Geochemical and Isotopic Characteristics of Geothermal Water in the Gonghe Basin of the Northeast Tibetan Plateau, China

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ABSTRACT
The Gonghe Basin locating in the Northeast Tibetan Plateau contains layers of low-to-median-temperature geothermal reservoirs, underlain by the granite hot dry rock (HDR) with temperature exceeding 180°C at the depth of 3000 m. It has been considered as a potential EGS demonstration site for the HDR exploitation in China. To understand the geothermal processes and to estimate the quantity of exploitable thermal resources in the Gonghe Basin, water and granite samples were collected and measured for chemical and isotopic compositions. $\delta^{18}$O and $\delta$D in water samples obtained from the upper geological layers suggested that the thermal water in the Gonghe Basin is recharged from meteoric water in the South-Qinghai Mountains. The maximum residual time of the thermal water in deep reservoir reaches 40000 years by $^{14}$C dating. The $^{3}$He/$^{4}$He value in thermal water collected in deep reservoir is 4.65-9.52 $\times 10^{-8}$, suggesting radiogenic heat source in the crust of earth. The $^{87}$Sr/$^{86}$Sr was measured to be 0.710987-0.712655, which indicated that strong interaction between geothermal water and granite at temperature more than 100°C. Temperature distribution in deep geothermal reservoir was determined by using geothermometers based on chemical ions in water, with the maximum reservoir temperature at 2440m estimated at 151°C.

1. INTRODUCTION
The Gonghe Basin locates in the Northeastern Tibetan Plateau. Due to multiple stage of tectonic activities, the base rocks in the Gonghe Basin is abnormally hot. In 2014, one exploration borehole was drilled in the Gonghe Basin with a depth of 3000 m. It was observed that the maximum temperature at the well bottom exceeds 180°C, which confirmed the existence of Hot Dry Rocks (HDR) in the Gonghe Basin (Yan, 2015). Overlying the HDR, two layers of hydrothermal reservoirs were revealed, with the average temperature of 60°C and 30°C, respectively. One demonstration EGS project will be soon launched in China, to jointly exploit the geothermal energy stored in the hydrothermal reservoir and HDR in the Gonghe Basin.

Before exploitation it is necessary to understand the geothermal processes in the Gonghe Basin, by using geochemistry and isotopes. Multiple layers of geothermal reservoir exists in the Gonghe Basin (Tan et al., 2012) and the deep thermal fluid could mix with the shallow groundwater. When estimating the reservoir temperature in the Gonghe Basin with the water samples collected in the springs, the results of classical geothermometer may be affected by the mixing and re-equilibrium processes.

In order to estimate temperature of the reservoir more accurately, the integrated multicomponent geothermometry (IMG) is here applied to reconstruct the chemical composition of deep fluids, which takes the advantages of complete fluid analyses and numerical calculations (Spycher et al., 2014a). Furthermore, various isotopic analyses, including $^3$H, $^{14}$C, D-$^{18}$O, $^3$He/$^4$He and $^{87}$Sr/$^{86}$Sr were applied to understand the hydrothermal system in the Gonghe Basin.

2. GEOLOGICAL SETTING
The Gonghe Basin is located in Qinghai Province, Northwestern China. The basin tilt from north to south, with South-Qinghai Mountains in the northern having an elevation > 3400 m and the maximum elevation of 4472 m (Figure 1). Alluvial-proluvial plain exists in the south of the basin, with elevation about 2700-2900 m, and the lowest elevation at the Longyangxia Reservoir is about 2573 m. TheQiabuqia River and Ayihai Riverflow through this study area. Both rivers flow from north to south, and discharge into the Longyangxia Reservoir.

The Gonghe Basin is an intermontane basin formed in the Cenozoic, located at the junction area of the East Kunlun Mountains, West Qinling Mountains, and South Qilian Mountains. The volcanic activity in the Gonghe Basin is strictly controlled by major faults, and the intrusive igneous rocks are mainly Indosinian and Yanshanian intrusions. Among them, the Indosinian dominates the lithology with granite and granodiorite. The depth of bedrock in the Gonghe geothermal field is between 900 m and 1500 m.
3. SAMPLING AND ANALYSIS METHODS

From 2015 to 2017, in order to study the geochemical and isotopic characteristics in the Gonghe Basin, a total of 20 water samples were collected from springs, wells and rivers (Figure 1). All water samples we collected were mainly along the faults in the Gonghe Basin. Ten thermal waters were sampled. Two of them (G11 and G20) are from boreholes located near N-S trending faults (F1, F1-1 and F5). Three of them (G05, G13 and G17) are from hot springs. G05 and G13 are located at the intersection of F2 and F3, while G17 is located near the F2, where the surface geothermal manifestations are the most obvious and a mass of low temperature geothermal water discharges. The rest of samples (G03, G06, G12, G18 and G19) are from hot wells, with the depth from 100 to 300 m, located in the area surrounded by the faults. In addition, five non-thermal artesian springs (G01, G04, G07, G08 and G16) and one drinking water well (G09) with the depth of 15 m were sampled for comparing and illustrating the relationship between cold and hot groundwater. River water samples (S01, S02, S04 and S05) were also collected for studying the geochemical characteristics of surface water.
The hydrogen and oxygen rations in water samples were measured using gas-bench IRMS at the US Beta Laboratory. The obtained δD and δ18O values were referred to the SMOW standard and reported in conventional delta (δ) notation, with precisions of ± 0.5 and ± 0.05‰, respectively. The 14C dating results, for three water samples (G07, G11 and G13), were measured by Accelerator Mass Spectrometry (AMS) at the US Beta Laboratory. The 14C dating results are reported both as pMC and fraction of modern, and “Apparent Radiocarbon Age” are also listed without adjusting for any hydrogeochemical effects on meteoric water 14CO2. The 3H results, for eight water samples (including 1 cold spring, 6 hot springs and wells, 1 geothermal borehole), were measured by Ultra-Low Level Liquid Scintillation Spectrometer at the Testing Center of China’s Ministry of Land and Resources. A total of 23 87Sr/86Sr data, including 13 water samples and 10 rock samples, were measured by Thermal Ionization Mass Spectrometer (TIMS) at Analytical Laboratory of CNNC Beijing Research Institute of Uranium Geology.

4. WATER CHEMICAL COMPOSITION AND TRENDS

The sampling temperature range of thermal groundwater is 23.4 to 78°C, non-thermal groundwater samples have a temperature range of 10.5 to 19.8°C, and surface water in the range of 14 to 21°C. All samples collected were weak alkaline with pH slightly more than 7. Four groups were divided according to different locations. Group 1 includes S01, S02, S04 and S05, which were collected from the Qiabuqia River. Group 2 includes G01, G04, G07, G08, G09 and G16, which were collected from cold springs and wells, with depth from 0 to 15 m. Group 3 includes G03, G05, G06, G12, G13, G17, G18 and G19, collected from hot springs and wells, with depth from 0 to 300 m. Group 4 collected from boreholes (Borehole DR3 and DR4) includes G11 and G20, of which temperature are higher than Group 3. As shown in Figure 2, the dominant cations are Na+ and K+ in all thermal samples, and a considerable content of Ca2+ and Mg2+ also existed in non-thermal samples. The main anions (including Cl-, HCO3- and SO4-2) have a similar milligram equivalent, the concentration of Cl- is slightly higher in thermal samples, and the concentration of HCO3- is slightly higher in non-thermal samples.

Figure 2: Piper diagram for groundwater and surface water samples in the Gonghe geothermal field.

5. GEOTHERMAL RESERVOIR TEMPERATURE ESTIMATIONS

5.1 Integrated multicomponent geothermometry approach

GeoT, a simulation program based on existing method of multicomponent chemical geothermometry (Reed and Spycher, 1984), developed based on TOUGHREACT (Xu and Pruess, 2001; Xu et al., 2006; Xu et al., 2011), is used in this study (Spycher et al., 2016; Spycher et al., 2014b; Spycher et al., 2011). Based on complete chemical composition analyses, GeoT can calculate the saturation indices of minerals (log(Q/K)) over a range of temperatures. Coupled with numerical optimization program PEST, an external parameter estimation software (Doherty, 1994), GeoT can estimate unknown or inaccurate input parameters necessary to reconstruct the deep fluid composition (e.g., concentration of Al and/or Mg). Geothermometry simulation combined with fluid reconstruction and numerical optimization is here called Integrated Multicomponent Geothermometry (IMG).

In order to get more accurate geothermal reservoir lithological data, granite and sandstone rock samples were collected in field of the Gonghe Basin and analyzed by X-ray diffraction at Jilin University. A mineral assemblage is selected including quartz, albite, microcline, calcite, tremolite, muscovite, clinoclore, illite and montmorillonite-Ca. In addition to the 9 detected minerals, as common hydrothermal minerals, dolomite and kaolinite are also taken into account in our study.
5.2 Insights from a single spring

Because of limited deep drilling information, there is no accurate data about the deep reservoir temperature of the Gonghe Basin. In this study, the sampling temperature of G20 borehole is 78°C. Other geothermal drilling data derived a temperature range of 80-90°C (Yan, 2015). Using a variety of classical geothermometers and Si-enthalpy graphic method, Li (2016) obtained an average value of 94-140°C. Synthesizing the results of previous investigations, a reasonable deep geothermal temperature in the Gonghe Basin should be more than 80°C.

The hot spring sample G05 has a relatively high temperature, large flow and high TDS value (1746.72 mg/L, close to deep borehole). Therefore, G05 is chosen for illustrating the method of integrated multicomponent geothermometry.

The base-case, without deep fluid reconstruction and parameter optimization, is shown in Figure 3a, b. The calculated mineral saturation indices (SI), which contains all the 11 minerals, show poor clustering as a function of temperature with an estimated temperature around 71°C (Figure 3a). Since GeoT program provides 4 kinds of statistical analyses for all minerals SI values at any specific temperature, and these statistical analyses help us determine the estimated temperature and judge the clustering of minerals curves accurately and directly. The minimum of median analysis (RMED) is used for the final temperature determination, and other statistical analyses (RMSE: mean-root-square error; SDEV: standard deviation; MEAN: average) are computed to provide information on the quality of the clustering (Spycher et al., 2014b). When the minimum of log(Q/K) statistics is less than 0.1, the clustering is generally considered to be good. As shown in Figure 3b, the minimum of RMED is 0.26 and the other 3 statistical analyses are even greater than 0.7, so it can indicate that the multicomponent geothermometry without deep fluid reconstruction and numerical optimization may show a poor performance.

In order to correct the effect of dilution and steam loss when the deep fluid ascend to the surface, parameters optimization is applied by an external software (PEST). Two parameters are unknown or poorly constrained input parameters like Al and Mg contents, because the concentration of Al is usually lower than the detection limit and the concentration of Mg is affected by the re-equilibrium when deep fluid ascended to shallow aquifer. It should also be taken into account if there is other unknown or poorly constrained parameter. The other two parameters are dilution/concentration factor and steam fraction. The dilution/concentration factor is used to correct the dilution or concentration effect by adjusting its value more than 1 or less than 1, further explanation is that this parameter multiplies input concentrations. The steam fraction is used to add back the steam loss by boiling to deep fluid, which represented the fraction of gas in the total discharge. The gas composition from analyzing geothermal spring gas samples (Shangguan et al., 2000) is listed as follows: 99.86 mol% H2O in all steam loss, 0.14 mol% of gases contained CO2 (95.41%), H2 (0.43%), H2S (0.023%), CH4 (0.01%).

The optimized case based on the IMG method is shown in Figure 3c, d. After the numerical optimization for inaccurate parameters, a temperature of 93°C of deep geothermal water reconstruction is achieved. A large spread of temperatures (over 80°C) is indicated by the log(Q/K) curves of minerals crossing the equilibrium point (zero log(Q/K) values), and even the curve of calcite is above the equilibrium line in all temperature range (Figure 3c). It shows that these 11 kinds of minerals may not all achieve equilibrium in the deep reservoir. Thus, a subset of best-clustering minerals (main minerals: albite, microcline, kaolinite, quartz, muscovite, clinochlore and dolomite) are used to estimate temperature, and yields a temperature of 92°C with a better-clustering (Figure 3e, f). The steam fraction is 0.00, which indicates that there is no steam loss in deep fluid reconstruction. The dilution/concentration factor is 3.4, suggesting that the input water composition is concentrated by this factor, to correct the significant dilution effect mixed with shallow groundwater. The optimized concentration of Al is 0.004 mg/L, which is about three times lower than the measured value (0.014 mg/L). The optimized concentration of Mg is 0.0025 mg/L, which is three orders of magnitude lower than the measured value (2.35 mg/L).
Figure 3: Simulation results of sample G05 obtained by the integrated multicomponent geothermometry method. (a) Mineral saturation index variation with temperature for the base-case. (b) Statistical analysis for the base-case. (c) Mineral saturation index variation with temperature for the optimized case. (d) Statistical analysis for the optimized case. (e) Base on the optimized case, this case only considered the main minerals. (f) Statistical analysis for the optimized case, only considered the main minerals.

5.3 Reservoir temperature estimations

Through the method of deep fluid reconstruction using IMG method, the results for all 10 thermal water samples are listed in Figure 4. The low-TDS group (G03, G12, G17, G18 and G19) yields similar estimated temperatures (111°C, 101°C, 107°C, 102°C and 97°C). It indicates that the measured temperatures (27.5°C, 25.0°C, 23.4°C, 29.3°C and 30.9°C) are far below the estimated temperature, because the samples were taken from hot spring and shallow wells, which reflects the mixing process between shallow groundwater and deep hot water. The IMG method can recover the common original state (if the water samples come from a common reservoir), but the measured temperatures were affected by the amount of mixed shallow cold groundwater. The high-TDS group (G05, G06 and G13) also yields similar estimated temperatures (92°C, 102°C and 116°C). The boreholes G11 and G20 yield estimated temperatures of 94°C and 151°C. Except for the abnormal high temperature in G20, other 9 water samples have obtained similar estimated temperature (102±7°C) (with an average temperature and standard deviation). It indicates that these 9 geothermal water samples are recharge by common deep
geothermal fluid. For the sample of G20, the high estimated temperature of deep reservoir (151°C) indicates the maximum circulating depth of deep fluid, and there may be a granite fracture zone for geothermal fluid circulation.

The comparison of the IMG estimated temperatures with classical geothermometer results is shown in Figure 4. It includes 5 kinds of common classical geothermometers (chalcedony, quartz, Na-K, Na-K-Ca, and K-Mg). The results of chalcedony geothermometer are close to the hot water sampling temperatures, conforming that chalcedony controls the SiO$_2$ concentration in low-temperature geothermal system (Fournier, 1989). However, the quartz geothermometer does not obtain a reasonable temperature when dealing with the mixing effect. The performance of the Na-K geothermometer in estimating deep reservoir temperature is not very good, which works well in low-TDS group but fails in other samples. The Na-K-Ca geothermometer is also not stable, although it aims to correct abnormally high Na-K results in the condition of Ca-rich geothermal fluid. Neither Na-K nor Na-K-Ca geothermometer can give a reasonable result. In general, concentration of Ca and Mg in shallow groundwater is high, because the re-equilibration process in corresponding minerals is rapid, so the temperatures determined by K-Mg geothermometer are close to the shallow reservoir temperatures.

![Figure 4](image)

**Figure 4:** Comparison of temperatures obtained from the Integrated Multicomponent Geothermometry (IMG) with those calculated by classical geothermometers for different samples in the Gonghe geothermal field. The measured temperatures refer to the hot water sampling temperatures.

6. ISOTOPIC CHARACTERISTICS

6.1 Isotopic dating

Both the content of $^3$H and $^{14}$C were measured in two hydrothermal reservoir and also in the shallow unconfined aquifers. $^{14}$C dating suggested that the groundwater age in the deeper geothermal reservoir is older than 40000 years, while in the shallow geothermal reservoir reaches 30000 years. However, the detectable $^3$H (1-2 TU) contended in the geothermal reservoirs as well, which suggested that the thermal water mixing with the young water during their upward migration to the land surface. This indicated that the renewable capability of the geothermal water in the Gonghe Basin is weak, and during the geothermal exploitation, the sharp temperature drop is possible due to the hydraulic communication between the geothermal reservoir and the shallow cool aquifers.

6.2 Isotopic tracing

The $\delta^{18}$O and $\delta^D$ values in different water samples are compared with the local meteoric water line (LMWL) of $\delta D=7\delta^{18}O+3.2$, which is determined in the adjacent Xining Basin (Tan et al., 2012). It is observed that all the $\delta^{18}$O and $\delta D$ are close to the LMWL, suggesting that the water in the geothermal reservoir originates from the meteoric water. According to the elevation-isotope gradient of $\sim 0.3‰/100$ m estimated in the northeastern Tibetan Plateau (Hren et al., 2009), the recharge altitude for the thermal water is estimated at 4500 m. South-Qinghai Mountains is the highest mountain in this study area with the elevation over 4472 m, which is most likely the recharge area of the geothermal water. In addition, due to the water-rock interaction in geothermal system, $\delta^{18}$O shift relative to LMWL is observed in hot water samples, especially G05, G11 and G20.
Figure 5: Plot of $\delta^{18}$O and $\delta D$ for groundwater and river water in the Gonghe geothermal field.

The isotopes of noble gases can help understand the heat source. Helium isotopes were measured in three hot water and one cold water (Figure 6). As shown in Figure 6, $^{3}$He/$^{4}$He in hot water with temperature $> 60^\circ$C ranges between 0.03 and 0.07 Ra, which is lower than that in the air and mantle helium composition ($>8$ Ra). This represents the characteristic of crustal radiogenic helium isotope ratio (typically $<0.1$ Ra). Moreover, the $^{3}$He/$^{4}$He ratio generally decreases with the increase of temperature in Figure 6. This confirms that the contribution of mantle helium in the thermal water is not likely, because the input of mantle source helium would increase both the temperature and helium ratio in water significantly (Jiang et al., 2018).

Figure 6: $^{3}$He/$^{4}$He (Ra, relative to $^{3}$He/$^{4}$He of $1.37 \times 10^{-6}$ in the atmosphere) versus temperature in the hot and cold water in the Gonghe Basin. The temperatures of G05 and G11 are derived from the results of IMG method.

To understand the flow paths of water circulation, $^{87}$Sr/$^{86}$Sr were measured in 10 rock samples, and 13 water samples collected in the Gonghe Basin. Figure 7a illustrated the $^{87}$Sr/$^{86}$Sr values in four typical types of rocks in the Gonghe Basin. As shown, in the granites formed in 230 Ma in the Gonghe Basin $^{87}$Sr/$^{86}$Sr ranges from 0.7082 to 0.7100, in the Neogene sandstone ranges from 0.7100 to 0.7161, in the slate is 0.7187, and in the calcite veins is 0.7198. The comparison of $^{87}$Sr/$^{86}$Sr values in water samples to that in the typical rocks indicates that the water mainly flows in the sandstones, while the flow through fractured granite and slate is not suggested (Figure 7b). The values of $^{87}$Sr/$^{86}$Sr increasing with temperature due to the stronger water-rock interaction in the high-temperature reservoirs.
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Figure 7: (a) The values of $^{87}\text{Sr}/^{86}\text{Sr}$ and isotopic age for different rock samples in Gonghe Basin. Four granites were formed in the Indosinian with an isotopic age of ca. 230 Ma, four sandstone were formed in the Neogene with an isotopic age of ca. 20 Ma, and the age of slate and calcite samples were not measured. (b) The values of $^{87}\text{Sr}/^{86}\text{Sr}$ for different water samples in Gonghe Basin. The temperatures of hot water samples in Gonghe are estimated by IMG method.

7. CONCLUSIONS
Geochemical characteristics and isotopic analysis ($^3\text{H}$, $^{14}\text{C}$, D, $^{18}\text{O}$, $^3\text{He}/^4\text{He}$ and $^{87}\text{Sr}/^{86}\text{Sr}$), were used to improve the understanding of hydrothermal systems in the Gonghe Basin, China. The integrated multicomponent geothermometry (IMG) was used to reconstruct the original deep water compositions, and to estimate reservoir temperatures. The following major conclusions were drawn:

Through the analysis of geochemical characteristics, the thermal water samples mixed with different quantity of deep fluids based on the TDS values. The estimated geothermal reservoir temperature is 92-116°C with an average temperature and standard deviation of $102\pm7$ °C by the results of 9 hot water samples. In addition, the granite fractured zone exists with an estimated temperature of 151°C reflecting the largest circulation depth of the geothermal fluid in the Gonghe Basin.

$^3\text{H}$ age dating and $^{14}$C age dating indicate that the residence time of geothermal water in Gonghe Basin is very long (more than 30000 years). Because of different residence time in hot water samples, it indicates that there may be different geothermal layers in Gonghe Basin. All the hot samples have a similar $^3\text{H}$ value (1.0, 1.3, 1.0, 1.0, 1.0, 1.0, 1.1 TU), indicating that these samples are a mixture of deep geothermal fluid with long residence time and shallow cold water with short residence time.

The thermal water source is from meteoric water in South-Qinghai Mountains, according to the measured $\delta^{18}\text{O}$ and $\deltaD$. The results of $^3\text{He}/^4\text{He}$ illustrate that the deep fluid has the characteristic of crustal radiogenic helium isotope ratio. From the $^{87}\text{Sr}/^{86}\text{Sr}$ values in hot water and cold water samples, it is generally recognized as deriving from the earth’s crust consisting with the helium isotopic conclusion, and the hot samples have experienced a stronger and more persistent water-rock interaction than cold samples in sandstone formation.

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