

## Thermal Fluid Geochemistry in Caldera Academy Nauk (Kamchatka, Russia)

Smyshlayeva A.A.\*, Karpov G.A.\*, Bortnikova S.B.\*\*\*, Kuzmin D.Yu.\*

\*Institute of Volcanology and seismology, Piip boulevard 9, Petropavlovsk-Kamchatsky 683006, Russia

[annasm@kcs.iks.ru](mailto:annasm@kcs.iks.ru)

[karpovga@kcsiks.ru](mailto:karpovga@kcsiks.ru) [devis@kcs.iks.ru](mailto:devis@kcs.iks.ru)

\*\*Institute of Geology, Koptyug Pr. 3, Novosibirsk 630090, Russia

[sveta@uiggm.nsc.ru](mailto:sveta@uiggm.nsc.ru)

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### ABSTRACT

In lake Karymskoe (Russia, Kamchatka) in 1996 has taken place underwater eruption therefore the structure of water of lake and his (its) physical and chemical parameters has essentially changed, and on his (its) coast has taken place reorganization gasgeothermal outputs (exits). The basic purpose of the works spent since 1996 on present time - studying and an estimation of consequences of underwater eruption on water object and an environment. At once after eruption outputs (exits) highly mineralized sources which part has gradually disappeared were observed, and in some there was a gradual decrease (reduction) of a mineralization. By change of the maintenance (contents) of chlorine and a pine forest having obviously deep origin, took place saturation superficial waters. And, alongside with simple saturation atmospheric waters occurred and adulteration lixiviate from the fresh cast out breeds (and also ashes from be in eruption Karymsky volcano) easily mobile components, first of all sulfur, calcium, sodium, magnesium. The wide range of fluctuations of physical and chemical conditions of solutions in a modern output (exit) gasgeotherm clearly correlates with change of a chemical compound. Deep sodium chloride solutions of sources of the Academy of sciences gravitate to a field of alkaline regenerative conditions, while for solutions with the greater share of a sulfate - ion (it is obvious, formed at mixture with superficial waters) less alkaline conditions are characteristic at same variations Eh. Occurrence of a significant amount of a hydrocarbonate typically for subalkaline oxidizing conditions.

Displays endogenous fluid system in caldera Academies of sciences are characterized by the raised(increased) maintenance(contents) in waters of thermal sources of such elements, as B, Li, Sr, As, Mo, V, Ni, Ga, Ge, Zr, Cu, Zn, Br. By much sulphatic structure of water and sour lakes Karymskoe up to pH-3.2 as a result of eruption of 1996, in structure deep flying prevailed SO<sub>2</sub> and H<sub>2</sub>S, that it is more typical for andesite magmas. In the volcanic centre now with the big dynamism processes of formation of new structures, volcanogenic and sedimentary formations(educations), a chemical compound of reservoirs proceed.

Now observation proceed as regime.

### 1. INTRODUCTION

Acidic lakes have been known in Japan (Yugama, Kusatsu-Shirane), Indonesia (Keli Mutu volcano, Crater Lakes; crater lake of Ijen Volcano, East Java), New Zealand

(Ruapehu crater lake), South America (Copahue crater lake - " Sulfur Lake ", Andes Mountains, Neuquen Province, Argentina), on Kuriles, Kamchatka and in other regions with active volcanism. They arise in places of output of acidic volcanic gases in active volcanoes craters and exist short time between eruptions. Condensation steam-gas volcanic fluids containing acid gases HCl, HF, SO<sub>2</sub>, H<sub>2</sub>S cause acidity of water in these lakes. The sizes of such lakes varied in a wide range - from the first meters up to hundreds. Usually this one does not have drain, or discharge from them is very small. In paroxysmal stage activity of volcano eruption often occurs in the center of lake. In this case there are breaks of walls of crater and slop the big weights of acidic waters in a vicinity that is lead to ecological accidents.

Caldera acidic lakes take a special place among types of acid lakes of areas with active volcanism. They are exist long time and characterized by wide variations of the general mineralization, inconstancy of a chemical compound and varying acidity. These lakes arise in hollows of caldera and fix zones of tectonic breaks, on which besides high-temperature fluids from superficially deposited magmatic centers and the top parts of magmatic body not left on ground surface. On periphery this calderas often occurs active volcanoes. Usually in this calderas located large high-temperature hydrothermal systems. The salt composition of water acidic caldera lakes basically represents a mix of salts sulfuric and hydrochloric acids - as products of transformation of deep haloid-sulphurous emanations and their reaction with breeds.

The hydrothermal system of caldera Academy Nauk have special interest of various researchers after underwater phreatic-magmatic eruption in January 1-2, 1996 in northern sector Karymskoe lake filling all caldera. Consequence of this short-term but powerful eruption was formation of volcanic construction of type maar with a crater in topmost part with diameter about 600 m and depth of 56 m. The southern sector of a crater is under water. Northern, east and western boards of this construction have generated peninsula Novogodny, combined sand-scoria-bomb a material of mainly basalt composition (Figure. 1). On a rather narrow inundated terrace Karymskaya river on her new coast, in 200 m from a source was appeared the group with temperature 70-98°C which has named "Piipovskye". The spring of descending thermal sources have generated groove "Goryachy" with width 2-3 m and length about 100 m. In some griffons (especially high-temperature) are observed outputs of gases. Besides thermal sources have appeared in the channel Karymskaya river (a Burlyashy source) and a few sources on both coast of this river (sources Razlomnyi, Beregovoi) traced on distance about 200 m a direction submeridional interstitial

трещинной а zone well shown as a powerful extended crack in a right board of a socle terrace Karymskaya river (Leonov V.L., 1998).

In the beach zone of Karymskoe lake framing from the north crater Tokareva almost on all his perimeter is observed warming zone, and in prospect-hole found thermal waters with temperature 50-96°C (sources Plyazhnye) and in southwest sector - outputs of hydroterm with temperature to 52°C are opened. In north-northeast sector Karymskoe lake coast in 1 km from a source Karymskaya river have appeared sources Medvezhy in 1996.

The big group of thermal sources is found in east frame of lake. The majority of sources set near shore line (Beregovoy, Serdity, Carbonatny etc.). Ushakovsky sources were appeared above 25 m higher shore line. Exact data on formation time of these sources are not present. Probably, they existed before eruption in 1996 as/since here are observed metasomatite disgraces – argillit formation typical for the centers of discharge of modern hydrothermal systems. Apparently, they were naked after sharp downturn lake level in May, 1996. In this zone plentiful outputs of free gases from depth of 1-2 m at a coast of lake are observed also.

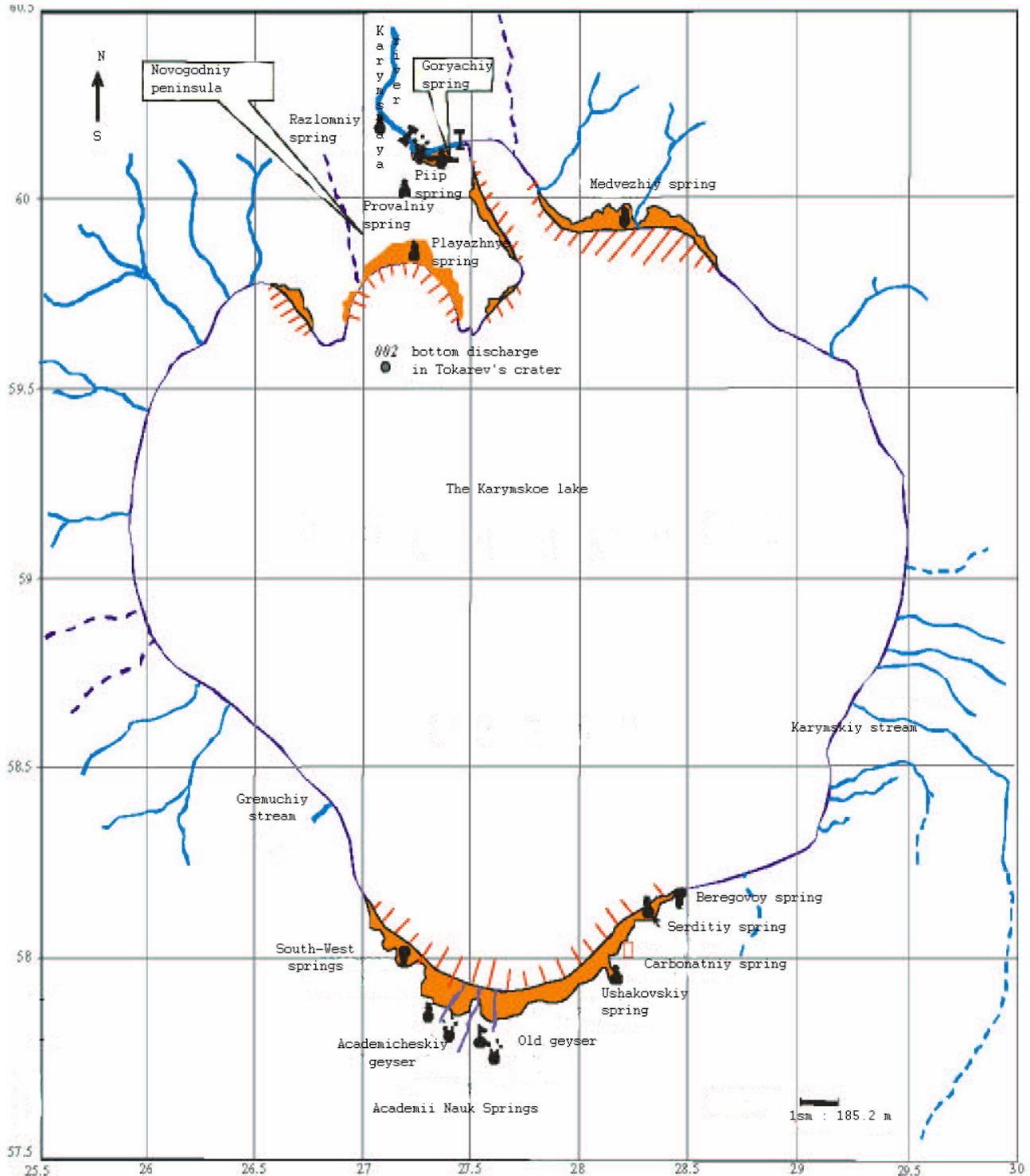


Figure 1: Location thermal springs in caldera's Academy Nauk (Kamchatka (map made by Nikolaeva A.G., Marushhak V.O., scientific editor Karpov G.A.).

Sources of the Academy Nauk were known earlier. But after eruption of 1996 there was some regrouping of outputs a hydroterm and there was found a new western group of thermal sources among with the geyser. It has received the name "Academicheskyy" (Vakin E.A., Pilipenko G.F., 2001).

Besides this geyser some tens outputs pair on which place pulsing sources and mud boilers with condensate water are formed here are observed. The basic purpose of hydrogeochemical studying of sources Karymskoe lake system was construction of qualitative model of their genesis on the basis of definition of physical and chemical conditions in solutions and also their basic and microelement composition. In article are used the data long-term monitoring supervision and gaugings of the specified parameters in different groups of sources and the results of their system approbation received in 2002. Detailed characteristics of the used methods are given by Bortnikova S.B., Karpov G.A., Bessonova E.P., Smyshlyayeva A.A., 2003.

## 2. THE SHORT CHARACTERISTIC OF A GEOLOGICAL STRUCTURE OF THE ACADEMY NAUK VOLCANO

The volcano of the Academy Nauk is allocated in structure Karymsky volcanic center and named by Vlodavets V.I. (1939). Karymsky volcanic center is one of the most active geological structures in East volcanic belt of Kamchatka. Its sizes about 50 x 35 kms. Volcanic activity began here more than 2 million years back and to present time, in this structure are allocated 21 volcanic construction, including 6 calderas. Masurenkov Yu.P. (1980) mark out four rhythms of volcanism which generated whole Karymsky volcanic center. The final (fourth) rhythm characterized by catastrophic eruptions pyroclastic flow in the structure sector of Academy Nauk about 110-80 thousand years ago (the end of average - the beginning of top Pleistocene). It is considered, at this time was generated caldera of Odnobokiy volcano in northern sector of that subsequently has formed small stratovolcano Academy Nauk.

The Karymskoe lake is located in East Kamchatka volcanic belt in 6 kms from active volcano Karymsky and belong to Karymsky volcanic center (KVC) Here are known two groups of thermal sources belong to calderas. Caldera Academy Nauk and Karymskaya caldera are allocated among other structures KVC with powerful modern hydrothermal activity. In caldera Academy Nauk at southern part of lake, have discharge high-temperature (boiling) hydrotherms and their less hot derivatives. Karymskaya caldera, located at bottom Karymsky volcano an arrangement to the most powerful center on Kamchatka of discharge medium-temperature carbonic therms (Vakin E.A., Pilipenko G.F., 1998). Modern hydrothermal activity is concentrated near a large break submeridional direction, transversal ring structure in this western part (Vakin E.A., Pilipenko G.F., 2001).

## 3. METHODS OF RESEARCH

For measurements temperature on vertical structures and sampling water from depths lake were applied to overturning bathometer HYDRO-BIOS KIEL the Swedish manufacture in volume 2 litre and slamming bathometer the same firm in volume 5 litre.

At approbation of hydroterm the sample were filtered and definition, also was determined pH and Eh. Then one portion of solutions was acidified by the overtaken nitric acid to pH ~ 2 for the subsequent definition microelement

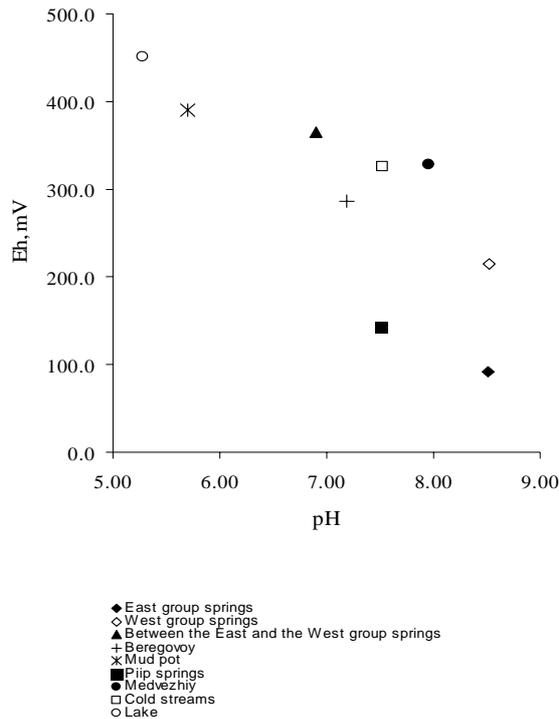
composition. Another was left without fixing for definition of the basic salt composition. Field definition pH and Eh was made portable field pH-OPR-meter by HANNA.

The analysis of a chemical compound was carried out in the certificated Central chemical laboratory of IV FED Russian Academy of Science by standard techniques for the analysis of natural waters and all-Union State Standard with a mistake of definition no more than 5 %. At the analysis ardent-photometric methods calorimetric, volumetric, potentiometric were applied. The microelement structure of solutions was analyzed by method ISP on device IRIS of firm Jarell Ash Corporation (USA).

## 4. THE HYDROCHEMICAL CHARACTERISTIC OF THERMAL SOURCES

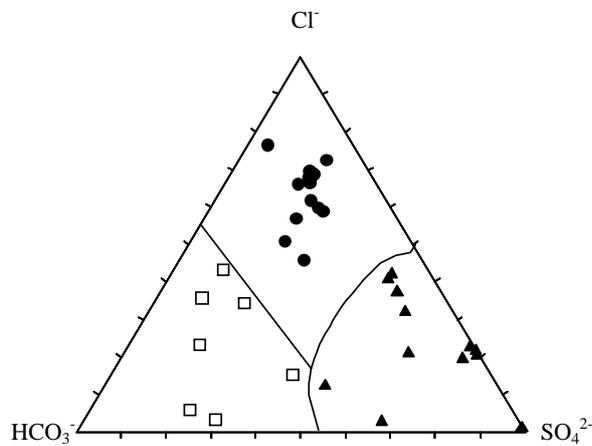
In group of hydroterm appear after underwater eruptions on peninsula Novogodny one year after eruption was formed failing raven with depth about 4 m at the bottom was found the output boiling hydroterm chloride-sodium composition (tab. 1). Water of this source had typical - high for this type a hydroterm contents of chlorine, sodium, potassium, a pine forest and silica acid and on the general mineralization more than twice surpassed water as old and new geyser in southern group a hydroterm. But in 1998 in crater have taken place collapse of the walls and the source has disappeared. A mineralization close to this source, had in the beginning of the existence in 1996 source #1 in Piip group of sources on the left coast Gorychy groove. But mineralization has essentially decreased after time. Similar changes were taking place in due course with a mineralization of water and other sources of Northern group. By change of the contents chlorine and a pine forest having obviously deep origin, took place desaturation meteoric waters. With occurred simple dilution by atmospheric waters and adulteration подмешивание with leachable from the fresh cast out breeds (and also ashes from be in eruption извергающегося Karymsky volcano) easily mobile components, first of all sulfur, calcium, sodium, magnesium take place.

In the modern plan of outputs hydrotherms on Karymskoe lake perimeter is looked through the certain law - they are grouped in northern and southern sectors of coast. In both groups heat developable wide variations of physical and chemical parameters of solutions (fig. 2) and their hydrogeochemical composition are observed. Distinctions of oxidation-reduction conditions and acidities - alkalinity the hydroterm allows to plan trend changes of these characteristics determined, obviously, genetic features of their origin and ways of an output on a surface. Regenerative conditions of subalkaline solutions of east group of the Academy Nauk on practically linear dependence is replaced on practically neutral and further - oxidizing conditions with downturn of values pH for different groups of hydrotherms (the Western group of the Academy Nauk, Piip sources, Beregovoy, Medvezhy, cold streams). Extreme values of these parameters are characterized for mud boilers of the Academy Nauk and Karymskoe lake - oxidizing conditions with subacidic- practically neutral environment.

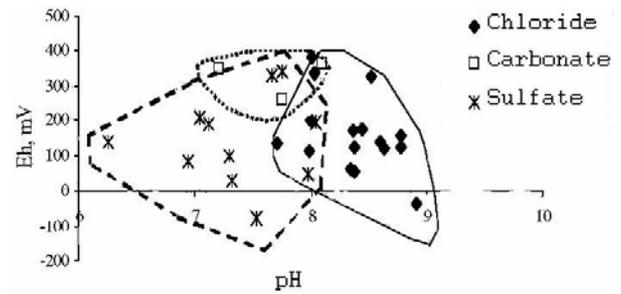


**Figure 2: The pH-Eh diagram parameters springs of Karymskoe lake (The average values for different groups).**

With regard to absence coarse hydrochemical ash value hydroterm, all the same, can divide sources into three groups on a ratio of the basic anions: a hydrocarbonate, chloride, sulfate. That in the majority the hydroterm the basic anion is chloride (sources of the Academii Nauk, Medvezhny, group of hydroterm in east sector of lake), in some sources (Piip, Beregovoy) the leading part plays sulfate (fig. 3). But meet the sources with composition where prevalence  $\text{HCO}_3^-$ -ion (except for above named Carbonatny to this type prevails concern small, but the numerous sources located on a coast of lake, between East and Western groups of geysers of the Academy Nauk). Variations in anion composition of solutions have quite distinct connection with change of physical and chemical parameters. Chloride-sodium sources occupy the right field on the diagram pH-Eh (sources from Academy Nauk, Medvezhny (fig. 4)).



**Figure 3: Relative contents of the basic anions in solutions of sources of system Karymsky lake.**



**Figure 4: Values pH-Eh parameters in different hydrochemical composition.**

The degree abyssal of thermal waters is well determined by the contents in them such characteristic components as Cl, B, Si. The field sulfate-sodium hydrotherms shown in zones with the big capacity of a cover fresh eruptive breed, is located in regenerative, but less alkaline area (some sources near coast, Beregovoye, Piip, Razlomny). In these therms always highly contents of ions Ca and Mg. And carbonate sources presented by three small hydrotherms, are characterized by oxidizing conditions at subalkaline reaction. From these positions the hydrothermal system of caldera Academy Nauk in a deep zone, apparently, contains classical nitric-carbonic-acid therms chloride-sodium composition. All other types of waters arise both on peninsula Novogodny, and on other sites caldera are products of mixture chloride-sodium therm with waters of superficial formation.

Using these criteria, we can ascertain, that the most deep therms chloride-sodium composition in caldera Academy Nauk have specialization concerning such components as B, Li, Sr, As, Mo, V (tab. 2). For all types of waters high contents Cu, Zn, Br and the same Sr, Ge are characteristic. In mineral deposits of sources with these waters, except for vanadium and strontium increased contents of Ni, Ga, Zr, to a lesser degree Y is marked also.

The composition of free gases of thermal sources and centers underwater discharge in caldera Academii Nauk also has very wide variations (tab. 3). In a gas phase of a high-temperature source №1 in Piip sources group highly the contents of methane. In discharge under water in a channel Karymskaya river (source Burlyashhy) which leaves in 40 m from a source № 1, already carbonic-nitric structure of gases is observed, at the minimal contents of hydrocarbons. In a beach zone of discharge composition of gas essentially nitric, and outputs of gas directly from a bottom of Karymskoe lake (for example, on shoalness in a Zhelaniy bay) already have carbonic structure. It is typical, that these outputs spatially gravitate to a zone of display hydrocarbonate waters (source Carbonatny). Nitric therms sources of Academy Nauk are enriched with oxygen (more than 25 %  $\text{O}_2$ ), at practically normal composition of air on lake (height 624 m). Obviously, active mixture deep a term with atmospheric waters and boil-off nitrogen and to a lesser degree carbonic acids in near-surface conditions takes place.

The important information about dynamics of a stream of substance on sites of display managed hydroterm to be received according to research of a radio-activity of free gases. Pyroclastic sand-bomb material basically basalt structure composing forming Novogodny peninsula, in the first months after eruption was hot and actively degassed. In these emanations high radio-activity was marked: gamma-activity achieved 39 microroentgen per hour, and volumetric activity of radon – alpha-activity explosive and filing craters achieved 50 kilobecquerel per cubic meter. After 2 years

scale activity has decreased to 4 - 6 microrentgen per hour, and an alpha activity - to first units. Stably high alpha activity - up to 10- kilobecquerel per cubic metre - was kept only in a zone fissuring - in a channel and flood-land Karymskaya river. We explain marked changes of a volumetric radio-activity that was caused by an emanation of radon, sorbable pyroclastic material. In the magmatic products composing peninsula were few parent radioactive elements - U-238, Ra-226. Quickly finished disintegration sorbable radon was reflected by falling of a radio-activity in this site. Fissuring sites dated for zones of a stretching, apparently, drain a deep zone of hydrothermal system with an ascending stream of gases and solutions act also radioactive elements. Definitions of the contents of uranium testify to it in solutions Goryachy groove - up to 0.012 mg/l of uranium. In free gases of sources of the Academy Nauk volumetric activity of radon during all 6 years of supervision exceeded 100 kilobecquerel/m<sup>3</sup>. It is indicative, that in geyserite significant maintenances of lead which can be an end-product of disintegration of uranium and thorium were determined. Hence, it is possible to believe, that in this hydrothermal system already long time rises to a surface a flow from deep substance in which structure, alongside with radioactive, act and the specific elements marked above to considered composition: B, Li, Sr, As, Mo, V, Ni, Ga, Ge, Zr, Y, Cu, Zn, Br.

## 5. CONCLUSIONS

1. Evolution of structure gas-hydrothermal sources after phreatic-magmatic eruption 1996 consist in natural decrease of the general mineralization of solutions and change of a ratio of the basic components aside increases of a share of the ions acting with superficial waters that was expressed in distinct reduction of contents of ions Cl and Na, but increase silica acid and a sulfate-ion.

2. The Wide range of fluctuations of physical and chemical conditions of solutions in a modern output gas-hydrotherm clearly correlates with change of a chemical compound. Deep chloride-sodium solutions of sources Academy Nauk gravitate to a field of alkaline regenerative conditions, while for solutions with the greater share of a sulfate - ion (it is obvious, formed at mixture with superficial waters) less alkaline conditions are characteristic at same variations Eh. Arising of significant amount of a hydrocarbonate typically for subalkaline oxidizing conditions.

3. Displays endogenous fluid system in caldera Academy Nauk are characterized by the increased contents in waters of thermal sources of such elements, as B, Li, Sr, As, Mo, V, Ni, Ga, Ge, Zr, Cu, Zn, Br. By much sulphatic structure of water and acidifying Karymskoe lakes to pH=3.2 as a result of eruption of 1996, in structure deep flying prevailed SO<sub>2</sub> and H<sub>2</sub>S, that it is more typical for andesite magmas. The differentiation of fluid system after end eruptive expressed activity in prevalence over structure of free gases of nitrogen and carbonic acid. The question is not absolutely clear about is abnormal the high contents of methane in outputs Piip sources.

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Table 1. Change of a chemical compound of thermal sources caldera Academy Nauk.

| Name of sampling  | Date of sampling | T, °C | pH   | Na <sup>+</sup> | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | NH <sub>4</sub> <sup>+</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | HCO <sub>3</sub> <sup>-</sup> | F <sup>-</sup> | H <sub>3</sub> BO <sub>3</sub> | H <sub>4</sub> SiO <sub>4</sub> | Σ       |
|---|------------------|-------|------|-----------------|----------------|------------------|------------------|------------------------------|-----------------|-------------------------------|-------------------------------|----------------|--------------------------------|---------------------------------|---------|
|   |                  |       |      |                 |                |                  |                  |                              |                 |                               |                               |                |                                |                                 |         |
| Srping № 1 Piip group                                   | Oct.1996         | 89    | 7.76 | 550             | 58             | 124              | 16.9             | no data                      | 753             | 509                           | 140                           | no data        | 53.4                           | 291                             | 2495.3  |
|   | Apr 2001         | 82    | 7.36 | 390             | 34             | 42.1             | 9.7              | no data                      | 380             | 394                           | 81.8                          | 1.0            | 18.0                           | 274                             | 1624.6  |
|   | Jul. 2002        | 67    | 8.05 | 370             | 54             | 48.1             | 2.4              | 0.1                          | 380             | 442                           | 76.9                          | no data        | 28.4                           | 410                             | 1811.9  |
| Provalny  | Jul. 1997        | 96    | 7.80 | 850             | 85             | 92               | 2.4              | 0.1                          | 1220            | 317                           | 120                           | 1.1            | 57.8                           | 461                             | 3206.4  |
| Bottom discharge in crater Tokareva                     | Jul. 2002        | 64    | 7.74 | 98              | 7.5            | 37.7             | 8.3              | 0.2                          | 75              | 230                           | 50                            | no data        | 6.8                            | 127                             | 640.55  |
| Plyazhny  | Jan.1997         | 79    | 7.30 | 255             | 24             | 48               | 9.7              | 0.1                          | 282             | 240                           | 157                           | 1.0            | 16.3                           | 390                             | 1423.1  |
|   | Jun.1998         | 72    | 6.50 | 164             | 15.9           | 46.8             | 11.2             | 0.1                          | 122.5           | 300                           | 50                            | 0.2            | 8.2                            | 204                             | 922.9   |
|   | Jul. 1998        | 64    | 7.64 | 225             | 20             | 50               | 4.9              | 0.1                          | 176             | 336                           | 98.9                          | 1.2            | 10.9                           | 276                             | 1199    |
|   | Sept. 1999       | 57.2  | 7.59 | 280             | 30.2           | 38.1             | 3.6              | 0.2                          | 176             | 394                           | 92.8                          | no data        | 5.2                            | 293                             | 1313.1  |
| Medvezhiy   | Jul. 1997        | 37.   | 7.60 | 79.3            | 8.6            | 20               | 1.4              | 0.1                          | 110             | 28.8                          | 65.9                          | 1.14           | 8.1                            | 167                             | 490.34  |
|   | Sept 1999        | 38    | 7.33 | 115             | 11.9           | 20               | 1.9              | 0.1                          | 146             | 67.2                          | 76.9                          | 1.14           | 0.4                            | 290                             | 730.54  |
|   | Jul. 2002        | 37    | 7.34 | 115             | 15.3           | 14.4             | 1.5              | 0.1                          | 138             | 57.6                          | 76.9                          | no data        | 16.7                           | 272                             | 707.5   |
| Old Geyser (East group Academy Nauk springs)            | 1947             | 98    | 8.70 | 240             | 26             | 9.0              | no data          | no data                      | 355             | 92                            | 85                            | 2.3            | 48.0                           | 343                             | 1150    |
|   | 1974             | 65    | 8.90 | 300             | 30             | 2.4              | 1.5              | 0.1                          | 347             | 84                            | 74                            | 2.3            | 48.0                           | 144                             | 1033.3  |
|   | 1989             | 94    | 9,30 | 370             | 29             | 3.6              | 0.1              | 0.1                          | 418             | 105                           | 109                           | no data        | 52.0                           | 512                             | 1598.8  |
|   | 1997             | 98    | 9.20 | 320             | 14             | 6.8              | 0.2              | 0.4                          | 389             | 106                           | 51                            | 2.1            | 53.0                           | 372                             | 1314.5  |
|   | 2002             | 98    | 9.32 | 310             | 23.5           | 1.6              | 0.12             | 0.1                          | 401             | 106                           | 84.8                          | 0.3            | 51.9                           | 473                             | 1452.32 |
| Geyser Academicheskiy (West group Academy Nauk springs) | Jul. 1997        | 97    | 9.25 | 360             | 15             | 6.4              | 0.1              | 0.1                          | 453             | 96                            | 115                           | 1.93           | 44.9                           | 426                             | 1518.43 |
|   | Apr. 20.01       | 97    | 9.41 | 350             | 23.5           | 2.0              | 0.4              | 0.0                          | 426             | 106                           | 115                           | 2.1            | 36.0                           | 247                             | 1308    |
|   | Jul. 2002        | 97    | 9.25 | 302             | 21.3           | 4.8              | 2.4              | 0.1                          | 390             | 106                           | 87.5                          | no.data        | 47.0                           | 393                             | 1354.1  |

**Table 2. Geochemistry a hydroterm caldera Academy Nauk, (date of selection - July, 2002)**

| Name of sampling                  | T, °C | Mn    | Fe   | P       | B    | Ba    | Li   | Sr    | As      | Zn    | Cu      | Mo      | V       |
|-----------------------------------|-------|-------|------|---------|------|-------|------|-------|---------|-------|---------|---------|---------|
|                                   |       | ppm   |      |         |      |       |      |       |         |       |         |         |         |
| Srping № 1 Piip group             | 67.0  | 0.14  | 0.09 | 0.1     | 3.03 | 0.02  | 0.47 | 0.13  | 0.086   | 0.03  | 0.0013  | no data | no data |
| Razlomny                          | 77.0  | 0.06  | 1.05 | 0.05    | 2.35 | 0.009 | 0.26 | 0.03  | 0.12    | 0.06  | 0.11    | 0.014   | 0.035   |
| Voronka № 4                       | 16.0  | 0.05  | 0.61 | 0.09    | 0.18 | 0.009 | 0.21 | 0.015 | no data | 0.12  | 0.012   | no data | no data |
| Bottom discharge (Tokarev crater) | 64    | 0.67  | 0.21 | no data | 1.09 | 0.005 | 0.16 | 0.045 | 0.08    | 0.03  | no data | 0.017   | 0.012   |
| Medvezhiy                         | 38.6  | 0.08  | 10.8 | 0.04    | 2.67 | 0.014 | 0.14 | 0.062 | 0.27    | 0.35  | 0.435   | 0.019   | 0.005   |
| Beregovoy                         | 89    | 0.45  | 0.39 | 0.15    | 0.46 | 0.076 | 0.06 | 0.29  | no data | 0.02  | 0.008   | 0.004   | no data |
| Serditiy                          | 79.4  | 0.04  | 0.04 | no data | 5.89 | 0.049 | 0.52 | 0.071 | 0.83    | 0.01  | no data | 0.014   | no data |
| Ermakovsky                        | 93    | 0.01  | 0.06 | no data | 4.32 | 0.004 | 0.68 | 0.310 | 0.70    | 0.02  | no data | 0.016   | no data |
| Old Geyser                        | 93.7  | 0.003 | 0.06 | 0.018   | 7.30 | 0.004 | 0.86 | 0.045 | 1.30    | 0.016 | no data | 0.041   | 0.009   |
| Geyser Academicheskyy             | 83    | 0.004 | 0.33 | 0.012   | 7.96 | 0.01  | 0.95 | 0.021 | 1.48    | 0.057 | 0.012   | 0.048   | 0.013   |
| Pulsiruyshhiy spring              | 76    | 0.16  | 1.14 | 0.21    | 0.89 | 0.06  | 0.06 | 0.06  | 0.14    | 0.014 | no data | no data | 0.019   |

**Table 3: Composition of free gases of thermal sources and zones of discharge in caldera Academy Nauk (Karymskoe lake)**

| Name of sampling                                | Date          | T°C     | Gas composition of free gases, vol. % |                |                |                |      |                 |                 |                               |                               |                               |                               |                                 |                                 | N <sub>2</sub> /Ar | N <sub>2</sub> /O <sub>2</sub> |
|---|---------------|---------|---------------------------------------|----------------|----------------|----------------|------|-----------------|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|--------------------|--------------------------------|
|   |               |         | He                                    | H <sub>2</sub> | O <sub>2</sub> | N <sub>2</sub> | Ar   | CO <sub>2</sub> | CH <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> | C <sub>2</sub> H <sub>4</sub> | C <sub>3</sub> H <sub>8</sub> | C <sub>3</sub> H <sub>6</sub> | iC <sub>4</sub> H <sub>10</sub> | nC <sub>4</sub> H <sub>10</sub> |                    |                                |
|   |               |         | x10 <sup>-6</sup>                     |                |                |                |      |                 |                 |                               |                               |                               |                               |                                 |                                 |                    |                                |
| Spring № 1<br>Piip group                        | Apr. 1997     | 83      | 0                                     | 0.003          | 0.6            | 23.8           | 0.38 | 31.8            | 41.9            | 3000                          | 2140                          | 80                            | 20                            | 2                               | 1                               | 63                 | 40                             |
|   | Jul. 1997     | 80      | 0                                     | 0              | 0.8            | 29.7           | 0.49 | 21.9            | 54.6            | 3220                          | 2360                          | 90                            | 20                            | 2                               | 1                               | 61                 | 37                             |
|   | Jun. 2000     | no data | 0.002                                 | 0.0009         | 1.4            | 36.7           | 0.98 | 9.44            | 51.5            | 0                             | 0                             | 0                             | 0                             | 23                              | 109                             | 37                 | 25                             |
|   | Jul. 2001     | 76*     | 0.001                                 | 0              | 1.2            | 31.8           | 0.82 | 8.69            | 57.4            | 0                             | 0                             | 0                             | 17.4                          | 6.1                             | 7.8                             | 39                 | 26                             |
|   | Jul. 2002     | no data | 0.0110                                | 0              | 0.0            | 35.0           | 0.94 | 9.12            | 54.9            | no data                       | no data                       | 49.5                          | 88.9                          | 4.2                             | 8.7                             | 37                 | 2059                           |
| Burlyashiy spring<br>in Karymskaya<br>river-bed | Apr. 1997     | 92      | 0.004                                 | 0              | 0.9            | 20.5           | 0.30 | 78.1            | 0.2             | 1740                          | 170                           | 40                            | 20                            | 27                              | 30                              | 68                 | 23                             |
|   | Jul. 1997     | 90      | 0.007                                 | 0.005          | 1.5            | 39.7           | 0.52 | 58.2            | 0.05            | 700                           | 0                             | 50                            | 30                            | 71                              | 71                              | 76                 | 26                             |
|   | Jun. 2000     | 99      | 0.0055                                | 0.0042         | 3.4            | 53.8           | 1.03 | 41.6            | 0.169           | 1160                          | 49                            | 130                           | 25                            | 37                              | 33                              | 52                 | 16                             |
|   | Jul. 2001     | 92.1*   | 0                                     | 0.0002         | 4.9            | 84.3           | 1.77 | 8.8             | 0.234           | 0                             | 0                             | 119.7                         | 8.1                           | 21.9                            | 28                              | 48                 | 17                             |
|   | Jul. 2002     | no data | 0.011                                 | 0.00           | 0.4            | 81.9           | 1.67 | 15.7            | 0.30            | no data                       | 809.0                         | 101                           | 8.6                           | 19.6                            | 23.90                           | 49                 | 197                            |
| Crater Tokareva<br>beach                        | Apr. 2001     | no data | 0.002                                 | 0              | 2.0            | 95.8           | 1.51 | 0.63            | 0.079           | 480                           | 20.3                          | 44.3                          | 4.4                           | 10.9                            | 10.8                            | 63                 | 49                             |
|   | Jul. 2001     | no data | 0                                     | 0              | 2.2            | 95.5           | 1.42 | 0.79            | 0.058           | 0                             | 0                             | 32.8                          | 4.4                           | 6.6                             | 6.3                             | 67                 | 43                             |
| Provalny  | Aug. 1997     | 98      | 0                                     | 0.027          | 18.0           | 65.8           | 0.72 | 15.5            | 0.0039          | 54                            | 32                            | 2.2                           | 4.2                           | 3.5                             | 4.1                             | 92                 | 4                              |
| East group<br>Academy Nauk<br>springs           | Jun. 1984     | no data | no data                               |                | 14.7           | 62.0           | 1.33 | 21.7            | 0.167           | 0                             | no data                       | no data                       | no data                       | no data                         | no data                         | 47                 | 4                              |
|   | Sent. 1995    | no data | 0.0016                                | 0.002          | 18.9           | 75.3           | 1.57 | 4.20            | 0.03            | no data                         | no data                         | 48                 | 4                              |
|   | May 1996      | 68      | 0                                     | 0              | 18.8           | 78.3           | 1.50 | 1.30            | 0.051           | 1200                          | 0                             | 60                            | 10                            | 1                               | 21                              | 52                 | 4                              |
|   | Apr.0<br>2001 | 80      | 0                                     | 0              | 25.3           | 72.3           | 1.49 | 0.73            | 0.15            | 70.4                          | 16.4                          | 6.1                           | 5                             | 1.2                             | 1.7                             | 48                 | 3                              |
|   | Jul. 2002     | 82      | 0.00                                  | 0.00           | 22.2           | 70.2           | 1.13 | 6.48            | 0.0054          | 17.20                         | 7.10                          | 2.60                          | 4.10                          | 0.8                             | 0.7                             | 62                 | 3                              |
| Outputs in lake<br>near Academy<br>Nauk         | Apr. 2001     | no data | 0.001                                 | 0.003          | 2.5            | 10.4           | 0.29 | 86.0            | 0.902           | no data                       | no data                       | 6.6                           | 14.5                          | 1.1                             | 1.1                             | 37                 | 4                              |
|   | Jul. 2001     | no data | 0                                     | 0              | 2.2            | 14.1           | 0.40 | 82.0            | 1.301           | no data                       | no data                       | 24.6                          | 24.6                          | 1.1                             | 1.6                             | 36                 | 6                              |
| Bottom of a<br>Zhelannaya bay                   | Jul. 2002     | no data | 0                                     | 0              | 1.5            | 15.9           | 0.31 | 82.1            | 0.145           | no data                       | no data                       | 13.5                          | 4.3                           | 1.9                             | 0.7                             | 52                 | 11                             |
| Medvezhiy                                       | May 1996      | 37      | 0.002                                 | 0.0057         | 8.7            | 87.8           | 1.14 | 2.30            | 0.001           | 10                            | 0                             | 0                             | 0                             | 0                               | 2                               | 77                 | 10                             |
|   | Jun. 2000     | no data | 0.001                                 | 0              | 6.0            | 91.5           | 1.64 | 0.85            | 0.051           | 0                             | 81                            | 12                            | 1.5                           | 0.2                             | 0.3                             | 56                 | 15                             |
| Air on Tokarev<br>beach                         | Jul. 1998     | no data | 0                                     | 0              | 17.9           | 80.1           | 0.93 | 1.15            | 0.0006          | 9.4                           | 12                            | 2.1                           | 26                            | 1.8                             | 2.2                             | 86                 | 4                              |

The note: \*Analyses are executed in analytical laboratory IVGG FED Russian Academy of Science, By Shapar' V.N., Gartzeva L.N;

- there are no data or were not defined