in the hydrothermal springs of the Bang Deposit (Lo Voy) (Table 3). Based on the distribution of data points of hydrothermal springs of different chemical composition versus δ^{18} O and δ D, two genetic types of waters can be distinguished. The water component of the first group is mainly represented by meteoric waters with insignificant contribution of sea (thalassogenic) water, while the group of sodium water with the fumaroles-related maximum $δ¹⁸O$ and $δD$ has a deeper source. The position of the first group in terms of isotopic composition ($\delta^{18}O$ = $-7.3...$ –6.2‰ and $\delta D = -51.4...$ –39.3‰) (Fig. 4) is well consistent with data previously obtained for the Trang Bo geothermal field in Central Vietnam (Doan et al., 2015; Novikov and Doan, 2016; Novikov et al., 2018), closely plotting to the Global Meteoric Water Line (GMWL) (Craig, 1961). The measurements of $δ¹⁸O$ and $δD$ in the fumarole-related sodium waters $(\delta^{18}O = -1.6... - 1.3\%$ and $\delta D = -22.2... - 21.4\%$ revealed their strong difference from surface waters (marine and river). This fact is no exception. Isotopically, they have much in common with mud volcanic hydrocarbonate sodium waters of Azerbaijan ($\delta^{18}O =$ $-0.6-0\%$ and $\delta D = -32.0\%$ (Lavrushin et al., 2015), as well as with hydrothermal vents (crater, fumaroles) of El Chichen Volcano in Mexico (δ¹⁸O = $-2.2...-1.5\%$ and $\delta D = -22.0...-17.0\%$ (Taran et al., 1998). Such isotopic shift could be caused by the water interaction with host rocks and high-temperature transformations of their minerals. Thereby, the longer the interaction time, the higher the observed shift.

Obtained tritium data also indicate the different circulation time for two thermal groups studied at the Bang deposit. One group represented by sodium– magnesium hydrocarbonate–chloride waters contains 4.3–11.1 ТЕ tritium (Table 3). In contrast, the tritium concentration in the high-temperature sodium hydrocarbonate waters is as low as 0.5 ТЕ. The comparison of obtained data with studies of thermal waters in Turkey (Yurteri and Simsek, 2017), on Canadian shield (Douglas et al., 2000), in Spain (Gómez et al., 2006), as well with the Eastern Cis-Caucasus (Sokolovsky et al., 2010a), and West Siberian (Sokolovsky et al., 2010b) artesian basins, Far East (Kharitonova et al., 2012), and other regions around the world and application of different models for calculations of groundwater age (Ferronsky and Polyakov, 1983; 2009) showed that the "tritium" age (water-exchange time) is no more than 50 years for the first group and reaches over 1000 years for the second group.

CONCLUSIONS

Detailed hydrogeochemical and isotopic studies carried out for the first time for the thermal springs of the Bang (Lo Voy) deposit made it possible to determine compositional peculiarities, genesis, and preliminary age. It is established that the waters are subdivided into two genetic groups. The first group has an atmospheric genesis ($\delta^{18}O = -7.3... - 6.2\%$ and $\delta D =$ $-51.4... - 39.3\%$, temperature of $24.3 - 34.5$ °C, hydrocarbonate–chloride sodium–magnesium composition with the total mineralization of $44-87$ mg/dm³ and рН 5.71–7.84. The second group restricted to the Kien Giang–Bang fault intersection has a deeper origin $(\delta^{18}O = -1.6... -1.3\%$ and $\delta D = -22.2... -21.4\%$. temperature of 62.1–97.1°С, hydrocarbonate sodium composition, mineralization of $256-659$ mg/dm³, and pH from 8.03 to 8.51. Data on tritium (^{3}H) also indicate the different circulation time of these waters: 50 years for the first group $(^{3}H = 4.3-11.1$ TE), and over 1000 years for the second group (${}^{3}H = 0.5$ TE).

REFERENCES

- H. Craig, "Isotopic variations in meteoric waters," *Science* **133**, 1702–1703 (1961).
- V. T. Doan, T. K. V. Phan, F. V. Tran, and D. A. Novikov, "Features of hydrogeology of Central Vietnam," Proceedings of 2nd All-Russian Conference with Participation of Foreign Scientists "Geological Evolution of Water–Rock Interaction," (Dal'nauka, Vladivostok, 2015), pp, 234–237.
- M. Douglas, I. D. Clark, K. Raven, and D. Bottomley, "Groundwater mixing dynamics at a Canadian Shield mine," J. Hydrology **235**, 88–103 (2000).
- A. Duchkov, D. Nguen Chong Iem, Din Van Toan, and Chin Viet Bak, "First assessments of heat flow in Northern Vietnam," Sov. Geol. Geofiz., No. 5, 110– 115 (1992).
- V. I. Ferronsky and V. A. Polyakov, *Hydrosphere Isotopy* (Nedra, Moscow, 1983) [in Russian].
- V. I. Ferronsky and V. A. Polyakov, *Hydrosphere Isotopy* (Nauchnyi Mir, Moscow, 2009) [in Russian].
- P. Gómez, M. J.Turrero, A. Garralón, F. J. Peña, B. Buil, B. de la Crux, M. Sánchez, D. M. Sánchez, A. Quejido, C. Bajos, and L. Sánchez, "Hydrogeochemical characteristics of deep groundwaters of the Hesperian Massif (Spain)," J. Iberian Geol. **32** (1), 113–131 (2006).
- N. A. Kharitonova, G. A. Chelnokov, I. V. Bragin, and E. A. Vakh, "Isotopic composition of natural waters of southern Russian Far East," Tikhookean Geol. **31** (2), 75–86 (2012).
- V. Yu. Lavrushin, I. S. Guliev, O. E. Kikvadze, Ad. A. Aliev, B. G. Pokrovsky, and B. G. Polyak, "Waters from mud volcanoes of Azerbaijan: isotopic-geochemical properties and generation environments," Lithol Miner. Resour. **50** (1), 1–26 (2015).
- D. A. Novikov and Doan Van Tuen, "Thermal waters of Central Vietnam,*" Proceedings of 12th International Congress GEO-Sibir-2016* (SGUGiT, Novosibirsk, 2016), Vol. 1, pp. 94–98 [in Russian].
- D. A. Novikov, Doan Van Tuyen, Phan Thi Kim Van, and N. A. Kharitonova, "Hydrogeochemical features of thermal waters of South Trungbo (Central Vietnam)," Russ. J. Pac. Geol. **12** (1), 63–79 (2018)
- A. M. Plyusnin, L. V. Zamana, S. L. Shvartsev, O. G. Tokarenko, and M. K. Chernyavskii, "Hydrogeochemical peculiarities of the composition of nitric thermal waters in the Baikal rift zone, Russ. Geol. Geophys. **54** (5), 495–508 (2013).
- V. D. Skorduli, M. V. Khudyk, Le Van Ky, Nguen Ngok Ky, and K. M. Secastyanov, "Geological structure and petroleum potential of the Khanoi trough," Geol. Nefti Gaza, No. 5, 55–61 (1983).
- L. G. Sokolovskii, V. A. Polyakov, V. G. Timokhin, and S. V. Alibekova, Assessment of conditions of formation and protection of groundwaters of the Eastern Cis-Caucasian artesian basin from technogenic pollution," Razvedka Okhr. Nedr, No. 7, 24–31 (2010).
- L. G. Sokolovskii, V. A. Polyakov, A. V. Sokolova, N. A. Provotorova, and A. I. Chistyakova, Isotopehydrogeochemical study of ground and surface waters of the West Siberian artesian basin and Ural complex fold area," Razvedka Okhr. Nedr, No. 7, 65–71. (2010)
- Y. Taran, T. P. Fisher, B. Pokrovsky, Y. Sano, M. Aurora Armienta, and J. L. Macias, "Geochemistry of the volcano-hydrotermal system of El Chichón Volcano, Chiapas, Mexico," Bull Volcanol. **59**, 436–449 (1998).
- V. P. Utkin, Nguen Chong Iem, Ho Dak Hoai, Le Ching Kan, Nguen Din Tu, Lyi Hoi Thong, Chan Le Dong, Nguen Kuok Kyong, Le Van Chyong, and Le Min Kuok, "Geodynamic conditions of the formation of basins in Southeast Asia," Tikhookean Geol., No. 6, 12–23 (1986).
- Vo Cong Nghiep, *List of Mineral and Hot Water Sources in Vietnam*, (Vietnam Department of Geology and Mineral Resources, Hanoi, 1998) [in Vietnamese].
- A. Wysocka, "Sedimentary environments of the Neogene basins associated with the Cao Bang-Tien Yen fault, NE Vienam," Acta Geol. Polonica **59** (1), 45–69 (2009).
- C. Yurteri and S. Simsek, "Hydrogeological and hydrochemical studies of the Kaman-Savcili-Büyükoba (Kirsehir) geothermal area, Turkey," Geothermics **65**, 99–112 (2017).

Translated by M. Bogina