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Atom Trap Trace Analysis

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Abstract. A new method of ultrasensitive trace-isotope analysis has been developed based upon the technique of laser manipulation of neutral atoms. It has been used to count individual ⁸⁵Kr and ⁸¹Kr atoms present in a natural krypton sample with isotopic abundances in the range of 10^{-11} and 10^{-13} , respectively. The atom counts are free of contamination from other isotopes, elements, or molecules. The method is applicable to other trace-isotopes that can be efficiently captured with a magneto-optical trap, and has a broad range of potential applications.

INTRODUCTION

Much can be learned from the concentrations of the ubiquitous long-lived radioactive isotopes. W. Libby and coworkers first demonstrated in 1949 that trace analysis of ¹⁴C ($t_{1/2} = 5715$ yr, isotopic abundance = 1×10^{-12}) can be used for archaeological dating [1]. Since then, two well established methods, low-level counting [2] and accelerator mass spectrometry [3], have been used to analyze many more trace-isotopes at about the parts-per-trillion level and to extract valuable information encoded in the production, transport, and decay processes of these isotopes. The impact of ultrasensitive trace-isotope analysis has reached a wide range of scientific and technological fields. We have recently developed a new method, Atom Trap Trace Analysis (ATTA) [4], which is capable of analyzing trace-isotopes with an isotopic abundance at the parts-per-trillion level. This new method promises to enhance the capability and expand the applications of ultrasensitive trace-isotope analysis.

In this paper, we will first describe the motivation of analyzing ⁸¹Kr and ⁸⁵Kr. We will then survey the existing techniques, followed by a description on ATTA and our work on the detection of the rare krypton isotopes. Finally, we will discuss some other potential applications of ATTA.

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RARE KRYPTON ISOTOPES

Krypton gas constitutes 1 ppm of the earth atmosphere in fraction volume. It has six stable isotopes, ^{78}Kr (isotopic abundance = 0.35%), ^{80}Kr (2.25%), ^{82}Kr (11.6%), ^{83}Kr (11.5%), ^{84}Kr (57%), ^{86}Kr (17.3%), and two long-lived radioactive isotopes, ^{81}Kr and ^{85}Kr (Table 1). There are about 2×10^4 ^{81}Kr atoms and 3×10^5 ^{85}Kr atoms in 1 liter STP of air. There are roughly 10^3 ^{81}Kr atoms in one kilogram of modern water or ice.

^{81}Kr is produced in the upper atmosphere by cosmic ray induced spallation and neutron activation of stable krypton isotopes [5]. Throughout its long lifetime in the atmosphere, ^{81}Kr is well mixed and distributed over the earth with a uniform isotopic abundance. Human activities on nuclear fission have had a negligible effect on the ^{81}Kr concentration, largely because the stable ^{81}Br shields ^{81}Kr from the neutron rich isotopes that are produced in nuclear fission [6]. These physical and chemical properties make ^{81}Kr an ideal tracer for dating ice and groundwater that are older than 100,000 years [7], which is beyond the range of ^{14}C -dating.

^{85}Kr is a fission product of ^{235}U and ^{239}Pu . Its present-day concentration in the environment has primarily been released by nuclear fuel reprocessing plants. As a result, its abundance in the atmosphere has increased by six orders of magnitude since the 1950s. It has been used as a general tracer to study air and ocean currents [8], date shallow groundwater, and monitor nuclear-fuel reprocessing activities [9]. Due to its fast mobility, it may be used as a leak sensor to check the seals of nuclear fuel cells and nuclear waste containers.

Noble gas tracers in general have the advantages that they can be chemically separated from large amount of raw samples, and that their transport processes in environment are easier to understand.

Table 1. The properties of Kr-81 and Kr-85.

Isotope	Half-life (year)	Atmospheric Isotopic abundance	Applications
Kr-81	2.3×10^5	$(5.9 \pm 0.6) \times 10^{-13}$, LLC [5] $(4.5 \pm 0.3) \times 10^{-13}$, LLC [10] $(5.3 \pm 1.2) \times 10^{-13}$, AMS [6] $(1.0 \pm 0.4) \times 10^{-12}$, ATTA [4]	Geological dating of polar ice and groundwater
Kr-85	10.8	$\sim 10^{-11}$, LLC [8]	Monitor nuclear-fuel reprocessing activities

EXISTING TECHNIQUES

Here we briefly review the existing techniques with an emphasis on the analysis of the rare krypton isotopes.

Low-Level Decay Counting (LLC)

Long-lived trace-isotopes decay in various ways including α -decay, β -decay, or e-capture. A single decay event releases energy in the range of 10^4 – 10^7 eV, and can be readily detected with a scintillation or a proportional counter with high efficiency

(>50%). The overall detection efficiency is usually limited by the short counting time (t_c) compared with the half-life of isotopes ($t_{1/2}$) since the fraction of nuclei decayed during the counting time, $f \approx \ln 2 \times (t_c/t_{1/2})$ when $t_c \ll t_{1/2}$. For example, in one week of counting, 10^{-3} of ^{85}Kr , 10^{-6} of ^{14}C , or 10^{-7} of ^{81}Kr would decay. The shorter the half-life, the more efficient this method is.

LLC is often carried out in a specially designed underground laboratory in order to avoid background due to cosmic-rays and the radioactivity present in common materials. Environmental samples often contain other radioactive isotopes, which can be reduced by chemical purification or, in the case of short-lived impurities such as ^{222}Rn ($t_{1/2} = 3.8$ days), by waiting.

LLC is used to analyze ^{85}Kr [8]. It was also used in the first observation of atmospheric ^{81}Kr [5], but can no longer be used because in today's air the decay activity of ^{85}Kr is 10^5 times that of ^{81}Kr . Pre-nuclear-age samples are also affected, and are now extremely difficult to analyze with LLC due to the inevitable small contamination of modern krypton during the sampling and preparation stages.

Mass spectrometry (MS)

Atom counting has a number of advantages over decay counting. The efficiency and speed of atom counting is not fundamentally limited by the long half-lives of isotopes, nor is it affected by radioactive backgrounds in the environment or in samples.

The most popular atom-counting method is mass spectrometry, which can separate and detect individual ions of a chosen mass. However, the sensitivity of this method is limited by interference from isobars, i.e., atoms of other elements or molecules with the same mass number, which are present in trace amount even after the most careful chemical purification. Mass spectrometry in general has a detection limit at an isotopic abundance level of 10^{-9} [11], and is not suitable for analyses at the PPT level.

Accelerator mass spectrometry (AMS)

Isobar contamination can be eliminated in some cases by performing mass spectrometry with a high energy ($\sim\text{MeV}$) beam from an accelerator [12, 13, 14]. First, molecular isobars can be eliminated by passing the accelerated beam through a thin foil where molecules disintegrate. Second, some isobar atoms can be eliminated by exploiting the stability property of negative ions that are used in the first acceleration stage of a tandem accelerator. For example, $^{14}\text{N}^-$, the only abundant isobar of $^{14}\text{C}^-$, is not stable, and consequently not accelerated.

The advantages of atom counting are indeed realized with AMS, which has replaced LLC as the standard method of ^{14}C -dating. Furthermore, AMS has opened up new applications by analyzing other long-lived trace-isotopes that were previously impossible to do. The most utilized isotopes in AMS are ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , ^{41}Ca , and ^{129}I [3]. The AMS community has grown steadily since the late 1970s, even at a cost of several million U.S. dollars for a typical AMS setup. As of 1998, there were

about 40 dedicated AMS facilities around the world, and more facilities where AMS works are carried out [15].

Krypton isotopes can not be analyzed at a standard AMS facility that uses a tandem accelerator because they do not form negative ions. A new approach has been developed by P. Collon et. al. [6], who used an ECR source to produce positive krypton ions, and a high energy (GeV) cyclotron (K1200 Superconducting Cyclotron, MSU) to produce a fully stripped krypton ion beam. Once fully stripped, $^{81}\text{Kr}^{+36}$ can be cleanly separated from its abundant isobar ^{81}Br ($Z=35$). They have thus realized radiokrypton dating and determined the ages of groundwater, ranging from 200 to 400 kyr, at several sites in the Great Artesian Basin in Australia [15]. In a typical run, 16 tons of groundwater were processed to extract 0.4 cm^3 STP of krypton gas, and resulted in 60-100 ^{81}Kr counts with a detection efficiency of $\sim 1 \times 10^{-5}$. Because old ice is much more difficult to extract than old groundwater in similar quantities, an improved efficiency, at 10^{-3} or higher, is needed before dating ice can be realized.

Resonance ionization mass spectrometry (RIMS)

An alternative method of reducing isobar contamination is to use resonant photons to selectively ionize the element of choice [16, 17]. Figure 1a shows a two-step ionization scheme where the first step is a resonant excitation, followed by a second non-resonant ionization step [18]. More steps of resonant excitation can be added to enhance the selectivity. The combination of isobar selection by resonance ionization and isotope selection by mass spectrometry would, in principle, enable RIMS to reach a selectivity well below the PPT level. In practice, however, complications such as thermal or collisional ionization may limit the detection sensitivity and selectivity.

G.S. Hurst and coworkers have counted ^{81}Kr atoms using the excitation scheme illustrated in figure 1a [18]. Krypton is a difficult case because the first excitation needs a laser of 116.5 nm wavelength. In their work, ^{81}Kr had to be pre-enriched with a mass spectrometer three times to reach an isotopic abundance of $\sim 10^{-4}$ before counting was performed. The whole process, including the enrichment cycles, has a total detection efficiency of $>50\%$. This scheme, although extremely efficient, involves a multi-step operation that is difficult to implement in practical applications [19].

RIMS is successfully implemented in cases where cw narrow-bandwidth lasers are available to excite atoms. For example, K. Zimmer et. al. have analyzed ^{90}Sr , a nuclear fission product, in dust particles collected in Munich after the Chernobyl accident [20]. Applying collinear laser spectroscopy on a fast atomic beam, they have reached an isotopic selectivity (Sr^{90}/Sr) of $>10^{11}$ with a detection limit of 3×10^7 atoms. A simplified version [21], in which laser spectroscopy on a thermal atomic is applied, has demonstrated an isotopic selectivity (Sr^{90}/Sr) of $>10^{10}$ with a detection limit of 5×10^6 atoms. Work aimed at analyzing ^{41}Ca at a higher selectivity is in progress [22].

Photon-burst mass spectrometry (PBMS)

A single atom can also be detected by observing its fluorescence burst in a resonant laser beam [23]. By detecting multiple photons in coincidence during the short transit time, both the detector dark counts and the noise photon counts due to light scattered off walls can be suppressed. Furthermore, multiple photon detection also enhances isotopic selectivity.

Using PBMS, W. M. Fairbank jr. and coworkers detected ^{85}Kr at the isotopic abundance of 6×10^{-9} [24]. In their work, metastable krypton atoms in a fast beam, produced by neutralizing a mass-selected ion beam, are counted when passing through a photon-burst detection region that consists of ten avalanche photodiode detectors. They pointed out that, by doubling the number of photon detectors and thereby improving the photon collection efficiency, this method may detect ^{85}Kr at the atmospheric abundance level ($\sim 10^{-11}$).

B.D. Cannon et. al. proposed a new concept [25], in which a resonant laser beam is used to transversely deflect ^{85}Kr atoms out of the primary metastable krypton. The separated ^{85}Kr atoms are then detected with the photon-burst technique. They succeeded in enriching ^{85}Kr in the deflected beam by a factor of 1.2×10^4 , which is limited by non-resonant deflection due to collisions [26].

ATOM TRAP TRACE ANALYSIS (ATTA)

ATTA is a new laser-based atom-counting method [4]. It has been used to analyze both ^{81}Kr and ^{85}Kr in an atmospheric krypton sample with no other isotope enrichment processes. The atom counts contain no contamination from other isotopes, elements, or molecules. The isotopic selectivity ($\text{Kr}/^{81}\text{Kr}$) has reached 1×10^{13} , and is currently limited by the operation time. ATTA can tolerate impure gas samples, and does not require a special operation environment.

Our design is based on a type of magneto-optical trap system that had been used to trap various metastable noble gas atoms [27, 28]. Trapping krypton atoms in the $5s[{}^3/2]_2$ metastable level (lifetime ≈ 40 sec) is accomplished by exciting the $5s[{}^3/2]_2 - 5p[{}^5/2]_3$ transition (Fig. 1b). Two repump sidebands are generated via additional AOMs to optically pump the atoms into the $F=13/2$ level for ^{85}Kr and $F=11/2$ level for ^{81}Kr where they can be excited by the trapping light. In the analysis, a krypton gas sample is injected into the system through a discharge region, where about 1×10^{-4} of the atoms are excited into the $5s[{}^3/2]_2$ level via electron impact excitation. Two-dimensional transverse cooling is used to reduce the atomic beam divergence and amplify the atom flux in the forward direction by a factor of 20. The thermal (300°C) atoms are then decelerated with the Zeeman slowing technique [29, 30], and loaded into a MOT [31]. Atoms remain trapped for an average of 1.8 sec as the vacuum is maintained at 2×10^{-8} Torr. This trap system can capture the abundant ^{83}Kr atoms at the rate of $2 \times 10^8 \text{ sec}^{-1}$. The ratio of the capture rate to the injection rate gives a total capture efficiency of 1×10^{-7} .

With expected capture rates between 10^{-3} sec^{-1} and 10^{-2} sec^{-1} for the rare krypton isotopes, the system must be capable of detecting a single atom in the trap [32, 33]. In the trap, a single atom scatters resonant photons at a rate of $\sim 10^7 \text{ sec}^{-1}$, of which 1% are collected, spatially filtered to reduce background light, and then focused onto an avalanche photodiode with a photon counting efficiency of 25%. In order to achieve a high capture efficiency and a clean single atom signal, the setup is switched at 2 Hz between the parameters optimized for trap capture and for atom counting. The resulting fluorescence signal of a single atom is 16 kcps (kilo-counts per second) while the background level is 3.4 kcps (Fig. 2).

We have trapped and counted ^{85}Kr and ^{81}Kr atoms from a natural krypton gas sample. The frequency settings of the trapping laser and the two sidebands are in good agreement with previous spectroscopic measurements obtained using enriched ^{85}Kr gas and enriched ^{81}Kr gas [34]. We have also mapped the atom capture rate versus laser frequency (Fig. 3). Furthermore, repeated tests were performed under conditions in which a ^{85}Kr (^{81}Kr) trap should not work, such as turning off repump sidebands and tuning the laser frequency above resonance, and these tests always yielded zero atom counts. These tests show that the recorded counts are solely due to laser-trapped ^{85}Kr (^{81}Kr) atoms.

Previous efforts to develop a laser-based technique have encountered serious problems with contamination from nearby abundant isotopes. ATTA is immune from isotope contamination for several reasons: fluorescence is only collected in a small region ($\phi 0.5 \text{ mm}$) around the trap center; a trapped atom is cooled to a speed below 1 m/s so that its laser induced fluorescence is virtually Doppler-free; the long observation time ($>100 \text{ ms}$) allows the atom to be unambiguously identified ($S/N \approx 40$); and trapping allows the temporal separation of capture and detection so that both capture efficiency and detection sensitivity can be optimized. Our design also provides additional features, such as chopping off the atomic beam before detecting the trapped atom or sending in a laser beam to selectively push out (or de-excite) the atoms of contaminant isotopes.

The capture rate of our system depends on the discharge current, laser power, as well as optical alignment. At one particular setting, we measured capture rates of ^{83}Kr , ^{85}Kr , and ^{81}Kr , which were $(1.5 \pm 0.3) \times 10^8 \text{ sec}^{-1}$, $(1.9 \pm 0.3) \times 10^{-2} \text{ sec}^{-1}$, and $(1.3 \pm 0.4) \times 10^{-3} \text{ sec}^{-1}$ respectively. If we assume the same detection efficiency for all three isotopes, then we get isotopic abundances of $(1.5 \pm 0.4) \times 10^{-11}$ for ^{85}Kr and $(1.0 \pm 0.4) \times 10^{-12}$ for ^{81}Kr , which are in good agreement with previous measurements using other methods [5, 6, 10]. The capture efficiencies can be calibrated with enriched samples of known isotopic abundance to correct for any isotope-dependent effects and measure isotopic ratios in unknown samples. For example, in ^{81}Kr -dating, a known amount of ^{85}Kr can be mixed into the sample, thus allowing the ^{81}Kr abundance be extracted by measuring the ratio of $^{81}\text{Kr}/^{85}\text{Kr}$.

Efficiency

Our system has achieved an efficiency of 1×10^{-7} . Use of this system to measure the abundance of ^{85}Kr to within 10% would require 2 hours and a krypton sample of 3 cm^3 STP while measurement of ^{81}Kr to within 10% would require 2 days and a sample of 60 cm^3 STP. This limits the current system to atmospheric applications where large samples of gas are available. Improvements, such as a liquid-nitrogen cooled discharge source and recirculation of krypton gas [35], are presently under investigation.

The metastable level of krypton can also be populated via photon excitations (Fig. 1c, 1d). With a suitable laser or lamp, the excitation efficiency could be much higher than the $\sim 1 \times 10^{-4}$ currently achieved with a discharge. Furthermore, without the constraint on gas pressure imposed by a discharge, atoms can be well collimated and cooled, thus further reducing the inefficiency due to beam divergence.

Trace Analysis of Cesium Isotopes

By combining a mass separator and a MOT, Dave Vieira and coworkers have recently analyzed two long-lived radioactive isotopes, ^{135}Cs and ^{137}Cs [36]. Applications of this analysis are in environmental science [37] and nonproliferation monitoring. In this work, cesium is ionized, accelerated, mass selected, and implanted into a foil located inside a glass cell. Neutral atoms released from the foil are then captured by a MOT via the vapor cell loading technique, and detected by observing their fluorescence in the trap.

With a particular sample, where the isotopic abundances of ^{135}Cs and ^{137}Cs are about 10^{-6} - 10^{-5} , the MOT holds $\sim 20,000$ atoms. By comparing the trap fluorescence of both ^{135}Cs and ^{137}Cs . They have determined the abundance ratio $^{135}\text{Cs} / ^{137}\text{Cs} = 1.21 \pm 0.10^{\text{stat}} \pm 0.30^{\text{sys}}$.

OTHER POTENTIAL APPLICATIONS

Laser manipulation of neutral atoms has been demonstrated on alkali metal (Li, Na, K, Rb, Cs, Fr), alkali earth (Mg, Ca, Sr), noble gas (He, Ne, Ar, Kr, Xe), and individual cases including Al, Cr, Ag, and Yb. Based on these demonstrated cases, there are already 16 long-lived radioisotopes (Fig. 4) that can be analyzed with ATTA for a broad range of applications. The conference proceedings of AMS and RIMS are good references where the applications are discussed. Some examples are discussed here.

Solar neutrinos

Solar neutrinos were first detected with a radioisotope tracer [38]. In this experiment, ^{37}Ar ($t_{1/2} = 35$ days) were produced at the rate of 0.5 atoms/day in a

sealed tank containing 615 tons of perchlorethylene via the $^{37}\text{Cl}(\nu_e, e)^{37}\text{Ar}$ (threshold = 0.814 MeV) reaction. These ^{37}Ar atoms were recovered with over 90% efficiency and counted in a proportional counter. LLC works very well here due to the short half-life, and that the source material is artificially maintained in a clean environment. The measured neutrino flux disagrees with the prediction of the Standard Solar Model [39], indeed the measured ^8B and ^7Be neutrino flux is 2.56 ± 0.22 SNU while the theoretical prediction is 7.7 ± 1.2 SNU, thus establishing the so-called solar neutrino puzzle. The later experiments as well as theoretical works continue to support this disagreement [40].

An analogous detector that counts ^{81}Kr produced in the $^{81}\text{Br}(\nu_e, e)^{81}\text{Kr}$ (threshold = 0.471 MeV) reaction has been proposed [41, 39]. Due to a lower reaction threshold, this detector would be more sensitive to the ^9Be (31%) neutrinos than the chlorine detector (15%). For a detector containing 1000 tons of a Br-chemical, ^{81}Kr is produced at a few atoms per day. Thus an atom-counter of ~10% efficiency is required.

Besides of measuring the present-day solar neutrino flux, radioisotopes can play a unique role in measuring the long-term average of the solar neutrino flux, and testing the long-term thermal stability of the solar core [42, 43]. In such a geochemical experiment, tracer atoms (for example, ^{98}Tc) are chemically extracted from an ancient mineral deposit (for example, molybdenite), and then counted. The number of tracer atoms present in the target mineral is a measure of the solar neutrino flux integrated over the lifetime of the tracer. Suitable geological deposits have been located for the ^{98}Tc and ^{205}Pb experiments. However, an efficient (10^{-3}) and unambiguous method of counting these tracer atoms has to be developed before such experiments can be carried out. MS [44], AMS [45], and RIMS [46] have been attempted, but none has succeeded so far.

Table 2. Proposed radioisotope experiments on time-integrated solar neutrino flux.

Tracer	Half-life (yr)	Target	Threshold (MeV)	Reference
Ca-41	1.0E5	K-41	2.36	[47]
Kr-81	2.3E5	Br-81	0.471	[41]
Tc-98	4.2E6	Mo-98	1.68	[48]
Pb-205	1.5E7	Tl-205	0.062	[49]

Archaeological and geological dating

^{41}Ca ($t_{1/2} = 100$ kyr) tracer could be used to date bones ranging from 50 thousand to 1 million years old [50, 51]. This period, while covers an important stage of early human development, is beyond the reach of ^{14}C -dating. ^{41}Ca is produced on the ground by cosmic rays, therefore, its isotopic abundance varies depending on the exposure length and erosion rate of the ground. Early AMS work indicated that $^{41}\text{Ca}/\text{Ca}$ in different bone samples vary in the range of 10^{-15} to 10^{-14} . However, because the detection limit of AMS, at 2×10^{-15} , is so close to the measured level that systematic errors may contribute to some of the observed variation [52]. If ATTA can

push down the detection limit to 1×10^{-13} , then dedicated setups can be used to investigate in detail on the feasibility of ^{41}Ca -dating. In addition, $^{41}\text{Ca}/\text{Ca}$ can be used to determine exposure age of geological samples.

$^{40}\text{K}/^{40}\text{Ar}$ dating is one of the most commonly used of all radiometric techniques [53]. In a variation of this method, the task of measuring $^{40}\text{K}/^{40}\text{Ar}$ is converted to a much easier and more reliable one of measuring $^{39}\text{Ar}/^{40}\text{Ar}$. ^{39}Ar is produced by irradiating the sample with neutrons via the $^{39}\text{Ar}(n,p)^{39}\text{K}$, and the resulting abundance can be calculated from the known reaction rates and the $^{39}\text{K}/^{40}\text{K}$ ratio. Here the isotopic abundance of each argon isotope is quite high ($>10\%$) and mass spectrometry is the standard analysis tool, with a detection limit of $\sim 10^7$ atoms. ATTA may be useful here due to its immunity to contamination [54]. With ATTA, steps of gas purification could be reduced or eliminated, and thereby minimizing the contamination by environmental argon. By employing laser excitation to populate argon atoms into the metastable level, ATTA could lower the detection limit significantly and open up new applications of $^{39}\text{Ar}/^{40}\text{Ar}$ dating.

Medical diagnostics

Radioisotope tracers, ^{14}C and ^3H in particular, are widely used in biomedical research. With the advancements in AMS, other long-lived isotopes, such as ^{41}Ca and ^{26}Al , are also becoming available to the biomedical field. It is advantageous to use long-lived isotopes on human subjects due to the low radioactivity of these isotopes.

One particularly interesting proposal that is currently under investigation with AMS is to use ^{41}Ca -tracing to diagnose osteoporosis, a disease commonly found in women after menopause [55]. A patient of osteoporosis loses bones, and hence calcium, at an excessive rate. The current standard medical practice is to monitor the bone density with X-ray imaging. Measuring the bone loss rate directly could be more sensitive to the patient's condition, and a faster feedback in assessing treatments. In this proposal, a subject of the high-risk group would take a ^{41}Ca pill. ^{41}Ca in tissues would be depleted within a few weeks, but ^{41}Ca in bones would last a lifetime. ^{41}Ca in urine samples, with an isotopic abundance in the range of 10^{-13} - 10^{-9} , can then be measured on a regular basis as a monitor of the bone metabolism. Note that AMS has met the technical needs of this proposal. The advantage of using ATTA lies in a significant reduction of cost (more than a factor of 10).

Other biomedical applications are nutrition studies using isotopes such as ^{22}Na , ^{40}K , and ^{41}Ca , and toxic studies using ^{10}Be and ^{26}Al [56].

Mapping ocean currents

Earth climate depends closely on the global ocean currents, which are mapped and modeled with the help of radioisotope tracers [57]. Radioisotopes are used to determine the "age" of water, which is the time since the water was near ocean surface and exchanged gas with the atmosphere. While the analyses of ^3H and ^{14}C have been successfully implemented, ^{39}Ar -tracing is of strong interest because it can be used to map ocean currents in the range of 10^2 - 10^3 years and fill the gap between the dating

ranges of ^3H and ^{14}C . Counting ^{39}Ar atoms in water is difficult because 1 liter of surface water contains only $\sim 1 \times 10^4$ ^{39}Ar atoms and the isotopic abundance of $^{39}\text{Ar}/\text{Ar}$ is 8.1×10^{-16} . At present, LLC is used to count ^{39}Ar , but requires a large amount (~ 1000 liters) of water [58]. AMS has succeeded in detecting ^{39}Ar at the atmospheric level, but the efficiency needs to be improved [59]. A quick and efficient ($\sim 1\%$) atom-counting method would make a global mapping possible. Since $^{39}\text{Ar}/\text{Ar}$ is about 1000 times lower than $^{81}\text{Kr}/\text{Kr}$, incremental improvements of our current ATTA system are not sufficient to realize this application. However, populating metastable levels with laser excitation is promising.

Monitoring fission products

Fission products in environment are monitored for a number of reasons. It is used to assess the contamination of the environment neighboring to nuclear facilities. It serves as an early warning of nuclear accidents or bomb tests [60]. And it is a verification mean to ensure compliance to nuclear nonproliferation treaties.

The fission isotopes that can be analyzed with ATTA include ^{85}Kr , ^{90}Sr , $^{135,137}\text{Cs}$.

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Figure 1. Krypton energy diagrams. (a) Excitation scheme used in the resonance ionization spectroscopy of krypton; (b) Excitation scheme used in the laser trapping of krypton; (c) Populating the metastable level via a non-resonant UV+UV excitation; (d) Populating the metastable level via a resonant VUV+IR excitation.

Figure 2. Signal of a single trapped ^{81}Kr atom. The photon counter is only open during the detection phase. Single atom signal \approx 1600 photon counts, background \approx 340 photon counts.

Figure 3. (a) Fluorescence of trapped krypton atoms. Dark bands are the signal of stable isotopes measured with a low-gain photo-diode detector. Line markers mark the positions of the two rare isotopes. (b) Fluorescence of trapped ^{83}Kr atoms versus laser frequency. (c) Number of ^{81}Kr and ^{85}Kr atoms counted versus laser frequency. Each data point represents the number of ^{81}Kr atoms counted in 3 hours, and ^{85}Kr atoms counted in 0.5 hours.

Figure 4. Long-lived radioisotopes. Isotopes that can be analyzed using ATTA are marked with \times .







