^{81}Kr dating – A tool for finding and studying paleogroundwater

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Abstract. The study of paleogroundwater on a timescale of several thousands to a million years is interesting both in terms of understanding the aquifer system itself and water resource management. It may also provide valuable information about paleoclimate. ^{81}Kr is an ideal age tracer for paleogroundwater up to 1.3 million years old. Recent developments in the Atom Trap Trace Analysis method have made ^{81}Kr dating available to the earth science community at large.

1 Background

Paleogroundwater can be both a valuable water resource and an archive that holds the local precipitation record for the past millions of years [1-6]. Characterizing paleogroundwater requires a series of reliable age tracers capable of covering a large age range up to 1 million years and dealing with the complicated situations frequently encountered in large deep aquifer systems. Radiokrypton (^{81}Kr) dating was proposed by Loosli and Oeschger in 1969 as an ideal tool to study paleogroundwater ranging from 40ka to 1.3Ma [7]. However due to significant technical challenges it has been available only recently thanks to the development of the Atom Trap Trace Analysis technique (ATTA) [8-10]. Recent rapid progress on radiokrypton dating has enabled more and broader applications [11-16]. This paper describes these recent advancements, including the latest developments in our laboratory and discusses how this new technology may impact the study of paleogroundwater.

2 Recent Advances in ^{81}Kr dating

Recent progress on ^{81}Kr dating has been focused on reducing the sample size and increasing the method's accessibility. With a smaller sample, the weight, size and complexity of the sampling equipment, as well as the time needed for sampling, can all be reduced.

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2.1 Atom Trap Trace Analysis for ^{81}Kr dating

The sample size for an ATTA analysis of ^{81}Kr is determined by the minimum pressure required to operate the Radio-Frequency (RF) discharge source in the ATTA instrument. If the sample is smaller than the optimal size then the atom counting rate and efficiency will suffer accordingly [10]. The vacuum system of the ATTA apparatus has many stages. The pressures at different stages are maintained with differential pumping and the sample is recirculated among different stages. In order to make the sample size smaller, the volume of the high pressure part of the system needs to be reduced. To accomplish this, the flow conductance of different parts of the system needs to be calculated and the position of the pump must be carefully placed so that the pressure distribution allows minimization of the required sample volume. In the latest ATTA-Kr system at the University of Science and Technology of China, the typical gas sample size is reduced to about $2\mu\text{L}$ STP. This allows measurement of gas samples as small as $1\mu\text{L}$ STP routinely without adversely affecting the atom counting rate. For a modern Kr sample, a two-hour measurement has about 1000 ^{81}Kr atom counts.

Smaller samples present additional challenges. The most important of these is that small samples are prone to cross-sample contamination. Therefore, the measurement time is usually limited to 2 to 4 hours. In order to suppress the cross-sample contamination during the measurement, a Xe discharge wash specifically tailored for small samples is implemented between measurements [10]. The Xe pressure during the washing procedure alternates between high and low pressure modes, allowing the Xe to clean the vacuum system more thoroughly and quickly. After the wash, the Kr outgassing rate is less than $0.01\mu\text{L}$ STP/h. For a $2\mu\text{L}$ STP sample this leads to a cross-sample contamination of less than 1% in a two-hour measurement. If the sample is smaller than $1\mu\text{L}$ STP, extended washing can further reduce the outgassing rate (samples as small as $0.5\mu\text{L}$ STP have been measured successfully).

Fig. 1. ^{81}Kr dating performance of the ATTA-Kr system at the University of Science and Technology of China.

Fig. 1 shows the current performance of the ATTA-Kr system at USTC. The contours show the age uncertainty from ^{81}Kr dating. For a $1\text{--}2\mu\text{L}$ STP gas sample, the age uncertainty is about 10-20% between 100ka and 1.3 million years.

2.2 Portable sampling device for field sampling

With the sample size reduced to 20-40kg of water, the bulky field sampling equipment previously required can be replaced with a smaller portable device. This device utilizes hydrophobic membrane contactors, has a small footprint, and is lightweight (25kg). In a wide flow rate range (2-20L/min), the extraction efficiency is higher than 75%, ensuring that fractionation during the degassing process remains <1%.

2.3 Automated Kr purification system with large sample processing capability

With the increased accessibility of ^{81}Kr dating, it is anticipated that the demand for radiokrypton dating will increase. Samples obtained in the field need to be pre-treated before analysis with ATTA to separate the Kr from bulk gas (N_2 , O_2 , Ar, etc). Pre-treatment requires about 1.5-2 hours and is quite labor intensive [17]. To keep up with the increasing demand, a fully automated sample pre-treatment system was developed at USTC. All valves are pneumatic and computer controlled. This system can handle gas samples from 0.5L to 10L and can process up to 5 samples per day. Recovery and purity for Kr both exceed 90%.

3 ^{81}Kr dating as a tool for paleogroundwater studies

The wide application of ^{81}Kr could enable significant advancements in paleogroundwater studies in the future. Potential applications are discussed below.

3.1 Use ^{81}Kr to find and study paleogroundwater

Most of Earth's groundwater is paleogroundwater [18]. However, existing studies of very old groundwater are often complicated by conflicting results from traditional age tracers such as ^{14}C , ^{36}Cl , etc. Moreover, aquifers with a complex geologic framework may even prohibit the use of many traditional tracers.

By utilizing the ^{81}Kr dating method, studies previously thought to be impossible or very difficult can now be undertaken. Unlike traditional tracers, ^{81}Kr has a single, well-defined source, making computed ages more robust and much more straightforward to interpret. It is also insensitive to the gas loss during sample collection because it measures isotope ratios. ^{81}Kr should provide a clearer picture of the age of water in the system and help to achieve a better understanding of the aquifer.

In a recently published study ^{81}Kr is used to characterize the Baltic Artesian Basin aquifer where the brine posed challenges to the traditional tracers such as ^{36}Cl . The ^{81}Kr results provide the age of the bulk water. Together with other measurements a very old brine component beyond the ^{81}Kr dating limit is identified, and a complex flow pattern that was active in the past can be discerned [14].

3.2 The combination of ^{81}Kr and ^4He

The ^4He dating method is a common tool for dating paleogroundwater that is considerably less expensive and more convenient than the ^{81}Kr method. The concentration of ^4He can be used to infer the groundwater age because ^4He is a product of U–Th series decay and can accumulate in groundwater along flow paths. However, the ^4He flux that enters the water is hard to estimate accurately. Besides the in-situ production there also can be contributions

from external fluxes. Quantifying the internal release rate and external flux of ^4He are typically significant challenges in the quantitative use of ^4He as a groundwater dating tool [13,19-21]. ^{14}C has been used to calibrate ^4He , but this method only extends over a very a limited age range due to its relatively short half-life. ^{81}Kr is a reliable tracer that covers a large age range, therefore it can be used to calibrate the ^4He method. This approach has been successfully implemented in studies of the Guarani aquifer in South America and the North China Plain aquifer system [13,16].

The combination of ^{81}Kr and ^4He may become a very useful tool for paleogroundwater research. Since ^4He is considerably easier to measure, it can be used in a screening campaign to identify samples potentially containing very old ground water [22]. Once suitable sampling locations are chosen based on the ^4He data, a second more strategically planned campaign for ^{81}Kr sampling can be undertaken. Based on existing joint studies through the IAEA CRP groundwater program, we have recommended a groundwater ^4He concentration of $>10^{-6} \text{ cm}^3\text{STP/g}$ as a screening threshold. Accurate age information from ^{81}Kr can be used to constrain hydrologic models and to calibrate ^4He production rates. Once ^4He is calibrated it can be used to perform denser sampling for a better understanding of the aquifer. It may also extend the age range beyond that of ^{81}Kr dating. For complex aquifer systems, the ^4He flux is less likely to be constant over the entire groundwater system. When local ^4He anomalies are observed, ^{81}Kr can be used to help resolve them. This approach combines the benefits of both methods, minimizing time and cost while maximizing scientific output.

3.3 Multiple tracer approach to cover wider age range and to study mixing

A growing number of groundwater studies are using multiple age tracers for the following reasons. First, the residence time of groundwater can span a wide range, from a few years to millions of years. A single tracer rarely covers the full age range in an aquifer. Therefore, employing multiple tracers with different age ranges is a natural approach to fully characterize aquifer age distributions. With the recent advances in dating technology, especially now that ^{81}Kr and ^{39}Ar dating have been made available by the ATTA method [10,23,24], we anticipate that ever more studies will be using a multi-tracer approach ($^3\text{He}/^{85}\text{Kr}$, ^{39}Ar , ^{14}C and $^{81}\text{Kr}/^4\text{He}$).

Second, the concept of a groundwater sample having a single age is highly idealized. In reality, dispersion and mixing usually result in samples that need to be characterized with an age distribution instead of a single age. The power of the multiple tracer approach is that it can disentangle the mixing and gives us a better picture of the age distribution in the sample because different tracers have different time responses. This allows transition from the simple piston flow model of groundwater flow to more sophisticated and realistic models. Multiple tracers also provide more constraints for numerical models of groundwater flow and reactive transport, which reduces the simulation uncertainty and in some cases helps to identify new transport mechanism [25, 26]. It is also worth mentioning that a single sampling can be used to measure all three radio-noble gas tracers (^{85}Kr , ^{39}Ar and ^{81}Kr), because these noble gas isotopes can be stripped from the groundwater simultaneously. This is particularly advantageous in multi-tracer studies because one can be sure that these tracers are really coming from the same volume of groundwater.

In conclusion, ^{81}Kr dating is a powerful new tool in paleogroundwater research, similar to ^{14}C . With the current suite of age tracers ($^3\text{He}/^{85}\text{Kr}$, ^{39}Ar , ^{14}C and $^{81}\text{Kr}/^4\text{He}$) that can cover the entire age spectrum of groundwater up to one million years now available, the field of groundwater dating is entering a new era of paleogroundwater research which should yield important new insights into this hidden resource deep under our feet.

This work is supported by National Key Research and Development Program of China (2016YFA0302200), by National Natural Science Foundation of China, NSFC (41727901) and by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB21010200).

References

1. E. Mazor, *Geochim. Cosmochim. Acta*, **36**, 1321 (1972)
2. J.N. Andrews and D.J. Lee, *J. of Hydrology*, **41**, 233 (1979)
3. M. Stute, et al., *Science*, **269**, 379 (1995)
4. W. Aeschbach-Hertig et al., *Nature* **405**, 1040 (2000)
5. J. Jouzel et al., *Quat. Sci. Rev.*, **19**, 363 (2000)
6. C.E. Weyhenmeyer, et al., *Science*, **287**, 842 (2000)
7. H. Loosli, H. Oeschger, *Earth Planet. Sci. Lett.* **7**, 67 (1969)
8. C.Y. Chen et al., *Science*, **286**, 1139 (1999)
9. X. Du et al., *Geophys. Res. Lett.*, **30**, 2068 (2003)
10. Jiang, W., et al., *Geochim. Cosmochim. Acta*, **91**, 1 (2012)
11. N.C. Sturchio et al., *Geophys. Res. Lett.*, **31**, L05503 (2004)
12. C. Buizert et al., *Proc. Natl. Acad. Sci. USA*, **111**, 6876 (2014)
13. P.K. Aggarwal et al., *Nature geoscience*, **8**, 35 (2015)
14. Gerber, C., et al., *Geochim. Cosmochim. Acta*, **205**, 187 (2017)
15. J. Li et al., *Science Bulletin*, **62**, 1181 (2017)
16. T. Matsumoto et al., *Earth and Planet. Sci. Lett.*, **493**, 208 (2018)
17. L.-Y. Tu et al., *App. Chem.* **86**, 4002 (2014)
18. S. Jasechko et al., *Nature Geosci.* **10**, 425 (2017)
19. T. Torgersen T. and M. Stute, in *Isotope Methods for Dating Old Groundwater* (eds. A. Suckow, L. Araguas-Araguas and P. Aggarwal). IAEA, Vienna, p179-216 (2013)
20. M.C. Castro, M. Stute, M. and P. Schlosser, *Applied Geochemistry*, **15**, 1137 (2000)
21. D.K. Solomon, ^4He in groundwater. In *Environmental tracers in subsurface hydrology* p425-439. Springer, Boston, MA (2000)
22. M.S. Brennwald et al., *Environ. Sci. Technol.*, **50**, 13455 (2016)
23. W. Jiang et al., *Phys. Rev. Lett.*, **106**, 103001 (2011)
24. Ritterbusch, F., et al., *Geophys. Res. Lett.*, **41**, 6758 (2014)
25. C.M. Bethke and T.M. Johnson, *Annu. Rev. of Earth and Planet. Sci.*, **36**, 121 (2008)
26. A. Suckow, in *Isotope Methods for Dating Old Groundwater* (eds. A. Suckow, L. Araguas-Araguas and P. Aggarwal). IAEA, Vienna, 179-216 (2013)