

Noble gas geochemistry and chronology of groundwater in an active rift basin in central China

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Abstract. Stable noble gas isotopes are excellent groundwater tracers. Radioactive noble gases are emerging new tools in the study of groundwater circulation dynamics. Among these, the ⁸⁵Kr and ⁸¹Kr, and ³⁹Ar have advanced very fast in recent years and exhibit strong potential in the reconstruction of the history of groundwater recharge and evolution in sedimentary basins at different scales. Here, we report the findings in groundwater circulation dynamics as relative to intensive water-rock interactions, heat transfer and He gas flux in Guanzhong Basin located in Xi'an, the geographical centre of China, which is a rift basin created by collision between the Eurasia and Indian plates, with active neotectonic activities. The recent technological breakthrough in noble gas isotope measurements, i.e. the atomic trap trace analysis (ATTA) techniques on Kr and Ar gas radionuclei, has revolutionized groundwater dating. Noble gas samples from shallow and deep wells to 3000 m depth have been collected to study isotope variations to reconstruct the history of groundwater recharge and understand the water-rock interaction processes. Stable isotopes of water show strong water-rock interaction in the formation, creating a strong positive O-isotope shift up to 10 ‰, a phenomenon that is rarely seen in a fairly low temperature environment. Analysis of ⁸⁵Kr and ⁸¹Kr show groundwater ages up to 1.3 million years old along both North-South and a West-East cross sections, which offers strong evidence about the slow moving flow, strong water-rock interaction, rich geothermal resources as well as He gas resources.

1 Introduction

The utilization of geothermal water from natural hot springs in Guanzhong Basin, Sha'anxi Province, China, began more than 1000 years ago in the Tang dynasty (618 to 907 A.D.). The well known Huaqingchi hot spring in Lintong city located about 20 km to the east of Xi'an city was then an imperial thermal spa. There are two geothermal fields that are located in Xi'an City and Xianyang City, respectively, separated by the Wei River. In Xi'an

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city more than 70 production wells are being used to supply hot water for bathing, space heating and fish farming. Some of the deep wells have reached 4000 m, offering a very good opportunity for groundwater sample collection.

In large sedimentary basins, groundwater circulation creates different scales of geological processes with different environmental and resources implications. However, groundwater circulation condition is crucial to the efficiency of geothermal resources development. Previous studies have showed that geothermal water in Xi'an city is low in ^{14}C activity, but close to the dating limit of ^{14}C method [1]. The ^{36}Cl dating method revealed a residence time of a few hundred thousand years up to one million years for the Tertiary thermal water aquifer [2]. We have studied the groundwater age using advanced ATTA technique which helped to interpret the hydrological conditions and geochemical evolution of the groundwater in the deep aquifer.

2 Geological setting and methods

2.1 Geological setting

Guanzhong Basin in the middle reaches of the Yellow River accommodates a thick cover of Cenozoic sediments greater than 5000 m (Fig.1). Xi'an and Xianyang geothermal fields are located in the central part of the Basin on the northern and southern sides, respectively. Four geothermal reservoirs are being exploited between 400 to 4000 m in depth. The shallowest reservoir is Quaternary sediments, with a depth of 400 to 800 m. The other three reservoirs are Neogene formations of Zhangjiapo, Lantianbahe and Gaoling groups. The three reservoirs are sandstone intercalated with mudstone and the main exploitation depth intervals are 800 to 1500 m, 1500 to 2700 m, and 2700 to 3200 m, with formation porosity of 10 to 20 %, 15 to 35 % and 5 to 20 %, respectively. Some wells have reached the underlying Paleogene formations.

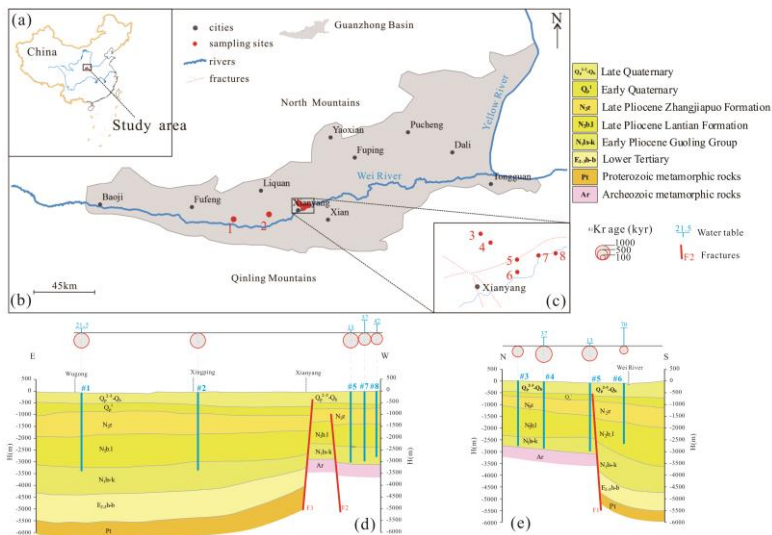


Fig. 1. Map of Guanzhong basin in China and the geothermal water sampling sites (a, b); ^{81}Kr sampling site in Xianyang geothermal field (c) and two schematic cross sections: East-West (d) and South-North (e). The size of the spheres denotes corresponding ^{81}Kr ages and the numbers above the spheres refer to the water table in the sampled well.

2.2 Methodology

For ^{81}Kr samples, dissolved Kr gas was extracted from several hundred liters of groundwater by using a portable membrane contactor (Liqui-Cel, PP X40) apparatus in the field. When water passes through the membrane contactor, only the gas phase can enter the hydrophobic semipermeable fiber tube. A diaphragm pump was connected to the gas output port to maintain a rough vacuum and to collect the sample gas. The gas was processed and purified in the laboratory to produce pure krypton for analysis. $^{81}\text{Kr}/^{83}\text{Kr}$ and $^{85}\text{Kr}/^{83}\text{Kr}$ isotopic ratios were determined using the ATTA technique. Moreover, samples from the same degassing system were collected under water for bulk gas analysis using 50 mL Pb glass bottles. The bulk gas compositions, $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{20}\text{Ne}$ ratios were measured. In our previous study [1], a series of geothermal water samples were also collected in this area.

3 Results and discussion

3.1 Groundwater dating

Generally, our ^{81}Kr ages are within the same order of magnitude of the ^{36}Cl ages. The ^{81}Kr ages between 0.3 and 1.3 Ma indicate good agreement with other methods including ^{14}C , ^4He and ^{36}Cl . According to samples 1, 2, 4 and 5, the oldest ^{81}Kr age was identified to occur in the centre of Guanzhong Basin, which can be considered as groundwater retention area with a relatively closed subsurface environment and a significantly low rate of groundwater renewal. Moreover, these sample sites are located on the north side of the Weibei fault (F1 in Fig. 1e). This groundwater retention area is also consistent with lower groundwater levels and higher groundwater temperatures. Higher piezometric levels were observed at Wells 6, 7 and 8 with relatively younger ^{81}Kr ages on the south side of the Weibei fault. There exists a positive correlation between wellhead temperatures and groundwater residence time as indicated by the ^{81}Kr ages. Samples from north (3) and south (6, 7 and 8), with relatively younger ^{81}Kr ages, indicate that groundwater is flowing from peripheries to the central retention area. Therefore, groundwater in the retention area is recharged by rain from both of Qinling Mountains to the south and North Mountains to the north [3]. The ^{81}Kr ages yield obvious evidence of groundwater recharge from both sides, which has confirmed our previous understanding regarding the geothermal waters in Xi'an which is recharged by precipitation from the Qinling Mountains in the southern side of the basin and the recharge of Xianyang geothermal field from both sides of the Guanzhong Basin [4]. The identification of the ^{81}Kr ages reveals the basin-scale groundwater flow regime in a Cenozoic rift basin.

3.2 Water-rock interaction

The geothermal waters with a water type of Cl-Na show slightly alkaline pH values (8.0 – 8.2). The total dissolved solids (TDS) in the geothermal waters range from 420 mg/L to 5033 mg/L. Water with low TDS is mainly composed of HCO_3^- and Ca^{2+} , Mg^{2+} , water with high TDS is mainly composed by Cl^- and Na^+ ; water with medium TDS is mainly composed of SO_4^{2-} and Na^+ , Ca^{2+} . The anion composition of geothermal water increases with TDS values and becomes Cl^- predominant which resulted that the geothermal water tend to be more mature. The reservoir temperature is calculated to be around 130 °C based on cationic geothermometers and FixAl method [4]. It is interesting to find out that strong water-rock interaction process is taking place in the formation, creating a strong positive oxygen isotope shift up to 10 ‰ (Fig. 2), a phenomenon that is rarely seen in a relatively

low temperature environment [5]. This phenomenon could be due to the fact that ^{18}O exchange between the geothermal waters and the carbonates extensively in a period as long as one million years.

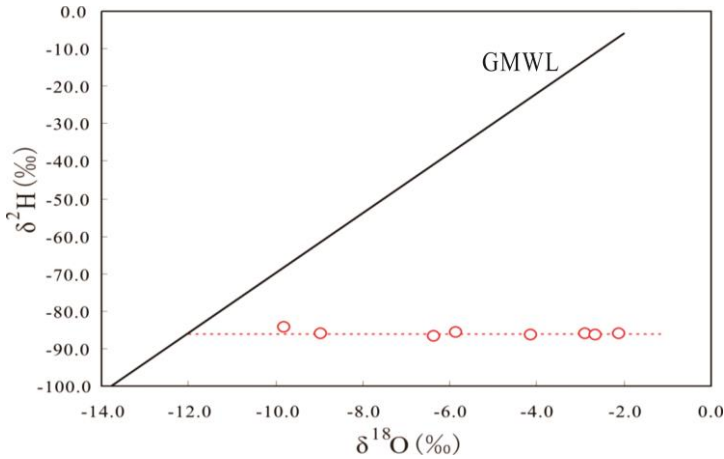


Fig. 2. A plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ showing a strong ^{18}O shift in the low-medium temperature geothermal system, indicating a relatively long time water-rock interaction (adopted from Qin et al., 2005).

3.3 Geothermal resources

Groundwater circulation is a process of transporting heat and dissolved gases. As shown in Figure 3, the wellhead temperature increases with the growing geothermal water age, implying heat accumulation during the long distance groundwater circulation underground. It is notable that the volume percentage of He in non-condensable gases accounts for more than 2 %, thus recognized as an exploitable He resource. The $^4\text{He}/^{20}\text{Ne}$ ratios and R/Ra values (Fig. 4a) indicate that He in groundwater samples is predominantly of crustal origin, mainly derived from radiogenic production by alpha decay of U-Th series elements, with negligible atmospheric contribution. A good fit between ^{81}Kr ages and ^4He percentages was obtained except for Well 7 (Fig. 4b). It is apparent that the old groundwater not only brings heat deep within the Earth to the surface, but also accumulated He.

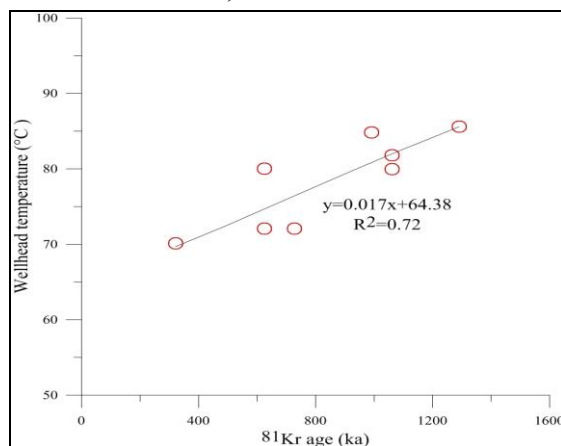


Fig. 3. A plot of wellhead temperature versus ^{81}Kr ages.

4 Conclusions

Groundwater ages of up to 1.3 Ma along both a North-South and a West-East cross section offer strong evidence on the recharge history and circulation dynamics of groundwater. Groundwater in Neogene formation at depth between the 2500 to 3000 m in the Guanzhong Basin has been replenished at a million-year time scale. This is in good agreement with a strong ^{18}O shift in this low-medium temperature geothermal system, which also indicates a relatively long time for water-rock interaction. The slow release of heat and helium and other gases ensured by low permeability cover has helped to keep them in place in this sedimentary basin that is formed by Cenozoic rifting bringing constant supply of heat and He gas.

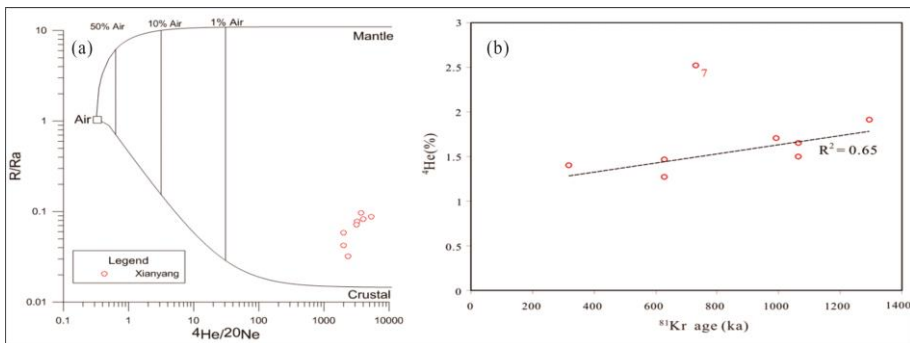


Fig. 4. (a) $^4\text{He}/^{20}\text{Ne}$ versus R/Ra ; (b) A good fit between ^{81}Kr ages and ^4He percentages except for Well 7.

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