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Geochemistry of Nitric Thermal Springs From Khoja-Obi-Garm Thermal Area (Pamir-Tien Shan Region)

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ABSTRACT

This paper presents data on the composition of the low-enthalpy thermal waters from the unique Khoja-Obi-Garm field located at the central part of the southern slope of the Gissar Range, in the gorge of the Khoja-Obi-Garm River, at an altitude of 1740-1960 meters. The eponymous SPA-center was built in this area. Groundwaters from springs and boreholes of the Khoja-Obi-Garm thermal area have temperatures from 57 to 93 °C, high pH (up to 8), and low TDS (less than 0.5 g/l). These waters belong to Na–SO_4–HCO_3 type with high content of H_2SiO_3 (~140 mg/l), F (up to 18 mg/l), and Rn (up to 814 Bq/l). The specific feature of these thermal waters is a predominance of N_2 in the gas phase (up to 83-98 vol.%) while other gases (O_2, CO_2, Ar, Kr, Xe, He, and Ne) are nonessential. The gas content at the Khoja-Obi-Garm spa waters is usually not high and does not exceed 30 ml/l. Data showed that N_2 and O_2 are atmospheric gases, but CO_2 is a biogenic gas ($\delta^{13}C_{TIC}$ -30‰ – -22 ‰). The estimated subsurface temperature is 193-197 °C based on the silica and K/Na geothermometer. Thermodynamic speciations indicate that these groundwaters are supersaturated with clay minerals and low-temperature zeolites but undersaturated with carbonate and aluminosilicate minerals.

1. INTRODUCTION

Low-enthalpy nitric thermal springs have been the focus of many scientists' interest for a long time due to their unique chemical characteristics and active use for geothermal and balneological purposes. In spite of numerous studies (Zamana, 2000; Plyusnin et al., 2008; Bragin et al., 2016, and others), several problems remain unsolved. The most significant questions, among others, are the genesis of such waters and their chemical composition transformation during upwelling: hydrogeological and tectonic settings of their formation and the depths of circulation, genesis of the gas phase, and the rate of water interaction with bedrocks.

New isotopic data for aqueous ($\delta^{18}O$, δD) and gas ($\delta^{13}C$, $^3He/^4He$, $^4He/^{20}Ne$) phases together with the detailed hydrogeological and geological study of the area allowed identification of the genesis of low-enthalpy nitric thermal waters from the unique Khoja-Obi-Garm thermal area (the Pamir-Alai mountain system, Central Asia).

The main aim of our study is to understand the genesis of thermal mineral waters at the Khoja-Obi-Garm thermal area. In addition to that, we tried to estimate the reservoir temperatures and depth of circulation.

2. GEOLOGY AND HYDROGEOLOGY

Khoja-Obi-Garm resort is a unique mountain climate spa located in the central part of Gissar mountain Range (western part of the Pamir-Alay system, Central Asia) 60 km north of Dushanbe. Spa elevation is 1740-1960 m asl.

Geologically, this territory represents the bend of the Himalaya-Hindukush mountain massif and was originated by the northward drift of the Indian craton and its final collision with Eurasia. Intensive seismic activity along the large fault system is fixed in this region. There are numerous deep faults along a NW strike direction in this area, many of them are very deep and serving as transport channels for thermal waters. The largest structure of this kind is Khoja-Obi-Garm fault. All thermal springs are localized within faults, most of which follow the area landscape.

The lithology of the study area consists of Mesozoic and Quaternary sediments and Paleozoic (C_2) effusive and intrusive complexes. Mesozoic (K_1) sediments are represented by sandstones, clays, conglomerates, etc. Quaternary (Q) deposits have limited distribution (boulders, pebbles, sand, clay, etc.). Paleozoic deposits are represented by volcanogenic complexes of Namur suite (basalts and basalt mandelstein) and Bashkirian suite (andesites, andesitic-dacite porphyrites, and tuffs with insignificant layers of marbled limestones) of the Lower Carboniferous period. Mesozoic sediments overlie the eroded surface of Palaeozoic ones. They are represented by sediments (sandstones, clays, conglomerates, etc.) of the lower group of the Cretaceous period (Figure 1).

The hydrogeological structure of Khoja-Obi-Garm Spa is very complicated, with fracture-vein waters circulating within the massive intrusions of granites localized within the zone of Alpine folding (Figure 2). Waters emanating from fractures appear as griffins localized in a small area (50 x 100 m) in the central part of the plot. Water in the fractured granite deposit area is unevenly distributed. The maximum flowrate of crack-vein waters from wells is limited to the main discharge zone. The remaining wells yield only a small amount of thermal waters of no practical significance.

Host rocks are represented by alkaline-feldspar granites, plagiogranites, and granodiorites. The main rock-forming minerals are quartz, potassic feldspar, and plagioclases. Accessory minerals are dominated by zircon, apatite, and REE-bearing carbonates. Mineral waters actively deposit drusy quartz and carbonate (two generations) in borehole pipes (Figure 3).

Scale 1:10 000

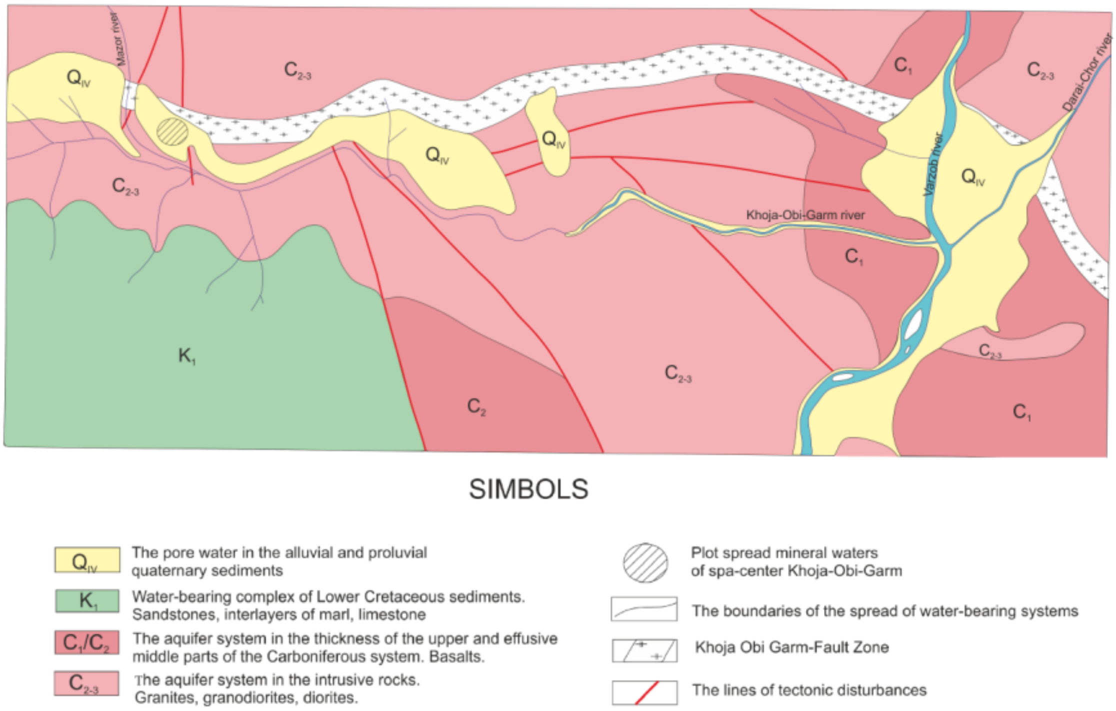

Figure 1: Hydrogeological map of the Khoja-Obi-Garm thermal waters area.

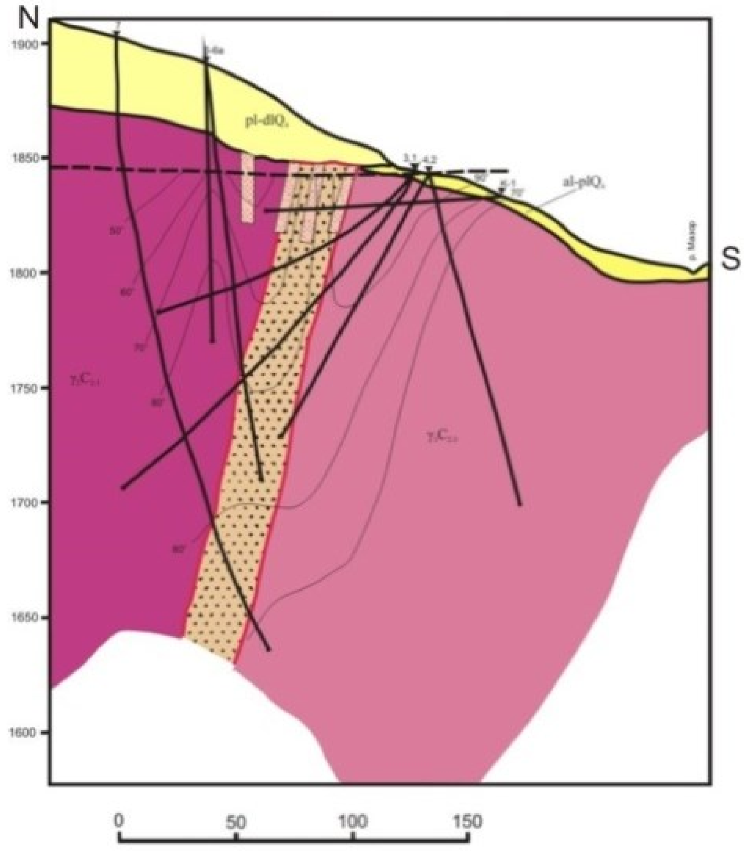

Figure 2: Hydrogeological cross-section within the Khoja-Obi-Garm thermal waters area.

Figure 3: Newly-formed mineral phases inside the borehole.

3. HYDROGEOCHEMISTRY

Thermal groundwaters from springs and boreholes in the studied area are characterized by temperatures varying from 57 to 93 ^oC, high pH (up to 8), and low TDS (less 0.5 g/l). The principal cation is Na^+ with concentrations up to 100 mg/l, whereas Ca^{2+}, Mg^{2+}, and K^+ contents are generally low (Figure 4). The dominant ion is usually HCO_3^- (up to 112 mg/l) and SO_4^{2-} is the second one. Sulfate concentrations vary from 2 to 133 mg/l. Concentrations of SiO_2 (up to 140 mg/l) and F (up to 18 mg/l) are high. In some boreholes high radon concentrations (at about 814 Bq/l) were detected. These thermal waters are also rich in Li, Rb, Cs, and Al. The distribution of trace elements in thermal groundwater samples is shown in Figure 5.

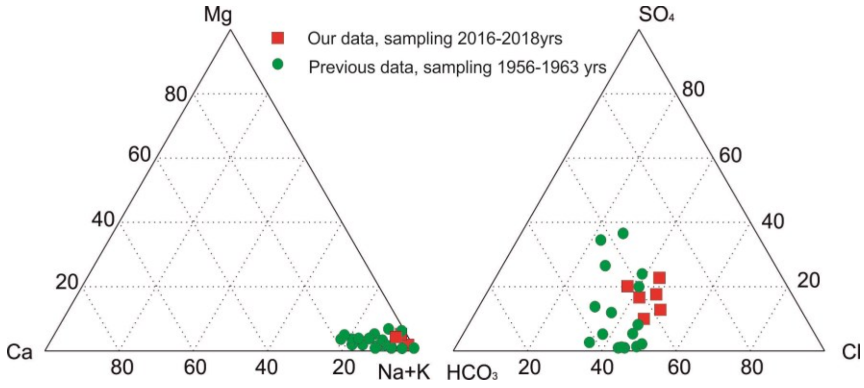

Figure 4. Ternary diagrams of the chemical composition of thermal waters of the Khoja-Obi-Garm field.

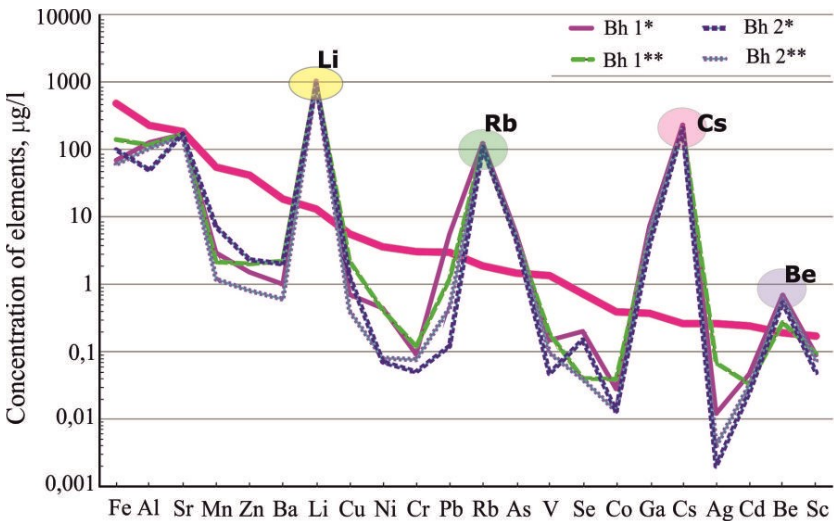

Figure 5: Trace element abundance in thermal groundwaters of the Khoja-Obi-Garm field. Data of water samples taken from boreholes #1 (Bh 1) and #2 (Bh 2): * - collected in 2015, **- collected in 2016. Redline indicates the average concentration of trace elements within the Earth's upper crust (Shvartsev, 1998)

According to the average content in thermal groundwaters, rare elements follow this sequence: Rb >>> Ga >> REE_{total}> U> Sc> Cd> Th. However. the sequence in aquifer rocks is different: REE_{total}> Rb> Th> Y> Sc> Ga> U >> Cd. The newly formed phase taken from boreholes scales is enriched with Sc, REE_{total}, Rb, and U, although all other elements have significantly lower concentrations.

An elevated Rb content is typical for all hydrothermal fluids worldwide. Most researchers believe that Rb is leached from the rock (Kharitonova et al., 2016; Chudaev et al., 2016). As pointed out by Arsanova (2014), Rb in the aquifer host rocks occurs mainly in mica (Rb-lepidolite, phlogopite) and potassium feldspar, which is the main rock-forming mineral (up to 95%). During the formation of scale, Rb stays in the fluid, so the secondary phases (new-forming) were depleted with Rb; its content does not exceed 2.1 g/t. To assess the aqua mobility of the chemical elements during groundwater-volcanic rock processes we used the coefficient of aqua migration Kam (Perel'man, 1982), which is expressed as follows: $K_{wm} = (mx*100)/(M*nx)$, where mx is the concentration of the element in groundwater (g/l), M – total dissolved solid (g/l) of groundwater and nx is the concentration of the element in bedrock (g/t), respectively.The coefficient of water migration (K_{wm}) for Rb is $3.5 - 4.8*10^3$, i.e., in this geochemical system, Rb is a strong migrant and can actively leach from the water-bearing strata. At the same time, the degree of accumulation of Rb in the waters is low, since the distribution coefficient is 0.001.

The content of Ga in the studied thermal waters is very low and ranges 6.2 - 7.2 µg/l, although in water-bearing sediments, the Ga concentration is very close to the Clarke value at 15 - 21 g/t. The main Ga concentrated minerals are mica and feldspar. In the secondary minerals, the amount of Ga is low (0.07 g / t). The low K_{wm} of Ga (0.12) indicates that it is a very weak migrant in this environment and accumulates very poorly.

The total concentration of REE in the studied waters is low with values ranging from 0.36–0.41 ppb, but the similar concentration is typical for thermal waters with alkalinity in the region of 8.98 - 9.18 (Kharitonova et al., 2016; Bragin et al., 2018). Very significant enrichment of light REE (up to 84%) was found and in general LREE >>> Y> MREE> HREE. On the contrary, the host rocks contain high concentrations of REE ranged from 100 to 780 g/t, while the newly formed phase is depleted by them (up to 4 g / t). The aquifer rocks are characterized by the prevalence of LREE (88 - 93 %) over MREE (5 - 10 %) and HREE (1 - 2 %). Intrusive rocks are enriched in Y (up to 29 g/t), and the carbonate phase concentrates a small amount of Y.

A large wide variety of secondary mineral phases concentrate REE and Y including apatite-(CaF) (La - up to 11%, Ce - up to 25%, Pr - up to 3% and Nd - up to 9%), (Y, Ce, Nd) - monazites (Y - up to 29.7 wt.%, Ce up to 1.6 wt.%, Nd up to 1.02 wt.%), silicate phases (Ce up to 1.9 wt.%, Nd up to 0.72 wt. %), zircons (Y - up to 4.8 wt.%) as revealed by microprobe analysis.

The Cl-normalized pattern of REY is quite flat, excluding slight negative Eu-anomaly, and shows a small decrease from LREE towards HREE (Figure 6). A similar anomaly is characteristic of the secondary phase and rock samples (G2, G4). A distinct positive europium anomaly is recorded in samples G1 and G3. The nature of this anomaly is not explicit. Perhaps, it appears in the case of depleting specimens by Sm and Gd or presenting a significant amount of Eu-bearing mineral phase (albite, for example) as we believed earlier (Bragin et al., 2018).

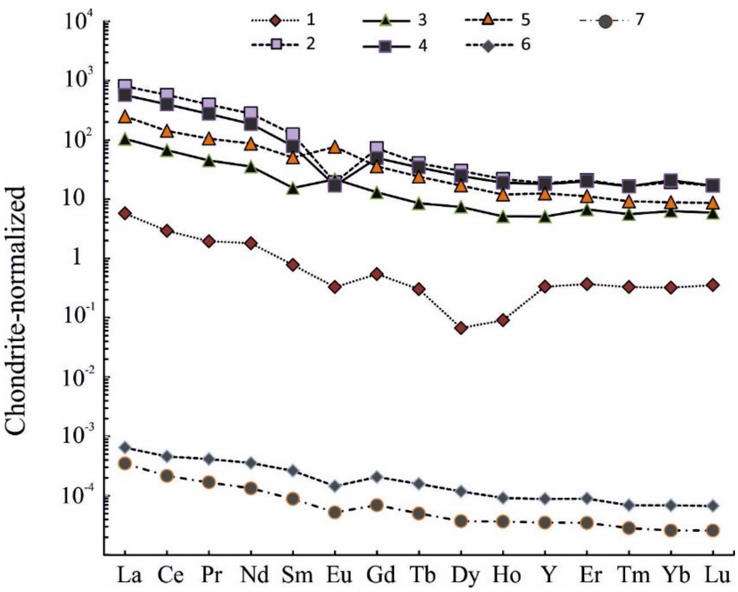

Figure 6: Chondrite-normalized plot of REY pattern within the host-rock, new-formed phase (scaled sediments), and thermal groundwaters from the studied area. 1 – scaled sediments; 2, 3, 4, 5 – bedrock's samples; 6, 7 – the thermal groundwater's samples.

The shape of REY pattern normalized to the host-rock is changed to more flat. However, the Eu-anomaly remained unchanged. From our point of view, the REY trends indicate the preferential flow of elements from bedrocks during water-rock-gas interaction under high temperatures and pressure. Almost all REYs excluding four (Ce, La, Nd, Y) have very small K_{wm} less than 0.1. The average intensity of water migration is characteristic of La, Nd, and Y, moreover Ce has K_{wm} ranging from 1.4 - 8.7 that argue for high mobility of Ce in aqueous solutions. The distribution coefficient for all REYs is very low $1\text{-}7 * 10^{-6}$, the maximum K_d is fixed for Ho and Y.

The content of U in the studied waters is low and varies from 0.06 - 0.13 μg/l. In thermal waters with high pH, U occurs mainly as hydroxy uranyls and carbonate uranyls in aqueous fluids. The main mineral-bearing U is zircon (up to 6.7 wt.%). The newly formed secondary phase contains U in small quantities (up to 1.2 g / t). The uranium K_{wm} (≈ 0.7) shows that the element is an average water migrant in this geochemical environment. The distribution coefficient U is low (about $1*10^{-5}$), but it is higher than that of REE, Th, and Sc.

The concentrations of Th in the waters is very low (at about 0.016 μg/l) although bedrock has high concentrations of the element (up to 92 g/t). This is due to the physicochemical properties of the component. As it is known, Th is one of the least mobile elements in the leaching process (Savenko, 1999). For example, the solubility in water of U^{6+} in water is three orders of magnitude higher than Th^{4+}. Thorianite is the main thorium-bearing mineral (up to 47 wt.% Th), but significant amounts of the element are also found in zircons (up to 7 wt.%) and monazites (up to 1.6 wt.%). K_{wm} for thorium is almost two times lower than for uranium. The content of Th in the waters is well correlated with HREE, so perhaps the water migration of elements occurs jointly.

The average content of Sc in the bedrocks is more than three times the Sc Clarke level in the Earth crust and is about 17 g/t. The main mineral bearing Sc is zircon (Sc up to 0.6 wt.%). Scandium concentrations in the secondary carbonates are significantly lower and do not exceed 4.5 g/t. In alkaline thermal groundwaters, the Sc content is very low, at 0.07–0.09 μg/l. K_{wm} is low (0.3 - 0.5), thus, the intensity of the water migration of the Sc is weak. The K_d is also low at less than $1*10^{-5}$.

The Cd abundance in the host rock is approximately equal to the Clarke of the element in the Earth crust. The Cd content in the secondary carbonate phase is an order of magnitude lower (about 0.03 mg/l), and in thermal waters another three orders of magnitude lower (≈0.03 μg/l). Cadmium has a very weak intensity of water migration with K_{wm} ranging from 0.001 - 0.003.

The specific feature of these thermal waters is the predominance of N_2 in the gas phase (up to 83-98 vol.%), while other gases (O_2, CO_2, Ar, Kr, Xe, He and Ne) are nonessential. Gas content at Khoja-Obi-Garm spa waters is usually not high and does not exceed 30 ml/l. Our data indicate that N_2 and O_2 are atmospheric gases, but CO_2 is biogenic ($\delta^{13}C_{TIC}$ -30‰ – -22 ‰). In boreholes $^3He/^4He_{cor.}$ values are below the atmospheric ratio (at about 0.02Ra) and very close to the crustal value. However in some thermal springs $^3He/^4He$ ratios is up to 0.3Ra. This is possibly caused by the presence of a weak mantle helium component (less 5%).

The isotope data obtained ($\delta^{18}O$ – - 13.1 ‰, δD –- -79.8 to -84,2 ‰) prove the meteoric origin of the waters since most of the data plotted along the Local Meteoric Water Line (Figure 7). The measured values of ^3H in the thermal groundwaters are very low (less 0.8 TE), which suggests a long residence time for these waters.

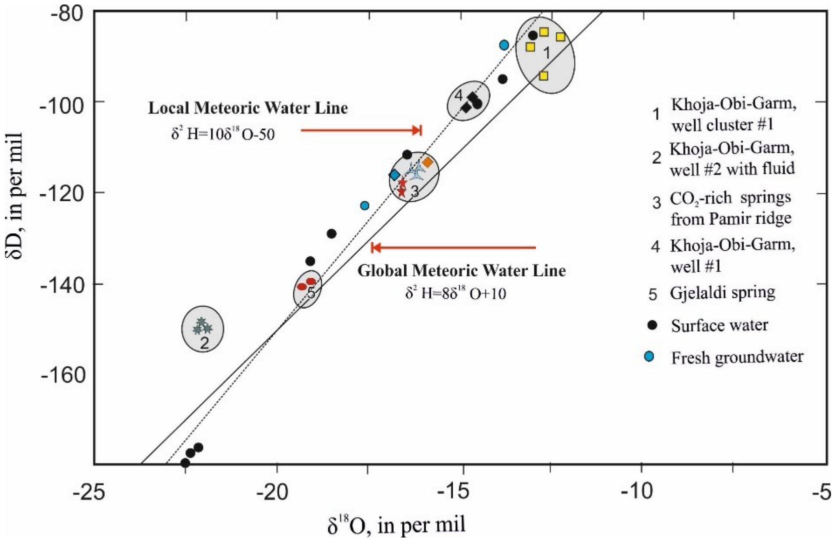

Figure 7: Plot of $\delta^{18}O$ vs δD for surface waters and thermomineral groundwater in the Pamir-Tien Shan Region.

Thermodynamic speciation indicated that these groundwaters are supersaturated with clay minerals and low-temperature zeolites but undersaturated with carbonate and aluminosilicate minerals. The estimated subsurface temperatures for these thermal waters vary from 140 °C to 156 °C based on the silica geothermometer and 193-197 °C using K/Na temperatures. Based on these temperatures and geothermal gradients of this area (at about 70°C/km), we suggest a circulation depth of about 2–3 km for the thermal groundwaters. We also conclude that the dissolution of albite, feldspar, and quartz plays a fundamental control on the groundwater chemistry.

4. CONCLUSIONS

The conducted studies indicate that the low TDS of the studied waters is a result of very limited and slowed down weathering of host igneous aluminosilicate rocks. High water temperature on the surface, up to 90-100 °C, reveals that the water circulation occurs at depths of up to 2-3 kilometers and depends on the fracturing that is developed in the rocks due to tectonic activity. The predominant gas is N_2, which is definitely of atmospheric in origin in contrast to CO_2 which is of biogenic origin. In boreholes $^3He/^4He_{cor.}$,values are below the atmospheric ratio (at about 0.02Ra) and very close to the crustal value.

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