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Short Communication

Million-year-old groundwater revealed by krypton-81 dating in Guanzhong Basin, China

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Groundwater age, defined as the mean subsurface residence time spent isolated from the atmosphere, is of crucial significance for managing water resources and industrial waste. It is also very useful for understanding subsurface contaminant transport, and for paleoclimate reconstruction. It is an important parameter for characterizing aquifer hydrogeology including aquifer storage capacity, the rate of groundwater renewal, and flow velocity. Environmental tracers that are sensitive to residence time have proven to be effective tools for estimating groundwater age. Short-lived radioisotopes such as ^{3}H, ^{85}Kr, and ^{3}H/^{3}He can indicate modern recharge, whereas those with long half-lives such as ^{14}C, ^{36}Cl, ^{4}He, and ^{81}Kr can be used to date old groundwater. With the advance of deep geological engineering such as nuclear waste disposal, carbon sequestration, and geothermal exploitation, dating of old groundwater has become increasingly important. The most routinely applied dating method by far is ^{14}C. However, because its half-life is 5730 years, the radiocarbon timescale is limited to less than 40 ka. Attempts with other isotope methods for dating older groundwater are under way. Chlorine-36, with a half-life of 301,000 ± 4000 years, is a potential tool that extends beyond the limits of radiocarbon. However, the ^{36}Cl method is complicated by variations of the initial ^{36}Cl activity and subsurface input of both stable chloride and nucleogenic ^{36}Cl. The ingrowth of helium (^{4}He) from radioactive decay in crustal waters offers a qualitative measure of time that significantly overlaps with ^{36}Cl. The ^{4}He age is influenced by factors such as atmospheric helium inputs gained during recharge and those from diffusion of He into the aquifer from other strata.

The ^{81}Kr tracer, with an atmospheric ^{81}Kr/Kr ratio of $(5.2 \pm 0.4) \times 10^{-13}$, is produced in the upper atmosphere by cosmic rays. It has a long residence time with a half-life of 229 ± 11 ka and a spatially homogeneous distribution in the atmosphere, making it an ideal tracer in its dating range. A pioneering attempt to use ^{81}Kr for groundwater dating was made with resonance ionization mass spectrometry (RIMS) through two steps of isotope enrichment from 10,000 L of water from the Milk River aquifer, Canada [1]. Accelerator mass-spectrometry (AMS) measurement of ^{81}Kr at a cyclotron facility were also conducted after extraction of Kr from groundwater samples of 16,000 L from the Great Artesian Basin, Australia [2]. Although both methods were successful in ^{81}Kr measurement, the huge amount of groundwater required during sampling and the low efficiency of the analytical process make it difficult to use them routinely in groundwater dating.

The Atom Trap Trace Analysis (ATTA) technique [3], due to its requirement for smaller sample size and relatively ease of operation, has enabled ^{81}Kr measurements for large-scale studies. Samples from Nubian Aquifer, Egypt; Guarani Aquifer, Brazil; the Waste Isolation Pilot Plant (WIPP), New Mexico; and Cambrian and Devonian aquifers, Baltic Artesian Basin have been measured for ^{81}Kr [4] so far using the ATTA technique. Although several studies have been attempted to use ^{81}Kr dating for groundwater studies in China, none of them has been published. Furthermore, international studies have mainly focused on aquifers at the depth of less than 2000 m. In this study we try to take a look at deeper aquifers in China. Guanzhong Basin has offered such a possibility.

Guanzhong Basin in the middle reaches of the Yellow River, in northwestern China accommodates a thick cover of Cenozoic sediments greater than 5000 m (Fig. 1). During development of geothermal resources in the basin, a lot of deep wells down to 4000 m have been drilled and many of them are in operation, offering a good opportunity for sample collection. Our previous studies in the basin show that, most of the thermal water samples in this area are low in ^{14}C activity [5], and close to the dating limit of ^{14}C

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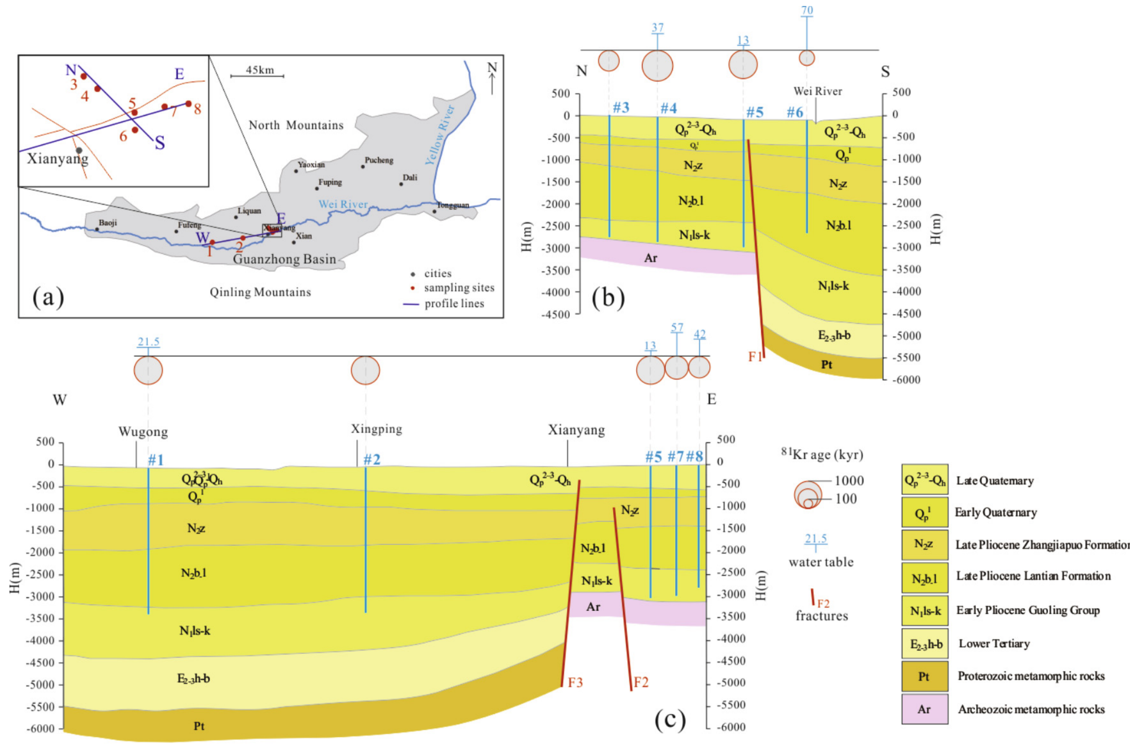

Fig. 1. Guanzhong basin with sampling sites (a) and two schematic cross sections: east–west (b) and south-north (c). The size of the spheres denotes corresponding ^{81}Kr ages; the numbers above the spheres refer to the water table in the sampled well.

method. A recent study using ^{36}Cl method reveals a residence time of a few hundred thousand years up to one million years for the Tertiary aquifer [6], making it possible to compare the ^{81}Kr and the ^{36}Cl methods.

For ^{81}Kr sampling of the environmental 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. Because this membrane contactor cannot sustain high temperatures of >40 °C, a cooling coil wrapped with flowing tap water and ice was equipped to cool the geothermal water (typically, 70 °C) before being transferred into the membrane contactor. In this first successful attempt to perform ^{81}Kr sampling in geothermal systems in China, eight gas samples were extracted from 100 to 160 L each of geothermal water in the winter of 2015. Moreover, samples from the same degassing system were collected for bulk gas analyses using 50 mL Pb glass bottles under water. Once the extracted gas filled approximately two-thirds of the glass bottle volume, the bottle was sealed with a rubber cap and was then encapsulated into a 500 mL polyethylene bottle filled with the geothermal water being sampled. The same geothermal water were also sampled for chemical and isotopic analyses.

The gas was processed and purified in the laboratory to produce pure krypton (purity 50%) for analysis. Krypton was extracted from the bulk gas at the USTC Laser Laboratory for Trace Analysis and Precision Measurements (http://atta.ustc.edu.cn) by cryogenic distillation and gas chromatography. ^{81}Kr/^{83}Kr and ^{85}Kr/^{83}Kr isotopic ratios were also determined at USTC using the ATTA. The bulk gas compositions were analyzed by using a gas mass spectrometer (MAT271) at the Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences in Lanzhou, China. ^{3}He/^{4}He and ^{4}He/^{20}Ne ratios were measured in the same laboratory with a Noblesse noble gas mass spectrometer (Nu Instruments, UK). Two ^{14}C samples were collected in 2014, and were measured by Beta Analytic Inc. (Florida, USA) with AMS.

The low concentrations of O_2 at <1.5% in the eight extracted gas samples indicate negligible contamination by air during and after sampling. However, we detected ^{85}Kr activity in the sample from Well 3 with a value of 12.2 ± 0.9 dpm/cc, which should be undetectable in deep geothermal water due to relatively short ^{85}Kr half-life of ~10.8 years. The high ^{85}Kr activity was finally confirmed to be introduced in the measuring process. For quality control in the analysis of environmental samples, ATTA is always calibrated with a standard modern atmospheric Kr sample after the analysis of a group of four or five environmental samples. The isotopic ratio of the standard gas was determined just prior to that of sample 3; the residual gas in the pipelines of ATTA introduced modern atmospheric Kr into the sample. The detection of residual gases in the pipelines of ATTA was thus added to the measurement procedure. The extent of possible modern atmospheric Kr contamination was assessed from the measured activities of ^{85}Kr in our samples. The isotopic abundance of ^{85}Kr in the standard gases at the time of measurement was 42.1 ± 0.6 dpm/cc. The fraction of standard Kr mixed into the groundwater can be estimated as:

$$f = \frac{12.2 \pm 0.9}{42.1 \pm 0.6} = 0.290 \pm 0.021.$$

Because the standard gases had the ^{81}Kr isotopic abundance of modern atmospheric air, the corrected ^{81}Kr abundance of $^{81}R_{gw}$ in sample 3 was obtained from the measured value (0.4 ± 0.04) as follows:

$$\begin{aligned} 0.4 \pm 0.04 &= f\,^{81}R_{st} + (1-f)\,^{81}R_{gw} \\ &= 0.290 \pm 0.021 + (0.710 \pm 0.021) \times {}^{81}R_{gw}. \end{aligned}$$

Therefore

$^{81}R_{gw} = 0.15 \pm 0.06.$

According to the exponential decay law, the time elapsed since the water was in contact with the atmosphere can be calculated as:

$$t_{^{81}Kr} = -\frac{1}{\lambda_{81}} \ln\left(\frac{^{81}Kr/Kr_{gw}}{^{81}Kr/Kr_{air}}\right), \quad (1)$$

where λ_{81} is the ^{81}Kr decay constant (3.03×10^{-6} a^{-1}), and $^{81}Kr/Kr_{gw}$ and $^{81}Kr/Kr_{air}$ are the ^{81}Kr/Kr ratios of the sample and modern air, respectively. The calculation yields ^{81}Kr model ages between 0.3 and 1.3 Ma.

In order to assess our ^{81}Kr ages, multiple methods including ^{14}C, ^{4}He, and ^{36}Cl were compared with ^{81}Kr in groundwater from Xianyang geothermal field (Data can be found in supplementary materials).

The ^{14}C dating range for groundwater is limited to about 40,000 years, which does not overlap with the effective dating range of ^{81}Kr. The decay of ^{81}Kr is still small when ^{14}C has decayed beyond the limit of practical application. However, the samples with relatively lower ^{81}Kr/Kr ratios should have ^{14}C activity close to zero. The ^{14}C activities of Wells 4 and 6 are 5.2 pmc and 3.0 pmc, respectively, which indicates that the ^{14}C models cannot yield useful groundwater ages for these deep wells.

The accumulation of ^{4}He along a groundwater flow path has long been explored and evaluated as a groundwater dating tool. Multiple He sources are likely in groundwater systems, including atmospheric source, *in situ* radiogenic production from alpha decay of U–Th series elements; and crustal and mantle fluxes. The ^{4}Ne/^{20}He and R/Ra values (Figure S1) indicate that helium in our eight groundwater samples originated chiefly from the crust, with negligible atmospheric contribution. Therefore, the atmospheric and mantle inputs to the total ^{4}He concentrations were neglected in this study. A good fit between ^{81}Kr ages and ^{4}He percentages was obtained except for Well 7. This outlier, with a higher ^{4}He percentage, may have been affected by additional He sources. It should be noted that ^{4}He percentages (%) but not ^{4}He concentrations (cm^{3} STP/g) were used in this study. Moreover, we could not differentiate the ^{4}He accumulation by *in situ* radioactive decay and the crustal flux under the present data and then obtain absolute ^{4}He ages. Fortunately, studies have shown that ^{4}He ages calculated with models under *in situ* ^{4}He production and stable crustal fluxes have the same increasing trend [7].

^{36}Cl, which has been used to study groundwater movement over time scales of several hundred thousand years, is one of age tracers that significantly overlaps ^{81}Kr. Chloride is conservative in the subsurface, and ^{36}Cl is rarely retarded with respect to the water velocity by adsorption or geochemical reactions. Therefore, the groundwater age can be estimated by using the radiometric decay equation and the decrease in ^{36}Cl from the amount in the recharge water. The ^{36}Cl age calculation is expressed as:

$$t_{^{36}Cl} = -\frac{1}{\lambda_{36}} \ln\left(\frac{^{36}Cl/Cl_{meas} - {}^{36}Cl/Cl_{se}}{^{36}Cl/Cl_{0} - {}^{36}Cl/Cl_{se}}\right), \quad (2)$$

where λ_{36} is the ^{36}Cl decay constant (2.3×10^{-6} a^{-1}), and $^{36}Cl/Cl_{meas}$, $^{36}Cl/Cl_{se}$, and $^{36}Cl/Cl_{0}$ are the measured ratio, the secular equilibrium ratio, and the recharge ratio, respectively.

Therefore, if ^{36}Cl and ^{81}Kr dating methods are consistent, ^{36}Cl/Cl should fall along a trend determined by the following equation:

$$^{36}Cl/Cl_{meas} = ({}^{36}Cl/Cl_{0} - {}^{36}Cl/Cl_{se}) \exp(-\lambda_{36} t_{^{81}Kr}) + {}^{36}Cl/Cl_{se}. \quad (3)$$

The measured ^{36}Cl/Cl ratios of samples 4 and 6 have been fitted to Eq. (3) with $^{36}Cl/Cl_{0} = 199 \times 10^{-15}$ and $^{36}Cl/Cl_{se} = 8.1 \times 10^{-15}$. The $^{36}Cl/Cl_{0}$ result is comparable to the calculation of Ma et al. [6], which was estimated to be about 190×10^{-15}. However, our $^{36}Cl/Cl_{se}$ value has a larger magnitude than that of Ma et al. [6] (=9.5×10^{-16}). Our value is more similar to the calculated result obtained in the Nubian sandstone aquifer of Egypt [8] with a value of 8×10^{-15}. Generally, our ^{81}Kr ages are within the same order of magnitude as ^{36}Cl ages.

Our ^{81}Kr ages between 0.3 and 1.3 Ma results indicate good consistency with multiple methods including ^{14}C, ^{4}He, and ^{36}Cl above. According to samples 1, 2, 4 and 5, the oldest ^{81}Kr age was identified to occur in the center 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 (Fig. 1). Moreover, these samples sites are located on the north side of the Weibei fault (F1 in Fig. 1(b)). This groundwater retention area is also in good agreement 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 the Qinling Mountains to the south and the North Mountains to the north. 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 [5] and the recharge of Xianyang geothermal field from both sides of the Guanzhong Basin [9].

The identification of the ^{81}Kr ages reveals the basin-scale groundwater flow regime in a Cenozoic rift basin. Similarly, lower ^{14}C activities of <5.0 pmc are also found in other groundwater systems in China, and older groundwater may also be identified in these systems as long as the ^{81}Kr dating technique is used. Different from the shallow groundwater in the quaternary aquifers, the older ages of deep groundwater generally imply longer groundwater residence time and weak renewal ability. This residence time could be used to calibrate numerical groundwater flow models and to support research on groundwater/geothermal system dynamics.

It should be also highlighted that the identified ^{81}Kr groundwater age between 0.3 and 1.3 Ma may potentially bring us to the dawn of revealing the paleo-climate at a scale of million years. Current climatic information derived from the groundwater archives is restricted to approximately 35,000 years due to limitations of the ^{14}C dating method. The record preserved in stalagmites has shown approximately 640,000 years of changes [10], which covers the full U–Th dating range. In this case, paleoclimate reconstruction based on the stable isotopes of groundwater can be traced back to an older epoch on the order of million years. The climate in a larger time scale may be reconstructed on the one hand, and the dissolved noble gases themselves in water work as a good absolute palaeothermometer on the other. It could yield noble gas temperatures, and help to better understand climate history.

In light of the million-year-old groundwater found, several interesting hydrological questions could be proposed, including but not limited to: (1) what is the hydro-geochemical characteristics of the old groundwater? (2) How does the old groundwater interact with the surrounding rocks through the geologic history? (3) What is their hydrological flow path? (4) How can we extract the information from the old groundwater to provide insights into paleo-environment? Along with these questions, we believe the finding of old groundwater in China will provide new possibilities for both of hydrogeological and climate change studies.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.scib.2017.08.009.

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