

Chemical and Isotopic Approach to Groundwater Cycle in Western Qaidam Basin, China

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Abstract: Due to the extremely arid climate in the western Qaidam Basin, the groundwater almost becomes the single water source for local residents and industrial production. It is necessary to know the reliable information on the groundwater cycle in this region for reasonable and sustainable exploitation of the groundwater resources with the further execution of recycling economy policies. This study focused on the recharge, the flow rate and the discharge of groundwater in the western Qaidam Basin through investigations on water chemistry and isotopes. Hydrological, chemical and isotopic characteristics show that the groundwater in the western Qaidam Basin was recharged by meltwater from new surface snow and old bottom glaciers on the northern slope of the Kunlun Mountains. In addition, the results also prove that the source water is enough and stable, and the rates of the circulation and renewal of the groundwater are relatively quick. Therefore, it can be concluded that the groundwater resources would guarantee the regional requirement if the meltwater volume of the mountains has not a great changes in future, moreover, water exploitation should be limited to the renewable amount of the groundwater reservoir in the western Qaidam Basin.

Keywords: groundwater cycle; water chemistry; isotope; Qaidam Basin

1 Introduction

There has been considerable attention placed on better understanding the source of recharge, condition of runoff and patterns of discharge of groundwater, which is significant and essential for right evaluation, effective exploitation and management for the regional water resources. Due to the different hydrogen and oxygen isotopic composition for water from different sources, stable hydrogen and oxygen isotopic ratios (δD and $\delta^{18}O$) are excellent ways to fingerprint groundwater origin (Clarke and Fritz, 1997). All kinds of natural water have distinctive isotope signatures depending on their mode of formation (Craig, 1961; 1966; Calyton, 1966). Radioactive tritium isotope is always introduced into the hydrological cycle and dated with the fallout from atmospheric nuclear weapon tests mainly during the early 1960s. In a degree, it can be indirectly used to evaluate the ability of groundwater updating (Clarke and Fritz, 1997). Strontium isotope ratio has proven to be a valuable tracer for

understanding earth surface problems related to regolith development, watershed processes, and global geochemical fluxes. Previous studies approved that some hydrological effects such as evaporation can change the Sr content in water, but $^{87}Sr/^{86}Sr$ ratio is very different from those light isotopes and always has no fractionation during the process of phase separation, chemical reaction, evaporation, and biosynthesis or assimilation (Palmer and Edmond, 1992; Douglas et al., 1995; Asahara et al., 1999). $^{87}Sr/^{86}Sr$ ratio also has no response to latitude or altitude changes and can keep invariable within the same geological periods and same hydrological system. Hence, strontium isotopes are always used to constrain on the origin and mixing process of groundwater, particularly to trace the degree of water-rock interactions and indirectly deduce the residence time of groundwater in the strata (Bullen and Kendall, 1998; Capo et al., 1998; McNutt, 2000; Blum and Erel, 2005; Shand et al., 2007). The noble gases and their isotopes are excellent natural tracers for fluid source and migration in the Earth's crust (Lup-

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ton, 1983; Kennedy et al., 1985; Hiyagon and Kennedy, 1992; Kennedy and Truesdell, 1996). Helium associated with crustal fluids that have experienced no mantle influence is dominated by radiogenic ^4He produced from radioactive decay of U and Th to Pb and is characterized by a $^3\text{He}/^4\text{He}$ ratio of 0.01–0.02Ra. Helium associated with mantle fluids is characterized by a $^3\text{He}/^4\text{He}$ ratio of $>1\text{Ra}$. Once the meteoric water enters into the ground, $^3\text{He}/^4\text{He}$ ratio will decrease from 1Ra to $<0.01\text{Ra}$ with long residence time and increased circular depth. Certainly, the $^3\text{He}/^4\text{He}$ ratio in groundwater will be very close to atmosphere ($\approx 1\text{Ra}$) if the meteoric water circulates quickly in the shallow layer. So, helium isotope can also be used to indirectly help to know about groundwater circular depth, residence time and rates of groundwater discharge and flow (Weiss, 1971; Tolstinkhin et al., 1996; Gisela et al., 2001; Kennedy and Matthijs, 2006; Antoni et al., 2006).

Qaidam Basin was granted as the mother batch of state test region for cyclic economy in 2005, which will bring the great opportunity for its development. The western Qaidam Basin, usually referred to Mangnai region, is an important base of oil field and salt chemical plant in Qinghai Province. Due to the extremely arid climate, there is almost no surface water can be used. Hence, groundwater becomes single water resources for resident existence and industrial production. Before the 1960s, the groundwater in Mangnai was drilled and utilized by oil industries and salt chemical plants, but nowadays, there has few researches on its water chemistry and isotope geochemistry. With the development of cyclic economy and increase requirement for water resources, to know the reliable information on the groundwater circulation becomes significant and essential for reasonable and sustainable exploitation of the valuable water resources. On account of this, this work is focused on finding the reliable information about the groundwater recharge, rates and patterns of discharge and flow in Mangnai region through discussion on the characteristics of water chemistry (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} and HCO_3^-) and particularly typical isotope geochemistry (δD , $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, T and $^3\text{He}/^4\text{He}$).

2 Methodology

2.1 Study area

Mangnai area (including old Mangnai Village, Alar pas-

toral area and Mangnai Town), located in the western Qaidam Basin, China, was selected as study area in this paper (Fig. 1). It is one of the most extremely arid areas in Qaidam Basin with very rare annual precipitation (less than 50mm) and high annual evaporation (more than 2,800mm). Besides some important salt lake resources and all of oil or gas resources have been mined, world-scale celestite and asbestos mines have also been discovered and developed in Mangnai area. Hence, Mangnai area has become an important base of chemical plant, petroleum production and mineral exploitation. However, for the extremely arid climate and wide desert distribution, there is almost no surface water to be used. Groundwater, therefore, becomes single water for resident existence and industrial production in Mangnai. There are several natural flowing wells (more than 40,000m³ of water is supplied every day) in Alar Basin in the southwestern Mangnai Town, which are used as water sources for regional resident living and industrial manufacture. Moreover, there has a very unusual wetland in extremely arid desert in the old Mangnai Village, which is formed by rich groundwater discharge. Many ascending springs and natural flowing wells can be found in the wetland. They also provide sufficient water for herdsman existence, oil and saline production. Despite several small rivers are perennial for mountain spring water (snow melt water) and groundwater recharge, they are quickly salinized by surface salts dissolved and extreme evapo-concentration once they flow from the front of mountain to discharge into Gas Hure Salt Lake. So river water has no much significant contribution to regional water resources utilization.

Within study area, from surface to the depth below 200m, about three main aquifers can be separated: the phreatic water aquifer in upper 10m depth from surface; the middle confined water from 70m to 120m depth and deep confined water aquifer below 200m depth from surface. The lithologies forming the aquifers are characteristically composed by a set of sandstone, gravelstone with high hydraulic conductivity. All the wells of confined water can keep high pressure of hydraulic head (from +50m to +60m) and large flux (natural flux 1500–5000m³/d in a single well) to supply water in several decades' exploitation.

2.2 Sampling methods

Groundwater samples were collected from six natural

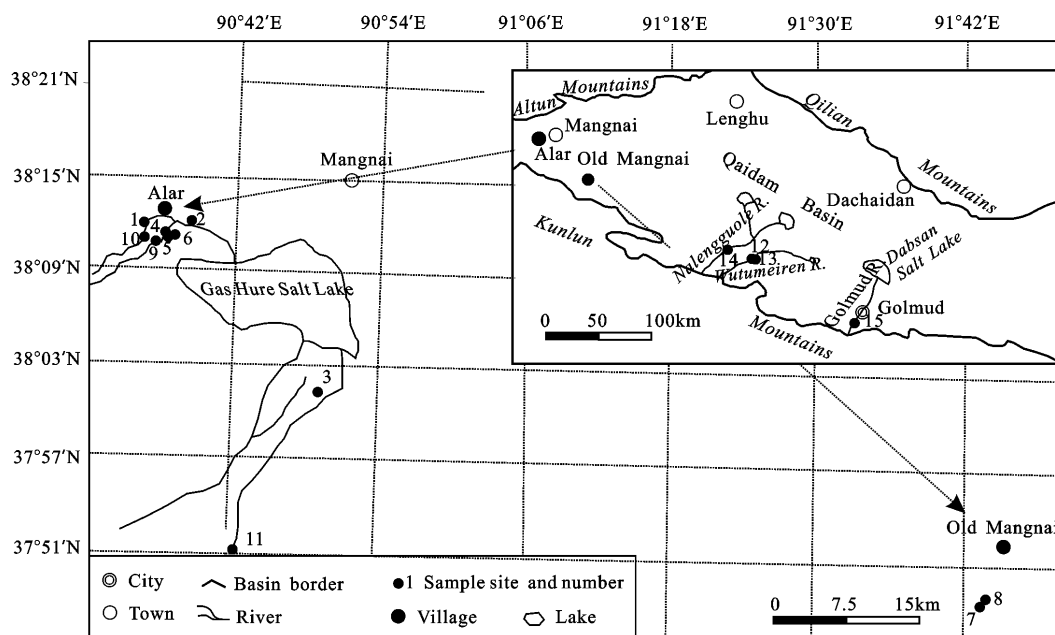


Fig. 1 Location of study area and sample section

flowing wells in Alar Basin and two wells from old Mangnai wetland (Fig. 1, Table 1). In order to compare with each other, three small perennial rivers in Mangnai area and three large rivers, one spring water typically sourced from snow melt water in the northern slope of the eastern Kunlun Mountains (including the Golmud River, the Wutumeiren River and the Nalengguole River) were also collected (Table 1).

pH, salinity and temperature were measured in the field. For each sample, three 500-mL bottles were used to col-

lect samples for cation, anion and hydrogen, oxygen, tritium and strontium isotope analysis. Cation aliquots were acidified with ultra-pure nitric acid. After that, the bottles were airproofed and sent to laboratory for isotope and element analysis in time. All of the water samples for helium isotope analysis were filled into glass bottles hermetically sealed in field and special care were taken to avoid air bubbles intrusion. We only obtained three deep well water samples in Alar and two well water samples in Mangnai wetland for helium analysis.

Table 1 Main physical and chemical parameters of different water types in western Qaidam Basin

Sample site	Sample number	Altitude (m)	EC ($\mu\text{s}/\text{cm}$)	pH	Description
Alar basin	1	2874	1130	8.20	Deep confined water (70m depth)
	2	2861	1936	8.80	Shallow phreatic water
	3	2890	389	8.00	Deep confined water (200m depth)
	4	2870	1279	8.54	Deep confined water (100m depth)
	5	2870	1325	8.54	Deep confined water (100m depth)
	6	2869	1365	8.54	Deep confined water (100m depth)
Old Mangnai wetland	7	2896	853	7.70	Deep confined water (120m depth)
	8	2891	2459	7.50	Shallow phreatic water
Alar basin	9	2862	1315	8.70	Upriver water
	10	2864	1315	8.70	Upriver water
	11	3202	853	8.70	Mountain pass river
Rivers sourced from northern slope of eastern Kunlun Mountains	12	2840	3640	8.79	Middle Wutumeiren River water
	13	2840	1116	8.44	Wutumeiren Spring water
	14	2938	1457	8.44	Middle Nalengguole River water
	15	3138	1130	8.20	Middle Golmud River water

2.3 Analysis methods

Major cations and anions were analyzed by atomic absorption spectrometry (AAS) and ion chromatography. Electrical balances were excellent with all water showing less than 5% difference between cations and anions. δD , $\delta^{18}O$, T analyses were performed in the State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University. $^2H/^1H$ and $^{18}O/^{16}O$ ratios were measured on a MAT253 mass spectrometer, and the results were reported to be relative to SMOW with a standard deviation of $\pm 1\%$ to 2% and $\pm 0.20\%$ to 0.30% , respectively. For the determination of the tritium content, the water samples were condensed through electrolysis and then measured by a low-background liquid scintillation counting (Tri-Carb 3170 TR/SL), and the results were reported in tritium unit (TU). The maximum measurement uncertainties of tritium results were less than 0.3TU. $^{87}Sr/^{86}Sr$ analysis was performed in Nanjing University. Firstly, the primary water samples were filtered through $0.45\mu m$ to remove

solid particulates and the clean filtrates were prepared for equipment analysis. For the determination of $^{87}Sr/^{86}Sr$ ratio, sufficient water was loaded in a cation exchange column resin (Dowex-50 produced from US) to separate Sr from other cations, particularly from Rb. The strontium isotope analyses were performed on a VG 354 mass-spectrometer, with an analytical precision of $\pm 11 \times 10^{-6}$. Reproducibility is within the range of $\pm 2 \times 10^{-5}$. The standard used SRM 987 averaged 0.710250 ($n=8$). All the results were normalized to $^{87}Sr/^{86}Sr=0.1194$. About helium isotopic sample preparation, analytical techniques and the instrumentation used are similar to those described by Ye et al. (2007). The content and isotopic composition of noble gas He were measured by a MM5400 mass spectrometer in the Laboratory of Gas Geochemistry (Lanzhou), Institute of Geology and Geophysics, Chinese Academy of Sciences. Errors on $^3He/^4He$ ratios with reproducibility of duplicate analyses are good to 1%. All the results are expressed in Table 2.

Table 2 Results of main chemical and isotopic determinations for groundwater and river water in western Qaidam Basin

Sample	Section	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	CO ₃ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	Sr (mg/L)	TDS (mg/L)	δD (‰)	$\delta^{18}O$ (‰)	T (TU)	$^{87}Sr/^{86}Sr$	$^3He/^4He$ (Ra)
1	Mangnai	206.3	4.7	40.1	56.2	127.1	158.9	0.0	451.0		691.5	-55.7	-7.86	1.7		
2	Mangnai	285.8	8.0	47.0	75.5	226.1	295.8	7.4	477.2		1008.6	-59.8	-7.17			
3	Mangnai	34.0	2.3	32.2	9.0	40.1	51.5	0.0	120.6		206.9	-58.8	-8.77	1.8		
4	Mangnai	156.4	4.1	41.1	39.4	113.7	118.2	17.9	362.1	0.71	557.8	-57.2	-8.00	4.2	0.711881	0.656
5	Mangnai	158.8	4.3	37.0	42.9	119.4	128.9	17.9	350.0	0.71	572.2	-45.9	-7.90	4.2	0.711807	0.826
6	Mangnai	177.8	4.7	35.1	43.6	123.8	167.2	17.9	342.8	0.71	607.7	-59.6	-7.78	<0.8	0.711812	0.727
7	Mangnai	102.5	18.7	25.2	12.4	120.2	91.4	1.2	115.1	0.50	381.6	-43.4	-8.46	2.6	0.711153	0.680
8	Mangnai	344.5	24.2	76.8	36.1	421.6	399.0	3.0	129.6	1.85	1302.3	-44.6	-7.20	1.2	0.711355	0.687
9	Mangnai	204.4	6.7	76.0	41.5	208.1	127.5	0.0	316.2		798.7	-54.5	-7.74	1.8		
10	Mangnai	109.3	5.0	59.7	32.2	121.1	116.2	0.0	272.0		539.3	-52.8	-7.50	2.6		
11	Mangnai	71.0	3.6	79.9	15.1	140.5	89.7	0.0	155.1		554.6	-51.0	-8.07	4.4		
12	Wutumeiren											-57.6	-7.87			
13	Wutumeiren											-59.0	-8.55			
14	Nalengguole											-51.5	-7.91			
15	Golmud											-55.6	-9.25			

3 Results and Analyses

3.1 Major chemical characteristics of groundwater

The pH and total dissolved salts (TDS) values of groundwater in Mangnai area are limited within the III grade of Chinese State Groundwater Quality (Table 1, Table 2, Fig. 2). Compared to the deep confined water with lower TDS, shallow phreatic water in Alar (Sample 2) and old Mangnai (Sample 8) presents much higher

TDS and higher electrical conductivity (EC) due to evapo-concentration. The TDS and EC of shallow phreatic water are also much higher than those of up-river water (including samples 9–11). From the field observation, the source water of rivers mainly origins from snow melt water in the northern slope of the Kunlun Mountains with very low TDS, and for the large fall, short distance and quick rate of flow, they can keep lower TDS when flowing out of the mountain pass. All

the deep confined waters (at a depth greater than 70m from the surface) have lower TDS values which are close to those of upriver water. In an anion and cation triangle of Piper diagram (Fig. 3), all data points are rather centralized in the mixed facies. Groundwater and rivers do not display any significant variation. Sample 8, however, is slightly offset toward the Na^+ and Cl^- poles only for evapo-concentration or salts dissolved, but as a whole, the water chemical characteristics show that groundwater has the same source with rivers, which indicates that the groundwater probably origins from snow melt water. In addition, from the source of rivers in the mountain to the groundwater discharge to rivers, wells or springs, the relatively steady proportion of the chemical composition also indicates that groundwater circulation is quick and the condition for runoff should be well.

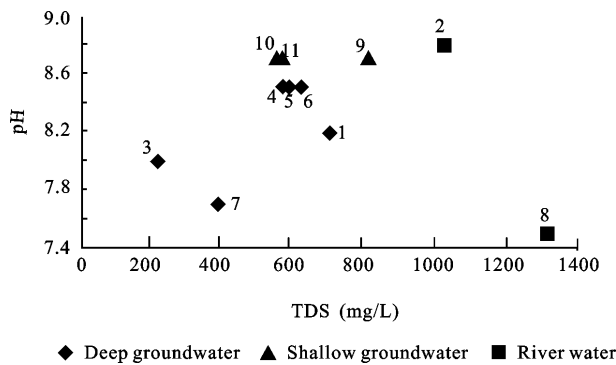


Fig. 2 Diagram of pH-TDS variation of groundwater and river water in Mangnai area

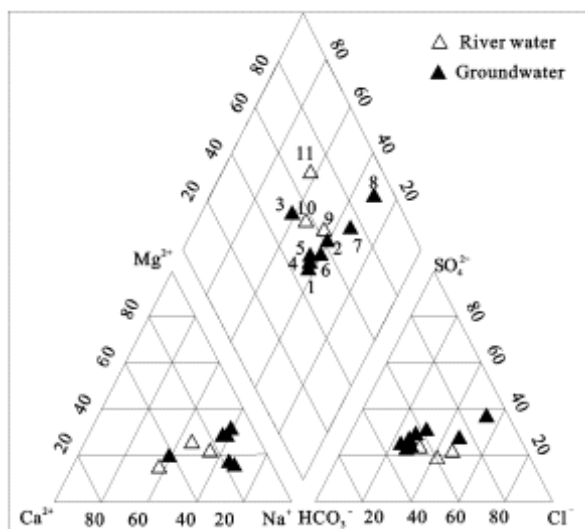
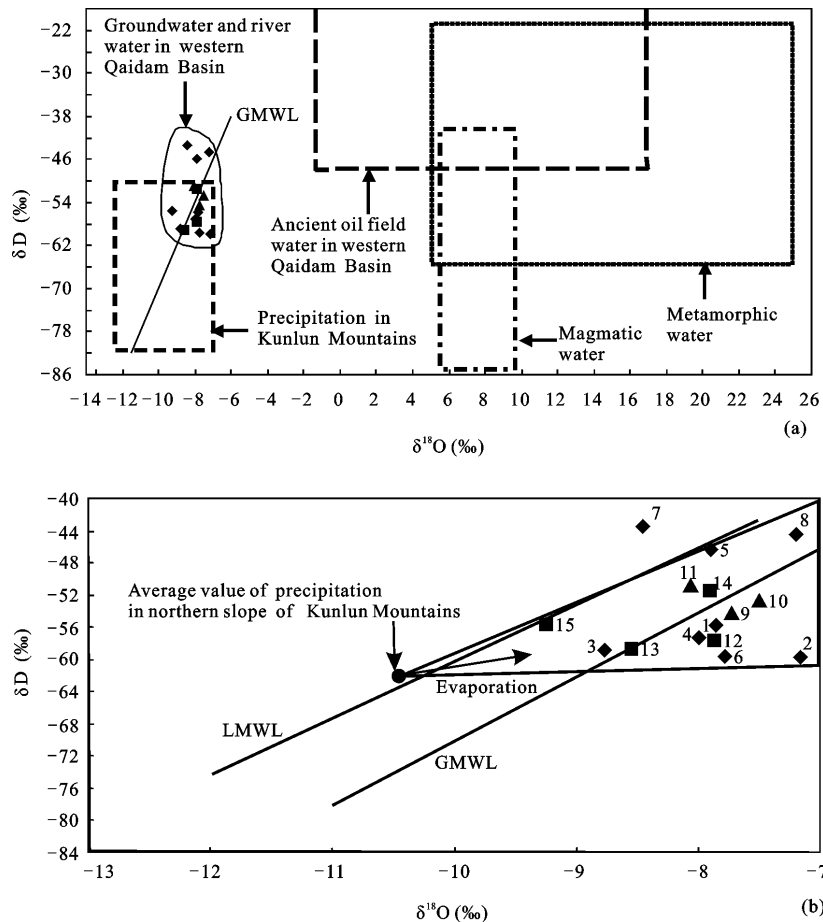


Fig. 3 Trilinear (Piper) diagram of groundwater and river water in Mangnai area

3.2 Hydrogen, oxygen and tritium isotope compositions of groundwater and river water

As a whole, either groundwater or river water shows rather homogeneous compositions in $\delta^{18}\text{O}$ (from -8.77‰ to 7.17‰ and its average value is -7.86‰) and δD (from -59.8‰ to -43.4‰ and its average value is -53.0‰) values in Mangnai area (Table 2). By contrast, their isotope compositions are very close to river water sourced from the northern slope of the Kunlun Mountains (from -9.25‰ to -7.87‰ and its average value is -8.40‰ in $\delta^{18}\text{O}$ and from -59.0‰ to -51.5‰ and its average value is -55.9‰ in δD). In Fig. 4a, the distribution ranges of δD versus $\delta^{18}\text{O}$ in the western Qaidam Basin are obviously different from the so-called magmatic water, ancient sedimentary water or metamorphic water, which always have an obvious trend of positive excursion in $\delta^{18}\text{O}$ values due to strong water-rock interaction. For example, for the ancient oil field water in the Tertiary strata in Mangnai area, their δD and $\delta^{18}\text{O}$ values are obviously positive, particularly the $\delta^{18}\text{O}$ values generally higher than 1‰ . Most sample points of groundwater and rivers all fall close to the Global Meteoric Water Line (GMWL) defined by Craig (1961) if the different altitudes and different degrees of evaporation in research area are considered. With respect to the values of precipitation ($\delta^{18}\text{O}$ values changing from -12.6‰ to -7.6‰ and its average value is -10.1‰ ; δD from -82.6‰ to -51.2‰ and its average value is -66.9‰) in the northern slope of the east Kunlun Mountains (Li et al., 2007), almost all the sample points are confined within their variable range. Relative to average value of precipitation, there is a slightly positive trend in δD and $\delta^{18}\text{O}$ of groundwater and rivers and their plots are located in the area of right corner of diagram (Fig. 4b), which should be attributed to evaporation during the circulation. A few of them have a slightly positive excursion in δD values (Sample 7), which is probably attributed to isotopic exchange between groundwater and hydrogen-bearing gas (H_2S , CH_4) near oil field during circulation. Summarily, the characteristics of hydrogen and oxygen isotope show that the groundwater and river water have the same source, i.e., they all origin from precipitation of the northern slope of the eastern Kunlun Mountains.

Either groundwater or river water in Mangnai area is water with ^3H activities lower than 5TU, which indicates that they are not tritium water with much higher nuclear explosion-formed ^3H for nuclear weapons tests



◆ Groundwater in Mangnai area; ▲ River water in Mangnai area; ■ River water sourced from northern slope of eastern Kunlun Mountains; LMWL: Local meteoric water line; GMWL: Global meteoric water line

(a) Plots of study area water samples and all kinds of natural water samples; (b) Enlarged study area plots of groundwater samples and typical rivers sourced from northern slope of eastern Kunlun Mountains

Fig. 4 Diagram δD versus $\delta^{18}O$ of groundwater, river water in Mangnai area and river water sourced from northern slope of eastern Kunlun Mountains

since from 1952 to 1980. Although the 3H activities are lower than 5TU, they all can be detected within the measurement error ($>0.3TU$) and are much higher than 0.8TU except for Sample 6 from deep hole ($<0.8TU$). The tritium content is the highest surface snow melt water recharge as well as the mountain springs. Hence, the 3H activity represents the mixed water with older water supplied before 1952 ($<0.8TU$) and recent water ($>5TU$). According to field observation, we think that old water should origin from the bottom melt water of old glaciers and recent water origin from surface melt snow water in summer. Moreover, for the other two rivers in Alar Basin, the 3H activities are 1.8TU and 2.6TU, respectively. They receive not only groundwater recharge in the basin but also receive water from mountain

springs. The 3H activities of the shallow or deep groundwater are very close to rivers. Thus it can be seen that the groundwater in Mangnai has steadily recent precipitation recharge and the renewal speed is relatively quick. That is why so many natural flowing wells can keep high pressure of hydraulic head and large flux to supply water in several decades, even in more than 50 years. In addition, in the extremely arid desert with very rare precipitation and strong evaporation, there exist perennial small rivers in Alar Basin, which also show the quick hydrogeological circulation in Mangnai area.

3.3 Strontium isotopes of groundwater

$^{87}Sr/^{86}Sr$ values of shallow, deep groundwater samples measured in Mangnai (Table 2) range from 0.711153 to

0.711881. Their variations are very small and close to inland snow and rainwater values reported by Jacks et al. (1989) and Aberg et al. (1989). The values are also close to source water values (0.711573) of the upper Kunlun River and snow of the Kunlun Mountains (0.710070) (Zhao et al., 2003), where the water-rock interactions are relatively weak and Sr isotopic compositions mainly represent the background values of regional natural precipitation water. The Sr content ranges from 0.71mg/L to 1.85mg/L, which belongs to natural water contents (0.003mg/L to 3.0mg/L). So, the strontium isotopic characteristics prove that the groundwater in Mangnai area keeps much more like natural water composition and the interaction of water-rock is weak during the process of circulation, which indirectly indicates that the circular period may be short from the source of snow melt water recharge-infiltrate to aquifer and runoff-discharge of wells or springs.

3.4 Helium isotopes of groundwater

According to five groundwater samples (samples 4–8) in Mangnai artesian wells, their ratios of $^3\text{He}/^4\text{He}$ (expressed as Ra, the ratio with respect to atmosphere) are distributed between 0.656 and 0.826Ra (Table 2), being somewhat lower than atmosphere (1.0Ra) but much higher than deep crustal radioactive values (0.02Ra). The depth of groundwater is limited about 200m from the surface and close to source area. The deep mantle-derived He with high $^3\text{He}/^4\text{He}$ ratios is unlikely to enter into shallow groundwater. Thus, a possible explain is that the groundwater circulates quickly in the strata and the radiogenic ^4He dissolved in groundwater may be very few for short residence time and shallow circulation in the crust. This is correlated with the discussion on Sr isotopic research conclusions in this paper.

4 Conclusions

(1) Characteristics of general chemical compositions, hydrogen, oxygen, strontium and helium isotopic distribution in groundwater of Mangnai area in the western Qaidam Basin conformably show that the groundwater is recharged by summer snow melt water in surface and old glacier melt water in bottom on the northern slope of the Kunlun Mountains.

(2) Due to the enough and stable source of water recharge, large fall from source to discharge and quick

circulation and renewal for the groundwater in Mangnai area, many natural flowing wells can keep high pressure of hydraulic head and large flux to supply water in several decades' exploitation. Hence, the water resources can guarantee the regional requirement if the precipitation in the Kunlun Mountains has no great changes and the water exploitation is always limited within its renewable amount of deposit.

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