

Analysis of Geochemical Characteristics of Geothermal Water in Beijing

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ABSTRACT

Based on 80 geothermal water and groundwater samples analysis, the hydrochemistry type of the thermal spring is $\text{SO}_4\text{-Na}$, the deep oil field water is Cl-Na , the quaternary groundwater is $\text{HCO}_3\text{-Ca}$ or $\text{HCO}_3\text{-Mg}$ and the geothermal water is $\text{HCO}_3\text{-Na}$. The hydrochemistry types of difference water samples have zone variation, which change from $\text{SO}_4\text{-Na}$ in the northern mountain area to $\text{HCO}_3\text{-Na}$ in Beijing Depression and Cl-Na in the southern edge of Beijing plain. The concentrations of F^- , SiO_3^{2-} , BO_2^- and H_2S in geothermal water are higher than in cold groundwater. The result showed that the ratios of Na/K , Cl/F , Cl/B , Cl/SiO_2 have little influence by evaporation concentration or the cold water dilution. The K-Mg geothermometer temperature is calculated from 35 to 140°C, the quartz temperature ranges from 55 to 155°C and the well head temperature of geothermal water ranges from 22.0 to 118.5°C. The K-Mg geothermometer temperature is higher than the the well head temperature when the well head temperature is lower, and the K-Mg geothermometer temperature is lower than the well head temperature when it's higher. The K-Mg geothermometer temperature is considered as the temperature the bore can get. The quartz temperature is considered as the highest temperature the hole ever reached during the drilling.

1. INTRODUCTION

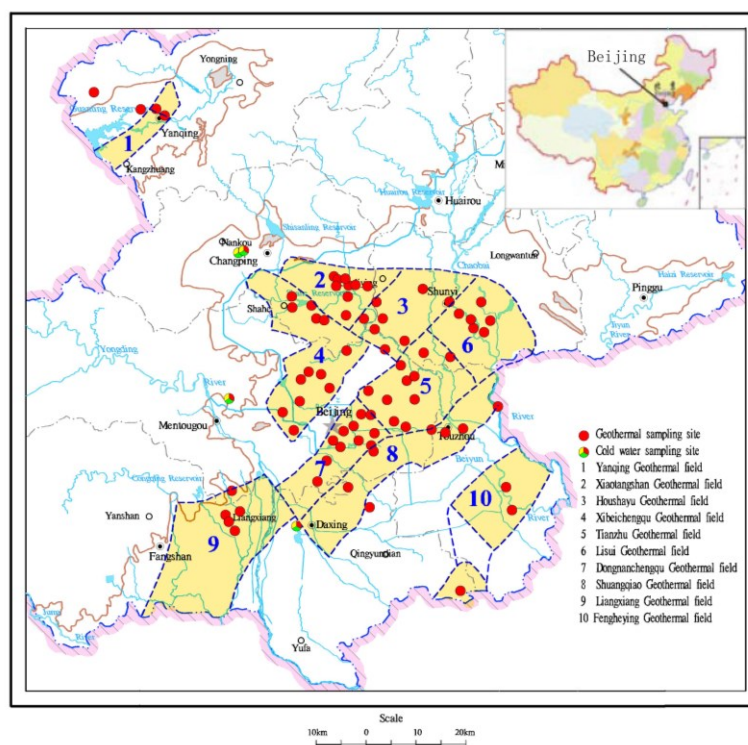


Figure 1: Sampling sites.

Beijing is rich in geothermal resources. The geothermal resources are mainly distributed in ten geothermal fields, such as the urban area, Xiaotangshan and Liangxiang (Bin D Z et al., 2002). The geothermal water has been identified and developed for nearly 60 years. As a kind of clean and pollution-free energy, it has been widely used for space heating, hot water, health spa, recreation,

greenhouse, fish farming and other aspects (Chen, 2002; Yang and Pan, 2002; Ding H H et al., 2007; Sun Y et al, 2009), which has made remarkable social, economical, ecological and environmental benefits.

Geothermal water is hosted in geothermal reservoir, Compared to the groundwater, it has decidedly different geochemical environments, the specific geochemical environment created the different geochemical geothermal water. The study of hydrogeochemical characteristics can reveal the source of the geothermal fluid migration, origin, age, storage condition, reservoir temperature, as well as the rock with water balance pointing out information related to geothermal geological conditions, etc. Previous study of hydrogeochemical characteristics of geothermal water in Beijing was based on a certain geothermal well or a geothermal field (Pan and Wang, 1999; Liu J R et al., 2002; Lv J B et al., 2006; Ke, 2009), which has certain limitations and did not achieve modern levels of accuracy. The present work includes 80 sampling sites (Fig.1) and present modern analyses for majors of 76 samples from geothermal wells, 4 samples from groundwater wells. Based on the analysis of hydrological characteristics of the 80 samples from different geothermal fields, an overall study, focusing on the hydrochemistry type, special components, component ratio, temperature scale of the geothermal water in Beijing, is performed.

2. GEOLOGICAL SETTING

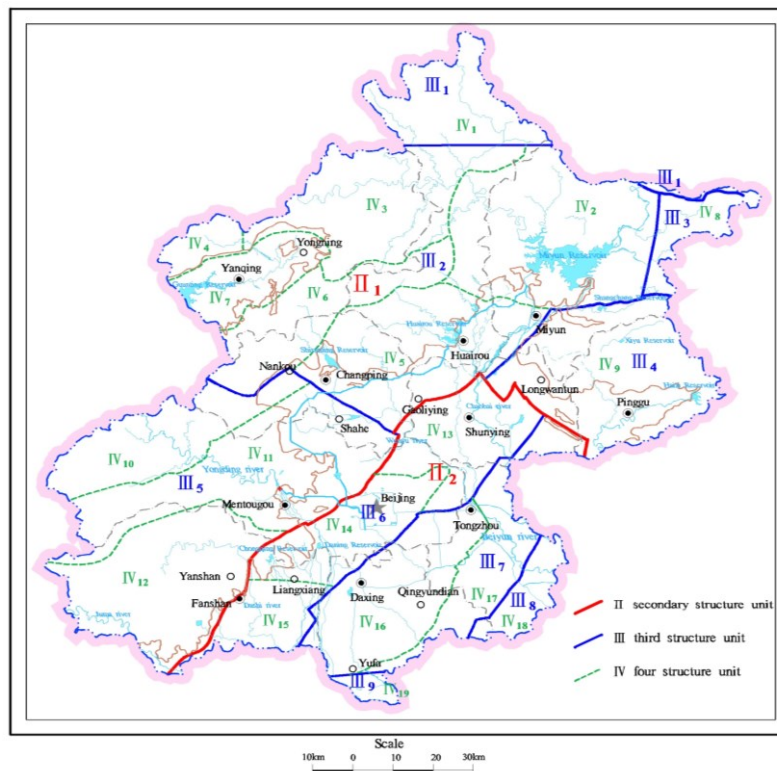


Figure 2: Classification of tectonic units.

Beijing area is tectonically located in the middle part of the Yanshan platform fold belt which belongs to the Sino-Korean paraplatform. It has gone through repeated tectonic disturbances and multistage and polycyclic evolutionary processes since the Archean. The primary regional tectonic framework is featured by early E-W-trending uplifts and depression or folds and faults being intersected and compounded by NE- and NNE-trending folds and faults of late stages, demonstrating rather complex geological structures in this area (Regional Geology of Beijing Municipality, 1991). There are a few large-scale faults that parallel to each other and strike in NE direction. The whole Beijing Plain is divided into a few grabens and hosts by these faults. There are Cenozoic Yanqing fault-subsidence, Beijing multiphase fault-subsidence, Cenozoic Dachang fault-subsidence from northwest to southeast of Beijing (Fig 2, Table 1). These fault-subsidence are covered by the thick sediment. The geothermal temperature in the area of Beijing is of mid-low-temperature resources stored in the sedimentary basin. The geothermal reservoirs are Proterozoic siliceous dolomite, as well as Ordovician and Cambrian limestone, and the caprock is composed of conglomerate, siltstone, shale, tuff, basalt, sandstone of different geological time, as well as Quaternary loose sediment. The rock type and thickness of the caprock is different in each area (Bin D Z et al., 2002).

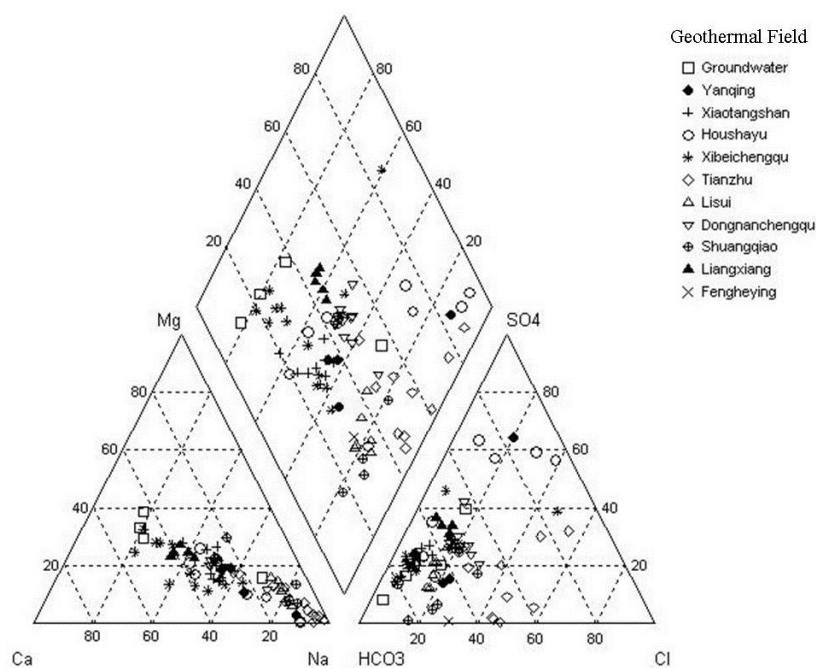
3. METHODS

Samples were taken from Quaternary cold water aquifer, Ordovician and Cambrian limestone geothermal reservoir and the Wumishan dolomite geothermal Reservoir in the ten geothermal fields of Beijing. The samples were taken by inserting a sampling tube against the pressure of a water discharge main. Temperature and pH were measured in-situ, other analysis were made in laboratory. K^+ , Na^+ , Li^+ and a wide range of metal ions were analyzed by atomic absorption. Total acidity, total hardness and most anions were analyzed by titration. NH_4^+ , Fe^{2+} , Fe^{3+} , metaboric acid, metasilicic acid, metaphosphoric acid and some halide ions were analyzed by spectrophotometry. NO_3^- was analyzed by ultraviolet spectrophotometry. Selenium, metaarsenic acid and mercury were analyzed by atomic fluorescence, and total dissolved solids were analyzed by gravimetry.

Table 1: Classification of Tectonic Units in Beijing Area.

Order I	Order II	Order III	Order IV
Sino-korean paraplatform	Yanshan platform fold belt (II ₁)	Chengde multiphase uplift-fault(III ₁)	Mesozoic Sanchakou-Fengning dome-fault(IV ₁)
		Mesozoic Miyun-Huailai uplift-fault(III ₂)	Miyun multiphase dome-fault(IV ₂), Huapen-Sihai multiphase subsidence fold(IV ₃), Mesozoic Dahaituo dome-fault(IV ₄), Mesozoic Changping-Huairou dome-fault(IV ₅), Mesozoic Badaling dome-fault(IV ₆), Cenozoic Yangqing fault-subsidence(IV ₇)
		Xinglong multiphase depression fold(III ₃)	Mesozoic Xingchengzi subsidengce fold(IV ₈)
		Mesozoic Jixian depression fold(III ₄)	Mesozoic Pinggu dome-fault(IV ₉)
		Xishan multiphase depression fold(III ₅)	Mesozoic Qingbaikou dome-fault(IV ₁₀), Mentougou multiphase subsidengce fold(IV ₁₁), Mesozoic Shidu-Fangshan dome-fault(IV ₁₂)
	NorthChina fault-depression(II ₂)	Beijing multiphase fault-subsidence(III ₆)	Shunyi multiphase sag(IV ₁₃), Tuoli-Fengtai multiphase sag(IV ₁₄), Liulihe-Zhuoxian multiphase sag(IV ₁₅)
		Daxing multiphase uplift(III ₇)	Huangcun multiphase convex(IV ₁₆), Niubaotun-Dasuangezhaung multiphase sag(IV ₁₇)
		Cenozoic Dachang fault-subsidence(III ₈)	Cenozoic Mizidian sag(IV ₁₈)
		Cenozoic Gu'an-Wuqing fault-subsidence(III ₉)	Cenozoic Gu'an sag(IV ₁₉)

4. RESULT AND DISCUSSION

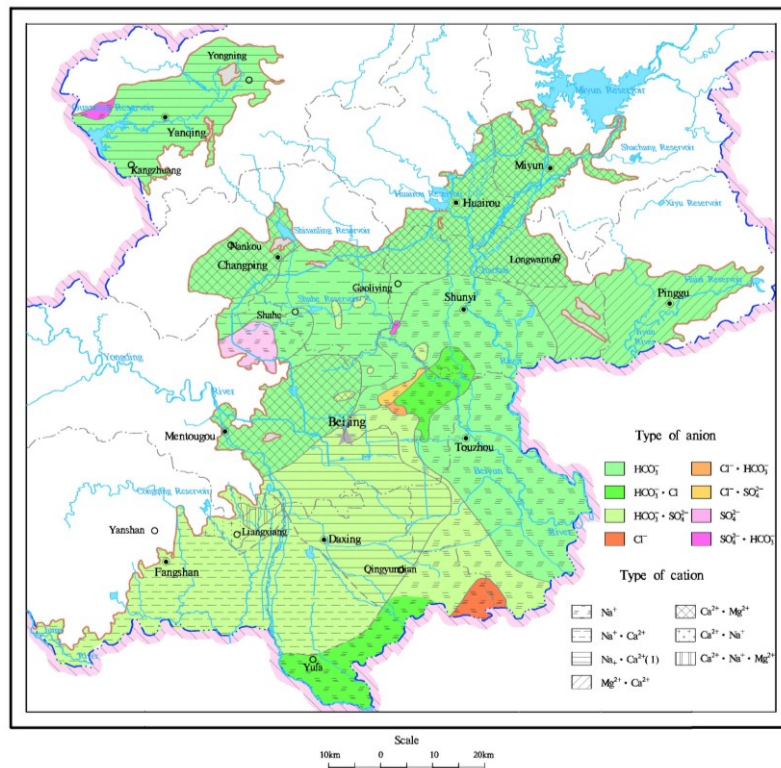
**Figure 3: Hydrochemical diagram of geothermal water and groundwater in Beijing.**

4.1 Hydrogeochemistry

The chemical constituents of the geothermal water are derived from the country rocks, they are markedly different, which indicate the difference of background value of country rocks and the difference of the effect of water-rock reaction. (Wu and Ma, 2010). The hydrochemical characteristics and major compositions of the geothermal water are listed respectively (Table 2), and the hydrochemical diagram of geothermal water and groundwater are shown on Figure 3. The geothermal systems in Beijing are low-medium temperature geothermal systems. The geothermal water contains some mineral components, the total dissolved solids of geothermal water is low, generally less than 1 g/L. The hydrochemistry types of different water samples have zone variation, which change from $\text{SO}_4\text{-Na}$ in the northern mountain area to $\text{HCO}_3\text{-Na}$ in Beijing Depression and Cl-Na in the southern edge of Beijing plain (Figure 4). Most hydrochemistry types of bedrock is $\text{HCO}_3\text{-Ca}$.

Table 2: The table of chemical characteristics in part of the geothermal water samples.

Geothermal field	Name	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻	Metasilicic acid	Metaboric acid	Hydrogen sulfide	TDS	T	PH	Hydrochemistry type
		(mg/L)												(°C)		
Yanqing	RS01	6.18	115	37.9	10.4	307.5	17.2	83.3	4.34	27.4	1.06	<0.05	603	33.7	7.97	HCO ₃ -Na
	RS02	2.85	141	14	2.4	61	44.8	198	14.7	45.9	0.44	<0.05	524	36	8.34	SO ₄ -Na
Xiaotangshan	RS03	10.2	76.5	46.5	15.2	305	25.6	67.4	7	40.2	1.2	0.08	554	53.8	7.57	HCO ₃ -Na·Ca
	RS04	16.2	81.2	45.1	13.6	277	22.9	68.8	6.1	44.4	0.6	<0.05	544	48	8.24	HCO ₃ -Na·Ca
Houshayu	RS05	32.6	219	50.1	16.2	219.7	41.1	396	11	43.8	2.18	<0.05	1035	70	8.12	SO ₄ ·HCO ₃ -Na·
	RS06	31.6	308	101	26.6	333.2	130	586	6.77	59.8	12.1	<0.05	1570	70	7.77	SO ₄ ·HCO ₃ -Na·
Xibeichenqu	RS07	8.57	56.9	49.1	13.4	262	15.2	71.8	5.6	58.4	0.19	2.1	488	72	7.59	HCO ₃ -Na·Ca
	RS08	10.7	62.7	42.5	8	233.1	13.8	57.8	7.04	54.6	0.79	0.11	480	68	7.82	HCO ₃ -Na·Ca
Tianzhu	RS09	13.4	516	12	6.7	753	358	18.2	18	46	48	7.93	1700	64	7.8	HCO ₃ ·Cl-Na
	RS10	17.5	434	17.8	7.4	628.5	331	2	21.2	33.4	41	0.29	1510	57	8.13	HCO ₃ ·Cl-Na
Lisui	RS11	15.1	161	21	13.1	378	51.7	51.3	10.4	34.2	3.28	<0.05	703	42.5	7.98	HCO ₃ -Na
	RS12	5.45	119	12.6	4.6	250	36.2	49.5	7	13.4	1	0.12	485	43	7.93	HCO ₃ -Na
Dongnanchengqu	RS13	13.2	82.5	52.1	20.7	247.7	50.7	113	5.52	44.7	1.09	<0.05	620	56.5	7.75	HCO ₃ ·SO ₄ -Na·Ca
	RS14	7.44	79	46.1	18.2	256	47.2	91.4	5.3	40.9	9	<0.05	554	52	7.65	HCO ₃ ·(SO ₄)-Na·(Ca)
Shuangqiao	RS15	7.23	149	12	6.4	281	50.6	14	12.6	16.4	2.4	5.39	546	51	8.48	HCO ₃ -Na
	RS16	3.84	127	13	6.7	268	51.4	18.8	9.4	28.8	0.88	0.08	507	42	8.13	HCO ₃ -Na
Liangxiang	RS17	10.3	63.8	78.2	26.1	293	47.7	133	5	39	0.28	0.12	667	36	7.44	HCO ₃ ·(SO ₄)-Ca·Na
	RS18	9.37	70.8	56.1	22.5	255	29.9	123	5.4	36.7	0.78	<0.05	573	51	7.43	HCO ₃ ·SO ₄ -Na·Ca
Fengheying	RS19	2.3	136.5	17.03	12.4	335.6	84.84	2.4	8.4	31.23	9.2	/	/	43	7.89	HCO ₃ -Cl-Na
groundwater	RS20	1.36	23.7	53.5	22.5	254	14.4	42.8	0.32	11.4	<0.04	<0.05	439	15.8	7.59	HCO ₃ -Ca·Na

**Figure 4: Hydrochemistry types of geothermal water.**

The hydrochemistry types of geothermal water in northern areas and discharging springs in the mountains, including the north of Yanqing and Huairou, are SO₄-Na. Their pH are between 7.7-9.2, the content of total dissolved solids are between 0.23-0.67g/L. The hydrochemistry types of geothermal water in Beijing multiphase fault-subsidence and Cenozoic Yangqing fault-subsidence are mainly HCO₃-Na, because of the geothermal water in different tectonic units, hydrogeologic and geothermal settings, their hydrochemistry characteristics appeared different subtypes, such as Cl·HCO₃-Na, HCO₃-Cl-Na, HCO₃·SO₄-Cl-Na, HCO₃·SO₄-Na, HCO₃·SO₄-Na·Ca, etc. They all belong to the same general type (HCO₃-Na), they are called transitional types or mixed types. Their pH are between 7.1-8.2, the content of total dissolved solids are between 0.3-0.7g/L. The hydrochemistry types of geothermal

water in the Fengheying geothermal field of Daxing multiphase uplift, are mainly Cl-Na, in the north of Fengheying is $\text{HCO}_3\cdot\text{Cl-Na}$, their pH are between 7.2-7.8, the content of total dissolved solids are between 6.7-7.5g/L.

4.2 Special Components

The geothermal water in Beijing plain contains some special components, such as fluoride, metasilicic acid, metaboric acid, hydrogen sulfide. Their contents are significantly higher than the groundwater, the fluoride and metasilicic acid content are in the vast majority of geothermal well and the metaboric acid in some geothermal well, they are measured up to the value of medical standards, some samplings reach named mineral water. The special components of the geothermal water in different geothermal fields are listed in table 3.

Table 3: The table of special components in each geothermal field.

Geothermal field	F ⁻ (mg/l)	Metasilicic acid (mg/l)	Metaboric acid (mg/l)	hydrogen sulfide
Yanqing	5.20-19.00	33.00-61.20	0.94-1.04	0.05-0.37
Xiaotangshan	2.60-7.00	22.90-59.79	0.08-1.00	0.05-0.37
Houshayu	1.45-6.00	21.70-68.70	4.60-14.00	0.17-0.22
Xibeichenqu	1.05-7.64	12.20-74.10	0.40-1.20	0.05-0.54
Tianzhu	1.94-19.00	24.30-68.60	1.04-52.00	0.05-14.00
Lisui	7.60-11.60	25.20-31.70	0.52-4.60	0.05-0.09
Dongnanchengqu	1.40-11.80	20.00-129.00	0.008-9.40	0.05-4.10
Shuangqiao	4.50-12.60	16.40-39.90	0.49-5.00	0.11-5.39
Liangxiang	3.80-5.80	18.80-59.70	0.08-0.80	0.05-0.33
Fengheying	3.50-8.40	24.00-70.00	2.10-72.00	0.05-5.03
Groundwater	0.32	11.40	<0.04	<0.05

Generally, the content of fluorine in edrock water is less than 1.0mg/l, but all the contents of fluorine in geothermal water are higher than edrock water. Fluorine is the most typical symbolic component of geothermal water. The content of fluorine in geothermal water from southwest to northeast along the direction of Beijing multiphase fault-subsidence increases gradually, the content of fluorine in geothermal water from northwest to southeast direction perpendicular to the Beijing multiphase fault-subsidence increases slightly. The content of metasilicic acid in edrock water (11.40mg/l) is less than in geothermal water (>20 mg/l, max up to 129.00mg/l). The content of metaboric acid in geothermal water is in commonly 2 to 9 mg/l, the content of metaboric acid in northwes of Tuoli-Fengtai multiphase sag is low (0.08-0.80mg/l), other geothermal field overall level is lower than the urban thermal field, about 0.2 to 5 mg/l, but up to 52 mg/l in the Tianzhu geothermal field, 72 mg/l in the Fengheying geothermal field. The content of hydrogen sulfide in edrock water is aslo less than in geothermal water.

Table 4: The table of component ratio in each geothermal field.

Geothermal field	Na/K	Cl/F	Cl/B	Cl/SiO ₂
Yanqing	15.21-20.86	1.16-4.67	13.43-15.06	1.17-3.80
Xiaotangshan	8.91-97.39	1.71-17.78	6.08-73.56	0.58-2.09
Houshayu	8.19-16.02	2.58-11.95	2.91-9.53	1.29-6.82
Xibeichenqu	5.40-11.39	0.88-16.92	7.99-82.20	0.34-38.70
Tianzhu	8.26-73.48	1.64-19.51	8.43-24.99	0.34-26.92
Lisui	15.87-18.82	2.53-3.79	14.54-38.09	3.14-4.35
Dongnanchengqu	7.26-40.46	1.90-41.77	3.89-61.34	0.22-11.77
Shuangqiao	17.24-54.86	0.50-6.31	1.52-32.45	1.23-5.06
Liangxiang	9.75-16.88	2.98-28.16	22.92-261.10	1.32-6.54
Fengheying	21.34-23.43	4.96-297.57	11.39-68.88	5.98-96.80

4.3 Component Ratios

Component ratios of geothermal water are affected slightly by the evaporation concentration or cold water dilution, when the local geothermal water is recharged by the cold water, the symbolic element and component will be affected, but the ratio between them is seldom disturbed, it can display the connotation of the geothermal geochemistry. The Na/K, Cl/F, Cl/B, Cl/SiO₂ component ratios (Table 4) have remarkable regularity in Beijing geothermal fields.

4.3.1 Na/K Ratio

In general, low Na/K component ratio reflects the presence of water of high temperature conditions. About 70% of the Na/K component ratio is less than 20, about 10% of the ratio is between 20 and 30. The low ratio appears in the urban area near the fault

and relatively high Na/K ratio appears in tectonic sag of the buried geothermal storage, which is relatively shallow or near faults. The Na/K component ratio in Fengtai multiphase sag and north of it is similar low, the Na/K component ratio in south of Fengtai multiphase sag, such as Fengheying geothermal field and Tianzhu geothermal field is higher. The heat of geothermal field comes from deep sag. After the geothermal field exploitation, they are recharged by the cold water, which mainly come from certain fractures.

4.3.2 Cl/F Ratio

When the geothermal reservoirs are recharged by cold water, the Cl/F component ratio usually decreases, because the solubility of calcium fluoride will increase in low temperature condition, which leads to the fluorine ion increase. While the fluoride unites with calcium ions to form calcium fluoride in the high temperature condition, the Cl/F component ratio will increase. The hydrochemistry types of geothermal water in the Fengheying geothermal field is mainly Cl-Na, the chloride content is particularly high, so the Cl/F ratio is the highest. The Cl/F component ratio of urban geothermal field and the Tianzhu geothermal field is relatively high; the ratios of Xiaotangshan geothermal field, Li Sui geothermal field, Shuangqiao geothermal field, Houshayu geothermal field are relatively lower.

4.3.3 Cl/B Ratio

Generally, the same origin of geothermal water has the same Cl/B ratio. The Cl/B ratio is different in each geothermal field. The highest Cl/B ratio is in Liangxiang geothermal field, then in urban geothermal field, Xiaotangshan geothermal field, Shahe geothermal field, Shuangqiao geothermal field, Fengheying geothermal field. The Cl/B ratio in Li Sui and Tianzhu geothermal field is relatively low; the Houshayu geothermal field is lower. The Cl/B ratio also suggests that the geothermal field slightly different in origin.

4.3.4 Cl/SiO₂ Ratio

The Cl/SiO₂ ratio reflects the mixing of the geothermal water and the low temperature water. In the 70s-80s, The Cl/SiO₂ ratio in the urban geothermal is relative higher, generally between 3.0- 6.7, by the end of the 90 s the ratio of about Cl/SiO₂ is between 0.8- 5.5, it may be that the range of the geothermal field become widened than before, the influence of some neighboring geothermal wells may have a slightly higher proportion of the cold water supply. It also indicates that the underground water supply proportion to geothermal field increase, because of the excessive development geothermal field. The Cl/SiO₂ ratio in Tianzhu geothermal field and Xibeichengqu geothermal field is higher, then, in Lisui geothermal field, Shuangqiao geothermal field, Liangxiang geothermal field, Houshayu geothermal field, the Cl/SiO₂ ratio is relatively lower, and the Cl/SiO₂ ratio in Xiaotangshan geothermal field is lowest.

4.4 Geochemical Geothermometer

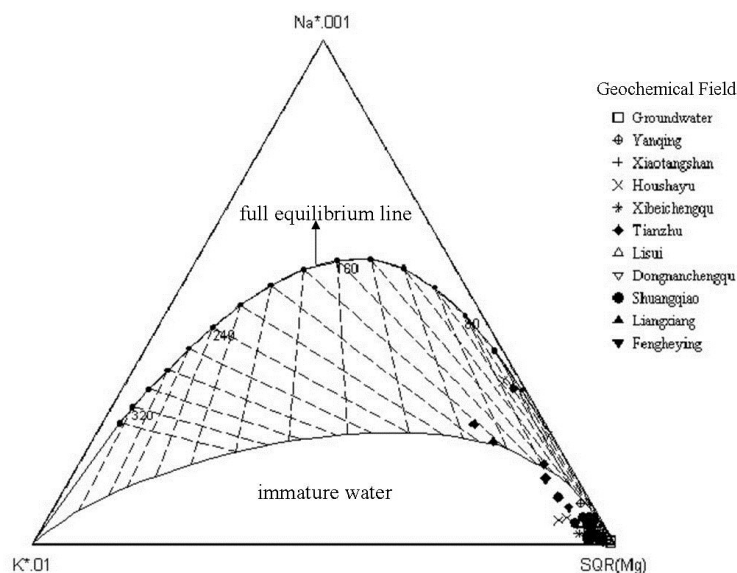


Figure 5: Na-K-Mg ternary diagram of water samples.

Geothermometer method is using relationship between the content of chemical components and temperature in geothermal water to estimate the temperature of deep thermal storage(Wang Y et al.,2001).Now it is widely used in geothermal exploration and research(Wang G C et al., 2003;Pan and Wang,1999;Wang H B et al., 2013;Huang W B et al., 2001; Wen Y H et al., 2011).The geothermometer methods mainly include four major categories: method of cationic geothermometer, silica geothermometer, isotope geothermometer and gas temperature scale. Cationic geothermometer method includes Na-K scale, Na-K-Ca scale, more mineral balance chemical scale, etc. (Wang Y et al., 2007).Before using geochemical geothermometer to estimate the temperature of deep thermal storage, the state of the water-rock interaction equilibrium should be evaluated. Giggenbach (1988) used Na-K-Mg ternary diagram for the first time to evaluate the state of the water-rock interaction equilibrium and the types of water samples. It is observed that most of the geothermal water are immature water in Beijing, only a few samples in Tianzhu and Houshayu Field are

partial equilibrium (Fig 5). This study uses K-Mg geothermometer and quartz geothermometer to estimate the temperature of geothermal reservoirs. The K-Mg geothermometer is suitable for low-medium geothermal field, and the quartz geothermometer is considered as the highest temperature of groundwater has been reached. Two kinds of scale calculation results and measured temperature data are listed in table 5.

Table 5: The geothermometer and measured temperature in geothermal field.

Geothermal field	K-Mg geothermometer(°C)	quartz geothermometer(°C)	measured temperature(°C)
Yanqing	55-95	90-115	46.0-71.0
Xiaotangshan	35-110	65-110	30.5-70.0
Houshayu	40-95	65-120	32.5-85.0
Xibeichenqu	55-85	60-125	35.2-76.0
Tianzhu	45-115	70-120	42.5-75.0
Lisui	45-75	70-85	22.0-55.0
Dongnanchengqu	40-110	60-120	30.6-88.0
Shuangqiao	40-65	55-95	28.0-58.0
Liangxiang	50-65	60-115	31.5-72.0
Fengheying	65-140	70-155	46.0-118.5

When the water temperature out of geothermal well is low, the calculate temperature using K-Mg geothermometer is generally higher than that of geothermal well water temperature. When the temperature of the geothermal well water is higher, K-Mg geothermometer may be lower than the water temperature, so The K-Mg geothermometer temperature is considered as the temperature the bore can get. The temperature of the urban geothermal fields is between 55-65°C, higher than the measured temperature of about 5-10°C. The K-Mg geothermometer of zhongshan park near the center of the tectonic sag is 82.5°C, higher than the measured temperature of 12°C. Other geothermal fields have a similar situation.

The calculated temperature using quartz geothermometer is generally higher than that of geothermal well water temperature about 10-20°C, some up to 30°C, it is not considered as the temperature the bore can get, it just shows the highest temperature the hole ever reached during the drilling. The quartz temperature of the urban geothermal fields is between 60-110°C, higher than the measured temperature of about 10-20°C; the quartz temperature of zhongshan park and dijing park near the center of the sag are 101.8°C and 112.6°C. Accordingly, the highest temperature of geothermal field should be located in the center of the tectonic sag, just as the deep burying geothermal reservoir.

5. CONCLUSIONS

The hydrochemistry types of geothermal water change from SO₄-Na in the northern mountain area to HCO₃-Na in Beijing Depression and Cl-Na in the southern edge of Beijing plain. Most of the geothermal water is medical thermal mineral water with many useful elements especially chlorine and metasilicate. The differences between their chemical element compositions shows different background value of the surrounding rocks and various water-rock reaction between geothermal water and surrounding rocks.

The component ratio of Na/K, Cl/F, Cl/B, Cl/SiO₂ have little influence by evaporation concentration or the cold water dilution. The result shows that various component ratios in different geothermal fields have different geochemistry characters.

Most of the geothermal water are immature water, only a few samples are partial equilibrium in Beijing. This paper uses K-Mg geothermometer and quartz geothermometer to estimate the temperature of geothermal reservoirs. The K-Mg geothermometer temperature is from 35°C to 140°C, the quartz temperature ranges from 55°C to 155°C. The result shows that the temperature the bore can get and the highest temperature the hole ever reached during the different geothermal fields. The results provide the hydrogeochemical evidence for geothermal water exploitation in Beijing.

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