

Characteristic Solutes in Geothermal Water from the Rehai Hydrothermal System, Southwestern China

Mingliang Liu¹, Qinghai Guo^{*1,2}, Xiaobo Zhang¹, Yanxin Wang²

1. School of Environmental Studies, China University of Geosciences, Wuhan 430074, China

2. State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China

ABSTRACT: Rehai, a high-temperature hydrothermal system located in the southern part of the Tengchong volcanic geothermal area of Yunnan Province, is characterized by intensive hydrothermal activities. The hot springs at Rehai that have been sampled so far are Na-HCO₃-Cl or Na-HCO₃ springs except for the one at Diretiyanqu (experience geothermal area) which is an acid sulfate spring. As typical characteristic solution constituents in high-temperature hydrothermal systems with magma as heat source, Cl, B and As in the Rehai geothermal waters originate mainly from the addition of magmatic fluid. However, both the mixing of magmatic fluid and the dissolution of reservoir hostrocks contribute to the enrichment of fluoride in the Rehai geothermal waters, although their fluoride concentrations are primarily controlled by the solubility of fluorite as indicated by a clear negative relation between solution fluoride and calcium concentrations. The much higher concentration of SO₄²⁻ in the Diretiyanqu Spring as compared to the other springs outcropping at Rehai implies a quite different geochemical genesis for this spring. The H₂S-rich vapor, separated from the deep geothermal fluid during boiling process (i.e., adiabatic cooling), can ascend to shallow aquifers where it is mixed with cold groundwaters and oxidized. Acid sulfate-rich hot springs are generally formed in this manner although only one spring of this type has been sampled during the field investigation of this study.

KEY WORDS: hot spring, characteristic constituent, magmatic fluid, fluid-hostrock interaction, Rehai.

0 INTRODUCTION

As a new and clean energy source, geothermal energy has increasingly attracted attention over the past years (Wang et al., 2013; Wu et al., 2012). The Tengchong volcanic geothermal area, located in western Yunnan Province of China, is famous for its abundant geothermal resource (Guo and Wang, 2012). Over the past decades, many investigations have been made in the Tengchong area for understanding the regional geology and hydrogeology (Peng and Jones, 2012; Gao and Fan, 1992; Liao et al., 1991; Tong and Zhang, 1989). Tengchong is one of the most promising areas in China in terms of geothermal energy exploitation, and therefore has the potential to play an important role in promoting the local economy.

There are numerous geothermal springs distributed in the Tengchong area. Tengchong can be further divided into fifty-eight hydrothermal areas, each of which has a group of hot springs that discharge to the surface (Tong and Zhang, 1989; Zhang et al., 1987). Among these hydrothermal areas, twenty-four are characterized by average spring water temperatures higher than 45 °C, and three of them have spring vent

temperatures equal to or slightly higher than the local boiling point (96 °C) (Guo and Wang, 2012).

Rehai, as the hydrothermal area with the highest estimated reservoir temperature in Tengchong, is defined as a geothermal field in view of its huge potential for geothermal resource utilization (Tong and Zhang, 1989). With a total area of around 10 km², the Rehai geothermal field is promising for electricity generation (Liao and Zhao, 1999). According to the hydrogeochemical survey made by Guo and Wang (2012), Zhang G P et al. (2008), Du et al. (2005), Tong and Zhang (1989) and Zhang Z F et al. (1987), the hydrochemical types of the Rehai geothermal waters are mainly Na-HCO₃-Cl and Na-HCO₃, although several acid sulfate-type springs were observed as well. Na, Cl, B, As, Li, Rb, Cs and SiO₂ are the major constituents in the neutral-alkaline springs, while SO₄²⁻ is predominant in the acidic springs (Guo and Wang, 2012; Zhang et al., 2008). In this study, a hydrogeochemical investigation was conducted in the Rehai field once again, with a focus on the geochemical behavior of characteristic solutes in geothermal water.

1 REGIONAL SETTING AND GEOLOGY

The Rehai geothermal field, 11 km southwest to the downtown of Tengchong County, is located in the southern part of the Tengchong volcanic geothermal area (Fig. 1a) (Wei et al., 2003; Jiang et al., 1998). With increasing depth the rock types of Rehai are as follows: Holocene alluvium, Middle Pleistocene basalt, Lower Pleistocene andesite, Miocene brecciated rocks,

*Corresponding author: qhguo2006@gmail.com

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Cretaceous granite, and Proterozoic gneiss and migmatite (Du et al., 2005). The cap-rocks of Rehai geothermal field consist of intensively altered gravel stone and sandstone, and the reservoir is composed of the Yanshanian granite and the Proterozoic metamorphic rocks (Guo and Wang, 2012). The major structures of the Rehai hydrothermal system are nearly N-S stretching faults. Besides, there are a few NE-SW and NW-SE stretching faults at Rehai. These stretching faults serve as the channels for the upward flow of geothermal fluids.

The heat source for the Rehai geothermal field is commonly regarded as the intrusion of mantle-derived magma (Du et al., 2005; Shangguan et al., 2005; Zhao et al., 1996), although the underlying Yanshanian granite (68.8 Ma) within the field may also contribute to its formation (Yan and Wan, 1998; Xu et al., 1997; Liao et al., 1991). According to the magneto-

telluric survey conducted by Chinese Academy of Sciences, the depth of this magma chamber was speculated to be not less than 7 km (Bai et al., 1994). Meteoric water, descending and penetrating into the subsurface, is the major source for the geothermal fluids in the reservoirs (Xu et al., 1997). Besides the contribution of water-rock interactions occurring in the reservoirs, the dissolved constituents in the geothermal waters originate from the addition of magmatic fluids as well (Du et al., 2005).

Strong geothermal manifestation has been found in the Rehai field, including hydrothermal explosion, hot spring, fumarole, steaming ground, hydrothermal alteration, and hydrothermally precipitated silica sinter. The hot springs are mainly located in the Liuhuangtang area and the Zaotang River valley (Fig. 1b).

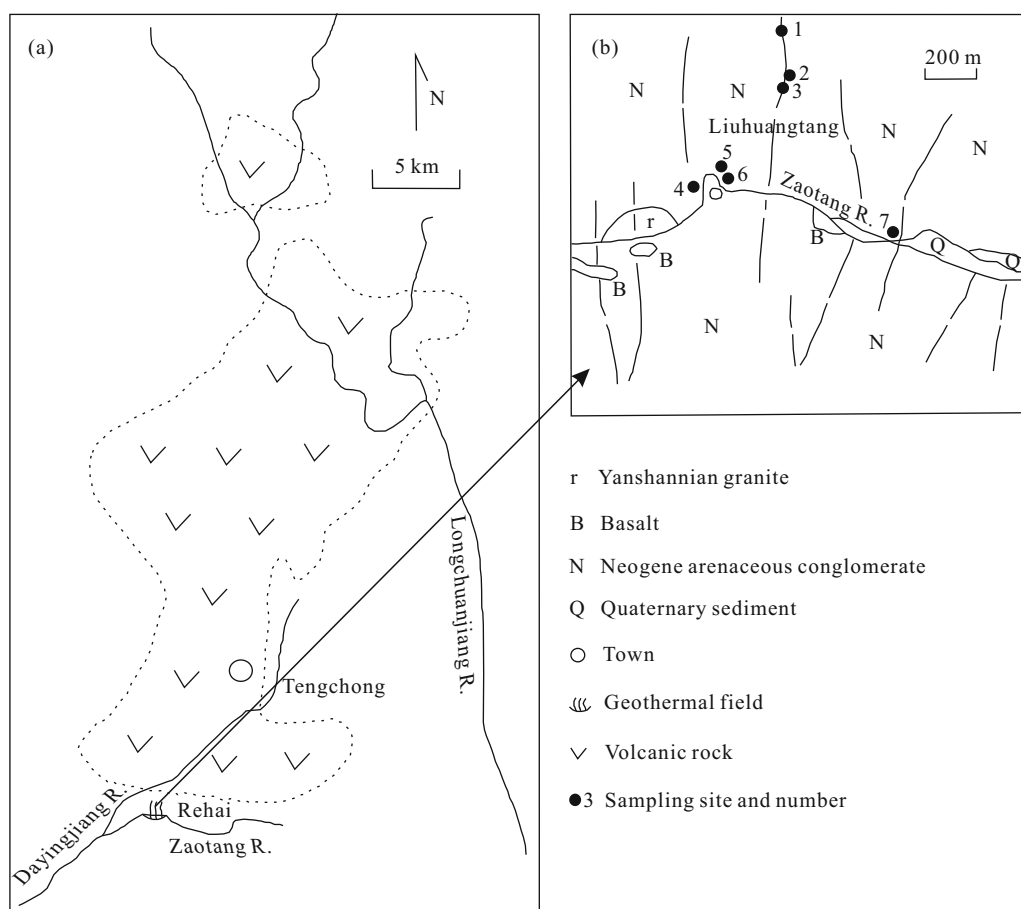


Figure 1. Geographic location of the Rehai geothermal field (a) and sampling sites for the Rehai geothermal waters (b) (modified after Zhang et al., (2008)). 1. Laogunguo; 2. Diretiyanqu (experience geothermal area); 3. Dagunguo; 4. Gumingquan; 5. Huaitaijing left; 6. Huaitaijing right; 7. nameless; R.. right.

2 SAMPLING AND ANALYSIS

Seven geothermal water samples were collected from the Rehai geothermal field in July, 2012, and the sampling locations are shown in Fig. 1b. All water samples were filtered through 0.45 μm membranes on site. Samples were stored in 500 mL polyethylene bottles which had been rinsed with deionized water three times before sampling. At each sampling point 3 bottles of water samples were collected and reagent-grade HNO_3 was added to one of them to bring the pH below 1 for

cation analysis. Unstable hydrochemical parameters, including temperature, pH, and electrical conductivity (EC), were measured using hand-held meters that were calibrated prior to sampling. The cation concentrations of all samples were determined by ICP-OES (inductively coupled plasma-optical emission spectroscopy), while the anion concentrations by ion chromatography. Alkalinity was measured using the Gran titration method (Appelo and Postma, 1996). The HCO_3^- and CO_3^{2-} concentrations of all samples were calculated from the meas-

ured alkalinity by use of PHREEQC.

Major chemical characteristics of all water samples collected in this study and the calculation results of their charge imbalances are presented in Table 1. The analytical results of trace elements in the water samples are summarized in Table 2. The hydrochemistry of several Rehai geothermal water samples collected by other researchers are also included in Table 1 and Table 2 for comparison. The geothermal waters sampled in this study are generally of high analytical accuracy, their charge imbalances being less than or around 15%. Moreover, there is a positive relationship between the TDS (total dissolved solids) and the EC values of the Rehai samples. The Dagunguo Spring has the highest TDS values among all samples. In contrast, the only acid water sample collected from the Diretiyanqu area is characterized by much lower TDS and EC values, indicating that its formation mechanism is possibly quite different from those neutral geothermal waters.

3 CHARACTERISTIC SOLUTES IN GEOTHERMAL WATER

The hydrogeochemical characteristics of the geothermal waters from Rehai have been investigated by quite a few researchers (Zhang G P et al., 2008; Du et al., 2005; Liao and Zhao, 1999; Tong and Zhang, 1989; Zhang Z F et al., 1987). The results of their hydrochemical analyses for the Rehai geothermal springs are very similar to those made in this study and show that they are basically neutral-bicarbonate-chloride waters except for several acid-sulfate springs at the Diretiyanqu area. Most neutral Rehai samples contain Cl^- and/or HCO_3^- as predominant anions and Na^+ as predominant cation, whereas their Ca^{2+} and Mg^{2+} concentrations are generally low.

Although there are dozens of geothermal springs at Rehai that are collectable, only the Dagunguo Spring has been sampled by most researchers and therefore has an available time series of hydrochemical analyses. Thus, it is selected as a representative to show the historical trend in chemistry of the Rehai geothermal waters (Fig. 2). Among the major constituents (HCO_3^- , SO_4^{2-} , Cl , F , Na , K , Ca and Mg) in the Dagunguo sample, HCO_3^- , Cl and K varied little over the past 40 years (from 1973 to 2012), whereas SO_4^{2-} , F , Ca and Mg changed a lot with time. The Na concentrations were generally stable before 1995, but afterwards there was a sharp decline. In view that HCO_3^- ,

Cl and Na are predominant constituents in the Rehai geothermal waters and the concentrations of HCO_3^- and Cl just changed slightly, the Na concentration variation after 1995 may be induced by the various analytical methods used in different laboratories. The Ca and Mg concentrations in geothermal water are primarily controlled by secondary processes, e.g., the precipitation of Ca - and Mg -bearing altered minerals or the mixing of Ca - and Mg -rich shallow groundwaters. So the changes of Ca and Mg concentrations of the Dagunguo Spring probably indicate that the mixing proportions of cold groundwaters have changed over time. It is interesting that the variation of F concentration shows a clear negative correlation with Ca , demonstrating that both F and Ca concentrations are affected by the solubility of fluorite.

3.1 Chloride

It has been widely acknowledged that Cl in high-temperature geothermal fluid with magma as heat source may be mainly owing to the addition of magmatic fluid (Guo, 2012; Browne and Rodgers, 2006). Tong and Zhang (1989) estimated the total amount of Cl^- discharged from the geothermal waters of the Rehai hydrothermal system. They assumed that the Rehai hydrothermal system had been discharging geothermal water at its present natural rate for the last 800 ka, and the total flux of Cl^- discharge could be 1.115×10^{15} g. By presuming that the circulation depth of the recharged waters at Rehai is 3 km, they figured out that the volume of rock reacting with geothermal waters is 25.5 km^3 . If 200 ppm Cl had been available from rock by leaching, 1.33×10^{13} g Cl could have actually been leached from the Rehai system during the past 800 ka. The results reveal that the Cl discharged by the Rehai hydrothermal system is much higher than those entering the system by rock leaching, implying that magmatic fluid (Giggenbach and Guern, 1976) is possibly the major source for Cl^- dissolved in the Rehai geothermal waters.

The plots of Na^+ , K^+ , B , Ca^{2+} , Mg^{2+} , and SO_4^{2-} vs. Cl^- in all geothermal water samples are shown in Fig. 3. The excellent linear relationship between Cl and Na , K and B suggests that there exists a deep parent geothermal liquid (PGL) below Rehai, and the geothermal springs within the Rehai field were formed by the adiabatic cooling, conductive cooling or mixing with shallow groundwater of this PGL with Cl , Na , K , B as

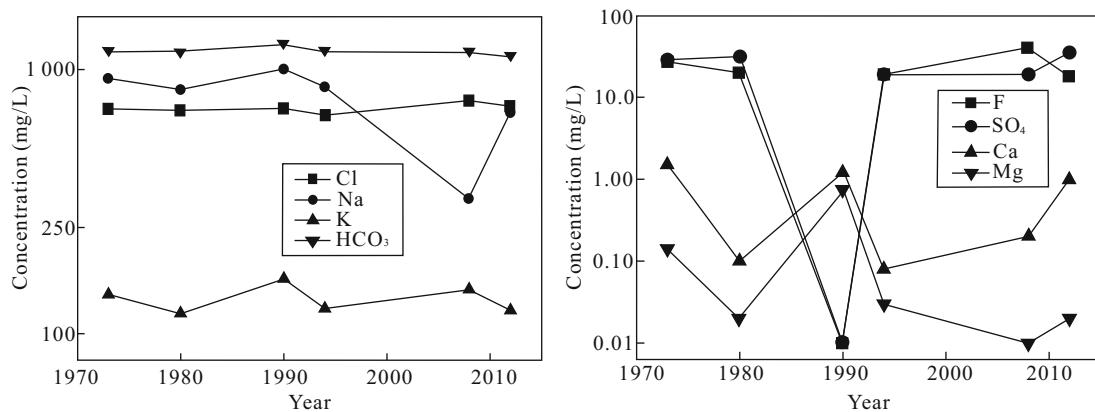


Figure 2. Temporal variation of Cl , Na , K , HCO_3^- , F , SO_4^{2-} , Ca and Mg concentrations in the Dagunguo Spring (from 1973 to 2012).

Table 1 Major geochemical characteristics of geothermal water samples and their saturation indices with respect to fluorite

No.	Name of spring	Sam-pling date	T (°C)	pH	EC (µs/cm)	TDS	SO ₄ ²⁻	Cl ⁻	F ⁻	HCO ₃ ⁻	CO ₃ ²⁻	(mg/L)					SI (fluorite)	Charge imbalance	Source	
												Ca	Mg	Na	K	As				B
1	Laogun-guo	2012	91	8.9	2 012	1 093	23.9	325	16.6	561	36.0	0.90	0.00	152	53.1	0.04	0.00	-1.2	-14.5%	This study
2	Direti-yanqu	2012	88	2.7	1 949	573	682	5.90	0.30	0.00	0.00	30.2	1.30	14.8	24.1	0.10	0.05	-5.06	-15.5%	This study
3	Dagun-guo	2012	96.6	8.3	4 210	1 686	35.2	725	18.2	1 132	35.6	0.97	0.02	689	123	1.10	12.4	-1.37	-15.0%	This study
		2008	97	8.8	4 140		18.4	759	40.0	1 171	66.0	0.20	N.D.	325	147					Zhang et al. (2008)
		1994	94			2 794	18.5	673	19.4	1 183	0.00	0.08	0.03	857	125					Du et al. (2005)
		1990	92	7.7		3 628	N.D.	712	N.D.	1 256	0.00	1.20	0.75	1 000	161					Du et al. (2005)
		1980	88	8.0		2 811	31.0	698	20.0	1 168	0.00	0.10	0.02	840	120					Du et al. (2005)
		1973	96.6			2 526	28.5	710	26.3	1 186	0.00	1.50	0.14	925	141					Du et al. (2005)
4	Guming-quan	2012	96	8.9	3 560	1 375	18.6	651	16.1	759.7	122	1.38	0.03	573	107	0.51	10.5	-1.48	-13.3%	This study
		2008	96	9.6	3 390		22.2	552	24.1	769	138	0.28	0.01	264	110					Zhang et al. (2008)
5	Huaitaijin-left	2012	88	8.4	3 350	1 251	20.1	559	13.8	857.3	40.8	1.54	0.06	538	96.8	0.38	9.56	-1.31	-11.8%	This study
		2008	81	7.9	1 939		77.2	331	15.4	476	N.D.	0.59	0.01	143	55.2					Zhang et al. (2008)
6	Huaitaijin-right	2012	88	7.6	2 464	991	38.3	455	8.10	628.5	0.00	1.61	0.05	400	71.1	0.59	7.23	-1.48	-12.5%	This study
		2008	89	8.9	3 260		20.5	585	29.3	817	102	0.27	N.D.	258	106					Zhang et al. (2008)
7	Nameless	2012	70	8.3	2 269	862	34.0	362	9.00	701.7	63.0	4.88	0.54	375	68.9	0.31	6.12	-0.94	-15.6%	This study

N.D., Not detected.

characteristic constituents. As compared to the geothermal waters, the shallow cold groundwaters have much lower Cl^- concentrations but higher Ca^{2+} , Mg^{2+} and SO_4^{2-} concentrations. For example, the Cl^- , Ca^{2+} , Mg^{2+} and SO_4^{2-} concentrations of a cold groundwater sample collected by Zhang et al. (1987) at Yangjiapo of Rehai are 1.0, 6.43, 0.83 and 16 mg/L, respectively. The reason is that the Ca concentration in geothermal fluid is controlled by the solubility of some hydrothermally altered minerals such as calcite, fluorite, wairakite and epidote, and similarly Mg and SO_4^{2-} concentrations are affected by the precipitation of chlorite and alunite or anhydrite respectively (Guo, 2012). Hence, the mixing with shallow groundwater to various extents results in the scattered distribution of geothermal water data points in the Ca^{2+} vs. Cl^- , Mg^{2+} vs. Cl^- , and SO_4^{2-} vs. Cl^- plots.

According to Table 1, the average concentration of Cl^- in

the Rehai geothermal waters is up to 440 mg/L, with the highest and lowest being 725 mg/L (Dagunguo) and 5.9 mg/L (Diretiyanqu), respectively. The big difference of Cl^- concentration between Dagunguo and Diretiyanqu is related to their formation mechanisms. As the parent geothermal liquid below Rehai with a certain chloride concentration ascended, it may experience adiabatic cooling to form Cl^- -enriched geothermal water and Cl^- -depleted vapor. Thus, the Dagunguo Spring, discharging the geothermal water that underwent a (or several) flashing process (processes), should have a higher Cl^- concentration than the PGL. In contrast, the Diretiyanqu Spring is basically the shallow groundwater heated by the H_2S -enriched and Cl^- -depleted vapor separated from geothermal fluid during the flashing processes, and therefore has much lower Cl^- concentration and pH value.

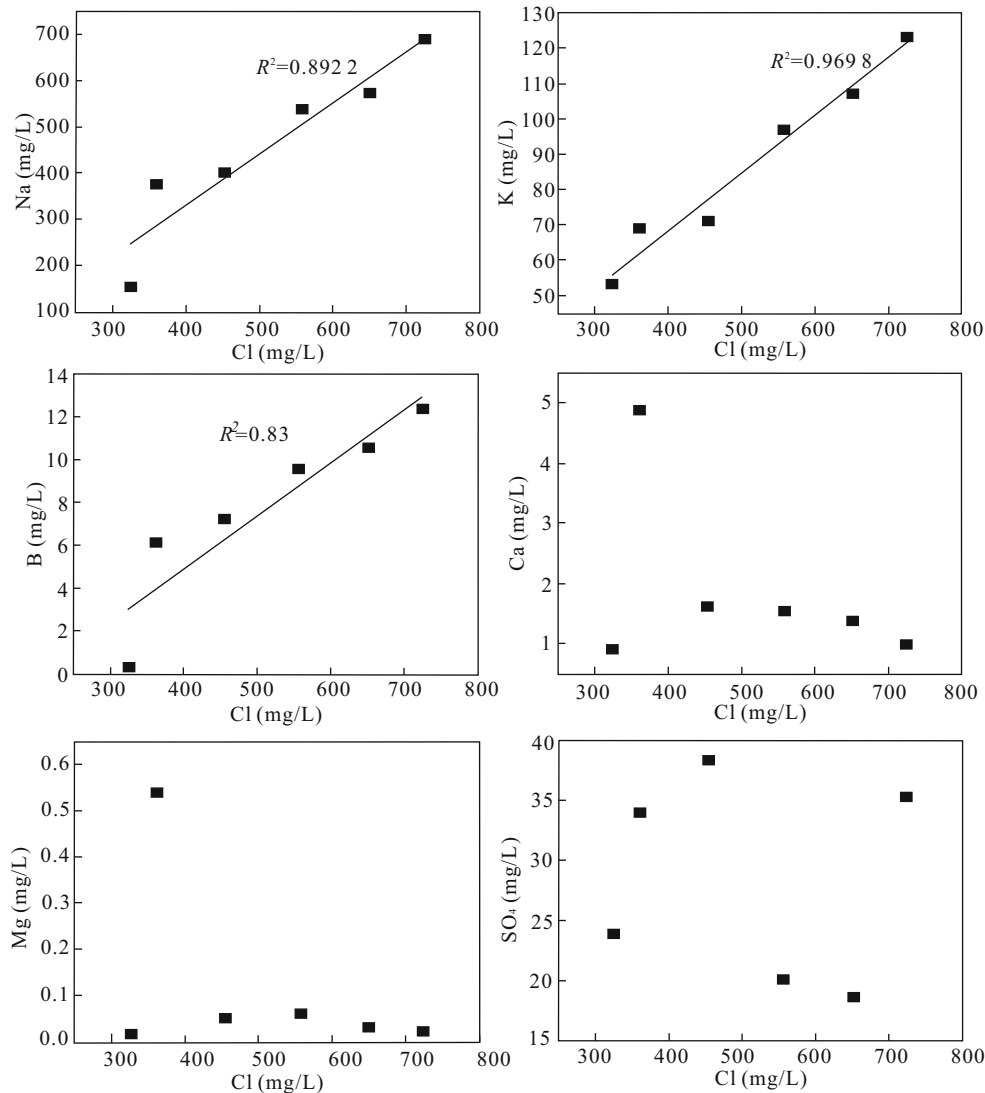


Figure 3. Plots of Na, K, B, Ca, Mg and SO_4^{2-} vs. Cl^- of the Rehai geothermal water samples.

3.2 Arsenic and Boron

As is regarded as a typical characteristic constituent for high-temperature geothermal waters because their total arsenic concentrations are usually higher than those of cold groundwaters (Ballantyne and Moore, 1988). This holds true for the Re-

hai geothermal waters as well. However, there is possibly a big difference of As concentration for geothermal waters discharged from different hydrothermal systems. For example, the As concentrations of neutral geothermal water samples collected from Rehai are comparable to those from the Yellow-

stone National Park hydrothermal system (USA) (Nordstrom et al., 2009), but much lower than those from the hydrothermal areas in Tibet, e.g. Yangbajing and Yangyi (Guo et al., 2009, 2007).

The good linear relationship between Cl and As indicates that As in the Rehai geothermal waters may come predominantly from the fluid released from magma chamber below Rehai as well. During the hydrothermal alteration process, As could precipitate from geothermal water as certain As-bearing minerals (Baba and Sözbilir, 2012). It was reported by Zhang et al. (2008) that the average concentration of As in the sinter deposited near the geothermal spring vents at Rehai is 113.2 mg/kg, much higher than the corresponding value for the crust (1.8 mg/kg) (Rudnick et al., 1988). Hence sinter may serve as an important sink for the arsenic derived from deep magmatic fluid.

Table 1 shows that all geothermal water samples have arsenic concentrations much higher than the Drinking Water Standard (10 µg/L) proposed by the World Health Organization (WHO, 1993). Among the species of arsenic, As (III) is 60 times more toxic than As (V), and organic arsenic is much less toxic than inorganic arsenic (Smedley and Kinniburgh, 2002). However, the arsenic in the Rehai geothermal waters exists primarily as As (III), and therefore its natural discharge poses a threat to the environment and the health of local residents.

The concentration of B in high-temperature geothermal waters is affected by multiple factors, such as source of boron, reservoir temperature, vapor pressure and hostrock type. It varies greatly in different hydrothermal systems (Dotsika et al., 2006). The average concentration of B in the Rehai geothermal waters is up to 15.4 mg/L (Table 1), much higher than that in the local shallow groundwater. Thus it may come from not only geothermal water-hostrock interactions but also magmatic fluid, as Arnórsson and Andresdóttir (1995) suggested for some hydrothermal systems in Iceland. The excellent linear relationship between B and Cl in the Rehai samples consolidates the above speculation.

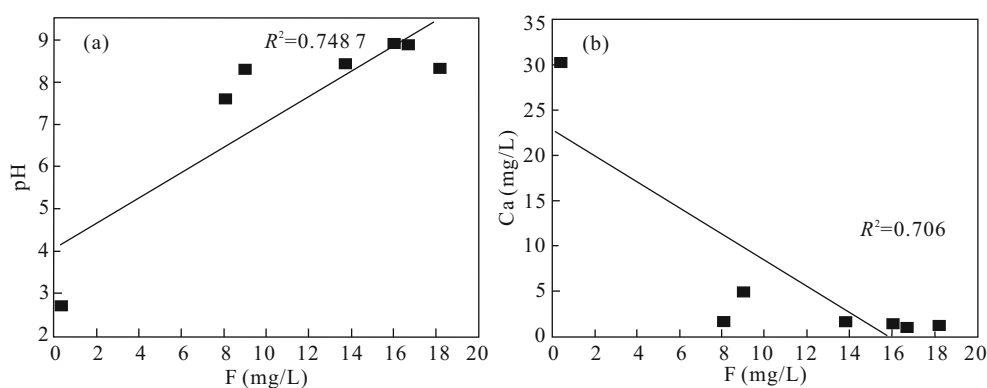


Figure 4. Plots of pH and Ca vs. F of the Rehai geothermal water samples.

3.4 Sulfate and Silica

Sulfate is usually not considered as a characteristic constituent for geothermal water. The sulfate concentrations of most Rehai geothermal samples are quite low, whereas that of the Diretiyanqu Spring is much higher (up to 682 mg/L). The formation mechanism for the Diretiyanqu Spring, as discussed

3.3 Fluoride

The average concentration of F⁻ in the Rehai geothermal waters is 11.7 mg/L (Table 1). Since F is believed to be one of the major components in acidic magmatic fluid (Capaccioni et al., 2011), the high-concentration fluoride in the Rehai geothermal waters may be associated with the recharge of deep magmatic fluid to some degrees. However, the reservoirs of the Rehai hydrothermal system are composed of Yanshanian granite and Proterozoic metamorphic rocks (Guo and Wang, 2012) in which fluoride-bearing minerals are generally not rare. So it seems that the interactions of geothermal water with reservoir hostrock have an effect on its fluoride concentration as well.

In addition, the F vs. pH plot for the Rehai samples (Fig. 4a) shows that there is a positive linear relationship between them. It means that alkaline environment facilitates the enrichment of fluoride in geothermal water. So the anion exchange between the OH⁻ in geothermal water and the exchangeable F⁻ in some silicate minerals, e.g., biotite, may also contribute to the fluoride dissolved in the geothermal waters. The reaction is as follows



The concentrations of Ca in the Rehai samples are quite low (Table 1), which is another favorable condition for the formation of the high-fluoride geothermal waters at Rehai. Under the solubility control of fluorite, the lower the Ca concentration is, the more likely the high-fluoride waters are formed. The negative correlation between F and Ca²⁺ in Fig. 4b validates the above argument. By use of PHREEQC, we calculate the saturation indices of fluorite in spring vents, which are between -0.94 and -1.48 (Table 1). According to Guo and Wang (2012), the reservoir temperature of Rehai geothermal field is between 200 and 300 °C, and the solubility product of fluorite in reservoir is slightly lower than in spring vent. Thus, the saturation indice in reservoir is close to 0 in Rehai geothermal system, which further confirms the speculation.

above, is quite different from the other geothermal springs discharged at Rehai. This spring is basically formed via the uptake of high-temperature vapor separated from geothermal fluid by shallow groundwaters. The vapor is enriched in H₂S that has been oxidized in the near-surface environment to form the sulfate-type geothermal waters with very low pH values.

Silica is generally of higher concentration in geothermal water than in cold groundwater, and therefore indicative of the occurrence of geothermal water (Gunnarsson and Arnórsson, 2005). Moreover, since its solubility is temperature-dependant, silica has been commonly used as a reliable geothermometer, especially for the geothermal waters with near neutral pH values (Verma and Santoyo, 1997; Vala Ragnarsdóttir and Walther, 1983; White et al., 1956). However, the application of silica geothermometers can be impeded in some cases, because the interpretation for sources of dissolved silica in hot springs may be somewhat ambiguous due to the uncertainties concerning the minerals controlling dissolved silica and the amount of steam possibly separated from geothermal fluid during a boiling process.

Different from Cl, B and As, SiO₂ in Rehai geothermal water come basically from the dissolution of aluminosilicate minerals in reservoir hostrocks. During the intense interactions between deep acidic fluid and hostrocks, the congruent dissolution of the reservoir rocks occurs, elevating the silica concentration in geothermal water to a very high level. This process is also called primary neutralization, implying the addition of Na, K, Mg, Ca and silica in proportions close to those of the original rocks. Although the early redeposition of Mg- and Ca-rich alteration products such as amphiboles, biotite, chlorite, anhy-

drite and fluorite reduces the solution silica concentration to some extents, the geothermal fluids at full equilibrium with hostrocks still have high silica concentrations. Afterwards, along with further ascent of geothermal water and subsequent boiling or conductive cooling, the solution re-equilibration happens and silica may precipitate from geothermal water once again (Guo et al., 2007). In the Rehai geothermal field, the silica sinter is widely distributed, and its distribution can be used to trace the hydrogeochemical temporal-spatial evolution of geothermal fluid (Guo, 2012).

3.5 Trace Elements

Table 2 shows the concentrations of trace elements (Sr, Se, Fe, Ba, Mn, Pb, Zn, Cd, Cu, Sn) in the Rehai samples. Different from those characteristic constituents, there is no significant difference in the concentrations of most trace elements listed in Table 2 between geothermal waters and local surface waters. However, the neutral and acid geothermal waters show quite different trace element chemistry. The Fe and Mn concentrations of the acid sample are much higher than those of the neutral samples, while the reverse is true for Pb and Cd. The high-concentrations of Fe and Mn in the acid waters should come from the dissolution of near-surface rocks in the strongly acid environment at the Diretiyanqu area.

Table 2 Concentrations of trace elements in geothermal water samples

No.	Name of spring	Sr	Se	Fe	Ba	Mn	Pb	Zn	Cd	Cu	Sn	Source
(µg/L)												
1	Laogunguo	20.0	N.D.	150	109	311	309	N.D.	7.9	3.7	N.D.	This study
2	Diretiyanqu	100	N.D.	750	31.8	549	13.4	100	0.12	2.2	0.12	This study
3	Dagunguo	92.2	N.D.	21.1	467	5.20	694	53.5	9.8	5.7	2.6	This study
4	Gumingquan	81.0	N.D.	13.9	533	10.4	540	173	5.7	5.3	2.1	This study
5	Huaitaijin-left	54.6	N.D.	31.2	582	28.6	489	96.0	6.0	4.4	4.4	This study
6	Huaitaijin-right	32.9	N.D.	21.6	17.5	16.5	394	218	5.9	5.7	1.1	This study
7	Nameless	61.3	0.000 4	146	307	35.5	282	144	6.5	5.2	N.D.	This study
	Zaotanghe 1	12.6	N.D.	0.83	0.46	10.9						Zhang et al. (2008)
	Zaotanghe 2	28.0	N.D.	2.35	1.40	15.5						Zhang et al. (2008)

N.D.. Not detected.

4 CONCLUSIONS

(1) The geothermal springs in the Rehai field are characterized with high Cl, B and As (the highest values being 725, 12.4 and 1.1 mg/L, respectively) as well as low Ca and Mg concentrations. Cl, B and As in the Rehai geothermal waters originate primarily from the addition of magmatic fluid. As an incompatible element, B usually remains in solution and does not readily enter secondary minerals during interactions between geothermal waters and reservoir hostrocks, and therefore shows good linear relationship with Cl.

(2) Although magmatic fluid should be a nonnegligible source for the fluoride in geothermal water from Rehai, the dissolution of hostrocks also contribute a lot to the formation of high-fluoride waters there. Anyways, the solubility of fluorite is the primary factor controlling the fluoride concentrations of the

Rehai geothermal waters.

(3) Magmatic sulfur, in the form of H₂S or SO₂, is a major source for the dissolved sulfur species in the Rehai geothermal waters. Due to the precipitation of some sulfur-bearing minerals (such as anhydrite, alumite and pyrite) during the neutralization process of acid magmatic fluid, the concentrations of both sulfate and sulfide in the parent geothermal liquid of the Rehai hydrothermal system should be not very high. However, the vapor separated from boiling geothermal fluids and enriched in H₂S gas could easily ascend to shallow aquifers and mix with low-TDS cold groundwaters. Oxidation of H₂S as well as evaporation process in near-surface environment results in the formation of geothermal waters with very low pH values and high SO₄²⁻ concentrations, just as the Diretiyanqu Spring.

(4) Different from other characteristic constituents, the

concentrations of silica in the Rehai geothermal waters are controlled exclusively by the dissolution of reservoir hostrocks and the precipitation of hydrothermally altered minerals. Similarly, the formation of Ca- and Mg-bearing altered minerals (e.g., calcite, fluorite, wairakite and chlorite) is the reason why the Rehai geothermal waters are so low in Ca and Mg concentrations.

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