DOI 10.7343/AS-109-15-0136

Physico-chemical model as a tool to explain the composition of thermal waters in tectonically active regions

Un modello fisico-chimico come strumento per spiegare la composizione delle acque termali nelle regioni tettonicamente attive

Elena A. Kuz'mina, Svetlana V. Veshcheva, Olga V. Zarubina, Nikolai V. Brianskii

Riassunto: Questo lavoro riguarda l'influenza delle condizioni strutturali e idrogeologiche del Sistema di Rift di Baikal (BRS) in Russia sull'origine delle acque, in un tipico ambiente di tettonica a zolle. E' stata condotta un'analisi comparativa degli elementi in traccia delle acque termali dei sistemi di rift e di quelli di arco insulare. Sono stati analizzati gli elementi in traccia di acque termali per capire meglio la loro origine mediante una modellazione chimico-fisica. Sono poi presentati i risultati di diverse simulazioni risultanti dalla modellazione termodinamica e finalizzate allo studio dei processi di formazione delle acque termali, tenendo conto della attività geodinamica della regione del BRS. I risultati del modello per la sorgente termale Alginsky del BRS hanno dimostrato che tutti gli elementi possono derivare da acque circolanti in graniti. Fanno eccezione U, Li, Rb, B, Mo, Sr e S, la cui origine può essere endogena.

Abstract: *In the present work, we address the structural-hydrogeological conditions for the Baikal Rift System (BRS) natural water formation in terms of lithospheric plate tectonics. A comparative analysis for the trace-element composition of thermal waters of rift and island-arc systems was made. We analyzed the thermal water trace elements to better understand the water origin through physico-chemical modeling. The results of different simulations of thermodynamic modeling are herein presented, in order to investigate the formation processes of thermal waters according to the geodynamic activity in the BRS region. Modeling results for the Alginsky Thermal Spring in BRS showed that all the elements can be accumulated in the waters from granites except for U, Li, Rb, B, Mo, Sr, S. These elements may have endogenous nature.*

Parole chiave: acqua termale, modello chimico-fisico, sorgente, elementi in traccia

Keywords: *thermal water, physico-chemical modeling, spring, microelements.*

Elena Aleksandrovna KUZ'MINA
Institute of the Earth's Crust of the Siberian Branch of the RAS
128, Lermontova St., 664033, Irkutsk, Russia
selenginsk2007@mail.ru

Svetlana Vadimovna VESHCHEVA
Institute of the Earth's Crust of the Siberian Branch of the RAS
128, Lermontova St., 664033, Irkutsk, Russia
veshcheva@gmail.com

Olga V. ZARUBINA
Nikolai V. BRIANSKII
A. P. Vinogradov Institute of Geochemistry of the Siberian Branch of the RAS
1a, Favorskogo St., 650033, Irkutsk, Russia
zarub@igc.irk.ru

Ricevuto: 2 marzo 2015 / Accettato: 1 giugno 2015
Pubblicato online: 30 giugno 2015

Introduction

The complex and polygenetic origin and composition of groundwater in the regions of rift remains a debate topic and is the focus of a wide range of specialists. These issues have received considerable attention in several studies (Didenkov 1998; Didenkov et al. 2007, 2010; Plûsnin and Cernavskij 2006; Ovčinnikov 1955; Lysak 1988), where the chemical composition of groundwater has been explained as due to water contact with the host rocks, excluding the participation of fluids of magmatic origin, while, on the contrary, others think that the occurrence of a number of trace elements in the water is associated with magmatic emanations.

The highly sensitive ICP-MS method allows to analyze trace-element composition of natural waters (saving significant time and covering a wide range of values). This method has great potential for analysis in solving the problems associated with the genesis of thermal water and specifically of the dissolved substances.

In a paper on the future development of the geochemistry, Vinogradov (1962) wrote that the main task of geochemistry at the moment is the "…development of physico-chemical theory of geochemical processes. And that means, that geochemists intensify research in the field of experiments and modeling processes. Without this, there is no theory of the process, and consequently, no science."

DOI 10.7343/AS-109-15-0136

The development of modern science has also led to the development of physico-chemical modeling software. The physico-chemical modeling can solve the problems associated with the inflow of elements in aqueous solution, the reconstruction process of their migration, analyzing the concentration and deposition of chemical elements, determining the forms of existence of elements in aqueous solutions, gas phase, solid phase.

This paper regards the Alginsky Thermal Spring located in the Barguzin Basin. The main objective of research is to establish the genesis of the chemical composition of the spring water.

The geodynamic environment

The Barguzin Basin is within the BRS (Baikal Rift System), which is one of the most extended intracontinental rift systems, associated with the boundary between the Sayan-Baikal area and the ancient Siberian platform (Fig.1). The BRS extends southwest-northeast for about 2,000 km, from the Busingol and Darkhat basins in northern Mongolia to the Tokkin Basin in southern Yakutia (Russia), forming an S-shaped pattern in the plan. BRS represents a boundary between the Eurasian and the Amur continental lithospheric plates.

The rate of spreading in this region is 3.4 ± 0.7 mm per year (San'kov et al. 2009).

Fig. 1 - The location of the studied area – the Baikal Rift System on the global scale.

Fig. 1 - Ubicazione dell'area di studio: il Sistema di Rift di Baikal (BRS) su scala globale.

According to Ufimcev et al. (2010), the Barguzin Valley is a complex of morphotectonic structure including three elements: 1) the Barguzin Basin s.s. that is 140 km long and 30–35 km wide; 2) a low-mountain massif between the Gusikha and Chichkan rivers; 3) the Ust'-Barguzin Basin, approximately 30 km long (Fig. 2).

Morphologically, the Barguzin Basin s.s. is an inclined-corrugated plain filled by the Barguzin River alluvial complex and edged with a piedmont strip of sandy rocks (Kuituns) along the south-eastern slope of the Ikat Ridge (Kolomiec and Budaev 2010).

Tectonically, the Barguzin Basin is considered as a unilateral graben with an abrupt northwest side and a series of faults that are followed by the Barguzin Range, and the gently sloping southeast side turning into the Ikat Range (Lysak 1988).

The Gusihinski lowland massif is a structural bridge that separates the Barguzin Basin from the Ust-Barguzin Basin. This last basin extends for about 7-8 km in width: on the west side is open to the waters of the Baikal lake's Barguzin bay, in the southwest the coast narrow low-mountain Holodyanochnym massif separates the basin from the lake.

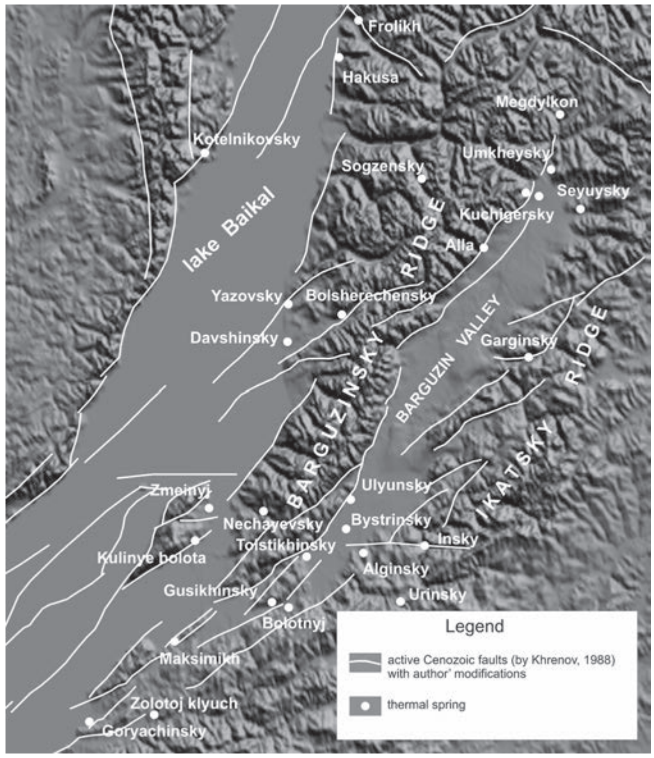


Fig. 2 - Digital elevation model of the study area and location of the thermal springs.

Fig. 2 - DEM dell'area di studio e ubicazione delle sorgenti termali.

The sedimentary cover of the Barguzin and Ust-Barguzin basins has a thickness varying from few hundred meters to 2.5 km, and is made up of deposits of glacial moraines, inequigranular sand, gravel, clay, siltstone, and silt. Boulder deposits are observed in the side basins. The substratum of the basin is constituted by igneous, seldom metamorphic rocks of the Lower Paleozoic and Upper Proterozoic (Lysak 1988). The Kuituns sands are of Pleistocene age and related to deposition in the marine environment (Kolomiec 2010).

The deep structure of the Barguzin Basin has been studied by geophysical methods (Bulmasov 1968; Èpov et al. 2007).

Holocene and current tectonic activity is manifested through active faults. In the study area the most of the seismic structures are normal faults and some of them are strike-slip faults.

Epicentres of instrumentally recorded earthquakes are grouped into two bands: the first is oriented along the Barguzin Basin on its south-eastern part, the second passes through the Svyatoy Nos Peninsula in the north-eastern part along the inner field of the Barguzin Range. The maximum hypocenter's location of the earthquakes has been detected at a depth of 15–20 km (Radziminovič et al. 2003).

The fault tectonics of the Barguzin Basin are considered in detail by Zamaraev et al. (1979). It was found that the faults of the territory were formed over a long period of time, i.e., from the Proterozoic to Cenozoic. The longest pre-Cenozoic faults are northeast-trending and the lesser long faults are spreading towards northwest. Activated Cenozoic faults basically follow the orientation of ancient fractures. The genetic type of the most active faults are characterized as normal faults, throws-shears, shears-throws, strike-slip faults (Zamaraev et al. 1979).

Results of structural-hydrogeological analysis

The proximity of the study area, i.e., the Barguzin Basin, to the continental Baikal rift system permits to investigate about the influence of the fluid geodynamics and lithosphere plate tectonics on the composition of groundwater. Rifting is the main driving force that affects the region's hydrogeological structures and the characteristics of its waters. The rifting geodynamic regime in the Baikal region determines, first of all, the current morphology of the area and thus the hydrogeological conditions.

In response to the main morpho-structures, three hydrogeological structures can be distinguished: rift depressions – hydrogeological basins; rift "edges" – hydrogeological massifs; disruptive tectonic disturbances of the rift – watered faults (Didenkov et al. 2006; Stepanov 1989). These hydrogeological structures differ in groundwater distribution and origin.

In the area under investigation several nitrogenous thermal springs are present and are characterized by temperature up to 84 °C, low mineralization (0.2–1.1 g/l), high pH values (7–9.3), and flow rate varying from 1–10 to 85 l/s (Lomonosov 1974). Water's chemical composition is sulfate sodium, bicarbonate-sulfate and sulfate-bicarbonate sodium, high in fluorine and siliceous acid. These thermal waters are associated with extensional structures (Mel'nikova and Radziminovic 2007) and are controlled by normal faults.

The Alginsky Thermal Spring is located on the eastern side of the Barguzin Basin of the Baikal Rift System, at the foot of the Ikat Ridge. It outcrops from a small sinkhole 1 m wide and 0.7 m deep in sand and silt (Fig.3). Fissure-vein thermal waters emerge through cleavage fractures, then mixing with the shallow cold waters circulating in the loose deposits of the basin. The mixing gives rise to temperatures of about 20 °C. The mineralization of the spring water is 593 mg/l, the chemical composition of water is sodium sulfate with pH 8.07.

Granitic rocks of Angaro-Vitimski batholith are the prevailing type of basement rocks in the Alginsky region. However, bedrock exposures of young volcanic rocks with an age of approximately 8 Ma (Rasskazov et al. 2013) have been found in this region. The andesitic composition of these rocks is not typical for the volcanic rocks of the BRS.

Trace elements for physico-chemical modeling

An important component of hydrogeological conditions in the region is the presence of thermal mineral groundwater with a wide chemical composition. There is general agreement on the association between features of groundwater origin and rifting. Nevertheless, it seems appropriate, from the standpoint of plate tectonics, to make a comparative analysis between the different areas of lithospheric plates with a corresponding geodynamic regime, regarding the formation and composition of current thermal springs.

For this purpose, we studied the data from chemical analysis of the trace-element's composition of the rift and island-arc groundwaters in order to specify their origin. We addressed both continental rifts (Tajura, Azal, Red Sea, the Sheba Range area, Ethiopian Great Rift Valley and Baikal) and oceanic rift areas of Northern Atlantic: Iceland, Reykjanes Ridge, East Pacific uplift area), as well as the present-day subduction regions (Kuril-Kamchatka trench and Pacific ring) (Kononov

Fig. 3 - Alginsky Thermal Spring in the Barguzin Basin.

Fig. 3 - La sorgente termale Alginsky nel bacino di Barguzin.

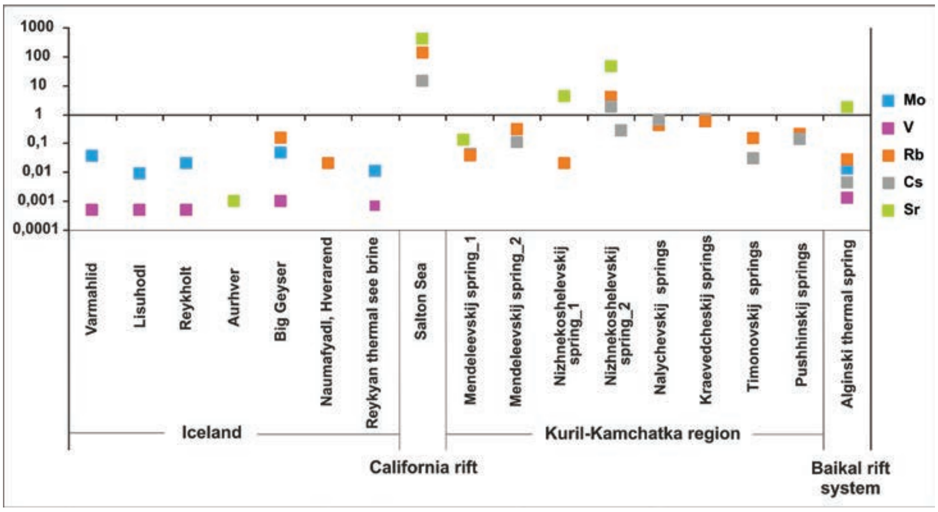
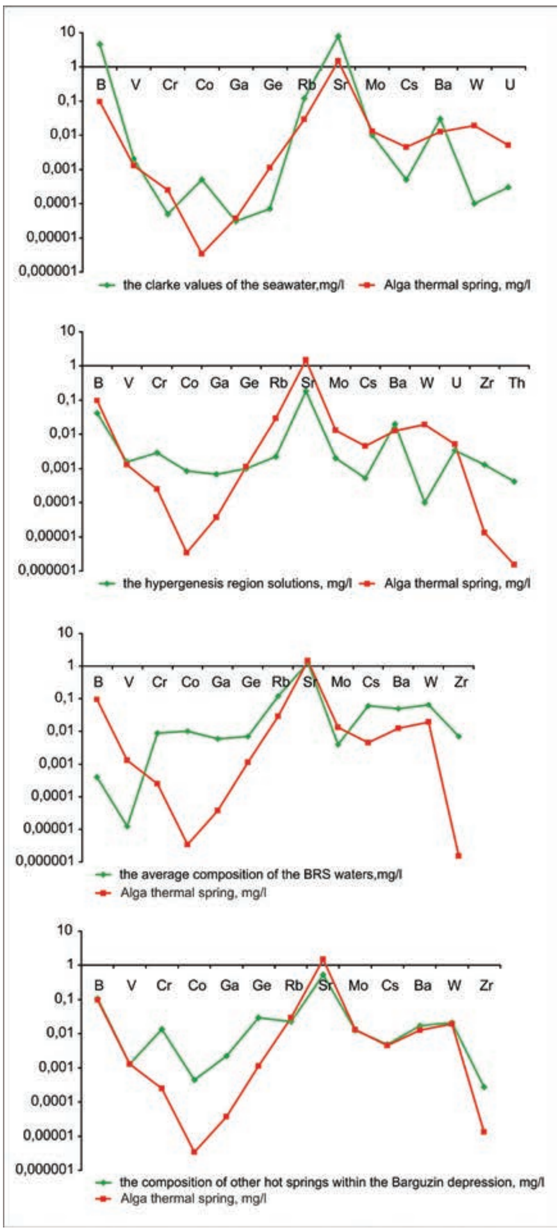


Fig. 4 - Trace-element composition of the Alginsky Spring waters against the water composition of rift and island-arc systems.

Fig. 4 - Elementi in traccia delle acque della sorgente Alginsky confrontati con quelli di acque di sistemi di rift e di arco insulare.



1983). These regions represent various margins of lithospheric plates, divergent and convergent, where ascending endogenic fluid components participate in groundwater composition.

As shown in figure 4, the content of elements of Alginsky Spring is close to the Icelandic geothermal waters.

Selecting specific microcomponents of a thermal water to determine its genesis, we compared chemical composition of the Barguzin Basin granite's to the clarke values of the elements in the Earth's crust and in the igneous rocks of both regional (Angara-Vitim batholith in general), and local prevalence (Angara-Vitim batholith Zazin Complex). This comparison showed that the concentration of the most of the elements corresponds to background concentrations (Fig. 5).

Upon comparing the values for average contents of elements in the Alginsky Spring to the seawater, to the hypergenesis region solutions, to the average composition of the BRS waters, and to the composition of other hot springs within the Barguzin Basin (Fig. 6), we found out that some of the elements, generally present in granites at the background level, have higher concentrations compared with the average values in the aqueous medium. Such elements are B, V, Rb, Mo, Sr, Cs, U.

Fig. 5 - The comparative characteristic of the rocks' chemical composition around the Alginsky Spring with the clarke values of igneous rocks, with the rocks of the Angara-Vitim batholite and with the rocks of the Zazin complex.

Fig. 5 - Comparazione della composizione chimica delle rocce dall'area della sorgente Alginsky con i valori tipici delle rocce ignee, delle rocce del batolite di Angara-Vitim e delle rocce del complesso di Zanin.

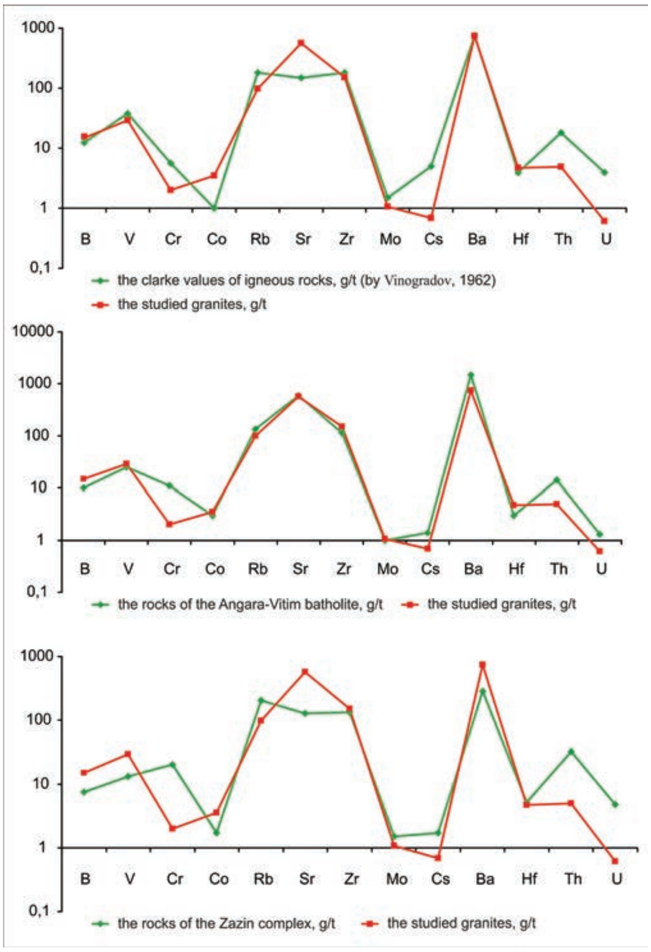


Fig. 6 - The comparative characteristic of the water's chemical composition of the Alginsky Spring with the clarke values of the seawater, of the hypergenesis region solutions, of the average composition of the BRS waters and of the composition of other hot springs within the Barguzin Basin.

Fig. 6 - Comparazione della composizione chimica dell'acqua della sorgente Alginsky con i valori tipici dell'acqua di mare, delle soluzioni ipergenetiche regionali, della composizione media delle acque del BRS e di altre sorgenti di acqua calda del bacino Barguzin.

Research methods

The water temperature of the spring and pH were measured on the site. Before taking the samples, the bottles had been rinsed several times with the water to be examined. The sample for macrocomponents determination has been stored in plastic bottles with a volume of 0.5–1 l. The sample for microcomponents was stored in a polypropylene tube of 15 ml. Initially, the membrane filter (pore size 0.45 µm) was pre-washed with water of the source, then it was used to filter the sample. Nitric acid was used for the preservation of the water sample, 0.1 ml of it was entered into the tube.

The rock sample has been selected from a granite massif near the thermal spring. From the rock sample of the size of 2.5–3 cm, microsections have been produced. For geochemical analysis another sample was taken from the same sampling point, not smaller than 10 cm in diameter and weighing more than 300 g. The selection criterion for these samples was the lack of weathered surfaces. Other characteristics of the examined rocks were observed on the field, such as material structure, presence of organic residues, relict textures and patterns, nature of the contact with other stratigraphic units, secondary changes.

The rock and water samples were analised at the Analytical Center of the "A.P. Vinogradov Institute of Geochemistry of the SB RAS" (Irkutsk). The petrographic study of the microsections focused on the mineral composition, the microstructure and microtexture of the rock. Hydrochemical analysis for the determination of the major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}) was carried out (Table 1).

Tab. 1 - Hydrochemical analysis of Alginsky Spring.

Tab. 1 Analisi idrochimica della sorgente Alginsky.

parameters		components	content (mg/l)
Eh (mV)	255	NH_4	0.001
Ec (µS/cm)	883	K	5.79
pH	6.2	Na	130.44
TDS (mg/l)	552.28	Ca	42.8
		Mg	3.16
		HCO_3	51.24
		Cl	15.98
		F	2.74
		SO_4	300
		NO_2	0.001
		NO_3	0.12
		SiO_2	41.06
		PO_4	0.01

Silicate analysis was done on the main rock-forming elements, which are represented in the form of oxides: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5 (Table 2). The oxide contents were determined by atomic emission flame photometry, semi-micro determination and spectrophotometric, potentiometric, atomic absorption, titrimetric, gravimetric methods.

For the determination of the microelements in the rock and the water ISP-MS analysis was used (Tables 3 and 4).

Tab. 2 - ISP-MS analysis of Alginsky Spring water.

Tab. 2 - Analisi mediante ISP-MS delle acque della sorgente Alginsky.

chemical elements	content (µg/l)	chemical elements	content (µg/l)
Li	126	Mo	13.1
Be	0.001	Cd	0.051
B	95	Sn	0.0001
Mg	1270	Sb	0.016
Al	11	Cs	4.51
Si	9052	Ba	12.5
P	3.7	La	0.006
S	119539	Ce	0.0058
Ca	49993	Pr	0.0007
Sc	0.0036	Nd	0.0024
Ti	0.60	Sm	0.0006
V	1.27	Eu	0.0007
Cr	0.25	Gd	0.0007
Mn	0.33	Tb	0.0006
Fe	1.70	Dy	0.0006
Co	0.0034	Ho	0.0013
Ni	0.046	Er	0.0006
Zn	1.37	Tm	0.0001
Ga	0.037	Yb	0.0001
Ge	1.12	Hf	0.0009
As	0.26	Ta	0.0007
Se	0.071	W	19
Br	41	Re	0.0006
Rb	29	Au	0.0002
Sr	1482	Tl	0.0067
Y	0.0091	Pb	0.0077
Zr	0.013	Th	0.0015
Nb	0.0014	U	5.1

Before the analysis, the rock sample (sample weighed: 0.02–0.1 g) was dissolved in a mixture of acids with melting in a muffle furnace at a temperature not exceeding 750 °C for 15–20 minutes. The analyzed water solutions were sprayed into the inductively coupled plasma discharge, which causes excitation and ionization of atoms, ions separation by the quadrupole mass analyzer for mass/charge ratio. The determination of the content of elements was conducted by comparing the measured intensities of the mass spectra of the samples' elements with the values of the intensities obtained in the construction of the calibration curve.

Tab. 3 - Silicate analysis of the granite.

Tab. 3 - Analisi del granito.

rock-forming components	content (%)
SiO_2	48.39
TiO_2	0.76
Al_2O_3	13.86
Fe_2O_3	2.18
FeO	4.7
MnO	0.14
MgO	6.9
CaO	19.98
Na_2O	1.04
K_2O	0.14
Li_2O	0.0092
P_2O_5	0.25
F	<0.02
S	<0.02
LOI	1.15
CO_2	0.2
B	4.5
Note: the content of B in g/t, LOI – loss on ignition	

Results and interpretation of physico-chemical modeling

The main question is whether the water's chemical composition of this sodium sulfate thermal spring is due to granite/andesite or from an endogenous source.

During our research, the structural and hydrogeological characterization was accompanied by physical and chemical modeling, a suitable tool for studying the characteristics of the formation of hydrogenic systems. A new approach for the modeling of hydrogenic processes through the software package "Selector" (Karpov et al. 2002) is herein proposed. "Selector" is a system of software and information modules which operate within a single integrated environment, and is based on the concept of minimizing the free energy of geochemical systems. The possibilities of the application "Selector" are shown in Figure 7.

The first step of thermodynamic modeling is the creation of a geological and geochemical model that includes theoretical understanding of the process and ex-perimental data. The second step consists in the creation of a physico-chemical and mathematical models. The physico-chemical model reflects the relationships of components of the geological model with the help of thermodynamic relations, the dynamics of

DOI 10.7343/AS-109-15-0136

Tab. 4 - ISP-MS analysis of the granite.

Tab. 4 - Analisi mediante ISP-MS del granito.

Chemical elements	content (g/t)	Chemical elements	content (g/t)
Li	50	La	28
Be	2.07	Ce	54
Sc	15	Pr	5.9
Ti	4357	Nd	22
V	152	Sm	3.58
Cr	69	Eu	0.87
Co	27	Gd	2.84
Ni	16	Tb	0.38
Cu	4.13	Dy	2.09
Zn	50	Ho	0.39
Ga	14.2	Er	1.09
Ge	0.88	Tm	0.17
Rb	6.1	Yb	1.12
Sr	735	Lu	0.20
Y	10.0	Hf	3.97
Zr	143	Ta	0.28
Nb	5.1	W	1.18
Mo	4.00	Tl	0.017
Sn	1.49	Pb	3.91
Sb	0.079	Th	6.6
Cs	1.48	U	3.67
Ba	110		

heat and mass transfer, the kinetics of chemical reactions. The main elements of the physico-chemical model are hydrodynamic conditions, which determine the physical and chemical evolution of hydrogeochemical systems (Byčinskij et al. 2004). The mathematical model describes quantitatively the physico-chemical process by a system of equations (the principle of minimum thermodynamic potential, the equations of heat and mass transfer, etc.) and includes methods and algorithms for calculating the equilibrium.

Algorithms for finding the minimum free energy have the advantage to not require determination of stoichiometric ratios. In addition, the method of minimizing the potentials gives the possibility of combining models of fluid dynamics and mass transfer in the megasystem, consisting of reservoirs, which are linked to each other and the environment by the direct, inverse and through-flows of matter and energy.

The main difficulty in applying the model is the choice of a conditional time of the process. To solve this problem, a solution of the degree of reaction was inserted. The physico-chemical characterization of the relations of the interacting water-rock mass simulates the water cycle. The slower the water exchange, the longer the water is in contact with the rock.

Another disadvantage of the minimization method is the necessity to approximate the local reactions to the state of chemical equilibrium of the whole system; local equilibrium is function of groundwater velocity, hence the achievement of a complete equilibrium in many cases is impossible.

The physico-chemical modeling of the water of Alginsky Spring followed several stages.

At first, the model validity was verified based on the chemical composition of the spring water. The water's chemical composition was entered as a system of independent components and was calculated at the temperature of 20 °C in and out of equilibrium with the atmosphere. The results of comparison of the model solution with the measured macrocomponents are presented in Figure 8.

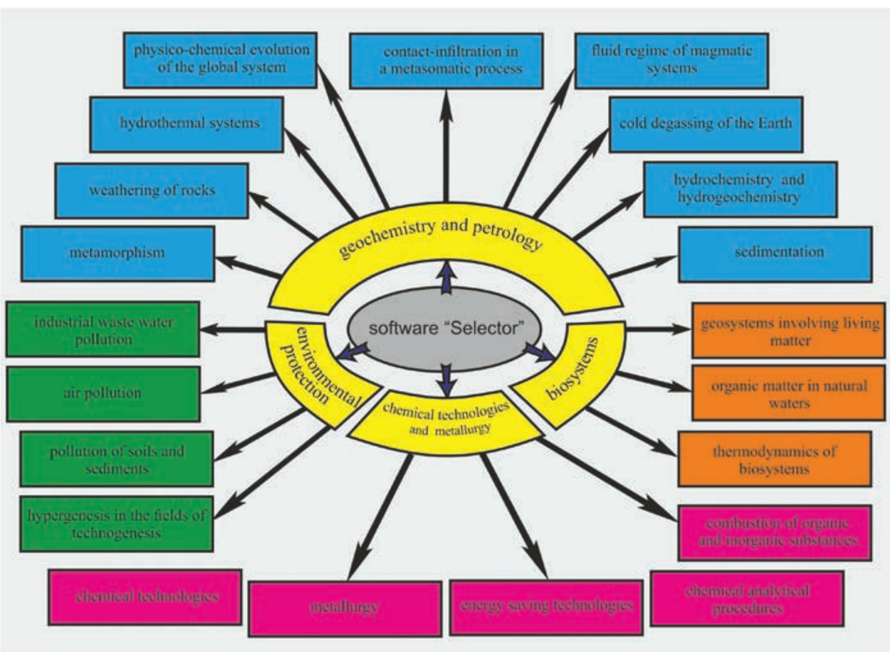


Fig. 7 - Application of the software "Selector" in various fields of science (modified from Byčinskij et al. 2004.

Fig. 7 - Applicazione del software "Selector" in vari campi delle scienze (modificato da Byčinskij et al. 2004).

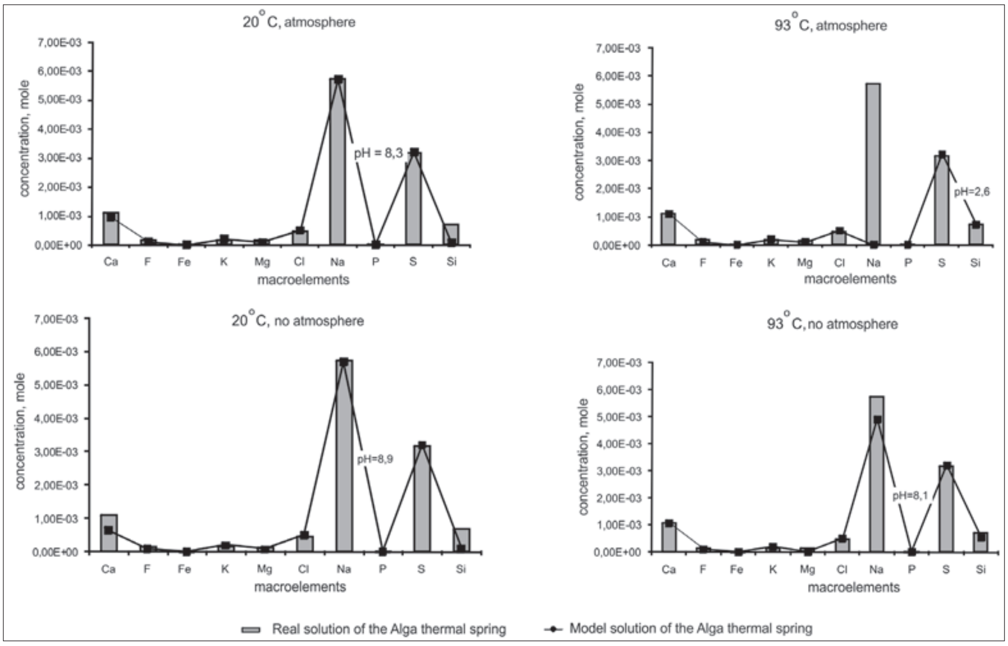


Fig. 8 - Results of the model test for adequacy.

Fig. 8 -Risultati della verifica del modello.

The closest values of the equilibrium chemical composition of the model water compared with the measured values were obtained in case of calculations at a temperature of 20 °C and at equilibrium with the atmosphere. The model was also verified at a temperature of 93 °C without atmospheric equilibrium. Figure 8 illustrates that at a temperature of 93 °C the value of pH is 8.1, which agrees with the pH-value of Alginsky Spring's water. The concentration of dissolved components is also the most closely corresponding to the composition of the hydrochemical analysis. Consequently, the model can be considered valid and able to describe the chemical composition of water solutions at the preset P–T conditions (see the Table 5).

To investigate about the origin of spring water composition, i.e., if water interaction with granites or andesites prevails or water requires participation of a juvenile substance source, two stages of analysis were carried out. At the first stage of physico-chemical modeling investigations of interaction between rainwater and rock (andesites/granites) at different P–T conditions were performed. In calculations the interaction degree between water and rock had changes. This interaction degree is expressed in terms of coefficients, reflecting the amount of rock interacting with 1 kg of water. This coefficient was changed from 5 to 20 g/kg H_2O. Figure 9 shows that the most probable source of macroelements in water are granites rather than andesites. The model that better approach the water composition is the one that involves the interaction of granites with pure water at the temperature 93 °C.

At the second stage of modeling, cooling process of the hydrothermal solution from 93 to 20 °C was considered. The

Tab. 5 -Composition of the Alginsky Spring water.

Tab. 5 - Composizione dell'acqua della sorgente Alginsky.

chemical elements	real composition of the Alginsky thermal spring water (mole)	model composition of the Alginsky thermal spring water (mole)			
		20° C atmosphere pH=8,3	20° C no atmosphere pH=8,9	93° C atmosphere pH=2,6	93° C no atmosphere pH=8,1
Ca	1,08E-03	9,51E-04	6,55E-04	1,10E-03	1,06E-03
F	1,46E-04	1,00E-04	1,00E-04	1,00E-04	1,00E-04
Fe	3,04E-08	1,69E-13	7,01E-14	3,00E-08	1,20E-09
K	1,50E-04	2,00E-04	2,00E-04	2,00E-04	2,00E-04
Mg	1,31E-04	9,46E-05	7,99E-05	1,00E-04	9,39E-07
Cl	4,55E-04	5,00E-04	5,00E-04	5,00E-04	5,00E-04
Na	5,73E-03	5,70E-03	5,70E-03	7,08E-10	4,90E-03
P	1,06E-07	1,32E-09	3,25E-10	1,00E-07	1,29E-10
S	3,16E-03	3,20E-03	3,20E-03	3,20E-03	3,20E-03
Si	6,91E-04	8,41E-05	1,01E-04	7,00E-04	5,42E-04

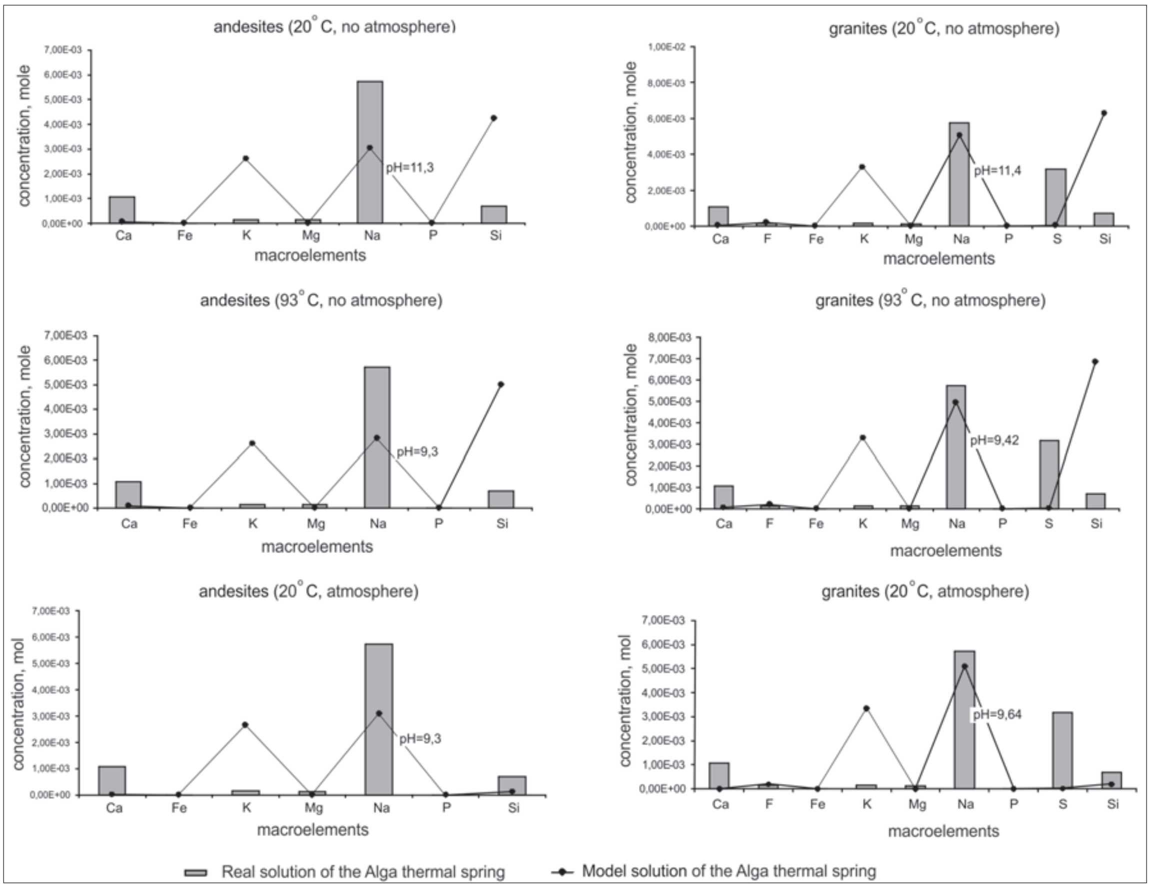


Fig. 9 - Results of interaction of rainwater-granites/andesites at different P–T conditions.

Fig. 9 - Risultati della interazione di acqua meteorica con graniti e andesiti in diverse condizioni di pressione e temperatura.

obtained equilibrium composition of cooled hydrothermal solution is strongly distinguished from the measured water composition according to the Si and Ca concentrations. One reason could be the introduction of the solid phases of calcite and α-quartz with essentially less solubility in the model. This is related to the replacement of α-quartz with amorphous form in solid components and to exclusion of equilibrium calcite. In this case, the result of the model matches with the analytical data. The only exception is the concentration of S. The high concentration of S observed in natural waters could be connected with either endogenous sources or microbial activity. From these experiments it can be therefore deduced that the origin of the Alginsky Spring can be related to atmospheric waters interacting with granites (when temperature is 93 °C and pressure reaches 840 Pa). The thermodynamic calculations show a comparable composition of the macroelements between the model and measured values (Fig. 10).

Thus, the Alginsky Spring water's formation process does not require an endogenous source of macrocomponents, with the exception of sulfur. However, it is necessary to have an endogenous source to explain the identified concentration of microcomponents, such as U, Li, Rb, B, V, Mo, Sr, Cs, (Fig. 10). The concentration of microelements in the model is often considerably lower than what observed in reality, although

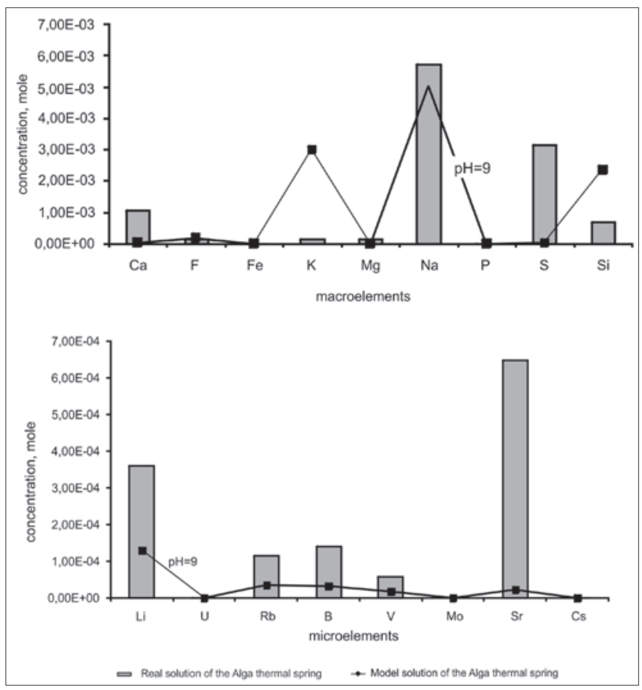


Fig. 10 - Physical and chemical model results for the hydrothermal solution cooling from 93 to 20 °C.

Fig. 10 - . Risultati del modello chimico-fisico per la soluzione idrotermale con raffreddamento da 93 a 20 °C.

the graph for microelements illustrates that modeled data tend to replicate the balance of components' concentration in natural waters, with the exception of Sr. Our findings are consistent with the results of investigations of He isotopes (Polâk 2000), which showed the existence of mantle marks in thermal waters of the Barguzin depression.

Conclusions

According to preliminary data of physico-chemical modeling, selected trace elements that distinguish Alginsky Spring from other natural waters of the region may have an endogenous nature.

For a more precise determination, further researches should continue the modeling of the formation processes of the studied thermal water composition, using the software "Selector" (Karpov 1981), according to the following scenarios: cooling model (increasing) of endogenous fluids, with a number of calculated equilibrium states of the system of a given composition, in combination with decreasing temperatures and pressures according to geothermobarometry (Zubkov 1998) and the model of deep fluid interaction with the host rocks (flow-through megasystem model) (Čudnenko 1999).

Acknowledgement: The authors are grateful to the reviewers Prof. Maria Dolores Fidelibus and Maurizio Barbieri, who contributed with their right and critical remarks to the improvement of the paper. The authors are also grateful to Christoph David Hohl and Francesca Lotti for helping with the translation.

REFERENCES

Bulmasov A.P. (1968). Nekotorye osobennosti geofizičeskih polej i struktury zemnoj kory Pribajkal'â // Bajkal'skij rift. "Some features of geophysical fields and crustal structure of the Baikal region// Baikal rift". Moscow: Nauka: 113–123.

Byčinskij V.A., Isaev V.P., Tupicyn A.A. (2004). Fiziko-himičeskoe modelirovanie v neftegazovoj geohimii. Teoriâ i metodologiâ fiziko-himičeskogo modelirovaniâ: učebnoe posobie. Čast' 1 "Physico-chemical modeling in oil and gas geochemistry. Theory and methodology of physical and chemical modeling: a tutorial. Part 1". Irkutsk.

Čudnenko K.V. (1999). Dinamika megasistem v geohimii: formirovanie bazovyh modelej processov i algoritmy imitacii "Dynamics of megasystems in geochemistry: formation of basic process models and algorithms for simulation" / K.V. Čudnenko, I.K. Karpov, S.I. Mazuhina, V.A. Byčinskij, M.V. Artimenko // Geologiâ i geofizika 40 (1): 45–61.

Didenkov Û.N. (1998). Formirovanie gidrosfery Bajkal'skogo regiona v svâzi s processami riftogeneza // Geologiâ, poiski i razvedka mestoroždenij rudnyh poleznyh iskopaemyh "Baikal region hydrosphere formation due to rifting processes". Sb. naučn. tr. Irkutsk: IrGTU. No. 22: 68–77.

Didenkov Û.N., Byčinskij V.A., Lomonosov I.S. (2006). O vozmožnosti suŝestvovaniâ èndogennogo istočnika presnyh vod v riftovyh geodinamičeskih usloviâh // Geologiâ i geofizika, "On possibility of existence of the fresh water endogenic source under rift geodynamic conditions". 47 (10): 1114–1118.

Didenkov Û.N., Byčinskij V.A., Lomonosov I.S., Altynnikova M.A. (2007). O genetičeskoj sistematizacii prirodnyh vod Bajkal'skogo rifta // Vserossijskaâ naučnaâ konferenciâ (s učastiem inostrannyh učënyh) "Problemy geohimii èndogennyh processov i okružaûŝej sredy" "On genetical systematization of the Baikal Rift natural waters". Irkutsk: Izd-vo Instituta geografii im. V.B. Sočavy SO RAN 1: 155–158.

Didenkov Û.N., Sklârova O.A., Černyšova Z.V., Brenzej V.I., Vergun A.V. (2010). Analiz mikrokomponentnogo sostava prirodnyh vod Bajkal'skoj riftovoj zony // Geologiâ, poiski i razvedka poleznyh iskopaemyh i metody geologičeskih issledovanij. "Analyzing the trace-element composition of the Baikal Rift Zone natural waters". Materialy Vserossijskoj naučno-tehničeskoj konferencii "Geonauki" Irkutsk: Izd-vo IrGTU No.10: 167–172.

Èpov M.I., Nevedrova N.N, Sančaa A.M. (2007). Geoèlektričeskaâ model'Barguzinskoj vpadiny Bajkal'skoj riftovoj zony "A geoelectric model of the Barguzinski depressions at the Baikal Rift Zone" // Geologiâ i geofizika 48 (7): 811–829.

Karpov I.K., Čudnenko K.V., Byčinskij V.A., Artimenko M.V. (2002). Selektor pod Windows// Geologiâ, geohimiâ i geofizika na rubeže HH i HHI vekov. RFFI v aziatskoj časti Rossii. Materialy Vserossijskoj naučnoj konferencii, posvâŝennoj10-letiû RFFI (1-4 oktâbrâ2002 g.) "The WINDOWS "Selector", Geology, geochemistry and geophysics at the turn of the 21st century Russian". Irkutsk.

Karpov, I.K. (1981). Fiziko-himičeskoe modelirovanie na ÈVM v geohimii [Physico-chemical modeling on a computer in geochemistry] / I.K. Karpov; otv. red. F.A. Letnikov. Novosibirsk: Nauka.

Karta razlomov ûga Vostočnoj Sibiri "Map of faults of Southeastern Siberia" (1988) / red. P. M. Khrenov. Moscow.

Kolomiec V.L. (2010). Sedimentogenez plejstocenovogo akval'nogo kompleksa i usloviâ formirovaniâ nerudnogo syr'â suhodol'nyh vpadin Bajkal'skoj riftovoj zony: avtoref. dis. … kand. geol.-min. nauk "Sedimentogenesis of the pleistocene aquatic complex and the conditions of formation of non-metallic minerals in upland depressions of the Baikal Rift Zone (Diss.)" (25.00.01). Irkutsk.

Kolomiec V.L., Budaev R.C. (2010). Paleoobstanovki sedimentogeneza pesčanogo massiva Verhnij kujtun (Barguzinskaâ dolina) // Geodinamičeskaâ èvolûciâ litosfery Central'no-Aziatskogo podvižnogo poâsa (ot okeana k kontinentu) "The Paleozoic environment of the sedimentation of sandy massif at Upper Kuitun (Barguzinskaya Valley) in: Geodynamic Evolution of the Lithosphere of the Central Asian Mobile Belt (from Ocean to Continent)": Materialy soveŝaniâ. Irkutsk: Institut zemnoj kory SO RAN 1 (8): 141–142.

Kononov V.I. (1983). Geohimiâ termal'nyh vod oblastej sovremennogo vulkanizma "Current volcanism thermal water geochemistry". Moscow: Nauka.

Kuz'mina E.A., Vergun A.V. (2009). Sopostavitel'naâ ocenka termal'nyh vod Bajkal'skoj riftovoj sistemy i Hangajskogo svodovogo podnâtiâ // Geologiâ, poiski i razvedka poleznyh iskopaemyh i metody geologičeskih issledovanij: Materialy Vseros. nauč.-tehn. konf. "Geonauki", posvâŝënnoj 110-letiû so dnâ roždeniâ professora S.A. Vahromeeva i 75-letiû so dnâ roždeniâ professora G.S. Vahromeeva "Comparative estimate of the thermal waters of the Baikal Rift System and the Hangay arc raise". Irkutsk: Izd-vo IrGTU No. 9: 164–168.

Lomonosov I.S. (1974). Geohimiâ i formirovanie sovremennyh gidroterm Bajkal'skoj riftovoj zony "Geochemistry and formation of the Baikal Rift Zone current hydrotherms". Novosibirsk: Nauka.

Lysak S.V. (1988). Teplovoj potok kontinental'nyh riftovyh zon "Continental rift zones' heat flow". Novosibirsk: Nauka. Sib. Otd-ie.

Mel'nikova V.I., Radziminovič N.A. (2007). Parametry sejsmotektoničeskih deformacij zemnoj kory Bajkal'skoj riftovoj zony po sejsmologičeskim dannym "Seismotectonic parameters of crustal deformation in the Baikal rift zone from seismological data" // DAN 416 (4): 543–545.

Ovčinnikov A.M. (1955). Obŝaâ gidrogeologiâ "General hydrogeology". Moscow: Gosudarstvennoe naučno-tehničeskoe izd-vo literatury po geologii i ohrane truda.

Plûsnin A.M., Černâvskij M.K. (2006). Vliânie temperatury na formirovanie mikrokomponentnogo sostava gidroterm Barguzinskogo Pribajkal'â // Podzemnaâ gidrosfera: Materialy Vserossijskogo soveŝaniâ po podzemnym vodam vostoka Rossii "Temperature effect on the formation of trace-element composition of the Barguzin Pribaikalye hydrotherms". Irkutsk: izd-vo IrGTU: 104–107.

Polâk B.G. (2000). Izotopy geliâ v podzemnyh flûidah Bajkal'skogo rifta i ego obramleniâ (k geodinamike kontinental'nogo riftogeneza) // Rossijskij žurnal nauk o Zemle "Helium isotopes in subsurface fluids from the Baikal rift and its framing (to the geodynamics of continental riftogenesis)" 2 (2): 109–136.

Radziminovič N.A., Balyšev S.O., Golubev V.A. (2003). Glubina gipocentrov zemletrâsenij i pročnost' zemnoj kory Bajkal'skoj riftovoj zony "The depth of the earthquake hypocenters and strength of the crust of the Baikal Rift Zone" // Geologiâ i geofizika 44 (11): 1216–1225.

Rasskazov S. V., Âsnygina T. A., Čuvašova I. S. (2013). Miocenovaâ smena magmatičeskih istočnikov na zapadnom zamykanii Ûžno-Bajkal'skoj vpadiny Bajkal'skoj riftovoj zony: ot neudavšegosâ passivnogo riftogeneza k aktivnomu // Kontinental'nyj riftogenez, soputstvuûŝie processy: materialy Vtorogo Vserossijskogo simpoziuma s meždunarodnym učastiem i molodežnoj naučnoj školy "Miocene change of magmatic sources of the South Baikal depression's western terminus in the Baikal Rift Zone: from a failed passive to an active rifting process". Irkutsk 2: 43–46.

San'kov V.A., Luhnev A.V., Mirošničenko A.I., Ašurkov S.V., Byzov L.M., Kale È., Deveršer Ž., Dembelov M.G. (2009). Rastâženie v Bajkal'skom rifte: sovremennaâ kinematika passivnogo riftogeneza // Doklady Akademii nauk "Stretching in the Baikal Rift: Current kinematics of passive rifting" 424 (5): 664–668.

Stepanov V.M. (1989). Vvedenie v strukturnuû gidrogeologiû "Introduction to structural hydrogeology". Moscow: Nedra.

Ufimcev G.F., Ŝetnikov A.A., Filinov I.A. (2010). Barguzinskaâ vpadina, eë sootnošeniâ s Bajkal'skim riftom i osobennosti kajnozojskogo riftogeneza na ûge Vostočnoj Sibiri "Barguzinskaya depression, its relationship with the Baikal rift and features of Cenozoic rifting in the south of Eastern Siberia" // Otečestvennaâ geologiâ No. 1: 32–37.

Vinogradov A.P. (1962). Srednie soderžaniâ himičeskih èlementov v glavnyh tipah izveržennyh gornyh porod zemnoj kory "The average content of chemical elements in the principal types of igneous rocks of the earth crust" // Geohimiâ No. 7: 555–571.

Zamaraev S.M., Vasil'ev E.P., Mazukabzov A.M., Ružič V.V., Râzanov G.V. (1979). Sootnošenie drevnej i kajnozojskoj struktur v Bajkal'skoj riftovoj zone "The relation of the ancient and Cenozoic structures in the Baikal rift zone". Novosibirsk: Nauka.

Zubkov V.S. (1998). Termodinamičeskaâ model' sistemy C-H v usloviâh vysokih temperatur i davlenij "Thermodynamic model of the C-H system at high temperatures and pressures" / V.S. Zubkov, A.N. Stepanov, I.K. Karpov, V.A. Byčinskij // Geohimiâ 36 (1): 95–101.