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An atom counter for measuring ^{81}Kr and ^{85}Kr in environmental samples

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Abstract

Due to its simple production and transport processes in the terrestrial environment, the long-lived noble-gas isotope ^{81}Kr is the ideal tracer for old water and ice in the age range of 10^5–10^6 years, a range beyond the reach of ^{14}C. ^{81}Kr-dating, a concept pursued in the past four decades by numerous laboratories employing a variety of techniques, is now available for the first time to the earth science community at large. This is made possible by the development of ATTA-3, an efficient and selective atom counter based on the Atom Trap Trace Analysis method and capable of measuring both ^{81}Kr/Kr and ^{85}Kr/Kr ratios of environmental samples in the range of 10^{-14}–10^{-10}. The instrument was calibrated with 12 samples whose ^{85}Kr/Kr ratios were independently measured using Low Level Decay Counting, including six samples that were measured in a blind arrangement. Compared to the previously reported ATTA-2 instrument, the counting rates of ATTA-3 are higher by two orders of magnitude and the required sample size lower by one order of magnitude. For ^{81}Kr-dating in the age range of 150–1500 kyr, the required sample size is 5–10 μL STP of krypton gas, which can be extracted from approximately 100–200 kg of water or 40–80 kg of ice. Moreover, a laser-induced quenching scheme was developed to enable measurements of both the rare ^{81,85}Kr and the abundant ^{83}Kr, whose isotopic abundances differ by 11 orders of magnitude. This scheme allows ATTA-3 to directly determine ^{81}Kr/Kr and ^{85}Kr/Kr ratios without other supplemental measurements. Combining the significant reduction in sample size with numerous advances in the measurement procedure, ATTA-3 represents the state-of-the-art instrument for routine analysis of these rare noble gas tracers in a wide range of earth science applications.

1. INTRODUCTION

Krypton permeates through the atmosphere at a concentration of one part per million. There are six stable krypton isotopes, and two rare, long-lived isotopes: ^{81}Kr ($t_{1/2} = 2.29 \times 10^5$ yr, isotopic abundance ^{81}Kr/Kr = 6×10^{-13}) and ^{85}Kr ($t_{1/2} = 10.8$ yr, ^{85}Kr/Kr $\sim 10^{-11}$) (Collon et al., 2004). Upon the discovery of ^{81}Kr in the atmosphere, Loosli and Oeschger (1969) 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 its long residence time, ^{81}Kr is expected to be distributed uniformly throughout the

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atmosphere. 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 the neutron-rich fission products (Collon et al., 1999; Lehmann et al., 2003). All of these favorable conditions combine to support the case for ^{81}Kr-dating. The other long-lived krypton isotope, ^{85}Kr, has a completely different production source. It is a fission product of ^{235}U and ^{239}Pu, and is released into the atmosphere primarily by nuclear fuel reprocessing activities. ^{85}Kr can be used as a tracer to study air and ocean currents, and determine residence time of young groundwater in shallow aquifers (Loosli, 1992; Winger et al., 2005).

For ^{85}Kr analysis, Low Level Decay Counting (LLC) is performed routinely in a few specialized laboratories around the world (Loosli and Purtschert, 2005; Momoshima et al., 2010). LLC was also the first method used to detect ^{81}Kr and to determine its abundance in the atmosphere (Loosli and Oeschger, 1969), but it is too inefficient for practical ^{81}Kr-dating because only a fraction 3×10^{-8} of ^{81}Kr atoms in a sample decays in a 100-h measurement. In general, counting atoms is preferable to counting decays for analyses of long-lived isotopes because of the enhanced efficiency, and because of the immunity to other decay backgrounds from both the sample and the surroundings. An Accelerator Mass Spectrometry (AMS) method for counting ^{81}Kr ions was successfully developed (Collon et al., 1997), and was used to perform ^{81}Kr-dating of four groundwater samples from the Great Artesian Basin of Australia (Collon et al., 2000; Lehmann et al., 2003) – the very first realization of ^{81}Kr-dating. However, due to the complexity of this technique, which required the use of a high energy (~4 GeV) cyclotron to produce fully stripped ^{81}Kr ions, and the large sample size required (~16 tons of water), the AMS effort on ^{81}Kr-dating was halted following these proof-of-principle measurements.

Atom Trap Trace Analysis (ATTA) is an atom-counting method capable of detecting both ^{81}Kr and ^{85}Kr in environmental samples (Chen et al., 1999). It 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 (MOT) and detected by observing its fluorescence. Following the first demonstration of ATTA (Chen et al., 1999), both the reliability and counting efficiency of the ATTA instrument have been steadily improved. An earlier version, ATTA-2 (Du et al., 2003), had a counting efficiency of 1×10^{-4} and, for each ^{81}Kr/Kr analysis, needed a sample of 50 μL STP of krypton gas extracted from approximately 1000 kg of water. The ATTA-2 instrument had a limited dynamic range: it could only be used to count the rare ^{81,85}Kr isotopes, not the abundant stable isotopes, for example, ^{83}Kr whose isotopic abundance is 11.5%. The isotopic abundance ^{81}Kr/Kr had to be measured in two steps: first, a controlled amount of ^{85}Kr was introduced into the sample and its ^{85}Kr/Kr ratio was determined with LLC; second, ATTA-2 was used to measure ^{81}Kr/^{85}Kr. The two ratios were then combined to obtain ^{81}Kr/Kr. Despite its dependence on additional measurements with other techniques and the relatively large sample size required, ATTA-2 was used successfully for ^{81}Kr-dating of old groundwater of the Nubian aquifer in western Egypt (Sturchio et al., 2004).

In this paper, we report on the performance of recently completed ATTA-3, a significantly improved ATTA instrument. We have used ATTA-3 to measure both the ^{81}Kr/Kr and ^{85}Kr/Kr ratios in environmental samples. The instrument was calibrated with 12 samples whose ^{85}Kr/Kr ratios were independently measured using LLC, including six samples that were measured in a blind arrangement. Compared to ATTA-2, the counting rates of ATTA-3 are two orders of magnitude higher, and the required size of water or ice samples for ^{81,85}Kr measurement is reduced by one order of magnitude. Moreover, by directly measuring the counting rates of both the rare ^{81,85}Kr and the abundant ^{83}Kr, the normalization procedure in the isotope-ratio measurements is done in one step – the measurement is now simpler and more reliable. ATTA-3 represents the state-of-the-art instrument capable of performing routine analysis of these rare noble gas tracers.

2. METHOD

The principle of the ATTA method has already been reported (Chen et al., 1999). Here, we briefly describe the ATTA-3 apparatus (Fig. 1) with emphasis on the new improvements that have resulted in gain factors over ATTA-2 (Du et al., 2003). Laser trapping and cooling of krypton atoms are achieved by the resonant excitation of the cycling transition $5s[3/2]_2$–$5p[5/2]_3$ (Fig. 2). The $5s[3/2]_2$ state is metastable, and is populated with an efficiency of $\sim 10^{-4}$ by sending the sample gas through a RF-driven discharge source (Chen et al. 2001). The newly developed discharge source is cooled by a liquid nitrogen reservoir, resulting in a slower beam of atoms and a gain by a factor of two in the trapping efficiency. A diverging beam of metastable atoms is collimated in a 20 cm long, two-dimensional transverse cooling zone. The forward atomic beam flux is enhanced by a factor of 140, resulting in a gain by a factor of two over ATTA-2. A mechanical beam chopper is used to periodically turn on the atomic beam in the capture phase and to turn it off in the detection phase. A two-dimensional trap is installed in ATTA-3 to focus the already collimated atomic beam, thus boosting the trap capture efficiency by a factor of three. A new Zeeman slower, containing a reverse-biased segment near the MOT, improves the transition of atoms from the slower into the trap, and improves the trapping efficiency by a factor of three. In addition, a factor of three increase in laser power (a total of 2 W) and complete sideband coverage for hyperfine repumping improve the trapping efficiency by a factor of four. Analyzing an atmospheric krypton sample, the new ATTA-3 apparatus can capture ^{83}Kr (11.5%) atoms at the rate of $\sim 1 \times 10^{11}$ s^{-1}, ^{81}Kr (6×10^{-13}) at the rate of 1000 per hour and ^{85}Kr ($\sim 10^{-11}$) at 20,000 per hour. This represents a combined improvement by two orders of magnitude over the previously reported ATTA-2 results. Finally, instead of an avalanche photodiode employed in ATTA-2, a sensitive EMCCD camera is used in ATTA-3 to record

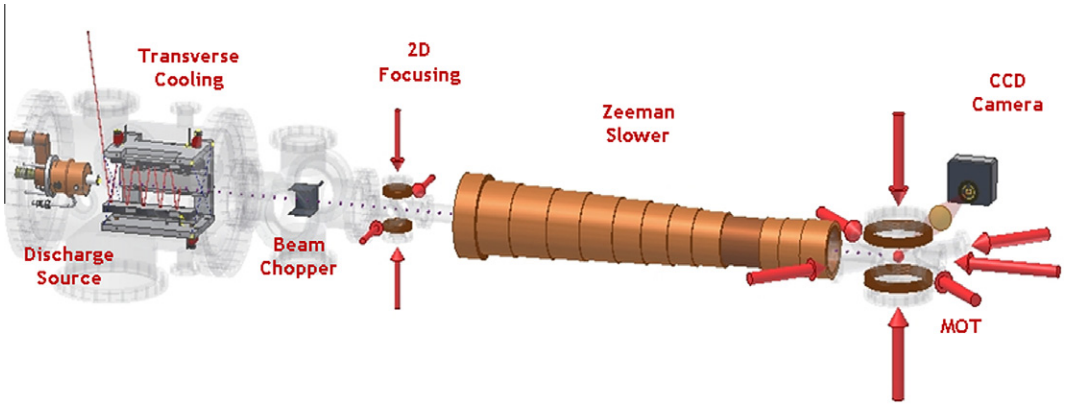

Fig. 1. Schematic of the ATTA-3 apparatus. The total length of the atomic beamline is approximately 2 m. Lasers and optics are located on an adjacent laser table of a similar length.

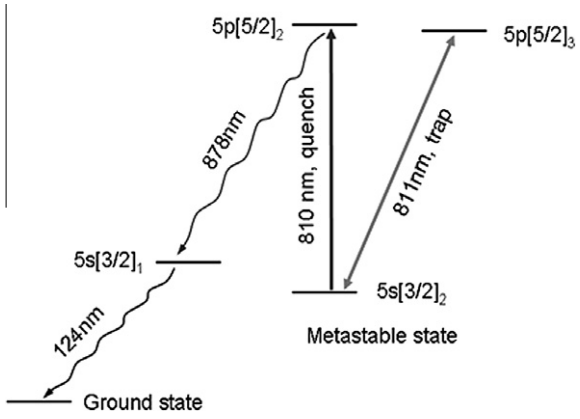

Fig. 2. Atomic level diagram of krypton. The $5s[3/2]_2$ state is metastable. The cycling transition $5s[3/2]_2$–$5p[5/2]_3$ is excited for trapping and its fluorescence detected for single atom counting of ^{81,85}Kr. The transition $5s[3/2]_2$–$5p[5/2]_2$ is excited to quench the metastable ^{83}Kr atoms, and the $5s[3/2]_1$–$[5/2]_2$ fluorescence is detected for ^{83}Kr measurements.

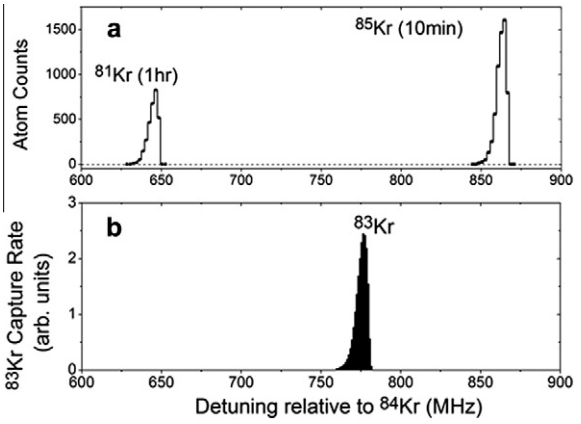

Fig. 3. Trap capture rate versus laser frequency detuning. (a) The integration time for each data point of the ^{81}Kr peak is one hour, and 10 min for ^{85}Kr. The atom is detected by collecting the 811 nm fluorescence on the cycling transition. Zero atom counts on both sides of peaks illustrate the immunity of ATTA to any contamination by other species. (b) For ^{83}Kr, 878 nm fluorescence is recorded in the laser induced quenching procedure (see text for details). In isotope ratio measurements, the laser frequency is fixed to the top of the peak for each isotope in order to count atoms at the maximum rates.

both the spatial and intensity information of the fluorescence image of the trapped atom. Under the optimum conditions, the signal-to-noise ratio of a single trapped atom is approximately 20. The threshold for single atom detection is set at seven standard deviations above background.

2.1. Selectivity

ATTA is immune to interference from any other isotope, element, or molecule. When the laser frequency is tuned to the resonance of the desired isotope, ^{81}Kr or ^{85}Kr, only atoms of this specific isotope are trapped (Fig. 3a). Other species are either deflected before reaching the trap or are allowed to pass through it without being captured. Indeed, the number of atom counts drops to zero on both sides of the ^{81}Kr or ^{85}Kr peak. There is no interference from counts due to the nearby peak of ^{83}Kr (Fig. 3b), an isotope that is more abundant by ~11 orders of magnitude. This superb selectivity is due to two characteristics of the MOT: resonance and repetition – laser trapping works only when the atom resonantly and repeatedly scatters photons at the rate of 10^7 s^{-1}.

2.2. Normalization: direct measurements of ^{81}Kr/^{83}Kr and ^{85}Kr/^{83}Kr ratios

Compared to single-atom counting of ^{81}Kr or ^{85}Kr, an accurate determination of the trap capture rate of the abundant isotope ^{83}Kr is surprisingly difficult, yet it is required in order to measure the isotopic abundances of ^{81}Kr/Kr and ^{85}Kr/Kr. Here, we assume that the ^{83}Kr/Kr ratio (=11.5%) is a constant throughout the near-surface Earth environment. Interaction among the large number (~10^9) of ^{83}Kr atoms in the trap causes loss of atoms due to ionization, quenching, and other forms of inelastic collisions. Consequently, the average time for an atom to stay in the

trap, the so-called trap lifetime, depends sharply on the number and the density of atoms in the trap, and is difficult to control and determine to the required accuracy (±5%). Since the fluorescence signal of the cycling transition at 811 nm from the trapped ^{83}Kr atoms is proportional to the trap lifetime – the longer an atom stays in the trap, the more fluorescence photons at 811 nm it emits – the large uncertainty in determining the trap lifetime causes a similar difficulty in accurately determining the capture rate of ^{83}Kr. This is not a problem for counting the rare ^{81,85}Kr isotope. For one, the number of trapped ^{81,85}Kr atoms is small, and their trap lifetime is long (~1 s) and stable. In addition, the signal size of the 811 nm fluorescence is discrete when there are only a couple of ^{81,85}Kr atoms in the trap, making atom counting of ^{81,85}Kr possible without knowing the trap lifetime.

In ATTA-2, this problem was bypassed by injecting a known amount of ^{85}Kr into the sample and using ^{85}Kr as a control isotope for ^{81}Kr measurement, and vice versa. This procedure introduced additional complexity and potential sources of errors into the final age determination. In ATTA-3, we have succeeded in measuring the capture rate of ^{83}Kr accurately with a laser-induced quenching procedure. A 200 μW laser beam of 810 nm is directed at the trapped atoms to resonantly excite the $5s[3/2]_2$–$5p[5/2]_2$ transition (Fig. 2). An atom excited to the $5p[5/2]_2$ state decays to the ground state through the intermediate $5s[3/2]_1$ state, emitting two photons at 878 nm and 124 nm, respectively. Once in the ground state, the atom no longer interacts resonantly with the laser beams and is lost from the trap. This quenching process actively reduces the lifetime and, thus, the number of ^{83}Kr atoms in the trap by one order of magnitude while the collisional loss rate is reduced by two orders. While the 811 nm fluorescence of the cycling transition is proportional to the trap lifetime, the 878 nm fluorescence is not. Instead, each ^{83}Kr atom in the trap emits a single 878 nm photon before dropping to the ground state. The fluorescence at 878 nm, although much weaker, is linearly proportional to the rate of atoms being captured by the trap, and is insensitive to any drifts of laser power and frequency. Detecting the 878 nm fluorescence of ^{83}Kr induced by the quenching laser beam, we have measured both the ^{81}Kr/^{83}Kr and ^{85}Kr/^{83}Kr ratios of a single test sample under a variety of trapping conditions and overall capture rates (Fig. 4), and found these ratios to remain constant within the statistical 1σ uncertainty of ±9% for ^{81}Kr/^{83}Kr and ±7% for ^{85}Kr/^{83}Kr. This new procedure is adopted in ATTA-3 for all isotope ratio measurements.

2.3. Memory effect

Cross-sample contamination remains the primary limitation on the sample size requirement and sample processing time of ATTA-3. While the discharge is used to excite the krypton atoms to the metastable $5s[3/2]_2$ state, it also ionizes the atoms and implants them into the surrounding walls, thus causing a slow loss of the sample. Later on, under the bombardment of the energetic ions, those embedded atoms of the current and previous samples can be slowly released back into the vacuum system. Over time, atoms from previous samples slowly accumulate in the system, causing an instrumental memory effect. This effect is mitigated by flushing the system for 36 h with a xenon gas discharge following each measurement. This solution does limit the sample processing speed as each measurement-flushing cycle takes two days of time. During flushing, the outgassing rate of krypton is recorded with a residual gas analyzer, and is observed to drop by two orders of magnitude down to an acceptable level of 0.015 μL STP per hour. In addition, both the ^{81}Kr/Kr and ^{85}Kr/Kr ratios of the outgassing krypton can be measured directly with atom counting. Although the contamination is small compared to the sample size of 5–10 μL, it is not entirely negligible, particularly when a sample is old and the ^{81}Kr/Kr abundance is much lower than that of the contaminant from previous samples. Since both the release rate and the ^{81}Kr/Kr abundance of the contaminant can be determined, a correction is made and its associated error is added to the result of each sample. In the future, the discharge source of metastable atoms may be replaced with a photon excitation scheme (Ding et al., 2007), thus avoiding the undesirable effects due to ionization in the discharge. The trapping and counting efficiency could be further improved; the 36-h flushing would no longer be needed. If successful, the photon excitation scheme would lead to even smaller required sample size and a higher sample processing speed.

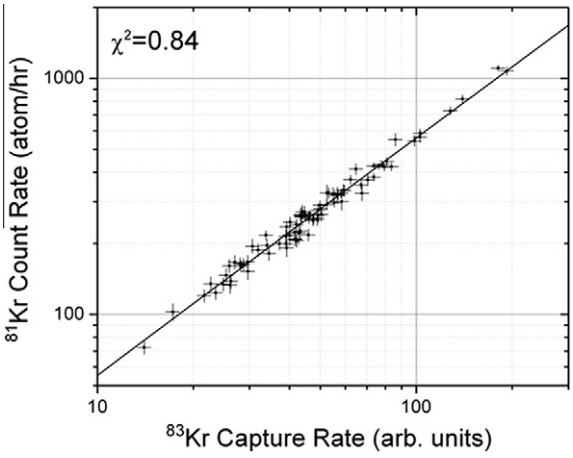

Fig. 4. Comparison of the atom capture rates between the rare ^{81}Kr and abundant ^{83}Kr for a single test sample under a variety of trapping conditions. The linearity of the fit demonstrates that the 878 nm signal can be used effectively for normalizing the ^{81}Kr/Kr (or ^{85}Kr/Kr) ratios.

3. RESULTS

The ^{85}Kr/Kr ratios measured at Argonne National Laboratory with ATTA-3 were compared to those measured independently at the University of Bern with LLC (Loosli and Purtschert, 2005). A total of 12 krypton samples were prepared in Bern by mixing varying amounts of modern atmospheric krypton with a krypton sample originally taken from air prior to the dawn of the nuclear age containing basically zero ^{85}Kr concentration. The resulting ^{85}Kr/Kr ratios among these samples vary from 0 to

1×10^{-10}. These ratios were determined both by the volume mixing ratios and by LLC of ^{85}Kr. The ^{81}Kr/Kr ratios are expected to remain constant among all these samples. Using ATTA-3, both the ^{85}Kr/Kr and ^{81}Kr/Kr ratios were measured several times for each sample, with each measurement consuming approximately 10 μL STP of krypton. During a measurement, the laser frequency was switched among ^{81}Kr, ^{83}Kr, and ^{85}Kr every few minutes to average out any drifts in trapping and detection efficiencies. The final isotope ratio results, after correction for the memory effect, are displayed in Fig. 5. ATTA-3 and LLC measurements agree on the ^{85}Kr/Kr ratios at the ±7% level ($\chi^2 = 1.1$). Moreover, the ^{81}Kr/Kr ratios measured with ATTA-3 indeed remain constant at the ±9% level ($\chi^2 = 1.0$). We note that ATTA-3 does not directly measure absolute isotope ratios. Instead, the measured ratios of unknown samples are normalized to those of a standard reference, a well-studied atmospheric krypton sample.

The required sample size for applications in ^{81}Kr-dating depends on both the sample age and the desired uncertainty in age determination (Fig. 6). ^{81}Kr-dating with ATTA-3 covers an effective age range from 150 kyr to 1.5 Myr, or 0.6–6 times the half-life of the isotope. On the side younger than 150 kyr, the change of ^{81}Kr/Kr is too small to provide adequate age resolution. On the side older than 1.5 Myr, the ^{81}Kr/Kr ratio itself is too small compared to the error introduced by the correction for the memory effect. Within the effective age range, a typical sample size is 5–10 μL STP of krypton gas, which can be extracted from approximately 100–200 kg of water or 40–80 kg of ice. For a ^{85}Kr/Kr analysis, the required sample size is in general smaller by an order of magnitude because of the isotope's higher initial abundance in the atmosphere. It should be noted that these are not absolute requirements; rather, they should be viewed as a guideline. If needed, extraordinary steps, for example prolonged xenon flushing in order to reduce the memory effect, can be taken to further reduce the required sample size and meet the special demands of a particular application. The chemical purity of the krypton sample is not important since the ATTA method is immune to contamination from any other species.

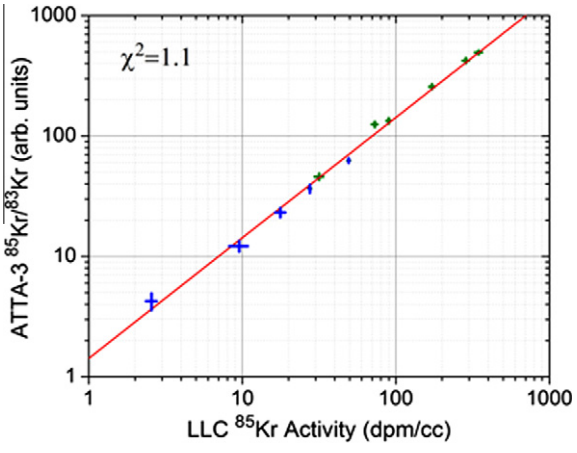

Fig. 5. Comparison of ^{85}Kr/Kr ratios measured by ATTA-3 and LLC. ATTA-3 measures the ^{85}Kr/^{83}Kr ratio in arbitrary units. LLC measures the ^{85}Kr decay activity in the units of decays per minute per cc-STP of krypton gas (dpm/cc). Six samples (blue data points) were measured in a blind arrangement: The ATTA-3 and LLC results were only revealed and compared after the measurements had completed. In addition to the points shown in the figure, a sample with ^{85}Kr below the LLC detection limit was also analyzed: LLC, ^{85}Kr activity <1 dpm/cc; ATTA-3, ^{85}Kr/^{83}Kr < 2.0 (90% C.L.). ATTA-3 and LLC results agree at the ±7% level ($\chi^2 = 1.1$).

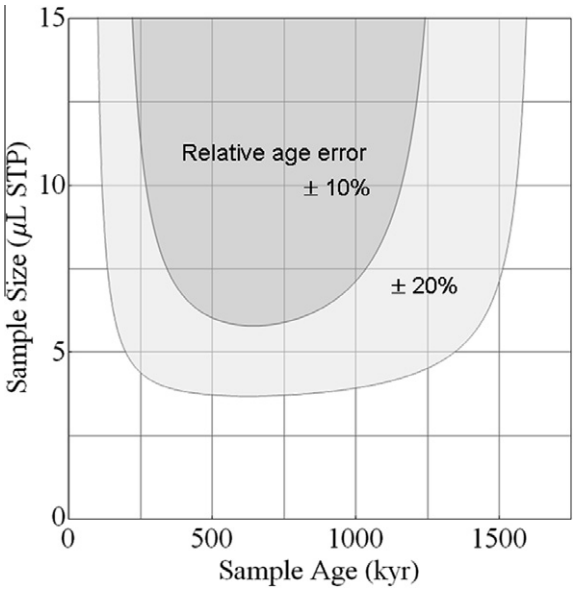

Fig. 6. Sample size *vs* sample age and desired accuracy for ^{81}Kr-dating. The two curves are for a relative age error of ±10% and ±20%, respectively.

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