The Studying of Gas and Hydrotherm Parameters and the Fluid-Conductor Geochemical Features with the Help of the “SELECTOR” Program Complex on the Example of the Golovnin Calder Sources

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Abstract. There is a discription of dynamical physical and chemical model of “flow reactor with an ideal piston displacement” type. With its help using the SELECTOR program complex (PC) for thermal solutions of Golovnin caldera (Kunashir Island, Kuril Islands) the numerical experiments were performed. The results of two “water-rock” type (W/R) systems modeling are represented: 1 – thermal solutions with pH=1.93; 2 – thermal ones with pH=6.35. The temperature range from 200 to 15 °C and the pressure of 1 and 10 bar in both experiments were used. As a results, data on the systems phase and chemical compositions were obtained; an evolutionary sequence of physical and chemical system states was identified with long-term water/rock (W/R) interaction; a metasomatism type for systems was gained; a metasomatic column was verified with ones near the orifice of thermal solutions. Thus, the complete correlation of model data with obtained in situ one was shown.

1. Introduction

Hydrothermal system orifices in the volcanic active areas are the results of interactions between fluids from igneous chambers, surface waters and host rocks. Such vapor-gas and water hydrothermal discharge zones are a kind of “window” into igneous systems, demonstrating an indicator of volcanic centers activity.

At present, an approach of equilibrium-dynamic modeling has been emerged, using the water/rock ratio (W/R) as an analog of a long period of time [1]. The imitation of system evolution has been modeled as the successive achievement of equilibrium in each reservoir with new fluid portions. Such method allows to obtain model calculations close to natural observations [2], as well as the information about the depths and location of thermal solutions in fluid conductors in the subsurface space (the first meters from the day surface). Such data is invaluable in the design, exploration and exploitation of thermal resources in the active volcanic zones.

2. Golovnin volcano caldera

The studied thermal springs are located along the shores of the Kipyashcheye Lake in the Golovnin volcano caldera. Springs aroses as a result of ones activity. The Golovnin volcano-caldera is
the southernmost volcano of the Great Kuril Ridge (figure 1), located in the south of Kunashir Island. It was the volcano's explosive activity that manifested for the most part in its history of existence (the process of caldera formation repeated twice with the destruction of a significant part of the volcanic structure).

![Figure 1. Geographic map of the Kuril Islands and adjacent territories.](image)

The young explosion funnel is about 350 m in diameter and is filled up by Kipyashcheye Lake. According to various data the depth of the funnel ranges from 16 to 17 m [3]. For the most part the eruptive activity of the Golovnin volcano is localized at the bottom and shores of the Kipyashcheye Lake (on land and underwater fumarole fields) and is represented by gas jets, mud boilers and hot springs.

3. Chemism of thermal springs

It is the sulphate-anion that dominates in the anionic composition of Golovnin thermal solutions over the others ones, the second most important component is the chloride-anion. The bicarbonate-ion is dominated in neutral-subalkaline sources. In addition, nitrate and fluoride anions (table 1) were found in significant amounts in solutions of some sources.

According to the cationic composition (table 1), the terms of Kipyashcheye Lake and Goryacheye Lake sources can be divided into the following types [4]:

1. **Ca-Na-Mg type** of mineralized waters. Almost all this type sources are of the sub-neutral - weakly alkaline environment. The potassium content is the first percent, while iron and aluminum are less than one percent. The five acid thermal boilers with Al and Fe concentrations reaching the 8 - 20 mEq% and 1 - 4 mEq% values respectively for macrocomponents can also be assigned to this solution type. Apparently, the genesis of these boilers waters is associated with surface waters and is noticeable influenced by the plutonic hydrothermal solutions.

2. **Na-Ca type**. There is the highest cations content (particularly, the Na) with an average level of total mineralization in this solution type among all ones. This type includes the acidic boiler solution, the lake one and the sub-neutral boiler one. The Fe and Al contents reach to several percents in the acidic solutions and are almost absent in the sub-neutral boiler.

3. **Na-Ca-Al** type. It is the increased of aluminum content (16 - 24 mEq%) and is the significant presence of iron (0.4 - 4 mEq%) that a distinctive feature among all types.

4. **Al-Ca-Fe** type. The boiler thermers located in the Central Thermal Field on the Goryacheye Lake shores are included in this type. According to the cationic composition of type solutions,
the different hydrotherms are responsible for the formation of ones in contrast to the Kipyashcheye Lake therms.

5. Al-Fe type. The solutions of the boiler on the bank of the Kislyy Creek are included in this type, as well as the stream water of one below the fumarole field with boilers are.

### Table 1. The composition of thermal source solutions of the Kipyashcheye Lake [4].

| Field     | Southeast | Northeast |
|-----------|-----------|-----------|
| Sample    | KG-1      | KG-2      | KG-3      | KG-4      | KG-5      | KG-7      | KG-8      | KG-9      | KG-10     | KG-12     | KG-13     |
| pH        | 6.35      | 2.25      | 2.29      | 6.03      | 1.93      | 2.26      | 2.48      | 2.13      | 1.82      | 2.15      | 4.39      |
| Eh        | -264      | -20       | -37       | -347      | -55       | -60       | -75       | 176       | 55.7      | 75.7      | -112      |
| T°C       | 47.7      | 53        | 41.5      | 68.9      | 90.25     | 51.4      | 97        | 84        | 96.9      | 93.7      | 94.2      |
| X         | 1.32      | 2.23      | 2.75      | 1.13      | 3.35      | 3.53      | 2.32      | 3.12      | 4.37      | 3.35      | 2.05      |
| mg/l      |           |           |           |           |           |           |           |           |           |           |           |
| SO₄       | 260       | 806       | 2100      | 230       | 1300      | 550       | 50        | 1050      | 1800      | 1400      | 590       |
| Cl        | 11        | 7.4       | 13        | 18        | 11        | 390       | 35        | 140       | 120       | 125       | 17        |
| F         | 0.2       | 0.3       | 0.5       | 0.3       | 0.8       | 2.1       | 1.5       | 4.6       | 2.5       | 0.6       | 0.3       |
| NO₃       | 2.7       | 1.9       | 3.6       | 2.2       | 3.3       | 21.7      | 5.1       | 68.2      | 8         | 11.1      |           |
| HCO₃      | 420       | -         | 214       | -         | -         | -         |           |           |           |           |           |
| PO₄       | 0.29      | 0.17      |           | 0.25      | 0.38      |           |           |           |           |           |           |
| Ca        | 132       | 71        | 125       | 109       | 62        | 83        | 162       | 84        | 63        | 127       | 106       |
| Mg        | 32        | 21        | 22        | 25        | 7.76      | 32        | 17        | 19        | 15        | 15        | 0.15      |
| Na        | 98        | 50        | 73        | 86        | 110       | 193       | 180       | 189       | 123       | 190       | 265       |
| K         | 8.1       | 5.1       | 8.1       | 9.0       | 11        | 21        | 15        | 15        | 6.4       | 16        | 24        |
| Fe        | 0.114     | 15        | 21        | 0.06      | 22        | 7.7       | 1.5       | 6.5       | 11        | 6.1       | 0.0084    |
| Fe²⁺      | 0         | 13        | 17        | 19        |           |           |           |           |           |           |           |
| Al        | 0.029     | 17        | 27        | 0.104     | 27        | 10.2      | 2.63      | 26        | 30        | 28        | 0.0798    |
| SiO₂      | 200       | 280       | 250       | 160       | 280       | 120       | 330       | 250       | 300       | 190       | 250       |
| B         | 0.50      | 0.31      | 0.56      | 0.92      | 9.1       | 15        | 3.6       | 15        | 6.8       | 13        | 5.6       |
| Mn        | 1.5       | 4.6       | 1.0       | 0.99      | 0.49      | 3.7       | 1.2       | 1.6       | 1.0       | 1.4       | 0.012     |
| mcg/l     |           |           |           |           |           |           |           |           |           |           |           |
| Ba        | 170       | 27        | 95        | 100       | 78        | 130       | 24        | 56        | 79        | 19        | 41        |
| Sr        | 320       | 100       | 270       | 280       | 140       | 180       | 87        | 97        | 100       | 220       | 81        |
| Li        | 25        | 37        | 29        | 32        | 42        | 130       | 45        | 39        | 47        | 67        | 100       |
| Rb        |           |           |           |           |           |           |           |           | 260       | 240       | 350       | 430       |
| Zn        | 11        | 39        | 62        | 110       | 2800      | 170       | 290       | 550       | 110       |           |           |
| V         | 3.8       | 55        | 52        | 49        | 34        | 12        | 37        | 62        | 41        |           |           |
| As        | 320       | 330       | 75        | 76        | 260       | 350       | 2400      | 170       |           |           |           |
| Sb        | 150       | 120       | 100       |           |           |           |           |           |           |           |           |

The microelement compositions that predominate in solutions are also contrasting. There are relatively high concentrations of both – rock-forming additions (Mn-Ba-Sr) and anionogens (Sb-Se-
Te-As) in 1st type. This type solutions with low mineralization basically are of an acidic environment. There is an assumption such waters are formed from surface reservoirs, and leaching of mechanical and chemical additives from the host rocks and minerals is the result of continuous “water/rock” (W/R) interaction. As a result of this process – the enriching the solution of some chemical elements. It is possible for mobile anionogens be entered the surface solutions from the vapor phase. The mobile anionogens migration from solutions leads to partial depletion of restite ones by these elements.

Both associations – B-Li-Be and metals Cr-Ni-Zn-Ag are contained in 2nd type. It is likely that the seawater infiltration into the underground chambers, followed by its penetration in discharge zones leads to an excess flow of Na into these solutions, that is reflected by chemical analysis.

An increase in the content of lithium and beryllium is affected by the interaction of solutions with metasomatically altered rocks containing various micas and hydromica. The presence of significant components of magmatic fluid in solutions is the reason of high nickel and chromium concentrations.

Relatively high concentrations of Pb-Cd and Rb-As are inherent in the solutions of 3th type.

The 4th type, represented by the most mineralized solutions, are characterised by Cu-Co, Ti-V, Zr-Y-Yb-La, and S-P associations. Elevated concentrations of such elements in Al-Ca waters can be associated with the acidic magmatic fluids rising from deep horizons. It is the interaction of magmatic fluid at great depth with the host rocks that leads to the destruction of the rock matrix and to the enrichment of solutions with such geochemically inert elements as Zr-Y-Yb.

4. Physical and chemical modeling

To study the components behavior in a fluid under subsurface conditions the next scenario was considered - a laminar continuous fluid stream motion of constant composition along a conductive channel composed of a certain geological rock. The chemical, physical, and mineralogical characteristics of this rock are constant at every point in its space (porosity, permeability, mineral phases, etc.). As a result of water/rock interaction (W/R) there is an exchange of components between fluid and host rock. Due to mobility of the solvent in this case and according to the Korzhinsky theory one can speak about infiltration metasomatism, i.e. the solvent flow penetration through cracks and channels into the rock. There is a formation of a metasomatic column with permanent zones along its entire length that is observed according to the characteristics of such metasomatism. To make the model as close as possible to the real object and for most fully reflection of the mechanism of fluid penetration into the rock considering the fixed composition of the substance (rock) added at each step, the model can be represented as a stepped flow reactor with ideal mixing. Thus, the scheme of overflowing of one fluid portion from one reservoir to another, filled with fresh (unchanged) host rock (granite), is considered.

To simplify the process, the scheme is devided into two steps. The first one is a stepwise flow of fluid:

**Stage1** Laminar movement of primeval fluid (I) to the first chemical reservoir;

**Stage2** Have reached the equilibrium between rock and fluid (I) in the first reservoir, the modified solvent with dissolved particles (II) flows into the second reservoir. In this case, there is an absence of primeval fluid I flow to the first reservoir;

**Stage3** Have reached the equilibrium between fresh rock of second reservoir and the (II) fluid, the resulted modified fluid (III) flows into the third reservoir. In this case also, there is an absence of primeval fluid I flow to the first reservoir;

**Stage4** The same process continues until the last reservoir.

Thus, the flow of the solvent with the dissolved components into the reservoirs occurs without the interaction of second portion primeval fluid (I) in system. (figure 2).

At the second period, have reached the equilibrium in last reservoir (have reached the end of fluid migration), there is its (fluid) total removing from the system. The next is entering the second portion of the original fluid (I) at system so the cycle repeats (figure 2, figure 3).

Each reservoir is a closed isobaric-isothermal “water-rock” (W/R) system [5], which local equilibrium is established in (the chemical potentials of all components are equal in system under the
Figure 2. The scheme of the first period: 1, 2, 3 – consistently located reservoirs; a, b, c, d – the system equilibrium composition for each reservoir; I - flow of primeval fluid; II, III and IV - flow of altered fluid; T\textsubscript{1}P\textsubscript{1}, T\textsubscript{2}P\textsubscript{2}, T\textsubscript{3}P\textsubscript{3}, T\textsubscript{4}P\textsubscript{4} - equilibrium conditions between fluid and rock for each reservoir.

specified P-T conditions). There are a lot of stages be set in model (multivave flow step reactor [2]) so it is a chance to trace the entire evolution of system while infiltration metasomatism during the big time.

The eight reservoirs and six waves (primeval fluid, fluid (I)) was used in models.

Constructing a model, the conditions of the infiltration metasomatism of Korzhinsky theory are satisfied:

- The fluid flow through homogeneous permeable rock is laminar one (the lack of hydrodynamic dispersion);
- The each point of rock reacts with the fluid at the same time (the interaction is instantly);

Covering all possible states of system while fluid migration through a fluid conductor, the temperature range from 200 to 80 or 50 °C (I group) and from 120 to 20 or 15 °C (II group) with a step of 20 °C or (in rare cases) 40, 10 and 5 °C was chosen. The step means the temperature in each reservoir is 20 °C (or 40, 10, 5 °C) lower in the previous one. Its allowed to approach the actual conditions of the natural infiltration metasomatism. The pressure has been taken a constant while the numerical experiment (P = 1 bar in reservoirs of I group and P = 10 bar in ones of II group).

Figure 3. The scheme of stages sequence. The legend is given in comments to figure 2.

The compositions of different thermal field solutions (Southeast and Northeast one) of most contrast physical and chemical parameters and chemical composition (KG-1 and KG-5 samples, table 1) were selected for modeling. It was the directly selected in the Golovnin caldera andesite that used as a host rock (the filling of reservoirs). As a transporting solvent for components the water was used in the amount of 1 kg (or 55.56 mol) - the mass of one fluid portion. Both the rock and the solutions component chemical compositions had been expressed in mol/kg.

In a numerical experiment, thus the T and P act as independent state factors. The initial acidity parameter — alkalinity (pH) had been set by the composition of the solutions. The chemical interaction had been reproduced by minimizing the isobaric-isothermal potential — the free Gibbs energy G (T, P).
5. Modeling results

5.1. The comparison of physical and chemical parameters

By wide temperature range an insufficiently rapid acid-base potential growth in the first experiments group at high temperatures (more than 100 °C) had been identified. It caused by low intensity of rock leaching with a small liquid phase proportion and a large gas one proportion in system (figure 4a, 4b). The II group is characterised by higher (alkaline) final pH value of both systems (8.85-11.02 for "acidic" and 8.90-11.11 for "subneutral") in comparison with I group (6.98-8.66 for "acidic" and 6.92-9.56 for "subneutral", (figure 5a, 5b)). A similar effect is explained by the presence of liquid phase larger amount in second group due to the P-T parameters chosen and, as a result, due to more intensive process of rock leaching while arriving new portions of primeval fluid (waves).

![Figure 4a. Acid-base properties of the “acidic” system (I group)](image1)

![Figure 4b. Acid-base properties of the “sub-neutral” system (I group)](image2)

![Figure 5a. Acid-base properties of the “acidic” system (II group)](image3)
Thus, the outflow to the surface of an “acidic” solution (pH = 1.93) is explained either by a short contact between the solution and rock, or (due to high temperature during the outflow (90.25 °C)) by the gas predominance all along its subsurface migration. It is the reason of great reducing of leaching intensity. The mixing with other thermal waters is also possible. The interaction between “subneutral” solution (pH = 6.35) and host rock is for a longer time and, taking into account the temperature of its outflow on the surface (47.7 °C), the leaching process is more intensive.

In I experiment group at T>100 °C, a smooth increase in the system Red/Ox potential had been observed. It caused by gas dominatind and by component accumulation actually in that one. Since anionogens under such P – T conditions exist in the molecular (gaseous) state predominantly, the number of free electrons decreases as more and more components enter the gas phase. As a result – the Eh parameter value increases (from -280 to -210 mV for “acidic” and from -250 to -190 mV for “sub-neutral” systems. As T value and the amount of gas decreases, the components had been transferred from the gas (molecular form) into a liquid (ionic form). A similar process had been accompanied by the release of electrons, had led to decrease of system Red/Ox potentials. In the II experiment group the is a domination of the liquid phase over the gas and the transition process is either smooth o r absent (in “sub-neutral” system the gas is absent). It causes the the Red/Ox potential growing during the numerical experiment (from -272 to -243 mV for “acidic” and from -268 to -202 mV for “sub-neutral” systems).

Taking into account the discharge tempe- rature of “sub-neutral” solution, its simulated values of Red/Ox potential is completely correlated with the measured in situ ones. Such discharge T of “acidic” solution (90.25 °C), math error may be associated with a measurement in situ (due to the careful attitude to the electrodes, the solution temperature while measuring does not exceed 25 °C). Besides, the real “acidic” system is caracterised by gas dominated upon the liquid before discharge. Therefore components go into solution just partly, some of ones go into the atmosphere in gas form.

5.2. The comparison of phase and chemical composition
The “acidic” solution source [4] is a large boiling boiler from black to greenish color of 2 m diameter. According to chemical analysis, it is caused by a high Fe$^{2+}$ and Fe$^{3+}$ content in solution. The source of the “sub-neutral” solution v.v. – is a beautiful bath surrounded by a large carpet of sediments (about 2 cm). Since the discharge system T is lower and the mineralization of liquid is higher than of the “acidic” one, both the components number and its concentration in “sub-neutral” solution is greater. It is caused the abundant mineral formation from the solution occurring along the bath edges which is confirmed by experimental modeling. Thus, the number of mineral phases in each group of experiments in “sub-neutral” system models is much higher than in of “acidic”ones. The “acidic” system is characterized by the accumulation of Fe$^{2+}$ and Fe$^{3+}$ cations in solution with each new additional portion of the primeval fluid to the reactor. According to modeling, in I group if T is equal to 120 °C or less, Fe$^{3+}$ is removed and the concentration of Fe$^{2+}$ in solution decreases by 100 times.
causing the formation of iron hydroxides, particularly the hematite. The "acidic" system (I experiment group) is characterised by the accumulation of Na⁺ and Mn²⁺ in dissolved form explaining the significant predominance of Na⁺ over K⁺ (more than 1000 times). In turn, Zn²⁺ and Ca²⁺ leave solution, forming mineral individuals. Notable is the absence of sulfur in the liquid and gas. All sulfur goes into the solid phase. Al³⁺, which is a part of alunite, glass, and various layered silicates, behaves in a similar way.

There is an accumulation of Na⁺ and Li⁺ in a dissolved form in the "sub-neutral" system. Divalent cations (Ca²⁺, Ba²⁺, Mg²⁺, Mn²⁺) have accumulated in the solution until 100 °C – the transition of Mn²⁺ into MnSO₄; at T<80 °C, Ba²⁺ becomes BaCO₃ (witherite); Ca²⁺ at 80 °C leaves the solution in the form of CaCO₃ (calcite); at T = 50 °C Mg²⁺ is used for crystallization of MgSO₄ (Epsom salt) and MgCO₃ (magnesite). Iron (III) is accumulated in the solution firstly and is completely transferred to hematite at T<100 °C. Zn²⁺ is similarly spent on sphalerite formation. The Cu²⁺ have present in the solution is passed into bornite and chalcozine at T<140 °C. Such divalent ions behavior (the formation of carbonates) can be explained by the dominant position of carbonate and bicarbonate anions in this type of solution. Sulfate and sulfide anion are in a subordinate amount.

5.3. Metasomatic column correlation

Petrographically "fresh" (unchanged) andesite from the Golovnin caldera is a rock with a massive, slightly porous or porous texture. The modified (developed by solution and gas) andesite is differ in chemical and mineral composition, although some textural features of the "fresh" rock are retained.

Comparing the modified and unchanged andesites, it is possible to note a higher content of SiO₂ in the modified rock samples compared to unchanged. This fact is explained by the leaching of andesite with a solution (described above). Besides SiO₂ during this process the Fe³⁺, Fe²⁺, Mg²⁺, Mn²⁺, Ca²⁺, Na⁺, Zn²⁺, Ga³⁺, Rb +, Sb³⁺, and As⁺⁺ are also removed (table 2).

| Samples Number  | KN-15 | KN-16 | KN-10 | KN-11 | KN-14 |
|-----------------|-------|-------|-------|-------|-------|
| Rocks Texture   | Changed rock | Porous | Unchanged ("fresh") rock |
| SiO₂            | 77.12 | 84.53 | 65.07 | 62.23 | 63.25 |
| TiO₂            | 0.69  | 0.79  | 0.59  | 0.60  | 0.60  |
| Al₂O₃           | 11.90 | 6.39  | 15.93 | 16.51 | 16.65 |
| Fe₂O₃           | 0.15  | 0.34  | 6.73  | 6.39  | 6.04  |
| MnO             | 0.00  | 0.00  | 0.12  | 0.12  | 0.12  |
| MgO             | 0.00  | 0.00  | 1.86  | 1.92  | 1.83  |
| CaO             | 0.15  | 0.20  | 6.37  | 5.05  | 5.77  |
| Na₂O            | 0.50  | 0.37  | 3.15  | 2.95  | 3.05  |
| K₂O             | 0.40  | 0.19  | 0.54  | 0.53  | 0.50  |
| P₂O₅            | 0.06  | 0.04  | 0.07  | 0.09  | 0.07  |
| BaO             | 0.02  | 0.03  | 0.03  | 0.02  | 0.03  |
| SO₃²⁻           | 0.07  | 0.06  | <0.03 | 0.12  | 0.09  |
| V₂O₅            | 0.02  | 0.01  | 0.02  | 0.02  | 0.02  |
| Cr₂O₃           | <0.002| <0.002| 0.002 | 0.003 | <0.002|
| NiO             | 0.005 | 0.004 | <0.003| <0.003| <0.003|
| LOI             | 8.86  | 5.28  | 0.39  | 2.15  | 1.58  |
| SUM             | 99.93 | 98.23 | 100.86| 98.71 | 99.58 |
| K,‰            | 0.44  | 0.18  | 0.34  | 0.35  | 0.28  |
| Ca,‰            | 0.55  | 0.23  | 4.43  | 3.53  | 3.44  |
| Ti,‰            | 0.566 | 0.59  | 0.312 | 0.303 | 0.26  |
Table 2. The chemical composition of andesites from Golovnin caldera, Kipyashcheye Lake. The contents of the main petrogenic components are in mass %, the rest - in mg/eq% [4].

| Samples Number | KN-15 | KN-16 | KN-10 | KN-11 | KN-14 |
|----------------|-------|-------|-------|-------|-------|
| Rocks Texture  | Changed rock | Porous | Unchanged ("fresh") rock | |
| V              | 111   | 79    | 58    | 52.4  | 51.8  |
| Cr             | 19.4  | 12.3  | 6.92  |       |       |
| Mn,%           | 0.005 | 0.003 | 0.096 | 0.098 | 0.083 |
| Fe,%           | 0.22  | 0.21  | 4.84  | 4.62  | 3.86  |
| Ni             | 28.9  | 21.5  | 14.4  | 19.6  | 26.3  |
| Cu             | 31.4  | 26.7  | 43.8  | 24.3  | 34.3  |
| Zn             | 22.2  | 14.6  | 73    | 69    | 70    |
| Ga             | 39.6  | 20.8  | 15    | 15.7  | 13.3  |
| Ge             | 6.56  | 4.37  | 3.46  | 2.14  | 2.64  |
| Br             | 3.01  | 2.98  | 1.96  | 0.75  | 0.54  |
| Rb             | 1.72  | 3.49  | 8.67  | 5.54  | 8.44  |
| Sr             | 201   | 77    | 193   | 164   | 190   |
| Y              | 2.95  | 5.22  | 27.4  | 22    | 24.7  |
| Zr             | 78    | 105   | 83    | 83    | 85    |
| Mo             | 1.04  | 1.19  | 1.21  | 0.97  | 0.91  |
| Ag             | 0.54  | 0.89  | 0.44  |       | 0.38  |
| Cd             | 0.18  | 0.3   | 0.55  | 0.47  | 0.35  |
| Sn             | 2.53  | 2.16  | 3.42  | 1.08  | 1.17  |
| Sb             | 154   | 104   | 4.38  | 2.77  | 3.29  |
| As             | 123   | 112   | 25.3  | 4.5   | 13.1  |
| Pb             | 6.6   | 5.1   | 12.3  | 13.2  | 9.2   |
| Th             | 1.1   |       | 2.2   | 1.1   | 0.9   |

It is obvious (table 3) in addition to main "primeval" SiO$_2$ modifications – tridymite and cristobalite, the hydrothermal α-quartz is also present in the rock.

Table 3. X-ray phase analysis of Golovnin caldera rocks. Samples KN-15, KN-16 and KN-19 - changed andesites; sample KN-17 is a changed tuff [4].

| Samples number | Mineral composition | Note |
|----------------|---------------------|------|
| KN – 15        | Tridimite, cristobalite, natroalunite, kaolinite, admixture of quartz, plagioclase, small admixture of anatase, disordered smectite, hydrargillite (gibbsite). | There is an x-ray amorphous component |
| KN – 16        | Cristobalite, tridimite, quartz, an admixture of kaolinite, hydrargillite (gibbsite), natroalunite, plagioclase, anatase, disordered smectite. | There is an x-ray amorphous component |
| KN – 17        | Quartz, cristobalite, tridymite, plagioclase, iron hydroxides, epidote. | There is a lot of x-ray amorphous component |
| KN – 19        | Quartz, cristobalite, tridymite, plagioclase, iron hydroxides, epidote. | There is an x-ray amorphous component |
Numerical experiments of I group had been similarly shown the presence of a large amount of redeposited (hydrothermal) quartz, and quartz in the “acidic” system is redeposited much considerably. In II group of experiments, quartz is absent at every stage. This phenomenon can be explained by insufficient leaching temperature, as well as by large amount of liquid phase in the systems.

The solution is saturated by components, leading to deposition of various silicate minerals with a T decreasing – talc, chlorite, albite, etc. As a result there is no free silica to form quartz. At high T, most components are in the gas phase, so the liquid phase is undersaturated with ones. The result is the formation of silicates – albite (due to a lot of Na+) and illite. There is a quartz precipitaion as a result of remaining free silica. It is confirmed by also disappearance of SiO$_2$ at T=120–80 °C. Because of the liquid phase increasing in ”sub-neutral” system (I group of experiments), is quartz dissolving, so heylandite, chlorites and talc are formed.

The presence of natroalunite (Na[Al$_3$(SO$_4$_2][OH)$_6$, [6]) in KN-15 and KN-16 samples have been confirmed by numerical experiments. Its formation, like the albite one (also present in samples of modified andesite) is directly related to high content of Na$^+$ compared to K$^+$ in solutions. It is also the reason of illite formation instead of muscovite (both in thermodynamic models and in situ). The content of Al$^{3+}$ in the modified rock is significantly lower than that in the unchanged one. Such phenomenon is explained by its dissolution and transition to liquid phase with subsequent partial redeposition, confirming by experiment (Al$^{3+}$ is absent in liquid). In the solid phase, however, various Al-containing minerals are present such as albite, natroalunite, illite, chlorite, glass, and diasporas.

In both groups of experiments for both types of systems, the presence of such minerals as heylandite (a family of zeolites), pumpellite-Al (ortho-diorto silicate) and pectolite (a group of wollastonite) is noted. Heylandite is located on the border of A and B fields (figure 6), and the conditions in experimental modeling chosen are most favorable for its formation, compared to other zeolites. The rest zeolites formation is impossible under such conditions (the coexistence with quartz).

Wairakite in this case is pure calcium zeolite Na$^+$ is high in the selected systems. Pumpellite as well as epidote is located in B field and is formed in experiments either at low T (I group where the SiO$_2$ amount is decreased), or at high T (II group where SiO$_2$ is absent). Pectolite is formed as geyllandite.
because of the high role of Na\(^+\) in systems. However, similar minerals or their counterparts have not been observed in situ.

The absence of heylandite, pectolite, calcite, chlorites (except for berterin) and pumpellite in situ can be explained by the hydrolysis of silicates according to the following schemes [6, 7]:

- Pumpellit-\(\text{Al}\) → calcite + phrenite → zeolites;
- Pectolite → zeolites;
- Heylandite (zeolite) → montmorillonite → kaolinite → gibbsite + quartz;
- Chlorites → montmorillonite → kaolinite (or a mixed-layer mineral).

It is the mixed-layer formations, the gibbsite, the silica and the kaolinite that have been existed near each surface orifice of thermal solution. Calcite and other carbonates are absent because of leaching with solutions. As a result the anion \(\text{CO}_3^{2-}\) → \(\text{HCO}_3^-\) and is dissolved (goes into solution). Thus, there is a complete correlation of metasomatic column in situ with the minerals obtained in the course of a numerical experiment.

6. Conclusion

The results obtained, based on numerical experiments is completely correlate with the data measured and selected in situ. The metasomatic column verification and the obtained relations of hydrothermal systems physical and chemical parameters to P-T conditions directly in the discharge areas, as well as to the hydrothermal solutions mixing with ground and meteoric waters, allow to assert about the models reliability. It can be concluded this research method (physical and chemical modeling) is promising, as well as predicting the use of this kind models in various branches of science (geochemistry, hydrogeology, geodynamics, etc.).

7. References

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