Geochemical peculiarities of nitric thermal waters in Jiangxi Province (SE-China)

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Abstract. The chemical composition of nitric thermal waters in Jiangxi Province, SE-China, is considered. It is shown that the studied thermal waters are characterized by low TDS (293-412 mg/l), but they always have alkaline or highly alkaline pH values. It should be noted that the content of Na⁺, Si, F⁻, HCO₃⁻, CO₃²⁻, sometimes SO₄²⁻ is predominant, on the other hand, the content of Ca²⁺, Mg²⁺, Cl⁻ is low. It has been established that the main factors responsible for low concentrations of some chemical elements and high concentrations of others are continuous dissolution of aluminosilicate minerals and simultaneous precipitation of the secondary minerals.

1. Introduction
Jiangxi Province is located in the Southeastern part of China and is one of the provinces where nitrogen-rich thermal waters are distributed most widely in the country. A systematic compilation of Province’s hot springs was done by Li Xueli in 1979 [4], later by Sun Zhanxue in 1988 [10], and it is continuing in the present time. In this Province, about 96 hot springs of different gas and chemical composition have been found. They are located in the following geothermal areas: the Ganbei (the northern part of Province), the Ganzhong (a central Province), the Gangxinan (the south-western Province) and the Gandongnan geothermal area (the southern Province). The nitric thermal waters are localized, mainly, in the Ganbei and the Gangxinan geothermal areas.

2. Geological background
Nitric thermal waters are widely spread, and they occur in the rocks of different types and ages all over Jiangxi. The majority of hot springs is located along the faults of different trends (fig.1). Nitric thermal waters are distributed all over geothermal areas, but, mainly, in the Ganbei and the Gangxinan.

The Ganbei geothermal area is situated in the north of Jiangxi. Thermal waters of the area are confined to the north-eastern trending Ganjiang deep fault, which is registered to be still tectonically active. Geologically, the studied area is composed of the Precambrian rocks represented by granites of migmatitic and biotite genesis [13].
The Ganxinan geothermal area is located in the south-western Jiangxi Province, where NNE-trending faults are widely distributed. The rocks are characterized by sandstone, conglomerates and granite of the Cretaceous and the Jurassic age [3].

3. Materials and methods
The factual data on chemical composition of nitric thermal waters are obtained due to the field works carried on in October, 2015. The macro component water composition has been analyzed by an ion exchange chromatography method using the ICS-000 «Dionex» device (the USA) in the accredited laboratory of «Water» Research Educational Center (Natural Research Tomsk Polytechnic University). Moreover, the earlier data of nitric thermal water chemical analysis (obtained by Sun Z. [11]) were used.

4. Results and Discussion
Experimental data on the chemical composition, temperature, pH and salinity of nitric thermal waters are given in Table.1. Firstly, it should be noted that the total mineralization dissolved solids (TDS) of thermal waters is extremely low, at the same time, pH is high. That is one of the peculiarities of nitric thermal waters all over the world [1], particularly, in Baikal Region [6]. The TDS values vary from 293 to 412 mg/l, the average value is 357 mg/l. The pH values are between 8.6 and 9.27, and the average value is 8.73.
The pH-TDS dependence in nitric thermal waters is difficult to see. However, relationship between pH and salinity of waters is characterized by a slight decline in their pH values with increasing TDS (Figure 2a). This type of correlation is not typical for the most fresh and saline natural waters [9].

According to chemical composition, nitric thermal waters are mainly sodium hydrocarbonate, excluding a single case, hot spring 8, where waters become sodium hydrocarbonate-sulfate.

Table 1. Chemical composition of nitric thermal waters in Jiangxi Province, mg/l.

| №  | T, C TDS pH HCO₃⁻ CO₃²⁻ Cl⁻ SO₄²⁻ Na⁺ K⁺ Ca²⁺ Mg²⁺ SiO₂ F⁻ Chemical type |
|----|----------------------------------------------------------|
| 7  | 36,8 293 8,70 110 12,2 5,3 14,8 71 1,3 3,8 0,6 56 16 HCO₃-Na |
| 8  | 83 343 8,66 86 18,3 3,8 44,0 59 3,1 6,4 0,1 113 10 HCO₃-SO₄-Na |
| 9  | 82,3 339 8,60 128 6,1 3,8 12,5 71 2,8 3,9 0,05 97 15 HCO₃-Na |
| 10 | 41,1 306 9,27 67 30,5 5,3 23,0 66 2,2 2,0 0,01 96 15 HCO₃-Na |
| 1S²| 71 412 8,60 177 8,5 5,5 14,4 110 - 1,7 0 80 15 HCO₃-Na |
| 2S²| 65 396 8,78 163 11,0 5,1 13,0 96 - 2,7 0,7 90 15 HCO₃-Na |
| 3S²| 65 399 8,62 177 8,3 5,4 11,4 110 - 1,9 0 70 15 HCO₃-Na |
| 5S²| 69 367 8,61 166 8,0 5,0 13,0 87 1,7 2,1 0,2 70 14 HCO₃-Na |
| Average| 70,6 357 8,73 134 12,9 4,9 18,3 84 2,2 3,1 0,2 84 14 HCO₃-Na |

*Data from Sun [10]

Figure 2. Dependence of TDS values on pH (a) and relation of Ca²⁺ and Mg²⁺ content to amount of carbonate ions (b). Water chemical type: 1 – HCO₃-Na; 2 – HCO₃-SO₄-Na.

As to cation content of nitric thermal waters, the dominance of sodium ion in calcium, potassium and magnesium is noteworthy. This is another peculiarity of nitric thermal waters chemical composition. It can be explained by inverse relations of Ca²⁺ and Mg²⁺ content to the amount of carbonate ions (Figure 2b), which confirms the equilibrium of nitric thermal waters with carbonate minerals, and, consequently, precipitation of these elements from the solution.

Dependence of studied waters salinity on their temperature is negligibly small. As temperature grows up, the TDS values increase (Figure 3). This tendency is related to falling of infiltration waters in the deep faults. Thus, interaction of water and water-bearing rocks takes more time, what leads to the salinity increase. But this evidence is concerned only with carbonate part of ions (Figure 4a), while sulfate ions behave in a different way: with the temperature increase the SO₄²⁻ content decreases (Figure 4b). According to this fact, it can be concluded that enrichment of nitrogen thermal waters by carbonate and sulfate ions comes from different sources. If carbonate salts are the result of aluminosilicates hydrolysis, sulfate salts are formed with sulphides and free O₂, which appears in water in the recharged areas.
Dependence of nitric thermal waters salinity on temperature.

Equilibrium with main minerals of water-bearing rocks has been calculated using the HydroGeo software system [2]. Despite the low salinity of nitric thermal waters, they are saturated not only with calcite (Figure 5a) and fluorite (Figure 5b), but also with such exotic minerals as albit (Figure 6a), glauconaphane (Figure 6b), as well as with microcline, muscovite, laumontite and others, which are not shown in the figures. At the same time, nitric thermal waters are non-equilibrium with endogenous Ca, Mg, Fe aluminosilicates of anorthite, forsterite, cheilitis types, etc. As far as chemical compositions and temperature of nitric thermal waters of Jiangxi province and Baikal Region are similar, the equilibrium character with minerals of rocks is identical, as well [6, 8].

Equilibrium of nitrogen thermal waters with calcite (a) and fluorite (b) at 25 °C (line 1) and 100 °C (line 2).
Therefore, it can be confirmed that a water-rock system is equilibrium-non-equilibrium: water dissolves some minerals and forms the other ones. In the studied nitric thermal waters the major portions of the elements passing into solution are precipitated into newly formed minerals: Ca - into calcite, montmorillonite, zeolites, and other aluminosilicates; Mg - into glaucophane, talc, chlorite, and zeolites; Na - into albite and zeolites; K - into illite, muscovite, microcline, biotite, phlogopite, etc.; Fe - into siderite and Fealuminosilicates; and F - into fluorite and, in part, micas. This allows the system reaching both chemical and dynamic equilibrium and establishing a balance between the amounts of elements released into and precipitated from the solution. Such a balance leads to the low salinity of hot spring waters, which tends to remain constant or increase slightly with time [8].

Figure 6 Equilibrium of nitrogen thermal waters with alominosilicate minerals: (a) – system SiO$_2$-Al$_2$O$_3$-K$_2$O-CO$_2$-H$_2$O at 100 °C; (b) – system HCl-H$_2$O-Al$_2$O$_3$-MgO-SiO$_2$ at 100 °C.

5. Conclusions
In Jiangxi Province, nitric thermal waters are widely distributed, and their chemical composition, salinity and pH values are similar with nitric thermal waters of other regions all over the world. These thermal waters and crustal bed rocks form a unique equilibrium–non-equilibrium system. This system evolves under conditions, when the majority of elements released from the host minerals tend to be continuously incorporated into newly formed secondary minerals. This leads to a dynamic equilibrium between the amount of elements liberated to and precipitated from the solution; as a result, the composition of the solution is stabilized, and the salinity does not longer increase, though, the interaction of water with the surrounding host rocks continues.

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