

^{81}Kr IN THE GREAT ARTESIAN BASIN, AUSTRALIA: A NEW METHOD FOR DATING VERY OLD GROUNDWATER

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Determining the absolute age of ancient groundwater is of general importance in any hydrologic study where the size of subsurface water reservoirs and their flow characteristics have to be quantitatively described. Sustainability of drinking water resources and the safety of potential sites for waste disposal are just two questions of public interest. A dating method based on the decay of a radioactive nuclide essentially needs to meet the following two requirements: (A) The input concentration into the aquifer has to be known and (B) any processes, other than radioactive decay that change the concentration in a groundwater sample as it flows along a path through an aquifer need to be quantified. ^{81}Kr with a half-life of $(2.29 \pm 0.11) \times 10^5$ years (1) is the one isotope with which many possible complications are of very minor importance. Since the time that this isotope was detected in the atmosphere (2) the radioactive noble gas isotope ^{81}Kr was considered to be an excellent candidate for dating very old groundwater. The reasons for this importance are that the atmospheric concentration of ^{81}Kr is known and constant and that the anthropogenic and subsurface production are negligible.

^{81}Kr atoms are produced by the interaction of cosmic rays with nuclei in the Earth's atmosphere. Neutron-capture by ^{80}Kr and spallation of heavier Kr isotopes ($A = 82$ to 86) are the most important reactions. Given a krypton mixing ratio of 1.14 ppmv in the atmosphere and a $^{81}\text{Kr}/\text{Kr}$ ratio of 5.2×10^{-13} , one can estimate that the total atmospheric ^{81}Kr inventory of ^{81}Kr is 6.4×10^{25} atoms. There is a total volume of 1.4×10^{21} liters of water in the world's oceans and 1130 atoms of ^{81}Kr per liter of water, the total ^{81}Kr ocean inventory is 1.6×10^{24} atoms, which corresponds to 2.5 % of the global inventory. The remaining 97.5% is atmospheric, in strong contrast to ^{14}C for which 93% of the global ^{14}C inventory is stored in the ocean with only 2% residing in the atmosphere and 5 % in the biosphere. Thus, it is easy to imagine that exchange between the ocean and atmosphere considerably effects the atmospheric ^{14}C content, whereas very little influence is expected by such exchange on the atmospheric ^{81}Kr inventory.

[Aside: For an air saturated water sample with a temperature of e.g. 15 degrees C in the recharge area of an aquifer, 8.1×10^{-5} cm³ STP of Krypton are dissolved per liter of water. The steady-state activity in the atmosphere of $1.5 \times 10^{10} \text{ Bq/m}^3$ STP of air corresponds to a $^{81}\text{Kr}/\text{Kr}$ ratio of 5.2×10^{-13} . Therefore one liter of a modern groundwater only contains 1130 ^{81}Kr atoms.]

In order to use ^{81}Kr as a dating tool, it is necessary to understand possible anthropogenic contributions. We have previously demonstrated (3) that anthropogenic production is negligible. No difference between pre-nuclear krypton and modern atmospheric krypton was detected (within an experimental uncertainty of $\pm 30\%$).

The subsurface production of ^{81}Kr is most likely also negligible (this is not the case for other radiotracers like ^{36}Cl or ^{129}I) because ^{81}Kr is shielded by stable ^{81}Br from the beta-decay chain along the isobar $A = 81$, produced in the spontaneous fission of ^{238}U . It was estimated that even in a geological environment with a larger than normal uranium concentration, the subsurface production of ^{81}Kr should be negligible (4). In addition, krypton is a noble gas and does not participate in any biological or chemical processes in the subsurface. Any analytical technique based on the measurement of the $^{81}\text{Kr}/\text{Kr}$ ratio will not be sensitive to changes in the absolute amount of Kr dissolved in recharging groundwater. In summary, ^{81}Kr is an almost perfect candidate for dating groundwaters in an

age range from about fifty thousand to several hundred thousand years.

The analytical requirements for the detection of ^{81}Kr are however extreme: less than 1200 atoms of ^{81}Kr per liters of water are available for counting. Such a low concentration represents an activity of only 1.1×10^{-10} Bq (about one radioactive decay every 300 years). A dating method utilizing ^{81}Kr must rely on counting the radioactive atoms in the sample before they decay. The present study is based on an AMS technique using positive krypton ions accelerated in a cyclotron developed by our collaboration at the National Superconducting Cyclotron Laboratory at Michigan State University, USA.

The principal experimental difficulty to develop a viable AMS counting method for ^{81}Kr resides in the separation of ^{81}Kr from the strong background of ^{81}Br , which is a stable (isobaric) nuclide with a relative mass difference of only 3.7×10^{-6} . Cyclotrons are excellent isotope separators because of their high mass resolution, e.g., the K1200 cyclotron at MSU has a mass-to-charge resolution is 10^{-4} . However, this resolution would not be sufficient to separate $^{81}\text{Kr}^+$ ions from $^{81}\text{Br}^+$ ions. As the source of the bromine contaminant at these low isotopic ratios is not known, a method based on full stripping at high energies was devised to obtain clear isobar separation. (Since the atomic number of ^{81}Kr is 36 and that of ^{81}Br is 35, ^{81}Br cannot acquire a 36+ charge state to mimic fully stripped ^{81}Kr ions). An overview of the experimental set-up for the detection of ^{81}Kr at the accelerator facility is presented in Figure 1 and the details of the analytical concept have been published (5). It is important to select support gas and ion source running conditions that reduced the number of accelerated bromine ions to a level at which the detection of the ^{81}Kr ions (at the natural level) could be distinguished from ^{81}Kr nuclei made in nuclear charge-exchange reactions of ^{81}Br in the stripper foil.

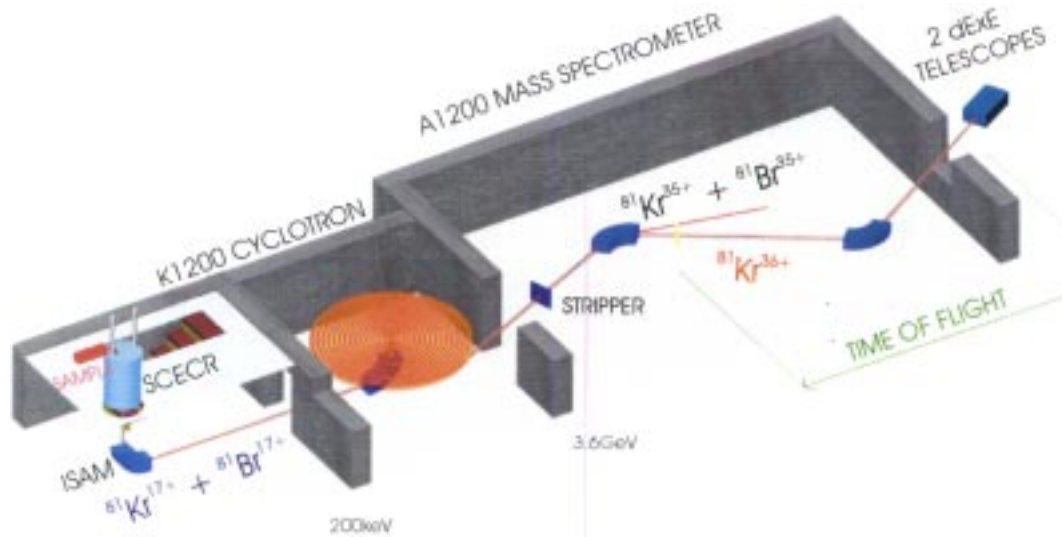


Figure 1: Conceptual presentation of the experimental setup at the NSCL.

A portable computer controlled gas handling system was developed (3) to handle the introduction of multiple small gas samples (as low as 0.4 cm^3 gas STP) into the ion that suppressed any bromine present in the sample through the use of a cold trap. The basic concept of the gas handling system was adapted from the Oxford CO_2 gas source (6).

Participants from Primary Industries and Resources, South Australia, from the University in Vienna and the University in Bern participated in a field trip to sample groundwater from the Great Artesian Basin of Australia (GAB) as a Coordinated Research Program (CRP) with partial support from the Hydrology Section of the IAEA, Vienna. This basin was selected for a demonstration of the new technique for three reasons: (a) based on previous studies the existence of very old groundwaters in an

age range accessible by the ^{81}Kr method was proposed based on hydrodynamic consideration as well as ^{36}Cl data (7), (b) Artesian conditions have the advantage that water samples reach the surface under their own pressure, and no pumping is necessary which minimises the danger of contamination with air during the sampling procedure, (c) the Great Artesian Basin in Australia is the largest Artesian groundwater basin in the world with water flowing in sandstones covered by extensive layers of shale. It provides water not only for the local population and agriculture in the arid interior of the Australian continent but also for major industries (Cu and U mining) with rather large demand for processing water.



Figure 2: Map of the Great Artesian Basin of Australia, the four sampling sites are indicated by the stars and well names: #1 is Oodnadatta, #2 is Raspberry Creek, #3 is Watson Creek, and #4 is Duck Hole. The arrows represent the general direction of the groundwater flow.

The sampling sites were in the south-west segment of the GAB, approximately 1000 km north to north-west of Adelaide, South Australia (Fig. 2). Very large water samples (16,000 liters) were degassed at each of the four wells indicated in the figure during a sampling campaign that took place during a field trip in January, 1998.

Krypton was separated from the extracted gases in a procedure developed at the University of Bern. Overall krypton losses had to be kept minimal. Analysis of the composition of the extracted gases and comparison with the absolute noble gas concentrations in the groundwater samples taken for NGT-determination (noble gas temperature) allowed the calculation of the overall yield of our gas extraction from groundwater in the field (82%) and of the Kr separation from the extracted gases in the laboratory

(60%). Krypton samples of 0.5 cm³ STP (containing about 3 million ⁸¹Kr atoms) for each well were sealed into quartz ampoules and shipped to the cyclotron laboratory at Michigan State University. From the initial water sample to the final detection of ⁸¹Kr the method covers almost 28 orders of magnitude.

The krypton samples were measured using our AMS method developed previously. Table 1 contains a summary of the results of the AMS measurements for all of the samples. Overall counting rates were typically 60 counts in 9 hours. Since a Kr groundwater sample of 0.5 cm³ STP represents about 3 million ⁸¹Kr atoms, the overall transmission from the gas handling system through the ECR ion source to the surface barrier ion detectors can be calculated to be about 2x10⁻⁵ in a standard experimental run.

From the measured krypton concentrations in the four water samples, atomic concentrations between 280 and 420 ⁸¹Kr atoms per liter of groundwater were calculated using the ⁸¹Kr/Kr ratios of Table 1. The corresponding ages were simply calculated from the change of the ⁸¹Kr/Kr ratios due to the radioactive decay, using the atmospheric Kr/Kr ratio as the starting value at the groundwater recharge.

Table 1: Summary of the measured data for extracted krypton gas.

Sample	⁸¹ Kr/Kr (10 ⁻¹³)	Mean Residence Time (10 ³ years)
Oodnadatta	1.78 +/- 0.26	354 +/- 50
Raspberry Creek	2.63 +/- 0.32	225 +/- 42
Watson Creek	1.54 +/- 0.22	402 +/- 51
Duck Hole	2.19 +/- 0.28	287 +/- 38
Atmospheric Kr	5.20 +/- 0.40	0

In summary, the present results confirm that ⁸¹Kr dating is a reliable method to determine the age of old groundwater (in fact, never have so old groundwater samples been reliably dated. Though measurements of ⁸¹Kr are still a major technical undertaking, this radionuclide shows every sign of an ideal tool for groundwater dating.

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