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Geochemistry of Selected Hot Springs in Jiangxi Province, SE-China

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ABSTRACT

The chemical and isotopic composition of ten selected hot springs in Jiangxi Province, SE-China, are analyzed. Five of them are N_2-dominated hot springs. The N_2-dominated geothermal waters are characterized by low TDS ranging from 0.135g/L to 0.294g/L, high pH values (>8.5), and nitrogen-predominate (>90%) in dissolved gases. The rest are CO_2-dominated hot springs. The CO_2-dominated thermal waters are distinguished by higher salinity from 0.245g/L to 1.33g/L but lower pH values (<8.0) and carbon dioxide-dominated (>96%) in dissolved gases. Fluid-mineral equilibrium studies suggest that the geothermal water-rock system is an equilibrium -nonequilibrium system in which geothermal waters are close to equilibrium with secondary minerals as carbonates and fluoride, but disequilibrium with endogenous minerals as albite and anorthite. The reasons for extremely low TDS of the nitric hot springs is also discussed based on geochemical modeling using geochemical code PHREEQC. Solute geothermometers and the Log(Q/K) method give subsurface temperatures ranging on average from 80 to 150°C for the nitric geothermal systems. The isotopic studies showed that the nitric hot springs were recharged by local precipitation and have a circulation depth approximately from 1200m to 2700m. Isotopic and gas study showed that the carbon dioxide of the CO_2-dominated hot springs are originated from magmatic inorganic sources and the nitrogen of the type is the mixture of mantle derived, crustal and atmospheric N_2, and that the CO_2 for the N_2-dominant type come from crustal organic sources and the $^3He/^4He$ ratios represents input of radiogenic ^4He in the crust.

1. INTRODUCTION

Jiangxi Province, located in SE-China, is one of the Provinces in the country with a wide distribution of hot springs. There are over 118 hot springs that have been found in the Province. The hot springs are mainly distributed along NNE and EW-trending uplift belts and controlled by the NNE and NE-trending faults.

The temperatures of most hot springs in the Province are lower than 90 °C. The highest temperature of them is 88 °C of the Tanghu Hot spring, located in the southern part of the Province. Most of the hot springs in Jiangxi Province belongs to medium and low temperature geothermal water (table1). There are two types of hot springs in the Province: one is the nitric geothermal water and the other is the carbon dioxide-domnated geothermal water (Sun et al., 2014). The nitric thermal waters has lower TDS of 0.2–0.6 g/L but higher pH values (>8.5), and the carbonate dioxide geothermal has higher TDS of 0.5–3.0 g/L but lower pH values (<7.6). The formation mechanisms of the geothermal waters in the Province are not very clear.

Table 1: Temperatures of hot springs in Jiangxi province

Temperature(℃)	20-40	40-60	60-80	>80
Numbers	66	36	13	3
Percentage (%)	56	30.5	11	2.5

Geochemistry plays a very important role in providing useful information on the origin of the geothermal fluids, the occurrence of mixing processes among different components, the role of water–rock and water–gas interactions, and the flow regimes (Ármannsson H,., 1989; Arnórsson S., 2000). This paper presents the formation mechanism of the nitric thermal waters in the Province by using geochemical data including water chemistry and isotopic analyses.

2. SAMPLING AND ANALYTICAL METHODS

This paper presents the results of 10 samples of hot springs collected. Temperature, pH, conductivity and redox potential were analyzed using Multi-function parameter 520M-01A in the field. The values of dissolved oxygen for the hot springs were analyzed using a dissolved oxygen meter, and the dissolved SiO_2 (Method 8185) and Fe concentrations (Method 8147) were determined by HACH DR2400 portable spectrophotometer on site. HCO_3^- and CO_3^{2-} were titrated with 10 ml micro-titrate tube. Major anions were analyzed by Ion ICS-1100 chromatography such as SO_4^{2-}, Cl^-, F^-, NO^{3-}, NO^{2-} and PO_4^{3-}, and major cations were analyzed by iCAP7400 spectrometer such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe, and Cu. Ten samples were analyzed for D and ^{18}O at the State Key Laboratory of Nuclear Resources and Environment of East China University of Technology. A Finnigan MAT253 mass spectrometer was used for the measurements. Samples of δD were equilibrated with mixture gas if 2% H_2 and He at a temperature of 45 °C for 40 minutes and then detected by MAT253, resulting in accuracy less than 2 ‰. Samples of $\delta^{18}O$ were equilibrated with a mixture gas of 0.3% CO_2 and He at a constant temperature of 28 °C for 20 hours resulting in accuracy less than 0.2‰. The samples were standardized using in-house standards of known composition relative to V-SMOW (Standard Mean Ocean Water).

3. RESULTS AND DISCUSSION

3.1 Chemical characteristics

Chemical analysis were as shown in Table 2, the charge balance error of all samples was less than 5%.

Table 2: Results of chemical analysis of hot springs（mg/L）

Sample NO.	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	F^-
1	93.3	126	121	11.8	10.8	42.6	673	/	4.41
2	15.2	10.9	57.1	2.89	2.05	50.1	140	/	4.5
3	19.5	221	37.6	0.15	16.9	451	31.5	/	8.51
4	59.2	703	86	4.98	28.9	257	1820	/	5.96
5	3.68	69.8	11.8	0.06	7.13	25.7	131	/	10.6
6	8.3	89.3	22.6	0.47	5.01	25.3	250	/	9.03
7	1.98	71.9	3.76	0.02	6.16	17.3	126.7	3.24	13.7
8	4.49	59.1	7.5	0.14	3.91	37.4	94.06	6.94	8.55
9	5.09	71.6	6.19	0.03	4.33	13.2	131.1	6.94	13.3
10	3.06	66.1	2.34	0.03	6.03	23.9	67.3	16.2	13.2

Sample NO.	TDS（mg/L）	T(℃)	pH	SiO_2	Hydrochemical type
1	651	35.8	6.3	73.5	HCO_3-Ca-Na
2	187	52.8	7.93	45	HCO_3-SO_4- Ca
3	568	58.1	6.86	107.1	SO_4-Na
4	1330	52.2	6.87	117	HCO_3-Na
5	245	72.0	7.72	76.1	HCO_3-Na
6	294	42.3	8.88	91	HCO_3-Na
7	173	37.8	8.82	61.8	HCO_3-Na
8	129	83.0	8.75	122	HCO_3-SO_4-Na
9	135	82.3	8.30	96	HCO_3-Na
10	135	41.4	9.23	104	HCO_3-Na

As shown in Table 2, the TDS values of the nitric hot springs (No. 6, 7, 8, 9, 10) are lower than those of the carbon dioxide type hot springs (No. 1, 2, 3, 4, 5). The Piper diagram (Figure 1) shows that most of the nitric hot springs are the HCO_3-Na type waters with lower TDS.

The average value of the γNa/γCl coefficient of the seawater is 0.85. If the groundwater is mainly dissolved from the rock salt, the γNa/γCl ratio is close to 1. The γNa/γCl ratios of nitric hot springs in Longnan area of the Province are much greater than 1, indicating that the hot springs have undergone strong water-rock interactions. In the magmatic and metamorphic rocks, the host rocks of thermal reservoirs contain lots of carbonates and aluminosilicate minerals, which were leached by CO_2 and H_2O. Those minerals such as feldspar are hydrolyzed to produce Na^+, and the aluminosilicate minerals are weathered and dissolved to form low TDS water mainly composed of HCO_3^- and Na^+.

The low content of K^+ and Mg^{2+} in hot spring may be due to K^+ and Mg^{2+} which are easily absorbed by plants. In addition, K^+ can form secondary minerals, such as hydromica, montmorillonite, sericite, etc., especially under the high temperature and pressure conditions, and the dolomitization may occur as the temperature increases (Equation 1), so that the hot spring is relatively lack of magnesium and rich in sodium and calcium.

$$2CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+} \quad (1)$$

Fluorine (F^-) is rich in nitric hot springs, ranging from 0.45 to 0.7 meq/L, and account for more than 15% of the total of anions. This element may be derived from fluorine-contained minerals such as biotite, amphibole and fluoroapatite in magmatic rocks.

The pH values of the nitric hot spring is higher than those of the carbon dioxide type hot springs. Due to leaching action, the pH value in the water should gradually increase with the increasing of the minerals (especially HCO_3^- present). For example, the hydrolysis of albite, the common mineral in the rocks of this area, results in increasing of OH^- in waters (see Equation 2).

$$2NaAlSi_3O_8 + 11H_2O = Al_2Si_2O_5(OH)_4 + 2Na^+ + 2OH^- + 4H_4SiO_4. \quad (2)$$

According to research by Shvartsev (Shvartsev, 2015), the alkalinity produced by the hydrolysis of silicate minerals is neutralized to some extent by acids (inorganic or organic acids) in geothermal systems. In the nitric hot springs of the Baikal region, it is difficult to produce large amounts of H_2CO_3 and CO_2 substances due to the scarcity of humus and organic matter in cold and barren landforms. Therefore, in the case where the carbon dioxide gas is extremely scarce, pH of the solution increase as the increasing of alkaline substances.

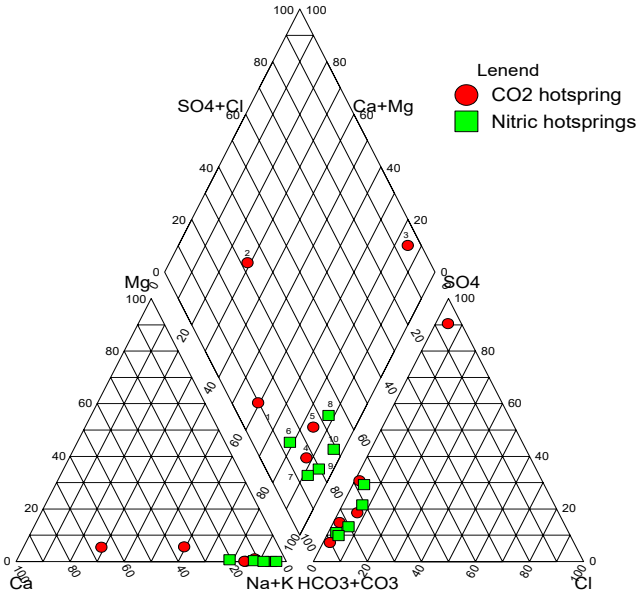


Figure1: Piper diagram of hot springs

3.2 Hydrogen and oxygen isotope characteristics

Craig (1961) first proposed that the precipitation points around the world fall on the line of $\delta D=8\delta^{18}O+10$. Further research has shown that the slope and intercept of atmospheric precipitation may vary within a small range, depending on the origin of water vapor that forms the precipitation process and other meteorological factors. The slope and intercept of the atmospheric precipitation line can be used to identify the recharge of groundwater. In this region, the local atmospheric meteoric water of Jiangxi province is (Sun et al., 2001):

$$\delta D=8.4\delta^{18}O+11.8 \quad \textbf{(3)}$$

For the hot springs in southern Jiangxi Province, $\delta^{18}O$ have shifted obviously (as shown in Figure.2), indicating that water-rock interactions are quite strong in the geothermal systems.

In the southwestern part of China, the altitude gradient of δD is -2.5‰/100m which is lower than that in the southwest with the elevation gradient of -2‰/ 100m (Sun Z. & Li L., 2001). According to the isotopic altitude effect, the recharge altitude of geothermal waters can be calculated using Equation 4.

$$H = \frac{R - R_1}{\rho} + h \quad \textbf{(4)}$$

where, H is the recharge altitude of the geothermal water, R is the $\delta^{18}O$ or δD value of the hot spring, R_1 is the $\delta^{18}O$ or δD value of the surface water without obvious evaporation near the sampling point, h is the surface water elevation, ρ is the altitude gradient of $\delta^{18}O$ or δD. Due to obvious oxygen-shift of the selected geothermal waters in the Province, the recharge altitude of the thermal waters can only be estimated by Equation 4 using altitude gradient of δD and the results are shown in Table 3.

Table 3: calculated Results for recharge altitude of hot springs

Hot spring No.	Sampling Altitude /m	δD/‰	Recharge Altitude/m
1	75	-53.1	230
2	62	-55.0	312
3	186	-59.0	636
4	228	-55.9	523
5	310	-60.6	840
6	290	-61.0	840
7	369	-57.8	759
8	341	-59.6	821
9	311	-66.2	1121
10	276	-66.6	1106

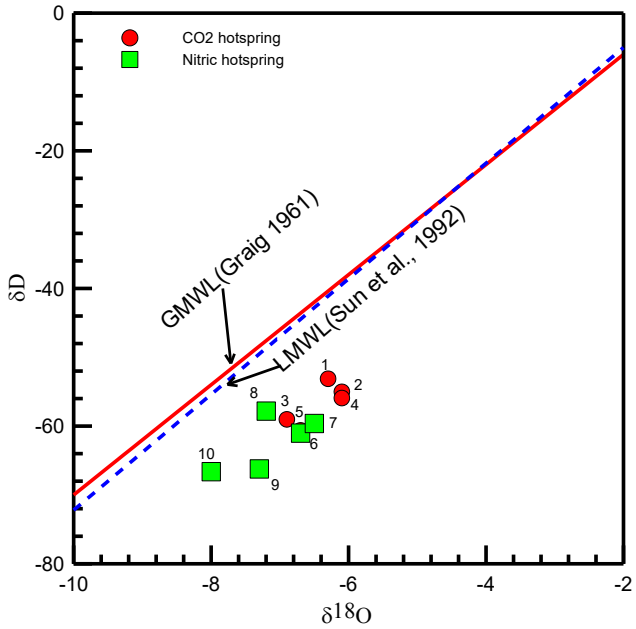


Figure 2: Relationship between δD and $\delta^{18}O$ of nitric hot springs

3.3 Fluid-mineral equilibrium

The saturation index (SI) is one of the most widely used hydrogeochemical parameters in groundwater research. When the mineral is in equilibrium in aqueous solution, SI = 0; when the mineral dissolves, SI < 0; when the mineral precipitates, SI > 0. The definition of saturation index (SI) can be expressed as Equation 5

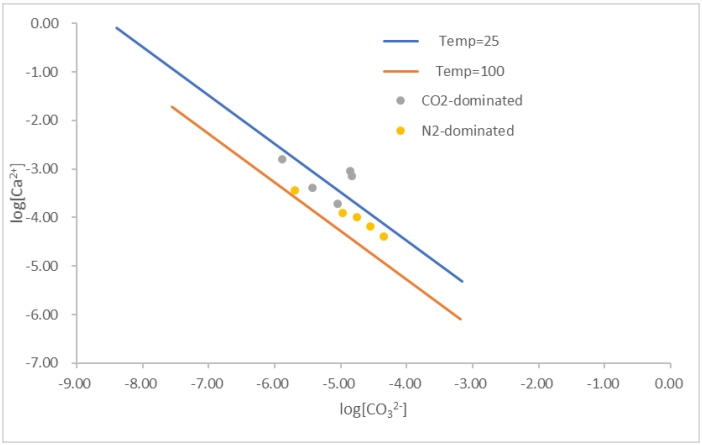
$$SI = \log IAP/K \quad (5)$$

where, IAP is ion activity product and K is the equilibrium constant. This equation is established at 25 ° C and 100 ° C. Here, PHREEQC2.15 was used to calculate the saturation indexes of some secondary minerals of the 5 nitric hot springs. The calculation results are shown in table 4.

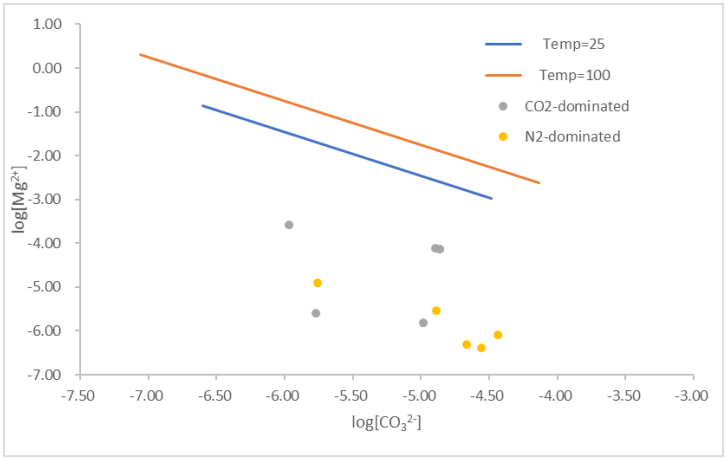
Table 4: Saturation indexes of secondary minerals in nitric hot springs

Sample NO.	Albite	Calcite	Chalcedony	Dolomite	Fluorite	Siderite	Quartz	Magnesite
6	-1.05	-0.53	0.29	-2.26	0.26	-2.32	0.67	-1.61
7	-5.79	-0.15	-1.19	-2.32	-0.06	-2.77	-0.80	-3.1
8	-4.08	0.30	-0.54	-0.99	-0.49	-1.71	-0.27	-2.62
9	-4.91	0.34	-0.80	-1.58	-0.19	-2.35	-0.52	-2.93
10	-2.48	0.09	-0.29	-1.26	-0.36	-1.95	0.088	-1.23

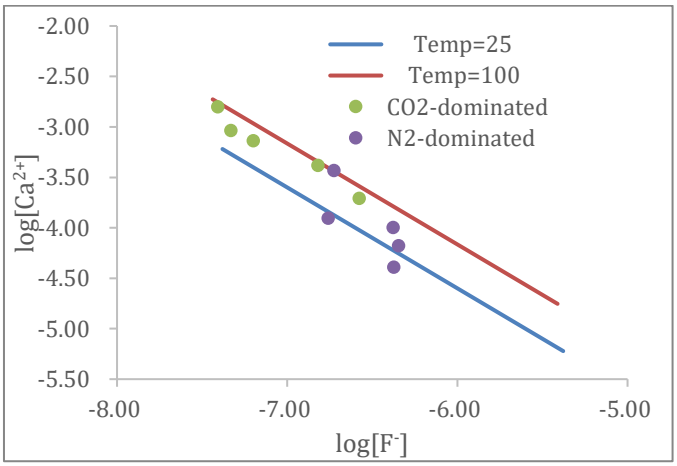
Figure 4 shows the saturated state of carbonate mineral calcite ($CaCO_3$), magnesite ($MgCO_3$) and fluorite (CaF_2). Figure 4 showed that the calcite minerals reach an equilibrium state, and magnesite is obviously below the line at SI=0, being in an undersaturated state. Since the solubility of carbonate decreases with increasing temperature, the equilibrium level of hot spring and carbonate minerals increases with depth. Fluorite (CaF_2) is another mineral that can reach saturation under moderate temperature parameters (Fig. 4c). It can be seen from the Figure 4 that the fluorite in the hot springs is mostly in equilibrium with the solution. Like calcite, fluorite in hot springs can reach saturation in the case of low salinity (<0.2g/L, pH>8).



(a)



（b）



（c）

Figure 4: Mineral equilibrium of calcite (a), magnesite (b) and fluorite (c) in hotspring at 25 ° C (dashed lines) and 100 °C (solid line))

3.4 Solute geothermometers

Solute geothermometers of SiO_2, chalcedony, Na-K, Na-K-Ca are widely used in geothermal studies. Mg-Na-K triangle diagram is one of the most useful geothermometers which was proposed by Giggenbach (1988).

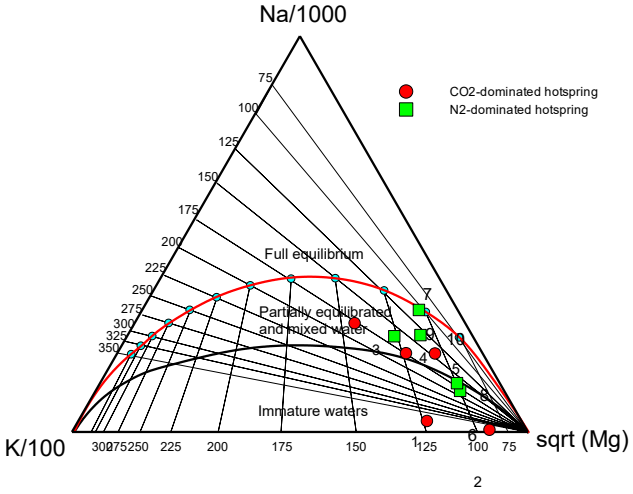


Figure 5: Na-K-Mg triangle diagram of hot springs

As shown in Figure 5, most of the nitric hot springs in the southern part of the Province are the immature waters or in partial equilibrium with relevant minerals. It is not suitable to use the cation geothermometers directly. Therefore, the chalcedony geothermometer and SiO_2 geothermometer are used to estimate the temperatures of the geothermal reservoirs. The calculation results are shown in Table 5. Temperature difference of these two geothermometers are about 20 °C. The result of chalcedony geothermometer (Equation 6) is relatively lower than those of SiO_2 geothermometer (Equation 7).

Chalcedony geothermometer (Fournier,1977), $T \in (0, 250℃)$

$$T = \frac{1032}{4.69 - \mathrm{Log}SiO_2} - 273.15 \quad (6)$$

SiO_2 geothermometer (Fournier,1973), $T \in (0, 250℃)$,

$$T = \frac{1309}{5.19 - \mathrm{Log}SiO_2} - 273.15 \quad (7)$$

Table 5: Results of estimation of temperature and depth of reservoir

Sample NO.	SiO2 geothermometers/°C	Chalcedony geothermometers/°C	Log(Q/K)/°C	Reservoir depth/m
6	132	105	80—120	1833
7	112	83	120—160	1179
8	149	123	140—150	2506
9	135	108	110—130	2690
10	139	113	90—120	2117

3.5 Log(Q/K) and T

The (logQ/K)-T diagram can be applied to estimate the subsurface temperatures of geothermal systems (Reed M. &Spycher N, 1984; Pang Z. & Reed M., 1998). The (logQ/K)-T diagram of the Rucheng Hot spring (No.8) of the western part of the Province showed that sepiolite, quartz and chalocedony converge at about 140-150°C. The temperature of the reservoir in Rucheng Hotspring may be estimated as 140-150 °C.

As shown in Figure 6(b), the calcite and chalcedony converge at 83 °C, and quartz at 118 °C. Therefore, the temperature of reservoir for Hetong Hotspring (No.6) is in the range of 80 °C to 120 °C. As shown in Figure 6(c), silica, chalcedony and aragonite are converged at 120 °C, 140 °C and 150 °C, respectively. Therefore, the temperature of reservoir for Dayu Hotspring (No.7) may be in the range of 120 °C to 150 °C. As shown in Figure 6 (d), forsterite and sepiolite are converged at around 110-130 °C. Therefore, the temperature of reservoir in Tanghu Hotspring (No.9) may be estimated as 110-130 °C. In figure 6(e), six minerals such as quartz, chalcedony, sepiolite, calcite, aragonite and clinoenstatite converge at 90-120 °C. Therefore, the subsurface temperature for Zhangmu Hotspring (No. 10) may range from 90 to 120 °C.

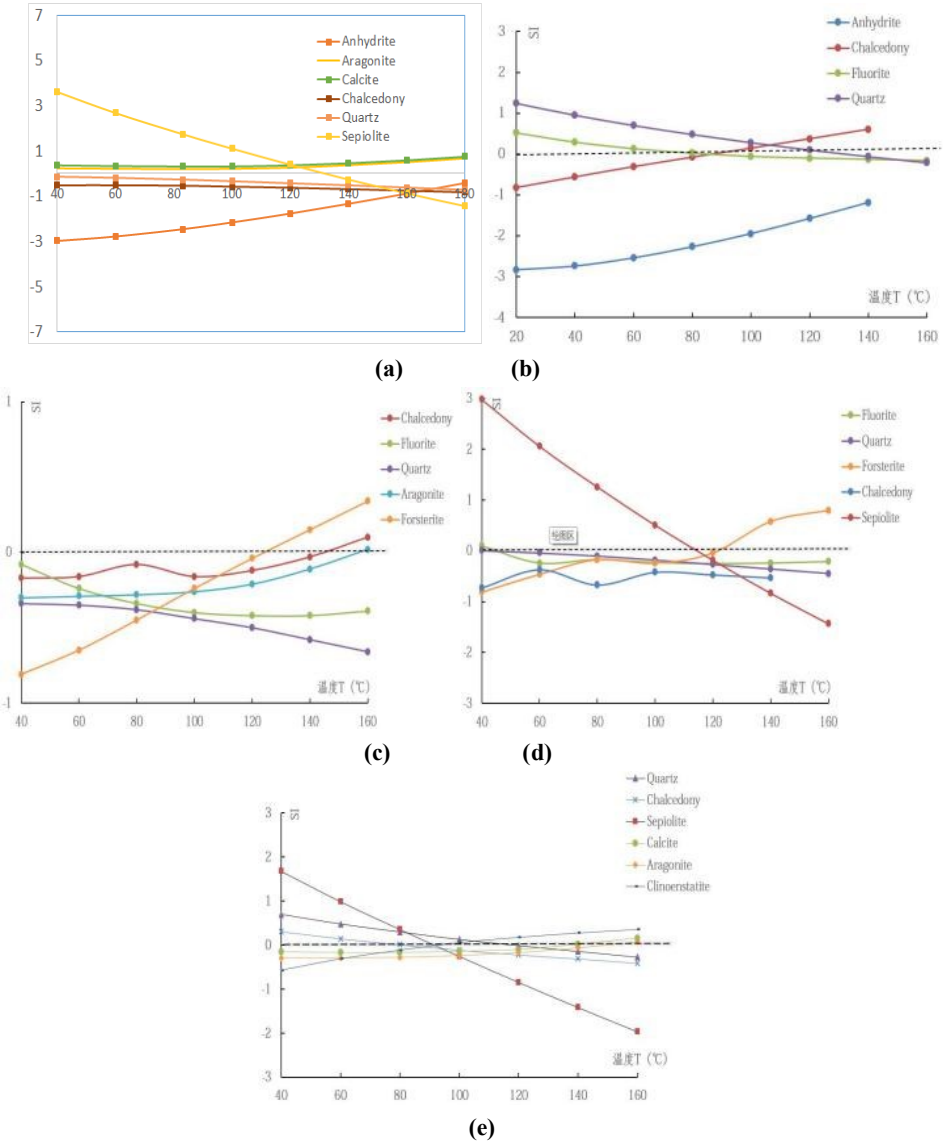


Figure 6: logQ/K of Hot springs (a: Rucheng Hotspring; b: Hetong Hotspring; c: Dayu Hotspring; d: Tanghu Hotspring; e: Zhangmu Hotspring)

3.6 Circulation depth

The isothermal zone is generally 15-20 m depth in the Province. The annual temperature change at this depth is less than 0.1 °C. Circulation depth of the hot spring is calculated by the following formula:

$$t=(D-h)\frac{\Delta t}{\Delta Z}+t_0 \quad (8)$$

where: t——subsurface temperature of geothermal reservoir (t°C);

D——Circulation depth (m);

H——depth of isothermal zone (m);

$\frac{\Delta t}{\Delta Z}$ ——Geothermal gradient（°C /m）;

t_0——local annual average temperature or normal temperature (°C)

In the study area, the geothermal gradient is 3.5 °C/100 m (Hu Shengbiao et al., 1992), t0 is the annual average ground temperature of the recharge area (22 °C), and the H is taken as 20 m. The results of estimated circulation depth for the hot springs are shown in Table 5.

3.7 Isotopic and geochemical evidence for origin of geothermal gases

3.7.1 Carbon isotopic composition and genesis of CO_2 and CH_4 in geothermal gas

The $\delta^{13}C$ of nitrogen-type geothermal gas in the western region of southern Jiangxi is -23.7‰ ~ -12.6‰ (PDB), and the average value is -17.82‰. According to the identification of CO_2 genesis (Dai Jinjin et al., 1994), this CO_2 gas is an organic factor of crustal origin. The $\delta^{13}C$ values of CO_2 for the CO_2-dominant type geothermal gases are-5.50‰ to-3.49‰(PDB) with a mean value of -4.66‰(PDB) showing that the carbon dioxide of the gases are originated from magmatic inorganic sources.

3.7.2 Noble gases and isotopes in geothermal gases

Geothermal fluids may contain helium from the mantle, crust, or atmosphere. Helium of different origins has characteristics of helium isotope composition, so it can be distinguished from different origin by the contribution of helium to geothermal fluid. The $^3He/^4He$ ratios of the N_2 dominant gases are from 0.06 to 0 .13Ra, representing input of radiogenic ^4He in the crust. The $^4He/^{20}Ne$ and $^3He/^4He$ demonstrate that the N_2 dominant gases are of atmospheric origin with some crustal contributions.

The $^3He/^4He$ ratio of carbon dioxide hot spring gas in the southeast of the Province ranges from 1.90×10^{-6} to 3.18×10^{-6}, and R/R_a from 1.36 to 2.27, all of which are greater than 1 (Sun Z. et al., 2014). Firstly, considering the origin of crust and mantle sources, 0.02 R_a and 8 R_a were taken as the $^3He/^4He$ of typical crust and mantle sources, and the proportion of mantle source helium in geothermal gas could be estimated by using the binary mixing model (Du J, 1994):

$$A = \frac{(R_s - R_c)}{(R_m - R_c)} \times 100\% \qquad (9)$$

where, A is the proportion of mantle source helium in natural gas, and R_s, R_c and R_m represent the $^3He/^4He$ values of samples, crustal sources and mantle sources, respectively. As R_s value is 1.36 R_a and 2.27 R_a respectively, it can be concluded from formula (1) that the proportion of hot spring mantle source helium in the total helium in this area is in the range of 16.8% to 28.2%. If the geothermal gas in this area is mainly derived from mantle source and air source, the proportion of mantle source helium in total helium is 5.1% ~ 18.1% with this calculation. In addition, it may be the mixing of crustal origin, mantle source and air. It indicates that the helium in the hot spring gas in the southeastern Jiangxi Province has different origin of mantle source. Results indicate that up to 28.2% of the total helium is derived from the mantle.

In this study, the $^3He/^4He$ -$^4He/^{20}Ne$ relationship of 6 samples collected from southern Jiangxi, as shown in figure 2. For comparison, data from Tengchong hot spring in yunnan (wang xianbin et al., 1993) are also shown in figure 2. The $^4He/^{20}Ne$ ratio of nitrogen-type geothermal hot spring gas in the western region of southern Jiangxi varies from 234 to 674. All samples falls on both sides of the line between air and crust, indicating that it is mainly caused by mixing of air and crustal gases. The hot spring gas in Tengchong volcanic area has mantle origin, air source and crustal source mixed origin, and a few spring points show mixed origin. Results indicates that the isotopic characteristics of helium and neon of nitrogen-type hot spring gas in the western region of southern Jiangxi province showing the shallow tectonic activity range in this area.

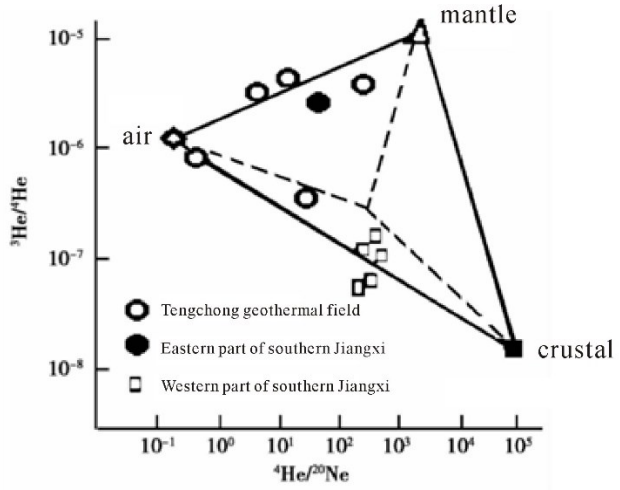


Figure 7: relation diagram of geothermal gas 3He/4He vs 4He/20Ne in southern Jiangxi province

Only one of CO2 geothermal gas in southeast Jiangxi with the data of $^3He/^4He$ vs $^4He/^{20}Ne$, falls in the mixing zone of crust, mantle and air, indicating that it is mainly the mixing origin of mantle source and air, and the contribution of crustal source.

3.7.3 The relative content of N2-He-Ar in geothermal gas

There are four types of N_2 sources in natural gas, atmospheric, biological, magma, and mantle sources. The relative composition of He, Ar and N_2 in gas were used to distinguish the different origins of geothermal and volcanic gases (Giggenbach ,1992; Zhao Ping,1992) . The N_2/Ar ratio in the atmosphere is 84, and the Ar/He ratio is close to 1800. The ratio of N_2/He is about 150,000. The atmospheric precipitation N_2/Ar ratio is about 38 with Ar/He ratio 6800, and the N2/He 260,000. The gas released from the plate collision zone, Anshan magma has a high N_2/Ar values (2500 ~ 5000) and high N2/He values (1700 ~ 5000). N_2/He values of basaltic magma and crustal source gases are 10 ~ 220.

The relative contents of He, Ar and N_2 of geothermal gas in southern Jiangxi were plotted on the He-Ar-N_2 map of Giggenbach (1992) (Figure 3). Hotspring gas in western of Jiangxi is mainly distributed in the mixing area of atmosphere and crustal origin, which is a shallow heat storage area. Its N_2/Ar value varies from 56.15 to 83.60, indicating that N_2 is mainly atmospheric origin. As mentioned above, in the west of Jiangxi geothermal gases helium isotope ratio (R/R_a) change in between 0.06 ~ 0.13, showing obvious crustal origin radiation causes He join, this is the ratio of N_2/He (in 116.44 ~ 388.56) is far lower than atmospheric N_2/He ratio (150000) and the Ar/He than (in 1.39 ~ 6.92) also is lower than atmospheric Ar/He ratio (1800). It can be seen that N_2 in the hot spring gases in the west of the Province mainly comes from the atmosphere, and may be added with crustal origin N_2.

Samples in the southeastern part of Jiangxi Province fall into the deep thermal area, and their N_2/Ar, N2/He, and Ar/H ratios are 9.53 to 20.11, 84.94 to 139.42, respetively. Relative He, Ar and N2 contents reveal that the nitrogen of the type of gases is the mixture of mantle derived, crustal and atmospheric N_2.

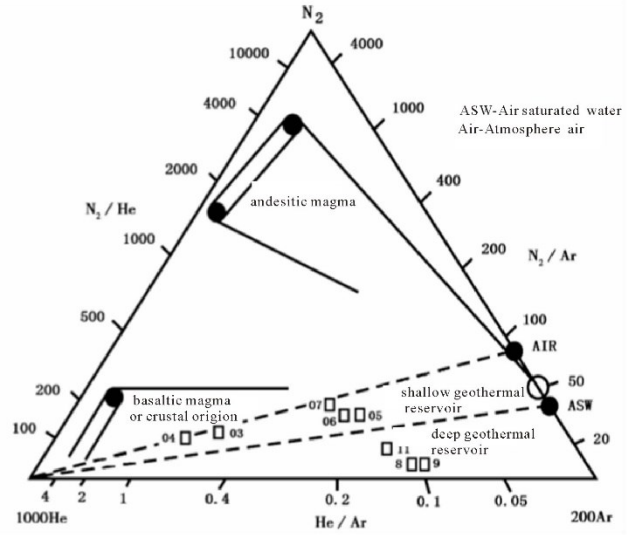


Figure 8: Relative N_2, He and Ar contents

4. CONCLUSIONS

1. The N_2-dominated geothermal waters in Jiangxi Province are characterized by low TDS ranging from 0.135g/L to 0.294g/L, high pH values (>8.5), and nitrogen-predominate (>90%) in dissolved gases. The CO_2-dominated hot springs in the Province are distinguished by higher salinity from 0.245g/L to 1.33g/L but lower pH values (<8.0) and carbon dioxide-dominated (>96%) in dissolved gases.

2. Fluid-mineral equilibrium studies suggest that the geothermal waters are close to equilibrium with secondary minerals as carbonates and fluoride, but disequilibrium with endogenous minerals such as albite and anorthite. Solute geothermometers and the Log(Q/K) against temperature method give subsurface temperatures ranging on average from 80 to 150°C for reservoir hosting the nitric waters.

3. The isotopic studies show that the nitric hot springs were recharged by local precipitation and have a circulation depth approximately from 1200m to 2700m. The carbon dioxide of the CO_2-dominated hot springs are originated from magmatic inorganic sources and the nitrogen of the geothermal gases is the mixture of mantle derived, crustal and atmospheric N_2, and the CO_2 for the N_2-dominant type come from crustal organic sources, and the $^3He/^4He$ ratios represents input of radiogenic ^4He in the crust.

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