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Atom Trap, Krypton-81, and Saharan Water

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Much can be learned from the analysis of the ubiquitous long-lived radioactive isotopes. In the late 1940's, Willard Libby and coworkers first detected the cosmogenic ^{14}C ($t_{1/2} = 5.7\times10^3$ yr, isotopic abundance ^{14}C/C = 1×10^{-12}) in nature and demonstrated that such analysis could be used for archaeological dating. Since then, two by now well established methods, Low-Level Counting (LLC) and Accelerator Mass Spectrometry (AMS), have been used to analyze ^{14}C and many other radioisotopes and to extract valuable information encoded in the production, transport, and decay processes of these isotopes. Ultrasensitive analysis of long-lived radioisotopes is presently used in a broad range of scientific and technological fields including earth and environmental science, archeology, cosmochemistry, physics, biomedicine, as well as applications designed to ensure nuclear safety and security. In this report, we introduce Atom Trap Trace Analysis (ATTA), a recently developed atom-counting method capable of analyzing trace isotopes at the parts-per-trillion level. This method was developed by our group at Argonne National Laboratory and was used to analyze both ^{81}Kr ($t_{1/2} = 2.3\times10^5$ years, ^{81}Kr/Kr ~ 1×10^{-12}) and ^{85}Kr ($t_{1/2}$ = 10.8 years, ^{85}Kr/Kr ~ 10^{-11}) in environmental samples. As the first real-world application of ATTA, ^{81}Kr dating was performed to determine the mean residence time, or the "age", of the old groundwater in the Nubian Aquifer located underneath the Sahara Desert.

The dream of radiokrypton dating began in 1969 when Heinz Hugo Loosli and Hans Oeschger of the University of Bern first detected the decay of natural ^{81}Kr in krypton gas extracted from the atmosphere. They proposed ^{81}Kr as the ideal tracer isotope for dating water and ice in the age range of 10^5-10^6 years, a range beyond the reach of ^{14}C dating. ^{81}Kr is mainly produced in the upper atmosphere by cosmic-ray induced spallation and neutron activation of stable krypton. Due to the constancy of the cosmic ray flux and the fact that the atmosphere is well-mixed and represents the only significant terrestrial krypton reservoir, the ^{81}Kr isotopic abundance is expected to be uniform throughout the atmosphere and constant on the time scale of its lifetime. Subsurface sources and sinks for ^{81}Kr other than radioactive decay are most likely negligible. Human activities involving nuclear fission have a negligible effect on the ^{81}Kr concentration because the stable ^{81}Br shields ^{81}Kr from the decay of fission products. All of these favorable conditions combine to support the case of ^{81}Kr dating. The situation is entirely different for the other long-lived krypton isotope, ^{85}Kr, which is a fission product of ^{235}U and ^{239}Pu, and is released into the atmosphere primarily by nuclear fuel reprocessing. Its abundance has increased by six orders of magnitude since the 1950's. ^{85}Kr can be used as a tracer to study air and ocean currents, determine residence time of young groundwater in shallow aquifers, and monitor nuclear-fuel processing activities.

For ^{85}Kr analysis, LLC is performed routinely in several specialized laboratories around the world. LLC was also the first method used to detect ^{81}Kr and measure its abundance in the atmosphere. However, LLC is too inefficient for practical analysis of ^{81}Kr because only a fraction 3×10^{-8} of ^{81}Kr atoms in a sample decay during a typical 100 hour measurement. In general, counting atoms (neutral or ionized) is much more preferable to counting decays for analyses of long-lived isotopes such as ^{81}Kr. An AMS method of counting ^{81}Kr ions was successfully developed by Walter Kutschera of the University of Vienna and his collaborators in the 1990's. Their effort culminated in the ^{81}Kr dating of old groundwater samples from the Great Artesian Basin of Australia – the very first realization of ^{81}Kr dating. The accelerator used in this experiment was the K1200 Cyclotron at Michigan State University. This large, high energy (~ 4 GeV) cyclotron was needed to produce fully stripped ^{81}Kr ions, which then can be cleanly separated from its abundant isobar, ^{81}Br.

Atom Trap Trace Analysis (ATTA)

Atom Trap Trace Analysis (ATTA) uses a table-top apparatus in a regular laboratory environment. In ATTA, an atom of a particular isotope is selectively captured by resonant laser light in a magneto-optical trap and detected by observing its fluorescence (Fig. 1). When the laser frequency is tuned to the resonance of the desired isotope, ^{81}Kr or ^{85}Kr, only atoms of this particular isotope are trapped. Atoms of other isotopes are either deflected before reaching the trap or are allowed to pass through the trap without being captured. An atom can be trapped and observed for 100 ms or longer, during which 10^6 fluorescence photons can be induced from a single trapped atom and as many as 10^4 photons can be detected, thereby allowing the counting of single atoms to be done with a high signal-to-noise ratio as well as a superb selectivity (Fig. 2). Indeed ATTA is immune to interference from other isotopes, elements, or molecules.

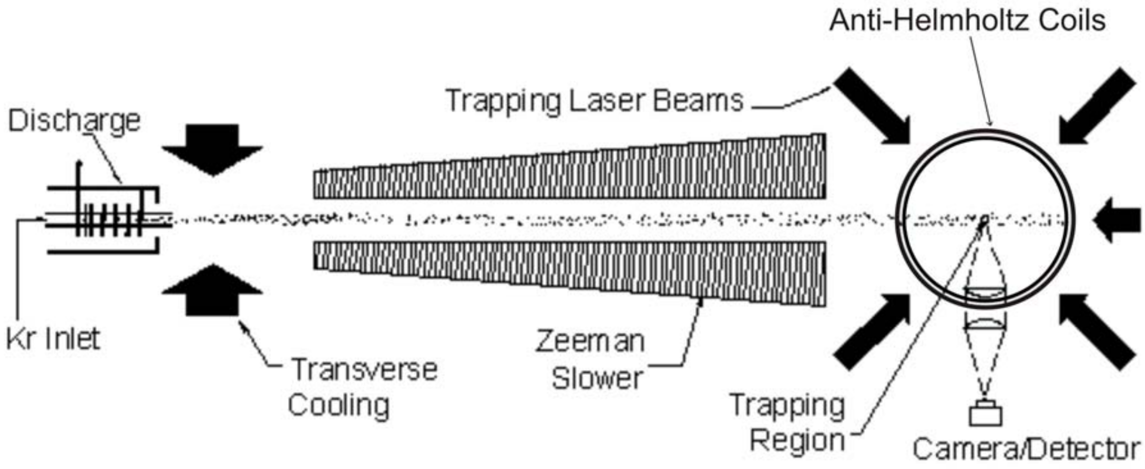

Fig. 1. Schematic layout of the ATTA apparatus. Metastable krypton atoms are produced in the discharge. The ^{81}Kr atoms are transversely cooled, slowed and trapped by the laser beams shown as solid arrows. The fluorescence of individual trapped ^{81}Kr atoms is imaged to a detector. Total length of the apparatus is about 2.5 meters.

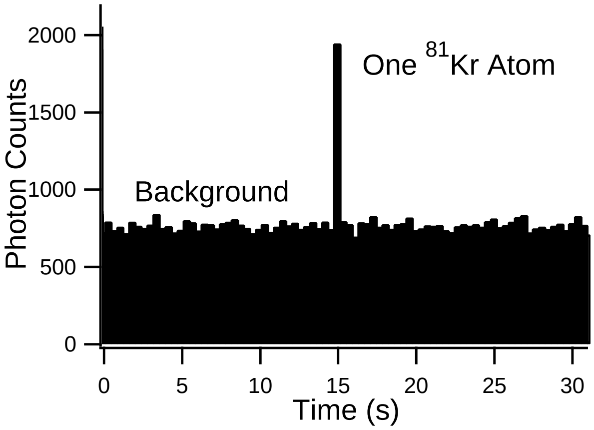

Fig. 2. Fluorescence signal of a single trapped ^{81}Kr atom. The background is due to light scattered off walls.

Following the first demonstration of ATTA in 1999, we have steadily improved the reliability and counting efficiency of the ATTA instrument. In 2003-2004, we completed the development of the ATTA-2 instrument. With a modern atmospheric krypton sample, ATTA-2 can count ^{85}Kr atoms at the rate of 240 hr^{-1} and ^{81}Kr atoms at the rate of 12 hr^{-1}. In order to achieve a statistical precision of ±10%, approximately 100 ^{81}Kr atom counts need to be accumulated. At the ATTA-2 counting efficiency of 1×10^{-4}, such an analysis requires a modern krypton sample of 50 μL STP, which can be extracted from either 50 L STP of air or 1000 L of water. This system has met the minimum requirements of implementing practical ^{81}Kr dating of old groundwater, as we have demonstrated in the study of the Nubian Aquifer in Egypt.

In order to demonstrate the validity of ATTA for quantitative analysis, we collaborated with a group led by Dr. Roland Purtschert at the University of Bern, and performed a set of inter-laboratory calibration measurements. The Bern group has expertise in noble gas sampling and LLC analysis of ^{85}Kr/Kr. They prepared ten different samples based on krypton extracted from modern air (age < 100 yr). Among the young samples, the ^{81}Kr/Kr ratios are expected to be identical; on the other hand, the ^{85}Kr/Kr ratios are expected to vary and were measured using LLC at Bern. The ^{85}Kr/^{81}Kr values independently measured using ATTA by our group were then compared with the ^{85}Kr/Kr values obtained using LLC by the Bern group. We demonstrated that the ratios measured by ATTA and LLC were directly proportional to each other within the measurement error of ±10% (Fig. 3); we calibrated the ^{81}Kr/Kr ratio of modern air measured using ATTA, which serves as the initial ratio in the calculation of groundwater residence times; and we showed that the ^{81}Kr/Kr ratios of samples extracted from air before and after the development of the nuclear industry are identical within the measurement error.

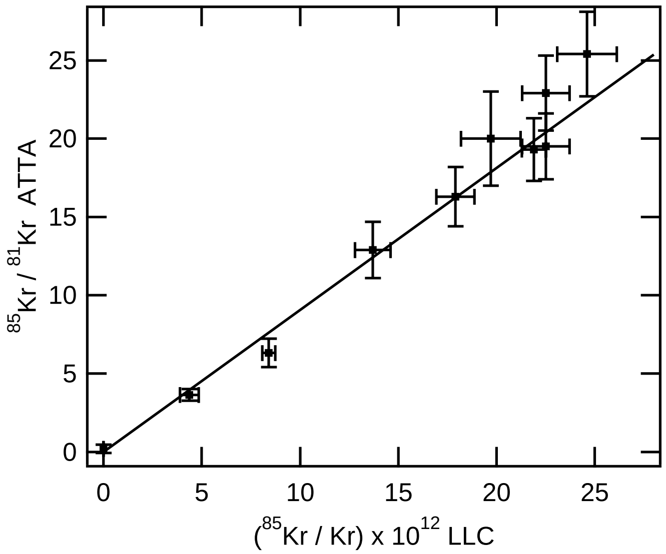

Fig.3. Proportional correlation between the ^{85}Kr/^{81}Kr ratios measured with ATTA and the ^{85}Kr/Kr ratios measured with LLC.

The efficiency of atom counting still has room for large improvements. Figure 4 shows our “ruler of progress” for the ^{81}Kr dating of old groundwater and polar ice. With the present ATTA-2 instrument, an analysis requires a sample of approximately one ton of water, which is not always feasible (e.g., for ice cores or submarine hydrothermal fluids). At present, we are developing ATTA-3 with the goal of further improving the efficiency to approximately 1% and reducing sample size for ^{81}Kr dating down to ~10 kg. From ATTA-2 to ATTA-3, we aim to make the transition from a physics experiment to a practical trace analysis method. Meanwhile, we are exploring technologies on and communicating with experts of vacuum ultraviolet sources for the excitation of krypton atoms, which may lead to further improvements.

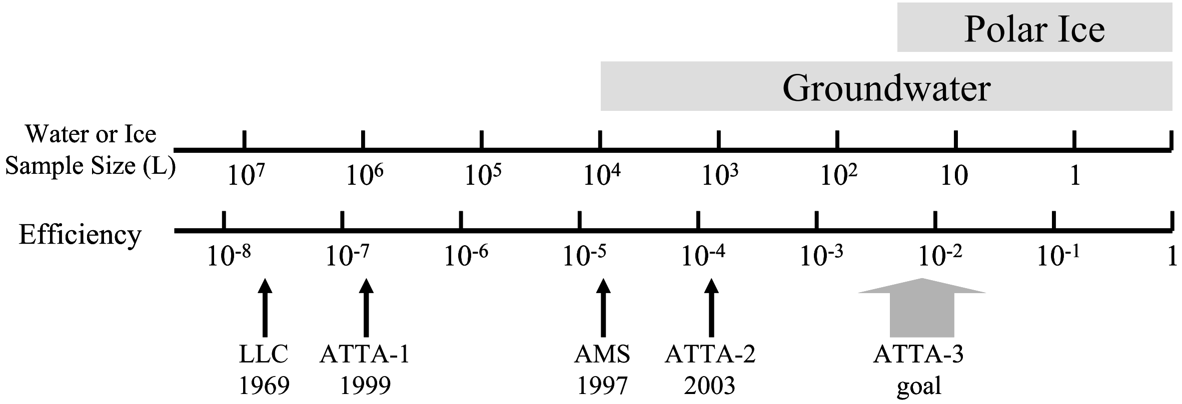

Fig. 4. Ruler of progress. As the efficiency of the analyzer approaches unity (100%), the required water or ice sample size for ^{81}Kr dating reduces to a fraction of one liter. Bars show the sample size required for dating water and ice.

Applications

For the first real-world application of ATTA, measurements of ^{81}Kr/Kr in deep groundwater from the Nubian Aquifer in the Western Desert of Egypt (at the eastern end of the Sahara Desert) were performed. This field study was done by a collaboration led by geologist Neil Sturchio of the University of Illinois at Chicago. For ^{81}Kr dating, dissolved gas was extracted from several tons of water in the field at six sites (Fig. 5). The ^{81}Kr data indicate that ages increase progressively along flow vectors predicted by numerical hydrodynamic models, verifying distant lateral flow of deep groundwater toward the northeast from a recharge area southwest of Dakhla. Furthermore, the ^{81}Kr data indicate relatively high flow velocities (~2 m/yr) from Dakhla toward Farafra, and low velocities (~0.2 m/yr) from Dakhla toward Kharga and from Farafra to Bahariya.

These observations are consistent with the areal distribution of hydraulically conductive sandstone within the aquifer and they provide support to some of the existing hydrodynamic models. Southwestward extrapolation of the ~2 m/yr flow rate inferred from the difference in ^{81}Kr ages for Dakhla and Farafra is consistent with recharge in the area of the Uweinat Uplift near the Egypt-Sudan border. In this area, the Nubian sandstone is exposed (or buried beneath sand sheets or dunes) at elevations between 200 and 600 m above sea level over a wide area, forming a broad catchment for recharge of the Nubian Aquifer.

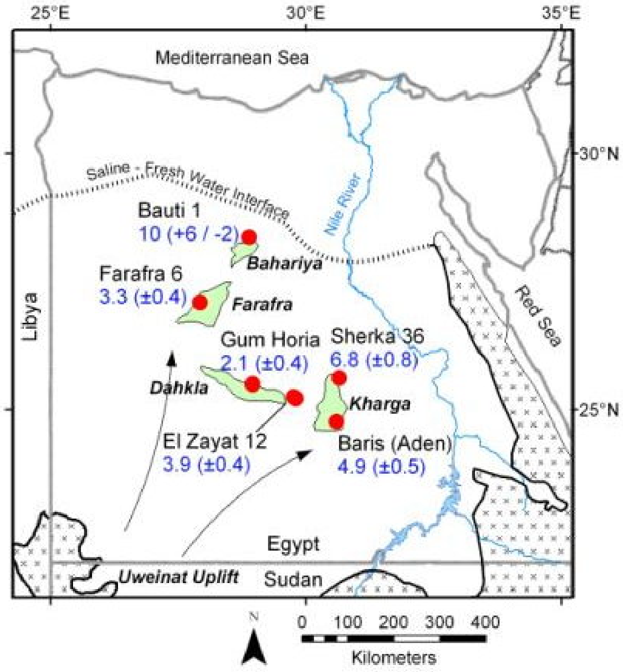

Fig. 5. Map showing sample locations (red circles) and their ^{81}Kr ages (in units of 10^5 years) in relation to oasis areas (shaded green), Precambrian basement outcrops (patterned), and other regional features. Groundwater flow in Nubian Aquifer is toward northeast.

Ice cores found in Greenland and Antarctica are the most important archives to study the composition of the atmosphere, reaching back in time perhaps one million years. Through precipitation and air bubble occlusion a direct imprint of atmospheric conditions is preserved in time. Ice cores can be dated most accurately as long as annual layers can be counted back in time (similar to counting tree rings). This can be accomplished by various methods such as annual grey-scale variations and seasonal δ^{18}O oscillations. However, eventually the annual structure disappears under the enormous pressure of the overlaying ice, and ice accumulation models have to be employed to determine the age of deep ice. In principle, ^{81}Kr would be well suited to date ice back to one million years, and perhaps beyond. The main obstacle so far is the low ^{81}Kr concentration in ice (~1000 ^{81}Kr atoms per kilogram of modern ice) combined with only small amounts of ice (a few kg) available from deep ice cores. The counting of such small amounts of ^{81}Kr atoms requires an extremely high efficiency (at least 10%), currently beyond the capabilities of both AMS and ATTA.

Acknowledgement

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Suggested Reading

1. P. Collon, W. Kutschera, and Z.-T. Lu. *Tracing noble gas radionuclides in the environment.* Annu. Rev. Nucl. Part. Sci. 54:39-67 (2004).
2. Z.-T. Lu and K. D. A. Wendt. *Laser-based methods for ultrasensitive trace-isotope analyses.* Rev. Sci. Instrum. 74:1169-1179 (2003).