Origin and Evolution Characteristics of Geothermal Water in the Niutuozhen Geothermal Field, North China Plain

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ABSTRACT: Statistical study of analyses of water from 43 samples from geothermal wells, three groundwater wells, and one sample of local rainwater along with rainwater data from the Global Network of Isotopes in Precipitation has been used to identify the origin and evolution of geothermal water in the Niutuozhen (牛驼镇) geothermal field and estimate the renewability rate of its geothermal resource. The results show that the geothermal waters of the Jixianian Wumishanian dolomite reservoir and the Ordovician limestone reservoir are of Cl-Na type, the geothermal water of the Pliocene Minghuazhen (明化镇) Formation sandstone reservoir are Cl-Na type and HCO₃-Na type and the groundwater of the Quaternary aquifer is HCO₃-Na and HCO₃-Na·Mg·Ca type. A linear relationship between silica concentration and temperature indicates that higher temperature probably enhances concentration of silica in Jixianian geothermal water. δ^{18} O shift in Wumishanian geothermal water averaged 1.57‰, and was less than 1‰ in the other geothermal waters. The minimum and maxi-

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Manuscript received June 14, 2013. Manuscript accepted October 22, 2013. mum ¹⁴C ages of Wumishanian geothermal water are 17 000 and 33 000 years from north to the south of the Niutuozhen geothermal field. Geothermal water and Quaternary groundwater belong to different groundwater systems with no hydraulic connections. Although the geothermal field receives some recharge from the Yanshan and Taihang mountains outside the northern and western boundaries of the geothermal field respectively, the renewability rate of geothermal water is on the scale of 10 000 years.

KEY WORDS: hydrogeochemistry, isotope, geothermal water, origin and evolution, Niutuozhen geothermal field.

INTRODUCTION

Geothermal resources can provide clean green energy and have recently received considerable attention. The Niutuozhen Geothermal Field is located in the Niutuozhen Uplift in North China (Fig. 1) and its geothermal resources have been developed for more than 30 years (Chen, 1988). Geothermal water is extensively used for space heating in Xiongxian, Gu'an and Baxian to construct smoke-free cities. There is an urgent need for further research on geothermal energy potential, reservoir temperature and water chemistry because of rapidly increasing demand (Dotsika et al., 2010; Wu and Ma, 2010; Gao et al., 2009; Liu H et al., 2009; Zhang et al., 2007; Liu J R et al., 2002; Giggenbach et al., 1995; Wang and Shen, 1993; Wang J Y et al., 1993; Wang Y X et al., 1993; Giggenbach, 1992, 1988; Dai et al., 1988). Chemical and isotopic components record the origin and evolution of geothermal water which reflect geothermal energy potential (Shen and Wang, 2002; Bi, 1998; Chen, 1998; Wang and

Shen, 1993; Wang Y X et al., 1993). Twenty years ago discussion of the origin and evolution of geothermal resources throughout the north China Basin was based on relatively few geothermal water samples (Yao, 1995; Chen, 1988; Zhou, 1987; Geothermal Group, 1983) and did not achieve modern levels of accuracy. The present work includes new sampling sites and presents modern analyses for major ions, δ^2 H, δ^{18} O, tritium and ¹⁴C ages of 43 samples from geothermal wells, three samples from groundwater wells and one rain water sample along with 14 rain water analyses obtained from the Global Network of Isotopes in Precipitation (GNIP).

GEOLOGICAL SETTING AND GEOTHERMAL RESOURCES

Geological Settings

The Niutuozhen Geothermal Field is located in the Niutuozhen uplift zone in the northern part of the Jizhong graben in the North China Basin bounded by



Figure 1. Location of the Niutuozhen uplift.

the Yanshan Mountains and the Taihang Mountains. The basin began developing by vertical crustal movement before the Late Triassic Period, followed by mountain building from Jurassic to Early Tertiary and Late Miocene subsidence. NE-SW striking horsts and grabens formed alternately from west to east. The Niutuozhen uplift (or horst) is bounded by the Niudong fault, Niunan fault, Rongcheng fault and Daxing fault initiated during Late Jurassic to Cretaceous earth movements and finally during Himalayan movements. The uplift continued to move up to the surface until the Late Oligocene when it became mature and was eroded. The Minghuazhen Formation was deposited over the entire horst by the Late Miocene (Fig. 2) and it was finally buried locally under Quaternary sediments.



Figure 2. Pre-Cenozoic geological map and cross-section of the Niutuozhen geothermal field.

The Neogene Minghuazhen Formation sandstone with an average effective thickness of 225 m and Jixianian Wumishanian Formation dolomite with a thickness more than 1 000 m are the main reservoirs in the Niutuozhen geothermal field. Quaternary clay with a thickness of 400 m is the main caprock of the Minghuazhen Formation reservoir, and mudstone of the Minghuazhen Formation and Quaternary clay more than 493 m thick are the caprocks of the Wumishanian dolomite reservoir.

The geothermal gradient in the cap rock of the Niutuozhen uplift is more than 3.0 °C/100 m, reaching a maximum of 11.5 °C/100 m in the axis of the uplift (Chen, 1988). The gradient in the Wumishanian reservoir is generally between 1.65 and 2.55 °C/100 m (Chen, 1988; Geothermal Group, 1983). Maximum wellhead pressure was measured at 3.74×10^5 Pa in 1970s (Chen, 1988), but has decreased to its present level of less than 1.01×10^5 Pa with drastic develop-

ment of the geothermal water and no reinjection. Wellhead temperature ranges from 59 to 84 °C. The permeability of the Minghuazhen Formation Reservoir is between 3.36×10^{-14} and 2.39×10^{-12} m⁻² and of the Wumishanian reservoir is between 2.10×10^{-11} and 6.15×10^{-10} m⁻².

METHODS

Samples were taken from a Quaternary cold water aquifer, the Minghuazhen Formation sandstone geothermal reservoir, an Ordovician limestone geothermal reservoir and the Wumishanian dolomite geothermal Reservoir and rainwater in the Niutuozhen geothermal field in order to compare geochemical characteristics between different waters (Fig. 3). 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



Figure 3. Sampling sites.

of metal ions were analysed by atomic absorption; total acidity, total hardness and most anions were analysed by titration; NH_4^+ , Fe^{2+} , Fe^{3+} , metaboric acid, metasilicic acid, metaphosphoric acid and some halide ions were analysed by spectrophotometry; and $NO_3^$ was analysed by ultraviolet spectrophotometry; selenium, metaarsenic acid and mercury were analysed by atomic fluorescence; and total dissolved solids were analysed by gravimetry.

Stable isotopes (¹⁸O, ²H) were analysed by isotope ratio mass spectrometry and Picarro L1102-i liquid water isotope analyzer and ¹⁴C samples were analyzed by Liquid Scintillation Counter.

RESULTS AND DISCUSSION

Hydrogeochemistry

Geothermal waters from the Wumishanian and Ordovician reservoirs are of Cl-Na type, and those of the Minghuazhen Formation reservoir are of Cl-Na type and HCO₃-Na type (Table 1, Fig. 4). Wumishanian geothermal water has higher total dissolved solid (TDS) ranging from 2 300 to 3 000 mg/L, than Ordovician reservoir water (2 206 mg/L) and Minghuazhen Formation (561–1 427.7 mg/L) geothermal water.

Symbolic Components

Silica (SiO₂) is the most significant symbolic component of geothermal water (Liu et al., 2002) and all water samples from Wumishanian geothermal reservoir are plotted in Fig. 5. The concentration of silica in Wumishanian geothermal water increases from 40 to 80 mg/L with temperature increase from 60 to 85 °C demonstrating a good linear relationship (R^2 =0.842) between silica concentration and temperature. The linear relationship indicates that temperature instead of lithology probably enhances the enrichment of SiO₂ in such a low-temperature geothermal system because the geothermal water is stored in the Jixianian dolomite geothermal reservoir (Li, 1982; Browne, 1978).



Figure 4. Piper diagram of compositions of geothermal water and groundwater.

components of the samples	
chemical	
le 1 The	
Tab	

Other		а	ы	ø	ы	q	ø	ы	ы	q	q	q	q	c	c	с	c	c	ø	ø	ы	ы	а
¹⁴ C age	(a)	$17\ 211\pm 874$	$22\ 912\pm 640$			22 185 \pm 365		25 704±1 566														33 536±3 697	
Tritium	(TU)							<0.5														<0.5	
$\delta^{18}O$	(0	-9.29	-9.11	-9.18	-9.18	-9.08	-9.08	-8.98							-8.70							-8.84	-8.66
$\delta^2 H$	%)	-77.40	-86.90	-79.30	-77.60	-81.90	-79.00	-76.80							-75.30							-79.30	-77.90
Т	(°C)	83	85	74	78	70	60	76	59	83	83	72	65	65	81	79	99	64	62	64	64	80	
TDS		2 886	2 868	2 879	2 889	2 833	2 929	2 814	2 940	2 910	2 800	2 830	2 850	3 005	2 820	2 790	2 781	2 622	2 853	2 683	2 533	2 821	
HCO ₃ ²⁻		442.4	469.8	485.1	485.1	524.7	701.7	655.9	669.0	646.0	647.0	671.0	677.0	687.1	631.0	622.0	621.0	676.8	654.7	668.1	660.5	631.5	
$\mathrm{SO_4}^{2-}$		0.5	0.2	0.6	0.0	0.0	0.5	0.2	<0.2	<0.2	<0.5	<0.5	1.4	68.3	6.7	8.6	8.5	8.0	39.7	6.4	25.5	1.3	
CI ⁻	(mg/L)	1 400	1 365	1 347	1 365	1 294	1 143	1 179	1 220	1 201	1 140	1 160	1 160	1 123	1 110	1 140	1 140	981	1080	984	938	1 179	
${\rm Mg}^{2+}$		21.88	25.53	27.96	25.28	35.25	31.00	24.07	27.70	22.10	23.10	25.90	27.70	26.69	22.60	24.30	24.20	23.83	20.27	22.33	23.97	20.66	
Ca^{2+}		39.08	39.08	40.08	46.09	32.06	55.11	56.11	56.70	54.10	51.70	55.10	58.10	60.21	60.10	52.10	52.09	61.01	49.06	55.77	49.91	52.10	
Na^+		910	006	910	006	880	838	832	897	911	867	848	858	897	865	824	825	743	865	812	602	870	
$\mathbf{K}^{\scriptscriptstyle +}$		58.0	57.0	58.2	57.0	56.0	57.8	58.0	62.8	66.2	70.3	63.3	53.8	55.9	51.4	57.8	57.7	47.8	53.8	50.0	42.4	58.0	
Wotor control	water source	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw	Jxw
Mamo	INALLIC	J1	J2	J3	J4	JS	J6	J7	J8	6ſ	J10	J11	J12	J13	J14	J15	J16	J17	J18	J19	J20	J21	J22
No	NO.	1	7	3	4	5	9	7	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22

Continu	led															
QN N	Name	Water cource	\mathbf{k}^{+}	Na^+	Ca^{2+}	${\rm Mg}^{2+}$	CI-	$\mathrm{SO_4}^{2-}$	HCO ₃ ²⁻	TDS	Т	$\delta^2 H$	$\delta^{18}O$	Tritium	¹⁴ C age	Other
N0.	INALLIC	watel source					(mg/L)				(C)	%)	(0	(TU)	(a)	
23	J23	Jxw										-75.10	-8.91			a
24	J24	Jxw										-78.00	-9.13			а
25	J25	Jxw										-74.10	-8.70			q
26	J26	Jxw										-73.70	-8.90			р
27	J27	Jxw										-73.90	-8.80			р
28	J28	Jxw										-72.90	-8.60			р
29	J29	Jxw										-73.70	-8.90			р
30	J30	Jxw										-73.70	-8.70			q
31	J31	Jxw										-73.30	-8.70			р
32	J32	Jxw										-73.70	-8.90			q
33	J33	Jxw										-73.10	-8.60			q
34	J34	Jxw										-73.70	-8.70			q
35	J35	Jxw										-73.60	-8.80			q
36	J36	Jxw										-72.80	-8.60			р
37	J37	Jxw										-73.50	-8.80			q
38	J38	Jxw										-73.70	-8.80			q
39	J39	Jxw										-72.20	-8.50			q
40	01	0	24.0	702	47.09	10.33	968	0.9	445	2 206	53	-75.80	-9.87		$12\ 461\pm419$	а
41	N1	Nm	10.0	449	28.06	11.55	573	12.6	339	1 428	58	-77.17	-10.64		$27\ 171 \pm 384$	a
42	N2	Nm	14.9	299	5.60	1.20	112	<0.5	603.0	1 050	54.5	-78.92	-10.02	<0.5	26900 ± 650	ø
43	N3	Nm	1.0	146	4.01	1.82	20	20.77	366.1	561	26	-78.00	-11.18		$25\ 142\pm400$	ø
44	Q1	ð	0.8	103	4.61	3.04	18	32.29	244.1	413	29.5	-89.20	-11.90			B
45	Q2	ð	0.5	67	34.07	23.10	20	42.17	320.3	508	15	-71.50	-10.44			а
46	Q3	Q										-66.36	-8.79	67.8		а

No.	Name	Woter course	$\mathbf{K}^{_{+}}$	Na^+	Ca^{2+}	${ m Mg}^{2+}$	CI-	SO_4^{2-}	HCO ₃ ²⁻	TDS	Г	$\delta^2 H$	$\delta^{18}O$	Tritium	¹⁴ C age	Other
140.	INALLIC						(mg/L)				(°C)	(%0	(((TU)	(a)	
47	Xiongxian	Rain										-58.79	-8.06			а
48	Shijiazhuang	Rain										-52.9	-7.44			e1986
49	Shijiazhuang	Rain										-48.4	-7.06			e1987
50	Shijiazhuang	Rain										-43.1	-6.8			e1988
51	Shijiazhuang	Rain										-57.4	-8.02			e1989
52	Shijiazhuang	Rain										-62.1	-8.36			e1990
53	Shijiazhuang	Rain										-63.5	-7.97			e1991
54	Shijiazhuang	Rain										-63.1	-8.67			e1996
55	Shijiazhuang	Rain										-54.3	-7.39			e1997
56	Shijiazhuang	Rain										-39.7	-6.5			e1998
57	Shijiazhuang	Rain										-51.3	-7.79			e1999
58	Shijiazhuang	Rain										-60.2	-9.1			e2000
59	Shijiazhuang	Rain										-56.9	-8.13			e2001
60	Shijiazhuang	Rain										-46.4	-7.22			e2002
61	Shijiazhuang	Rain										-52.5	-7.58			e2003

Continued

Geothermal Development Co. Ltd.; d. from Beijing Institute of Hydrogeology and Engineering Geology, analyzed by Laboratory of Water Isotopes and Water-Rock Interaction, Institute of institute was the Institute of Hydrogeology & Engineering Geology (Shijiazhuang, Hebei, China) (1986 means sampling year); f. the Quaternary groundwater is HCO₃-Na and HCO₃-Na·Mg·Ca type (Fig. 4) with TDS between 413.3 to 507.6 mg/L. The SO₄²⁻ concentration of the geothermal water was measured to be extremely low (some <0.2 mg/L), indicative of desulphurization in a a. From "Geothermal Survey Report of the Niutuozhen Geothermal Field in Hebei Province"; b. from Beijing Institute of Hydrogeology and Engineering Geology; c. from Shaanxi Green Energy Geology and Geophysics, Chinese Academy of Sciences; e. the isotope data of rainfall in Shijiazhuang meteorological stations, 207 km SW from Xiongxian, in a representative position in North China Plain were available from the Global Network of Isotopes in Precipitation (GNIP). The GNIP Database was accessible at http://www.iaea.org/water. The laboratory and management confined structure.



Figure 5. Relationship between well head temperature and SiO₂ concentration

Origin of geothermal water

Craig (1961) found that there was δ^{18} O shift when geothermal water is compared with the Global Meteoric Water Line, which was brought about by ¹⁸O exchange between geothermal water and rock under high temperature conditions (>300 °C). He found that change of δ^2 H due to depletion of H in the rock was negligible compared with δ^{18} O. Wen et al. (2010), Ma et al. (2008), Zhang et al. (2006), Pang (2004), Zhao et al. (2001), Wang Y X et al. (1993), Sun et al. (1992) and Pang et al. (1990a, b) have also used isotopic methods to study origin and mixing of geothermal water in different geothermal fields.

Stable isotope data for all geothermal waters (Fig. 6) show a δ^{18} O range from -8.66‰ to -11.90‰. It is obvious that the geothermal water from the Ordovician and the Minghuazhen Formation geothermal reservoir and from the Quaternary groundwater fall near the GMWL. However, samples from the Wumi- shanian geothermal reservoir demonstrate an average 1.57‰ ¹⁸O shift, slight compared with samples from a Tibet high temperature geothermal system (Zhou et al., 2009). Truesdell and Hulston (1980) found that the



Figure 6. δ^{18} O and δ^{2} H of different groundwaters.

mineral components of reservoir rock are a significant factor affecting δ^{18} O shift and that maximum shift occurred in carbonate rock systems. Exchange of ¹⁸O between deeply circulating meteoric water and hot carbonates in deep-seated aquifers for a long time (Zhou et al., 2004, 2001) may explain the slight O¹⁸ shift.

Evolution of geothermal water

In order to study the evolution characteristics of geothermal water along a flow line, Well O1 in the northernmost part of the geothermal field was taken as origin point. A plot of ¹⁴C age along the flow line shows a progressive increase indicating age increasing from north to south (Fig. 7a). A similar trend was also found in the studies of Chen (1988) and Geothermal Group (1983). There is a significant positive linear correlation between ¹⁴C age and δ^{18} O (Fig. 7b) which is good evidence that the extent of ¹⁸O exchange between geothermal water and reservoir rock was enhanced with the increasing residual time of geothermal water.



Figure 7. The relationship of ¹⁴C age with distance and δ^{18} O.

DISCUSSION

The high concentration of Cl and Na in the Wumishanian and Ordovician geothermal water indicates that the water experienced long time lixiviation from the recharge area during the process of flowing from north to south in the geothermal field (Wang et al., 1995), similar to the geothermal water in the geothermal fields of Tianjin and Beijing (Hu et al., 2007) and confirmed by the ¹⁴C age of the geothermal water.

The remarkably differences in geochemical characteristics between Quaternary, Minghuanian, Ordovician and Wumishanian geothermal waters suggests that they derive from different groundwater systems (Zhou, 1987). The Quaternary groundwater system is mainly recharged by local modern rain and groundwater recharge from mountains to the north and west (Chen et al., 2010). By contrast, geothermal water of the Minghuazhenian, Ordovician and Wumishanian reservoirs was recharged by paleo- precipitation at least 12 000 years ago (Table 1).

Its tritium isotope concentration 67.8 TU indicates that some Quaternary groundwater receives modern rain recharge. The δ^{18} O and δ^{2} H values of -8.79‰ and -66.36‰ of Quaternary geothermal water are close to modern rain water but its tritium isotope value <0.5 TU indicates that this water has not been recharged by modern rain, in agreement with the ¹⁴C results (Table 1).

¹⁴C ages indicate that the Wumishanian geothermal water flows from north to south at an average velocity of 3.6 m/a in the Niutuozhen geothermal field (Fig. 8).

With increasing time for water-rock ¹⁸O exchange processes, ¹⁸O in the geothermal water is progressively enriched along the flow line from north to south as demonstrated by the good linear relationship between δ^{18} O and ¹⁴C age in Fig. 7b.

According to research by Yan and Yu (2000) and Zhou (1987), the Niutuozhen geothermal field receives recharge both from the Yanshan Mountains in the north (about 100 km from the northern part of the geothermal field) and the Taihang Mountains in the west (about 50 km from the west boundary of the geothermal field) and moving Wumishanian geothermal water from the Yanshan Mountains may be diluted by water from the Taihang Mountains. Water from the Taihang Mountains is generally younger than water from Yanshan Mountains because of relative



Figure 8. A conceptual evolution model of Wumishanian geothermal water.

shorter flow distance. It could also be inferred that the water in the south of the geothermal field should be older than 33 000 year if it was only recharged by water from the north without being diluted by water from the west.

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