Review Article

Krypton 81: A New Method of Paleogroundwater Dating

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Abstract: Recently, because of $^{81}$Kr’s advantages of steady chemical property, long half-life and no extra source in the movement of groundwater, it is becoming an effective method to date old groundwater (age from 10$^5$-10$^6$ year). This paper summarizes the principles of $^{81}$Kr in groundwater dating and extraction method, presents the application of $^{81}$Kr in groundwater dating and discusses the problems of recent related researches, makes prospects of studies of radionuclide in hydrogeology chemistry, and provide scientific support for the measurement of $^{81}$Kr and the researches of old groundwater dating.

Keywords: $^{81}$Kr, Groundwater Dating, Radionuclide, Hydrogeology

1. Introduction

To study the origin, recharge and discharge of groundwater and to quantify the characteristics of groundwater transport, groundwater age dating is an important step. Recently, a large number of radioactive isotopes are used in groundwater dating studies [1]. For example, $^3$H, $^{85}$Kr and $^4$He/$^3$H can be used to measure the age of young groundwater (about 50 years); $^{39}$Ar is used to measure the age of groundwater from 50 to 1000 years. The method of using $^{39}$Ar as isotope tracer to determine the age of groundwater makes up for the blank stage between the range determined by $^3$H/$^3$He (< 50 years) and $^{85}$Kr (>1000 years) [2]. $^{14}$C is used to measure the age of groundwater between 1,000 and 40,000 years old. Although the $^{14}$C dating method is not absolutely accurate, it is an important method in solid phase or mesoscale measurement [3]. It is also very effective to use $^4$He for groundwater dating, whose accumulation can be calculated by the amount of U decay [4]. However, there are few isotopes that can be used to measure the age of extremely old groundwater [5]. Although $^{36}$Cl(half-life 3.01×10$^5$ years) and $^{266}$Hf(half-life 1.7×10$^7$ years) are two possible ways to analyze the age of old groundwater, they have complex chemical mechanisms in the process of groundwater movement, which makes the analysis more difficult and the age estimation results inaccurate. With the development of isotopic research and optimization of testing equipment domestic and abroad, as a radioactive nuclide of inert gas, $^{81}$Kr, with its very long half-life ((2.29±0.11)×10$^5$ years) and stable chemical properties, has become a possibility to measure the ancient groundwater (10$^5$-10$^6$ years).

In 1969, Loosli and Oeschger found $^{81}$Kr in atmosphere, making it an ideal tracer for the measurement of groundwater and glacier ages at the scale of 10$^5$ to 10$^6$ years [6]. Low Radiation Counting Technology (LLC) became the first method to measure the content of $^{81}$Kr [7, 8], but this method was subsequently phased out due to its slow speed and low efficiency. In 1997, Accelerator Mass Spectrometry (AMS) technology was developed [9], and it was successfully applied to the analysis and detection of $^{81}$Kr groundwater samples in the Great Artesian Basin region of Australia [10, 11]. In 1999, Atomic Trap Trace Analysis technology (ATTA-1) was developed, which is an atomic counting method based on laser technology to cool, trap and count atoms [12, 13]. In 2004, Sturchio et al. [14] applied the second-generation device (ATTA-2) to measure the age of $^{81}$Kr in deep groundwater in the desert of Nubian region in Egypt, which required several tons of groundwater samples, so it could not be widely popularized. As ATTA technology improved and developed, its efficiency and accuracy improved. In 2012, Jiang [15] et
al. developed a third-generation device (ATTA-3), which required only 6-8µL of krypton samples to measure, which means about 100-200L groundwater samples or approximately 2L extracted dissolved gas. ATTA-3 is currently the most advanced measurement tool with noble gas as tracer, which has been widely used in recent related researches [15]. It has been successfully applied in many areas and has become a definitely effective method for the measurement of krypton content. While the use of $^{81}$Kr for groundwater dating are relatively mature in some regions, such as the Great Artesian Basin in Australia, New Mexico, the Baltic sea artesian basin, etc., few studies are carried out in the most research field in the world, and the use of $^{81}$Kr for groundwater studies is just the start. Different conditions are required for age measurement by $^{81}$Kr and other methods under different circumstances. For example, some studies classify $^{85}$Kr from different sources, and then determine their content, leading to research results in different directions. For example, J. C. Zappala et al. limited the human’s contribution to $^{81}$Kr in the atmosphere by 2.5% [16]. The isotope $^{81}$Kr can be used as an ideal tracer for measuring young surface water [17]. In this paper, by searching relevant literatures on the application of $^{81}$Kr in groundwater dating, summarizing the principle of groundwater dating by using $^{81}$Kr, the measurement method of $^{81}$Kr and its practical application , providing ideas and research guidance for the application of $^{81}$Kr in the measurement of ancient groundwater age.

2. The Principle of $^{81}$Kr Dating

The method of measuring the age of groundwater by krypton radioisotope [18] needs to satisfy three conditions: (1) Groundwater and atmosphere are fully balanced in the recharge area; (2) The studied area is completely a closed system, and there is no groundwater mixing in different paths; (3) There is no krypton isotope diffusion exchange between groundwater aquifers and adjacent anhydrous aquifers during groundwater movement. If these conditions are met, groundwater age can be estimated by using the $^{81}$Kr decay equation, as shown in formula (1) and formula (2):

$$81\text{RS} = e^{-\frac{t}{\tau}}$$

$$t = -\tau \cdot ln^{81\text{RS}}$$

$^{81}$RS is the ratio of $^{81}$Kr abundance ratio of dissolved gas in groundwater to atmosphere; $\tau$ is the $^{81}$Kr decay constant; $t$ is groundwater age [Error! Bookmark not defined.]. When the ATTA measurement error of $^{81}$Kr is $\delta^{81}$RS, the age error of groundwater sample is shown in formula (3):

$$\delta t = -\tau \cdot \frac{\delta^{81}\text{RS}}{^{81}\text{RS} \cdot ln^{85\text{RS}}} \cdot t$$

3. $^{81}$Kr Measuring Technology

The amount of $^{81}$Kr in the atmosphere is constantly changing with months and years. For example, Andreas Bollhfer et al. have shown that $^{81}$Kr in Europe has changed over the past 50 years, and have suggested that its data can be used as a parameter for groundwater dating [19]. Inert gases are distributed uniformly and stably in the atmosphere [20-21]. The abundance of krypton in the atmosphere is (1.14±0.01) PPM [22], krypton has six stable isotopes ($^{80}$Kr, $^{82}$Kr, $^{83}$Kr, $^{84}$Kr, $^{85}$Kr, $^{86}$Kr) and two extremely low abundance radioisotopes ($^{81}$Kr, $^{85}$Kr). $^{81}$Kr is generated by the interaction between cosmic rays and atomic nuclei [23], with a half-life of (2.29±0.11)×10$^5$ years and abundance of 6×10$^-5$ [9, 23, 24]. The $^{81}$Kr generated by solar activity, human nuclear industry, nuclide spontaneous and neutron-induced fission is negligible [9, 13, 25-26]. As an inert gas, krypton is extremely stable in physical and chemical properties, and its mixed transport in groundwater is extremely simple, so it can be used to measure the age of ancient groundwater and old polar glaciers (10^5-10^6 years) [11, 27-28].

However, because of the extremely low content of $^{81}$Kr in groundwater, it is more difficult to use $^{81}$Kr in old groundwater dating. $^{81}$Kr extraction and purification experiments become the most important and difficult part of paleogroundwater dating. The $^{81}$Kr trap capture rate is extremely low, the amount of trapped atom $^{81}$Kr is small and its trap lifetime is long enough. W. Jiang et al. used a fluorescence signal way to analysis and counted the rare $^{81}$Kr isotope, and successfully counted the $^{81}$Kr abundance. They also used a control isotope $^{85}$Kr to assist their experiment [15]. Generally, to correctly measure the age of groundwater samples, three steps are required: (1) the extraction of dissolved gas from groundwater, (2) the isolation and purification of krypton from dissolved gas, (3) and the measurement of krypton radioactive isotopes. The sample size of $^{81}$Kr required for ATTA measurement is 6-8µL, which means about 100-200L groundwater samples, also means 2L dissolved gas should be extracted. In order to prevent the shortage of krypton samples caused by the diversification of dissolved gas components in water (such as rich of CH$_4$ or CO$_2$), the gas intake in the field is usually about 5L [29].

3.1. Extract Dissolved Gas from Groundwater

According to Henry's law, the solubility of gas in water is positively related to the equilibrium partial pressure of gas under isothermal and isobaric conditions. Therefore, in an environment with extremely low partial gas pressure, the ambient dissolved gas in the saturated dissolved sample will escape, and reach the equilibrium in the environment with lower partial gas pressure, so that the ambient dissolved gas can be extracted. Currently, there are two main methods for field groundwater dissolved gas separation: vacuum atomization method and degassing film method [33]. The idea is to increase the gas-liquid contact area to allow dissolved gas to escape. How these two methods work is shown in figure 1.
Because the collection of samples has a big influence to the measuring results in groundwater dating, and the amount of sample in groundwater dating by krypton 81 is larger than using other isotopes, the collection work should be very careful in the field. Considering the actual field condition, there are four requirements in the extraction of dissolved gas from groundwater in field:

1. Before collecting the samples, there should be a simple air tight test, to make sure that the total gas leakage rate in the system is less than 1%;
2. The time of collection should be controlled in 2 hours, and the devices should be effective, with 30L/min of samples generally;
3. Extracting gas should be efficient to reduce the influence of isotope fractionation;
4. When collecting samples, the local water temperature, water pressure, pH, depth, gas pressure and the amount of samples should be recorded.

### 3.2. Inert Gas Separation and Purification

Krypton has a volume fraction of 1.14 ppm in the air, and even more in groundwater and polar glaciers, at about 3 ppm, so it needs about 10L of air or 3-5L of dissolved gas from environmental samples to purify 10µL of krypton gas. Inert gas separation and purification are usually carried out by means of low-temperature distillation and enrichment, gas chromatography separation, physical or chemical adsorption and purification, and generally by a combination of these two or three methods.

The design ideas of krypton separation and purification system is: first, activated carbon adsorpts at low temperature to remove N₂, O₂ and other components, and krypton enriches 100 times; After that, non-inert gas components (N₂, O₂, CH₄, etc.) in residual gas are removed by high temperature sponge iron furnace. Finally, Kr and Ar are separated by gas chromatograph, and Kr is extracted from Ar. The flow chart of krypton separation and purification system is shown in figure 2 [33]:

The product from these two steps (the extraction of dissolved gas and the purification of krypton) is then used to measure the content of ⁸¹Kr by ATTA, and finally the decay equation is used to estimate the age of groundwater.

### 3.3. Analytical Instruments and Techniques

The core component of ATTA technology, which is based on laser technology to cool, trap and count atoms, is 3D magneto-optical trap (3D MOT), which captures atoms of different isotopes by changing the frequency of laser in the trap. Recently, Sapam Ranjita Chanu studied the cooling technology of transferring atoms from 3D magneto-optical trap [1]. Differs from the low radiation counting technology (LLC) isotope of radiation energy resolution and accelerator mass spectrometry (AMS) of isotope with the requirements of resolution of isotopes and isobars charge-mass ratio, the capture of ATTA technology only relates to the atomic transition frequency, thus it has a high selectivity, and is not influenced by any non-target atoms or molecules such as similar decay energy elements, isotope, isobars. Prior to the mature development of ATTA technology, accelerator mass spectrometry (AMS) was very inefficient in detecting krypton, requiring several hundred microliters of krypton samples and several tons of groundwater samples, which was extremely difficult to operate. As the sample size and isotope abundance decrease, the relative error of ATTA-3 technique increases. In order to make ATTA measurement error less than 10%, 6-8 microliters of pure krypton samples is required, which means 100-200L groundwater samples. The development of ATTA technology makes it possible to date groundwater by using inert gases.
4. The Application of $^{81}\text{Kr}$ in Groundwater Dating

$^{81}\text{Kr}$ can be used to estimate the age of old groundwater in deep aquifers (up to 5000m deep) and as a temperature indicator of the palaeoclimate. As a reference isotope, $^{81}\text{Kr}$ also has many applications. Compared with $^{14}\text{C}$ whose results are usually very accurate, $^{81}\text{Kr}$ can be used to date the age in its time range ($10^{5}$-$10^{6}$ years), as the verification of the results of $^{4}\text{He}$ [2]. The University of Science and Technology of China, the institute of hydrogeology and environmental geology, Chinese academy of geological sciences, and the International Atomic Energy Agency (IAEA) cooperated and collected seven deep groundwater samples from the west to the east region in the North China Plain and used the vacuum extraction and the membrane to extract the dissolved gas, and successfully separated and purified the krypton and measured. The results show that the groundwater is getting older from west to east in the North China Plain, and the most ancient groundwater is aged from 0.85 to 1.15 Ma. In Guanzhong Basin by applying the method of degassing membrane extraction from eight groundwater water samples (each sample 100L to 160L) and the separation and purification of krypton, as well as the atomic trap trace analysis technique (ATTA), Pang Zhonghe [3] measured the content of $^{81}\text{Kr}$ and estimated the age of groundwater in Guanzhong basin in the depth of 5000m, and compared the results with $^{14}\text{C}$, $^{4}\text{He}$ and $^{36}\text{Cl}$, indicating that the estimated age of groundwater by $^{81}\text{Kr}$ is basically consistent with other methods. He also illustrated that the age characteristics of groundwater estimated by $^{81}\text{Kr}$ can reveal the rules of groundwater movement in Cenozoic rift basin, and to some extent, it can reflect the temperature of paleoclimate on the scale of millions of years. Matsumoto [35] dated groundwater in the North China Plain (NCP) in combination with $^{81}\text{Kr}$ and $^{4}\text{He}$: In coastal areas, the age scale of groundwater samples measured by $^{81}\text{Kr}$ is between 0.5 and 1Ma years [36], $^{4}\text{He}$ in the underground water samples in the central and coastal areas of the North China Plain comes from the atmosphere, continental crust and mantle pool, which reflects the active tectonic activities in the continental crust of the North China Plain. The ages of $^{4}\text{He}$ and $^{81}\text{Kr}$ measured in the crust can be used to assess the patterns of $^{4}\text{He}$ inflowing into the aquifer and its vertical diffusivity in the aquifer. In addition, the age measured by $^{4}\text{He}$ is consistent with that of $^{81}\text{Kr}$, which proves the feasibility of the dating method of $^{81}\text{Kr}$. Therefore, $^{4}\text{He}$ can be used as a verification approach to assist $^{81}\text{Kr}$ dating.

$^{81}\text{Kr}$ was used to study the groundwater flow process and chemical solute transport rules, and $^{81}\text{Kr}$ concentration was measured from groundwater samples from two local monitoring Wells in Sturchio at the nuclear waste treatment plant (WIPP) in New Mexico, and the results were compared with the reverse hydrogeochemical simulation results [4]. $^{81}\text{Kr}$ can be used as a method to measure the age of old groundwater in aquifers, but the diffusion and exchange with surrounding aquifers complicate the estimation. If enough information about the hydrogeochemical interaction of groundwater with the surrounding aquifer, as well as other isotope results (such as $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, $\delta^{36}\text{Cl}$, etc.) as the complement and validation, the $^{81}\text{Kr}$ can be used as an effective way of the movement law of groundwater simulation and age. Gerber [5] analyzed the content of $^{81}\text{Kr}$ and inert gas to study the groundwater age in the deep aquifer of the Baltic Sea Artesian Basin (BAB) and revealed the groundwater flow pattern at the scale of millions of years. Analysis shows that the groundwater flow system consists of three parts: Holocene and Pleistocene interglacial precipitation, glacial meltwater, and ancient high-salinity salt water. Interglacial precipitation and glacial meltwater are based on the time scale of hundreds of thousands of years, while $^{4}\text{He}$ and $^{36}\text{Ar}$, as qualitative supporting evidence of $^{81}\text{Kr}$ results, prove that the residence time of high-salinity salt water components exceeds 1-5Ma years, and the high-salinity salt water components come from the evaporation enrichment of prequaternary seawater. In addition, isotope measurements of inert gas and stable environment isotopes can reveal the replenishment mechanism of glacier.

5. Conclusion and Recommendation

Atomic Trap Trace Analysis technology (ATTA) has experienced through the development of the first, second and third generations. For now, the measurement demand for krypton samples is 6-8µL, corresponding to the collection of groundwater samples of about 100-200L and the extraction of dissolved gas of about 2L. Although it is better than the previous equipment method, in fact, the collection amount of 100-200L deep aquifer groundwater in the field is still very large. The research and improvement of test equipment and measurement technology still need to be continued, so as to the improvement of work efficiency and the reduction of work difficulty.

$^{81}\text{Kr}$ for dating ancient deep aquifer groundwater aged from $10^5$ to $10^6$ is an effective way, but due to the errors in measuring instruments, improper operation result error such as the dissolved gas leakage, and the spread and exchange of krypton with weak permeable layer or aquiclude layer, the incalculable complex hydrogeochemical evolutions. $^{81}\text{Kr}$ cannot be the only way to date the ancient underground water. Other methods (such as $^{4}\text{He}$, $^{36}\text{Cl}$, reverse hydrogeochemical simulation, etc.) should be used as reference and validation when using $^{81}\text{Kr}$ to measure the groundwater age, and also the specific hydrogeochemical conditions should be considered and combined, to comprehensively and scientifically analyze the age and movement rules of local groundwater. The latest progress in $^{81}\text{Kr}$ dating is Aeschbachhertig W. et al. which has been used to measure very old groundwater [6]. Aggarwal et al. used $^{81}\text{Kr}$ as a constraint factor and $^{4}\text{He}$ as a combination to measure the age of paleogroundwater [7].

Besides ancient groundwater, $^{81}\text{Kr}$ dating samples can also be seawater, polar glaciers, etc. In addition to dating, it can also be used to study groundwater movement process and explore geological tectonic activities. It is also a prospect of...
81Kr in hydrogeology and paleoclimatology to be used as a temperature indicator to reconstruct paleoclimate characteristics, and combine meteorology and atmospheric dynamics to simulate climate change since ancient times. In addition, using 81Kr to study the age, origin, characteristics of recharge and discharge, and movement rules of groundwater can provide certain scientific basis for nuclear waste treatment and underground pollution in nuclear science and radiochemistry.

In summary, combined with the above prospects, this paper will serve as a suggestion guidance to provide a scientific basis for the measurement of 81Kr in the study of paleogroundwater dating.

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References

[1] P. G. Cook and A. L. Herczeg (Eds.), Environmental Tracers in Subsurface Hydrology, Kluwer Academic Publishers, Boston, MA, 2000, 529 pp.

[2] Mace E. Purification and Detection of 39Ar in Groundwater Samples via Low-Level Counting [C]/ AGU Fall Meeting. AGU Fall Meeting Abstracts, 2015.

[3] Hasegawa T, Nakata K, Tomioka Y, et al. Cross-checking groundwater age by 4He and 13C dating in a granite, Tono area, central Japan [J]. Geochimica et Cosmochimica Acta, 2016, 192: 166-185.

[4] Wen Wei, Werner Aeschbach-Hertig, Zongyu Chen. Identification of He sources and estimation of He ages in groundwater of the North China Plain [J]. Applied Geochemistry, 2015, 63.

[5] Collon P, Kutschera W, Loosli H H, et al. 81 Kr in the Great Artesian Basin, Australia: a new method for dating very old groundwater [J]. Earth & Planetary Science Letters, 2000, 182 (1): 103-113.

[6] Loosli H. H. and Oeschger H. (1969) 37Ar and 81Kr in the atmosphere. Earth Planet. Sci. Lett. 7, 67–71.

[7] Loosli H. H. and Purschert R. (2005) Rare gases. In Isotopes in the Water Cycle: Past, Present and Future of a Developing Science (eds. P. Aggarwal, J. R. Gat and K. Froehlich). IAEA, Vienna, pp. 91–95.

[8] Momoshima N., Inoue F., Sugihara S., Shimada J. and Taniguchi M. (2010) An improved method for 85Kr analysis by liquid scintillation counting. J. Environ. Radi. 101, 615–621.

[9] Collon P, Antaya T, Davids B, Fauerbach M, Harkewicz R, Hellstrom M, Kutschera W, Morrissey D, Pardo.

[10] Collon P, Kutschera W, Loosli H H, Lehmann B E, Purschert R, Love A, Sampson L, Anthony D, Cole D, Davids B, Morrissey D J, Sherrill B M, Steiner M, Pardo R C and Paul M. (2000) 81Kr in the Great Artesian Basin. Earth Planet. Sci. Lett. 182, 103–113.

[11] Lehmann B. E., Love A., Purschert R., Collon P, Loosli H., Kutschera W, Beyerle U., Aeschbach Hertig W, Kipfer R., Frape S. K., Herczeg A. L., Moran J., Tolstikhin I. andGroening M. (2003) A comparison of groundwater dating with 81Kr, 36Cl and 3He in 4 wells of the Great Artesian Basin, Australia. Earth Planet. Sci. Lett. 212, 237–250.

[12] Chen C.-Y., Li Y. M., Bailey K., O’Connor T. P., Young L. and Lu Z.-T. (1999) Ultrasensitive iso- tope trace analysis with a magneto-optical trap. Science 286, 1139–1141.

[13] Du X., Purschert R., Bailey K., Lehmann B. E., Lorenzo R., Lu Z.-T., Mueller P., O’Connor T. P., Sturchio N. C. and Young L. (2003) A new method of measuring 81Kr and 36Kr abundances in environmental samples. Geophys. Res. Lett. 30. http://dx.doi.org/10.1029/2003GL018293

[14] Sturchio N. C., Du X., Purschert R., Lehmann B., Sultan M., Patterson L. J., Lu Z.-T., Mueller P., Bigler T., Bailey K., O’Connor T. P., Young L., Lorenzo R., Becker R., El Alfy Z., El Kaliouby B., Dawood Y. and Abdallah A. M. A. (2004) One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. Geophys. Res. Lett. 31, L05505.

[15] Jiang W, Bailey K, Lu Z T, et al. An atom counter for measuring 81Kr and 36Kr in environmental samples [J]. Geochimica Et Cosmochimica Acta, 2012, 91 (5): 1-6.

[16] Zappala J C, Bailey K, Jiang W, et al. Setting a limit on anthropogenic sources of atmospheric 81Kr through Atom Trap Trace Analysis [J]. Chemical geology, 2017, 453: 66-71.

[17] Bishop M, Zappala J C, Bailey K G, et al. A New Radiokrypton Dating Facility at Argonne National Laboratory [C]/ AGU Fall Meeting. AGU Fall Meeting Abstracts, 2017.

[18] Sidle W C. Apparent 85Kr ages of groundwater within the Royal watershed, Maine, USA. [J]. Journal of Environmental Radioactivity, 2006, 91 (3): 113-127.

[19] Andreas Bollhöfer, Clemens Schlosser, Sabine Schmid, Martina Konrad, Roland Purschert, Roman Krais. Half a century of Krypton-85 activity concentration measured in air over Central Europe: Trends and relevance for dating young groundwater [J]. Journal of Environmental Radioactivity, 2019, 205-206.

[20] Mitchell J G. Noble gas geochemistry: M. Ozima and F. A. Podosek. Cambridge University Press, 1983, pp. 367, Price £40.00, $79.50, ISBN 0-521-23939-7 [J]. Physics of the Earth & Planetary Interiors, 1985, 37 (4): 292-293.

[21] Oliver B M, Bradley J G, Harry Farrar I V. Helium concentration in the Earth's lower atmosphere [J]. Geochimica Et Cosmochimica Acta, 1984, 48 (9): 1759-1767.

[22] Verniani F. The total mass of the Earth's atmosphere [J]. Journal of Geoph physical Research, 1966, 71 (2): 385–391.

[23] Kutschera W, Paul M, Ahmad I, et al. Long-lived noble gas radionuclides [J]. Nuclear Instruments & Methods in Physics Research, 1994, 92 (1): 241-248.

[24] KUZMINOV V V, POMANSKY A A. 81Kr production rate in the atmosphere [C]. 18th Int. Cosmic Ray Conference. Bangalore, India: [s.n].

[25] BAGLIN C M. Nuclear data sheets for A=81[J]. Nuclear Data sheets, 2008, 109 (10): 2257-2437.
Collon, Cole P /, Davids D /, et al. Measurement of the Long-lived Radionuclide $^{81}$Kr in Pre-nuclear and Present-day Atmospheric Krypton [J]. Radiochimica Acta, 1999, 85 (1-2): 13-20.

Buizert C, Baggenstos D, Jiang W, et al. Radiometric $^{81}$Kr dating identifies 120,000-year-old ice at Taylor Glacier, Antarctica. [J]. Proceedings of the National Academy of Sciences of the United States of America, 2014, 111 (19): 6876-81.

Aggarwal P K, Matsumoto T, Sturchio N C, et al. Continental degassing of 4He by surficial discharge of deep groundwater [J]. Nature Geoscience, 2015, 8 (1): 35-39.

Xu Leyi. The analysis of dissolved krypton gas in groundwater –the use in radioactive krypton dating [D]. University of Science and Technology of China. 2015.

Sapam Ranjita Chanu, Ketan D. Rathod, Vasant Natarajan. Generation of a cold pulsed beam of Rb atoms by transfer from a 3D magneto-optic trap [J]. Physics Letters A, 2016, 380 (37).

Takuya Matsumoto, Zongyu Chen, Wen Wei, Guo-Min Yang, Shui-Ming Hu, Xiangyang Zhang. Application of combined $^{81}$Kr and 4He chronometers to the dating of old groundwater in a tectonically active region of the North China Plain [J]. Earth and Planetary Science Letters, (2018) 208-217.

Zhonghe, Pang, Guo-Min, et al. Million-year-old groundwater revealed by krypton-81 dating in Guanzhong Basin, China [J]. Science Bulletin, 2017 (17): 1181-1184.

Sturchio N C, Kuhlman K L, Yokochi R, et al. Krypton-81 in groundwater of the Culebra Dolomite near the Waste Isolation Pilot Plant, New Mexico. [J]. Journal of Contaminant Hydrology, 2014, 160 (3): 12-20.

Gerber C, Vaikmäe R, Aeschbach W, et al. Using $^{81}$Kr and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale [J]. Geochimica Et Cosmochimica Acta, 2017, 205: 187-210.

Aeschbachhertig W. Radiokrypton dating finally takes off [J]. Proc Natl Acad Sci U S A, 2014, 111 (19): 6856-6857.

Aggarwal P K, Matsumoto T, Sturchio N C, et al. Continental degassing of 4He by surficial discharge of deep groundwater [J]. Nature Geoscience, 2014, 8 (1): 35-39.