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Analysis of ^{85}Kr: a comparison at the 10^{-14} level using micro-liter samples

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The isotopic abundance of ^{85}Kr in the atmosphere, currently at the level of 10^{-11}, has increased by orders of magnitude since the dawn of nuclear age. With a half-life of 10.76 years, ^{85}Kr is of great interest as tracers for environmental samples such as air, groundwater and ice. Atom Trap Trace Analysis (ATTA) is an emerging method for the analysis of rare krypton isotopes at isotopic abundance levels as low as 10^{-14} using krypton gas samples of a few micro-liters. Both the reliability and reproducibility of the method are examined in the present study by an inter-comparison among different instruments. The ^{85}Kr/Kr ratios of 12 samples, in the range of 10^{-13} to 10^{-10}, are measured independently in three laboratories: a low-level counting laboratory in Bern, Switzerland, and two ATTA laboratories, one in Hefei, China, and the other in Argonne, USA. The results are in agreement at the precision level of 5%.

Current atmospheric ^{85}Kr inventory is mainly attributable to nuclear fuel reprocessing activities. It has long been the most abundant man-made radioactive isotope in the troposphere[1]. The content of ^{85}Kr in the entire atmosphere continuously increased and reached 5.5×10^{15} Bq at the end of 2009[2]. A measurable disturbance of atmospheric electric properties due to ^{85}Kr has been examined[3]. The global exchange time of ^{85}Kr, mainly transport from the northern mid-latitudes to the southern hemisphere, was estimated to be 1.1 year[4]. As a noble gas isotope and with a half-life of 10.76 y, ^{85}Kr resides and mixes thoroughly in the atmosphere, reaching an isotopic abundance of $\sim 10^{-11}$. Known ^{85}Kr emissions are used for the validation and calibration of global atmospheric circulation models[5,6], while an undeclared temporary and spatially concentrated ^{85}Kr increase in the air can be an indicator for a nuclear leak accident or a clandestine plutonium separation[7]. In the next-generation experiments searching for dark matter[8], trace ^{85}Kr in liquid xenon detectors must be quantified and reduced via purification in order to suppress this significant source of background. ^{85}Kr is also an ideal tracer for environmental systems such as groundwater and ice[9,10]. It can be used for dating samples in the 2–50 y age range. Two other radioactive noble gas nuclides, ^{39}Ar and ^{81}Kr, with half-life of 269 y and 2.29×10^5 y, respectively, can be used for dating older samples[11–15].

At present, low level counting (LLC) of the decay radiation[16], accelerator mass spectrometry (AMS)[17,18], and atom trap trace analysis (ATTA)[19] can be used to analyze these rare isotopes. In LLC measurements, the minimal sample size for ^{85}Kr detection is 10 μL of Kr gas at the standard temperature and pressure (STP), and several hundred mL Ar gas for ^{39}Ar detection[20]. Due to its very long half-life, ^{81}Kr cannot be analyzed using LLC. ^{81}Kr detection by AMS has been demonstrated using Kr samples of 500 μL size[21]. ATTA is a laser-based instrument, utilizing a magneto-optical trap to capture atoms of the desired isotope, which only occurs when the laser frequency precisely matches the resonance frequency of a particular atomic transition. Any small changes in the atomic transition frequency, such as the isotope shifts caused by changes in nuclear size and mass, are sufficient to perfectly distinguish between the isotopes. ATTA is unique among trace analysis techniques as it is free of interferences from other isotopes, isobars, atomic or molecular species. The recent progress in ATTA reduced the necessary krypton sample size for ^{81}Kr detection to 5–10 μL[22]. Recently, first ATTA analysis of ^{39}Ar has also been performed[23], although the counting rate needs to be improved by a factor of 10–100 for practical applications.

Atom trap trace analysis is an emerging and novel technique for the analysis of environmental noble-gas radionuclides. Reliability and reproducibility of the method have to be examined and verified prior to its use in large-scale real-world applications. It is desirable to have an inter-comparison among different ATTA apparatuses and a cross check by a different analytical method. In this work, 12 samples with ^{85}Kr/Kr ratios in the range of 10^{-13} to 10^{-10} are measured using two separate ATTA instruments in Hefei, China, and Argonne, USA,

respectively. They are also measured in a low-level-counting (LLC) laboratory in Bern, Switzerland. The three laboratories conducted the measurements independently. The comparison shows that the ^{85}Kr/Kr ratios determined by both ATTA apparatuses agree well with the ^{85}Kr activities determined by LLC. The results demonstrate that the ATTA instruments can be used for dating environmental samples with a sample size as low as a few micro-liters of Kr gas at STP. Samples of such a size can be obtained from less than 100 liters of groundwater or 40 kg of ice, which are practical to retrieve and degas in field studies.

Results

ATTA determination of the abundances of the rare isotopes for a given sample is realized by simultaneously measuring the single atom counting rate of ^{85}Kr (or ^{81}Kr) and the trap loading rate of a stable isotope, ^{83}Kr, which has an abundance of 11.5% in natural krypton gas. Fig. 1 illustrates the correlation between the measured ^{85}Kr (or ^{81}Kr) counting rates and the ^{83}Kr loading rates. Two commercial Kr samples (Nanking Special Gas Inc.) were used, one acquired in 2007 and the other in 2012. In the experiment, a range of experimental parameters were deliberately changed, leading to considerable changes in the trapping efficiency. The measured results show good linear correlations between the single atom counting rates of rare isotopes and the loading rates of the stable isotope ^{83}Kr. Due to their differences in isotopic abundances, the rates in comparison differ by as much as 10 orders of magnitude. Linear fits of the data give the normalized rare isotope counting rates (k values shown in Fig. 1). The ^{85}Kr/^{83}Kr ratio of the 2007 sample is 71% of that of the 2012 sample. This drop in the ratio is consistent with the 10.76 y half-life and atmospheric history of ^{85}Kr.

To conduct a blind test of the quantitative analysis capability of the ATTA instruments, twelve krypton samples with different ^{85}Kr/Kr ratios were prepared at University of Bern, Switzerland, by mixing varying amounts of modern atmospheric krypton with a krypton sample collected from air prior to the dawn of the nuclear age containing basically zero ^{85}Kr concentration. The ^{85}Kr/Kr ratios of these samples, varying from $<1\times10^{-13}$ to 1×10^{-10}, were determined by LLC of ^{85}Kr at University of Bern. The ^{85}Kr/^{83}Kr ratios of the 12 samples were measured independently by ATTA setups in Argonne and in Hefei. Typically 5–10 μL Kr sample were used in each ATTA measurement. The results are listed in Table I and depicted in Fig. 2. Note that a log-log plot is employed in the figure (and also in Fig.1). The ^{85}Kr/^{83}Kr ratio of Sample No. 4, which is close to the 2012 commercial sample, is set as reference (1.00) in Table I. The value of the 2012 commercial sample is indicated by a horizontal line in Fig. 2. The ^{85}Kr/^{83}Kr ratios measured by both ATTA setups have excellent linear correlations with the ^{85}Kr activities measured by LLC. The statistical deviations of the linear fits are below 5% for both ATTA instruments.

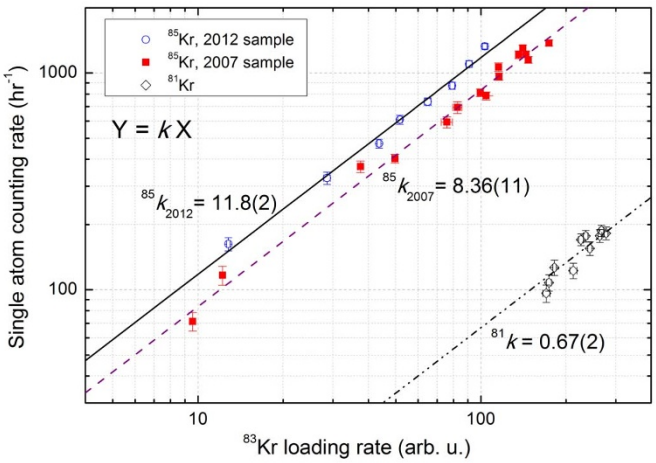

Figure 1 | ^{85}Kr counting rates measured by the ATTA-Hefei setup. Two commercial krypton gas samples were used, one acquired in 2012 (open circles) and the other acquired in 2007 (solid squares). Open diamonds are the measured ^{81}Kr counting rates. Note that a log-log plot is employed. The data were fitted with proportional functions, and the obtained proportional coefficients (k values) are given beside the lines, respectively. Values in parenthesis are the uncertainties (1σ) at the last digit.

Discussion

In the ATTA measurement, the sample size requirement is determined by the sample gas pressure needed to sustain the discharge and to reduce the impact of cross-sample contamination. For the ATTA-Hefei setup, the typical sample gas flow rate is about 0.7 μL/s (STP). The sample gas is re-circulated by sending the gas from the exhaust end of the turbo pumps back to the source chamber. In order to sustain the discharge, the total sample gas in the ATTA chambers is about 8 μL. A smaller Kr sample can also be analyzed by first mixing with pure Xe gas before measurement. Because some krypton atoms are embedded in the inner walls of the vacuum chambers during previous measurements, and subsequently released back into the vacuum chambers, cross sample contamination gradually increases over time during the measurement. The total observed ^{85}Kr counts N can be interpreted as:

$$N = N_0 + N_{\rm con} \qquad (1)$$

where N_0 is the counts from the studied sample, and $N_{\rm con}$ is those from the contamination. The $N_{\rm con}$ value is proportional to the volume and the ^{85}Kr/Kr ratio of the contamination gas released during the measurement.

Such a memory effect is reduced significantly by flushing the vacuum system using a xenon discharge for 40 hours between measurements. After this lengthy flushing, the outgas rate decreases significantly, which has been determined to be about 0.01 μL/hr. A typical ATTA measurement takes about 5 hours to acquire sufficient ^{85}Kr counts. In this case, the counts from contamination can be safely neglected unless the ^{85}Kr abundance in the present sample is much smaller than those in previous samples.

For samples with very low ^{85}Kr/Kr ratios, the influence from the memory effect is noticeable. A simple model was developed to estimate the contribution from the previous sample ("contamination") to the measured ^{85}Kr counts. In this model, the ^{85}Kr/Kr ratio of the contamination is set as that of the latest sample measured, and the outgas rate takes the value measured at the end of the Xe gas flushing process. The ^{85}Kr counts due to the contamination during the measurement, $N_{\rm con}$, can be calculated and then subtracted from the total observed ^{85}Kr counts N. The model was verified by measuring the ^{85}Kr counting rate using a Kr sample containing no ^{85}Kr. In this case, the measured ^{85}Kr counts should all come from the contamination. The model was used to correct the measured ^{85}Kr/Kr ratio by taking into account the "history" of the samples measured in the ATTA instrument. The corrected values are shown in brackets in Table I. Note that the memory effect has no influence for the samples with relatively higher ^{85}Kr concentrations.

The overall uncertainty of the determined ^{85}Kr/Kr ratio consists of the uncertainty in the measurement of the ^{83}Kr loading rate (typically about 2%), and the uncertainty in the ^{85}Kr counts. According to Eq. 1), the latter one consists of the statistical uncertainty ($1/\sqrt{N}$), and the uncertainty due to the memory effect. In this case, the uncertainty relates with the ^{85}Kr abundance of the sample as well as the sample size (Fig. 3). Generally, a smaller sample size or lower ^{85}Kr abundance in the sample (i.e., from an old groundwater) leads to less ^{85}Kr counts and larger uncertainties from both the statistical ($1/\sqrt{N}$) and the memory effect. The ATTA apparatus can be used for routine ^{85}Kr/Kr measurements at the uncertainty level of 5–10% with a size of

Table I | ^{85}Kr isotopic abundances in different samples measured by ATTA and LLC

Sample label	^{85}Kr activity, LLC dpm/cc	^{85}Kr activity, LLC relative	ATTA-Hefei	ATTA-Argonne
1	346(18)	3.85(20)	3.74(7)	3.64(13)
2	286(13)	3.19(15)	3.14(9)	3.17(16)
3	172(7)	1.91(8)	1.81(7)	1.92(10)
4	90(3)	1.00(3)	1.00(3)	1.00(5)
5	73(3)	0.81(3)	0.76(4)	0.93(5)
6	32(2)	0.35(2)	0.35(2)	0.34(2)
A1	0.0(3)	0.000(3)	$< 0.037^{a}$ [< 0.03]	$< 0.015^{a}$
A2	27.5(3)	0.306(3)	0.288(11) [0.286(11)]	0.271(18)
A3	17.7(13)	0.197(14)	0.195(9) [0.191(9)]	0.173(13)
A4	49.3(3)	0.549(3)	–[b]	0.487(27)
A5	2.6(2)	0.029(2)	0.037(3) [0.035(3)]	0.032(5)
A7	9.5(13)	0.106(14)	0.098(6) [0.097(6)]	0.090(8)

Numbers in parenthesis are the 1σ standard deviations at the last quoted digit. Numbers in brackets are the values after the correction of the memory effect.
[a]Value at the 90% confidence limit.
[b]Not available due to sample leak during transportation.

about 5 μL for samples with moderate ^{85}Kr/Kr abundance ($>2 \times 10^{-12}$, or 1/10 of the ^{85}Kr/Kr abundance in modern air). If needed, prolonged flushing of the vacuum chamber can further reduce the memory effect and allow longer measuring time using a smaller sample.

The absolute isotopic abundance of ^{85}Kr of a given sample can be determined by ATTA by comparing to a standard sample with known ^{85}Kr/Kr abundance. The method can also be applied for the other radioactive Kr isotope, ^{81}Kr, which has a much longer half-life (229 ky) and a lower natural abundance (6×10^{-13}). As shown in Fig. 1, the ^{81}Kr/Kr ratio can be obtained also using ^{83}Kr as the control isotope. Determination of the ^{39}Ar/Ar ratio using ATTA will also be feasible if the counting rate of ^{39}Ar can be improved by an order of magnitude. High efficiency (thus less sample size is needed) and high selectively (immune to the contamination from any other atoms or molecules) are the main advantages of the ATTA method compared to other trace analysis methods.

Methods

ATTA-Hefei. The configuration of the ATTA apparatus in Hefei is presented in Fig. 4. Krypton atoms in the metastable state $5s[3/2]_2$, marked as Kr*, are produced through a radio-frequency-driven discharge inside a ceramic tube cooled by liquid-N_2. The Kr* atomic beam is transversely cooled by 811 nm laser light tuned to the resonance of the $5s[3/2]_2$ - $5p[5/2]_3$ transition, and then slightly focused in a two-dimensional magneto-optic trap (2D-MOT). The Kr* beam flux is about 10^{16} atoms/s/sr in the trapping chamber two meters downstream from the discharge[24]. Kr* atoms are slowed down in a Zeeman slower and then trapped in a MOT. For abundant isotopes of Kr, about 10^8 cold atoms can be trapped simultaneously in the MOT.

For rare isotopes, ^{85}Kr and ^{81}Kr, due to their extremely low abundances, only individual atoms are trapped at a time. An electron-multiplying charge-coupled device (EMCCD) is used to record the fluorescence image of the trapped atom. The signal-to-noise ratio of a single trapped atom is about 15. Because the trapping efficiency slowly drifts over time due to various changes of the experimental conditions, the atom counting rate needs to be normalized by the trap loading rate of the stable isotope ^{83}Kr (isotopic abundance = 11.5%), which is measured with a "quench-and-capture" process. In the quench process, ^{83}Kr atoms in the trap are excited by an 810 nm laser beam from the metastable $5s[3/2]_2$ state to the $5p[5/2]_2$ state, then to the ground state through spontaneous decays (Fig. 4). In this way, the metastable atoms in the trap are quenched and removed from the MOT when the 810 nm laser beam is on. When it is turned off, new ^{83}Kr atoms are captured; their

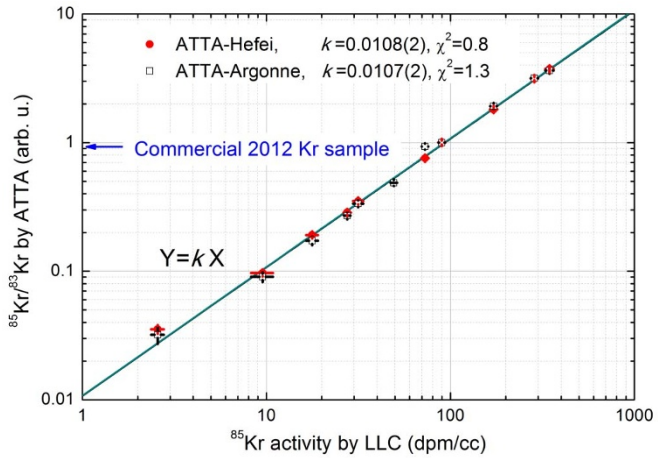

Figure 2 | Comparison between the ^{85}Kr/^{83}Kr ratios determined by ATTA-Hefei (solid circles), ATTA-Argonne (open squares) and the ^{85}Kr activity by LLC. Note that a log-log plot is employed. The data were fitted with proportional functions, and the obtained proportional coefficients (k values) are given for both data sets, respectively. Values in parenthesis are the uncertainties (1σ) at the last digit. The horizontal arrow indicates the corresponding ^{85}Kr/^{83}Kr ratio of the commercial 2012 Kr sample (see Fig. 1) determined by ATTA-Hefei.

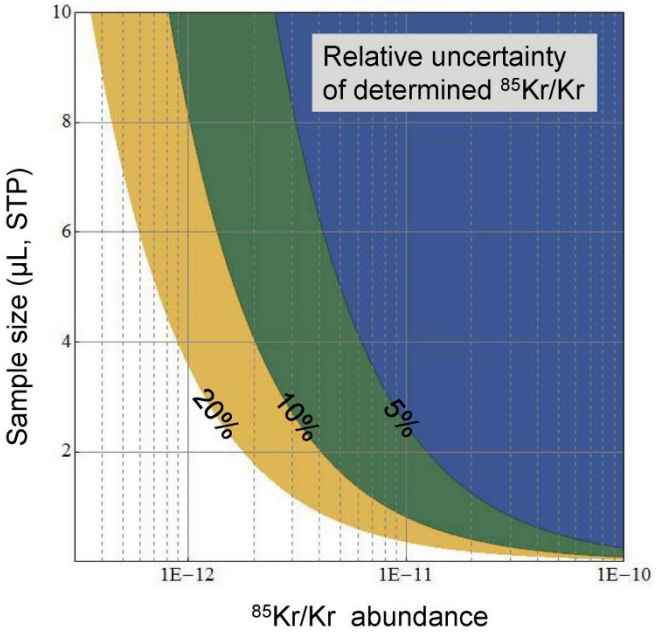

Figure 3 | Relative uncertainty of the ^{85}Kr abundance determined by the ATTA-Hefei instrument.

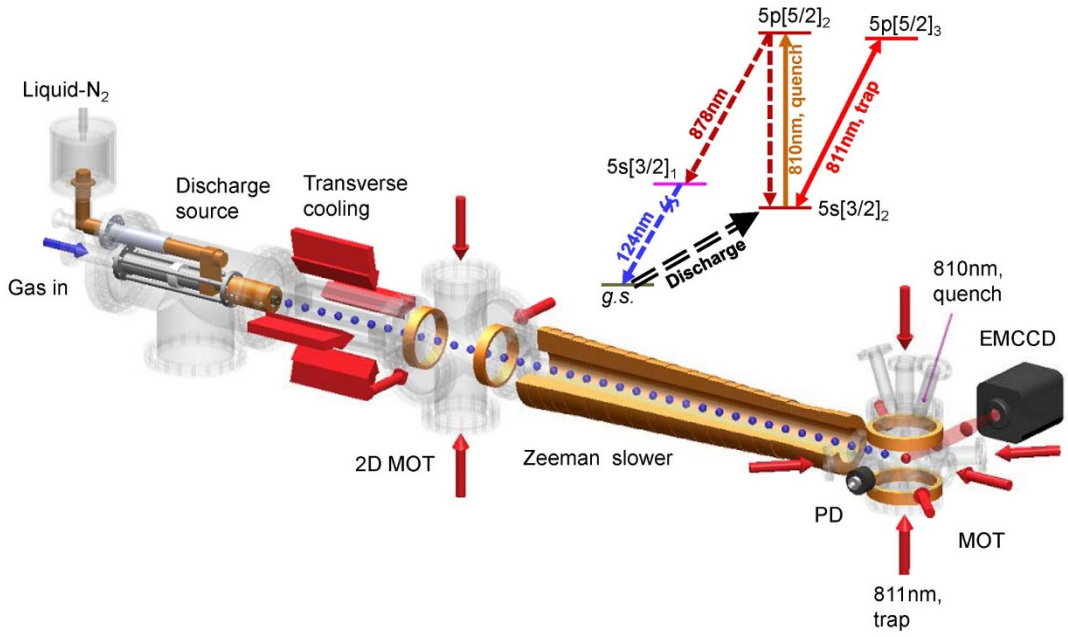

Figure 4 | Experimental setup of the ATTA-Hefei instrument. The diagram shows the lowest energy levels of Kr. Abbreviations: EMCCD, electron-multiplying charge-coupled device; *g.s.*, ground state; MOT, magneto-optic trap; 2D MOT, two-dimensional MOT; PD, photodiode detector.

number increases linearly at a rate almost equal to the trap loading rate in the first few milliseconds. By measuring the fluorescence (811 nm) light intensity emitted from the trapped atoms during this initial linear period, the number of trapped atoms is determined; a linear fit over time yields the loading rate of ^{83}Kr. We have demonstrated that the loading rate of a stable Kr isotope can be determined with an uncertainty of 2%, and it can be used to normalize the single atom counting rate of ^{85}Kr or ^{81}Kr in order to derive the ^{85}Kr/Kr or ^{81}Kr/Kr isotope ratios[25].

ATTA-Argonne. The ATTA apparatus at Argonne National Laboratory is similar to ATTA-Hefei. The details of the setup can be found in Ref. 22. The major difference between the two apparatuses is that the loading rate of the control isotope (^{83}Kr) is measured by two different methods developed by the Hefei group and Argonne group, respectively[22,25]. In ATTA-Argonne, a laser beam of 810 nm is also used to quench the metastable ^{83}Kr atoms in the trap. However unlike the "quench-and-capture" method used in ATTA-Hefei, the quench laser is left on all the time. Instead of measuring the 811 nm fluorescence, ATTA-Argonne monitors the 878 nm fluorescence emitted by the atom during the quench process (from $5p[5/2]_2$ to $5s[3/2]_1$ then to the ground state through spontaneous decay, see Fig. 4). Because each metastable Kr atom can only emit one 878 nm photon before it decays to the ground state, there is a one-to-one correspondence between the number of ^{83}Kr atoms in the trap and the photon number. Therefore, the intensity of the observed 878 nm fluorescence is proportional to the ^{83}Kr loading rate, and is insensitive to the variation of experimental parameters such as trap lifetime, laser power, etc.[22]. The uncertainty of ^{83}Kr loading rate determined using this method is 5% or less.

LLC-Bern. Low-level-counting measurements are preferably performed in a low-background environment[20]. One such state-of-the-art laboratory is located 35 meters (70 m.w.e) below the surface in an underground laboratory at the University of Bern in Switzerland. 99.6% of ^{85}Kr decays by β-radiation with a maximum energy of 0.69 MeV without γ-emission. Gas proportional counting is applied for the identification of ^{85}Kr decay. Because of the relatively high β-energy, the energy spectrum above the 3 keV electronic cut-off is taken into account. The deposition of the β-energy within the gas volume increases with pressure. In addition, a smaller volume of the counters reduces the background because the surface (and hence the influence) of self activity of the counter material (mostly high purity copper) are smaller. Gas proportional counters of different volumes (10-100 mL), pressures (10-23 bar), and methane/argon admixtures (p5-p40) are used at Bern. Depending on the configuration, counting time for ^{85}Kr ranges from 3 days to 6 days.

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Author contributions

G.-M. Y., C.-F. C., Y. R. S., L.-Y. T. and S.-M. H. developed the ATTA instrument in Hefei and conducted the experiments in collaboration with W. J. and Z.-T. L. W. J. performed the ATTA measurements in Argonne. R. P. conducted the LLC measurements in Bern and prepared the samples. S.-M. H. and Z.-T. L. wrote the manuscript. All authors reviewed the manuscript.

Additional information

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