

# 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 <sup>85</sup>Kr and <sup>81</sup>Kr atoms present in a natural krypton sample with isotopic abundances in the range of 10<sup>-11</sup> and 10<sup>-13</sup>, 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 <sup>14</sup>C ( $t_{1/2} = 5.7$  kyr, isotopic abundance =  $1 \times 10^{-12}$ ) 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 other 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], and utilized it to analyze two rare krypton isotopes, <sup>81</sup>Kr and <sup>85</sup>Kr, with isotopic abundances near the parts-per-trillion level. This new method promises to enhance the capabilities and expand the applications of ultrasensitive trace-isotope analysis.

In this paper, we will first describe the motivation of analyzing <sup>81</sup>Kr and <sup>85</sup>Kr. We will then survey the existing techniques, describe ATTA, and discuss some of the potential applications of ATTA.

## RARE KRYPTON ISOTOPES

Krypton gas constitutes 1 ppm of the earth's atmosphere in fractional volume. It has six stable isotopes, <sup>78</sup>Kr (isotopic abundance = 0.35%), <sup>80</sup>Kr (2.25%), <sup>82</sup>Kr (11.6%),

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$^{83}\text{Kr}$  (11.5%),  $^{84}\text{Kr}$  (57%),  $^{86}\text{Kr}$  (17.3%), and two long-lived radioactive isotopes,  $^{81}\text{Kr}$  and  $^{85}\text{Kr}$  (Table 1). There are about  $2 \times 10^4$   $^{81}\text{Kr}$  atoms and  $3 \times 10^5$   $^{85}\text{Kr}$  atoms in 1 liter STP of air. There are roughly  $10^3$   $^{81}\text{Kr}$  atoms in one kilogram of modern water or ice.

$^{81}\text{Kr}$  is produced in the upper atmosphere by cosmic-ray induced spallation and neutron activation of stable krypton isotopes [5]. As a result of its long lifetime in the atmosphere,  $^{81}\text{Kr}$  is well mixed and evenly distributed over the earth with a homogeneous isotopic abundance. Human activities with nuclear fission have had a negligible effect on the  $^{81}\text{Kr}$  concentration, largely because the stable  $^{81}\text{Br}$  shields  $^{81}\text{Kr}$  from the neutron-rich isotopes that are produced in nuclear fission [6]. These physical and chemical properties make  $^{81}\text{Kr}$  an ideal tracer for dating ice and groundwater that are older than 100,000 years [7], which is beyond the range of  $^{14}\text{C}$ -dating. The ages of ancient ice in this range are currently determined with the less reliable glaciological models [8].

$^{85}\text{Kr}$  is a fission product of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . Its present-day concentration in the environment has been released primarily 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 [9], date shallow groundwater, and monitor nuclear-fuel reprocessing activities [10]. 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 amounts of raw samples, and that their transport processes in environment are easy to understand.

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

Isotope	Half-life (year)	Atmospheric isotopic abundance	Applications
Kr-81	$2.3 \times 10^5$	$(5.9 \pm 0.6) \times 10^{-13}$ , LLC [5] $(4.5 \pm 0.3) \times 10^{-13}$ , LLC [11] $(5.3 \pm 1.2) \times 10^{-13}$ , AMS [6]	Geological dating of polar ice and groundwater; Detecting solar neutrinos via $^{81}\text{Br}(\nu_e, e)^{81}\text{Kr}$ .
Kr-85	10.8	$\sim 10^{-11}$ , LLC [9]	Monitor nuclear-fuel reprocessing activities; Short-term tracer for environmental studies.

## 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  $\alpha$ -decay,  $\beta$ -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 counter 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, factors of approximately  $10^{-3}$  of  $^{85}\text{Kr}$ ,  $10^{-6}$  of  $^{14}\text{C}$ , or  $10^{-7}$  of  $^{81}\text{Kr}$  in the initial sample 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  $^{222}\text{Rn}$  ( $t_{1/2} = 3.8$  days), by waiting.

LLC is used to analyze  $^{85}\text{Kr}$  [9]. It was also used in the first observation of atmospheric  $^{81}\text{Kr}$  [5], but this is no longer possible because in today's atmosphere the decay activity of  $^{85}\text{Kr}$  is  $10^5$  times that of  $^{81}\text{Kr}$ . 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 separates and detects individual ions of a chosen mass. However, the selectivity 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 amounts even after the most careful chemical purification. Conventional mass spectrometry in general has a detection limit at an isotopic abundance of  $10^{-9}$  [12], 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 (~MeV) beam from an accelerator [13-15]. First, molecular isobars can be eliminated by passing the accelerated beam through a thin foil where molecules disintegrate. Second, some atomic isobars 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  $^{14}\text{C}$ -dating. Furthermore, AMS has opened up new applications with other trace-isotopes whose half-lives are too long to be counted with LLC. The commonly utilized isotopes in AMS are  $^{10}\text{Be}$ ,  $^{14}\text{C}$ ,  $^{26}\text{Al}$ ,  $^{36}\text{Cl}$ ,  $^{41}\text{Ca}$ , and  $^{129}\text{I}$  [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 is performed on a routine basis [16].

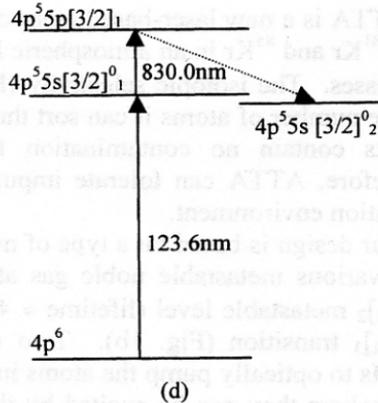
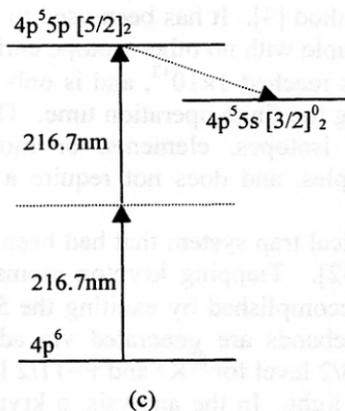
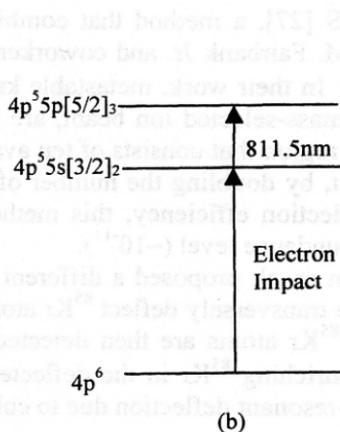
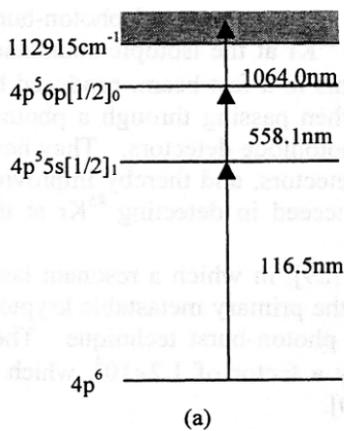
Krypton isotopes cannot be analyzed at a standard AMS facility that uses a tandem accelerator because krypton negative ions are unstable. A new approach has been developed by P. Collon et. al. [6], in which an ECR source is used to produce positive krypton ions, and a GeV-scale cyclotron (K1200, MSU) is used to produce a fully stripped krypton ion beam. Once fully stripped,  $^{81}\text{Kr}^{+36}$  can be cleanly separated from its abundant isobar  $^{81}\text{Br}^{+35}$  ( $Z=35$ ). 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 [17]. In a typical run, 16 tons of groundwater were processed to extract 0.4 cm<sup>3</sup> STP of krypton gas, and resulted in 60-100  $^{81}\text{Kr}$  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 [18, 19]. Figure 1a shows a three-step ionization scheme where the first two steps are resonant excitations that select an element and, in some cases, an isotope, followed by a third non-resonant ionization step [20]. Additional 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 limit both sensitivity and selectivity.

G.S. Hurst and coworkers have counted  $^{81}\text{Kr}$  atoms using the excitation scheme illustrated in figure 1a [20]. Krypton is a difficult case because the first excitation requires a laser of 116.5 nm wavelength. In their work,  $^{81}\text{Kr}$  had to be pre-enriched three times with a mass spectrometer in order to reach an isotopic abundance of  $\sim 10^{-3}$  before atom-counting was performed. The whole process, including the enrichment cycles, has a total detection efficiency of  $>50\%$  [20]. This scheme, although extremely efficient, involves a multi-step operation that is difficult to implement in practical applications.

RIMS is successfully implemented in cases where cw narrow-bandwidth lasers are available to excite atoms. For example, K. Wendt et. al. have analyzed  $^{90}\text{Sr}$ , a nuclear fission product, in dust particles collected in Munich after the Chernobyl accident [21]. Applying collinear laser spectroscopy to a fast atomic beam, they have reached an isotopic selectivity ( $\text{Sr}^{90}/\text{Sr}$ ) of  $\sim 10^{11}$  with a detection limit of  $3 \times 10^6$  atoms. A simplified version [22], in which laser spectroscopy is applied to a thermal atomic beam, has demonstrated an isotopic selectivity ( $\text{Sr}^{90}/\text{Sr}$ ) of  $3 \times 10^9$  with a detection limit of  $1 \times 10^4$  atoms. Work aimed at analyzing  $^{41}\text{Ca}$  at a higher selectivity is in progress [23, 24].



**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.

## Photon-burst mass spectrometry (PBMS)

A single atom can be detected by observing its fluorescence burst in a resonant laser beam [25, 26]. 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 [27], a method that combines mass spectrometry and photon-burst detection, W. M. Fairbank Jr. and coworkers detected  $^{85}\text{Kr}$  at the isotopic abundance of  $6 \times 10^{-9}$  [28]. 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 have pointed out that, by doubling the number of photon detectors, and thereby improving the photon collection efficiency, this method may succeed in detecting  $^{85}\text{Kr}$  at the atmospheric abundance level ( $\sim 10^{-11}$ ).

B.D. Cannon et. al. proposed a different approach [29], in which a resonant laser beam is used to transversely deflect  $^{85}\text{Kr}$  atoms out of the primary metastable krypton. The separated  $^{85}\text{Kr}$  atoms are then detected with the photon-burst technique. They succeeded in enriching  $^{85}\text{Kr}$  in the deflected beam by a factor of  $1.2 \times 10^4$ , which is limited by non-resonant deflection due to collisions [30].

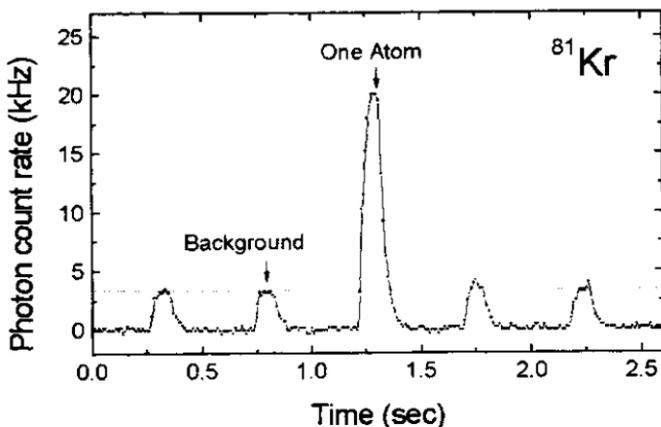
## ATOM TRAP TRACE ANALYSIS (ATTA)

ATTA is a new laser-based atom-counting method [4]. It has been used to analyze both  $^{81}\text{Kr}$  and  $^{85}\text{Kr}$  in an atmospheric krypton sample with no other isotope enrichment processes. The isotopic selectivity ( $\text{Kr}/^{81}\text{Kr}$ ) has reached  $1 \times 10^{13}$ , and is only limited by the number of atoms it can sort through during the finite operation time. The atom counts contain no contamination from other isotopes, elements, or molecules. Therefore, 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 [31, 32]. Trapping krypton atoms in the  $5s[^3/2]_2$  metastable level (lifetime  $\approx 40$  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  $^{85}\text{Kr}$  and  $F=11/2$  level for  $^{81}\text{Kr}$  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  $1 \times 10^4$  of the atoms are excited into the  $5s[^3/2]_2$  level via electron impact excitation. The thermal ( $300^\circ\text{C}$ ) atoms are then transversely cooled, decelerated with the Zeeman slowing technique [33, 34], and loaded into a magneto-optical trap (MOT) [35]. Atoms remain trapped for an average of 1.8 sec as the vacuum is maintained at  $2 \times 10^{-8}$  Torr. This trap system can capture the abundant  $^{83}\text{Kr}$  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  $1 \times 10^{-7}$ .

With expected capture rates between  $10^{-3} \text{ sec}^{-1}$  and  $10^{-2} \text{ sec}^{-1}$  for the rare krypton isotopes, the system must be able to detect a single atom in the trap [36]. 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 different parameters optimized for capture and for atom counting. The

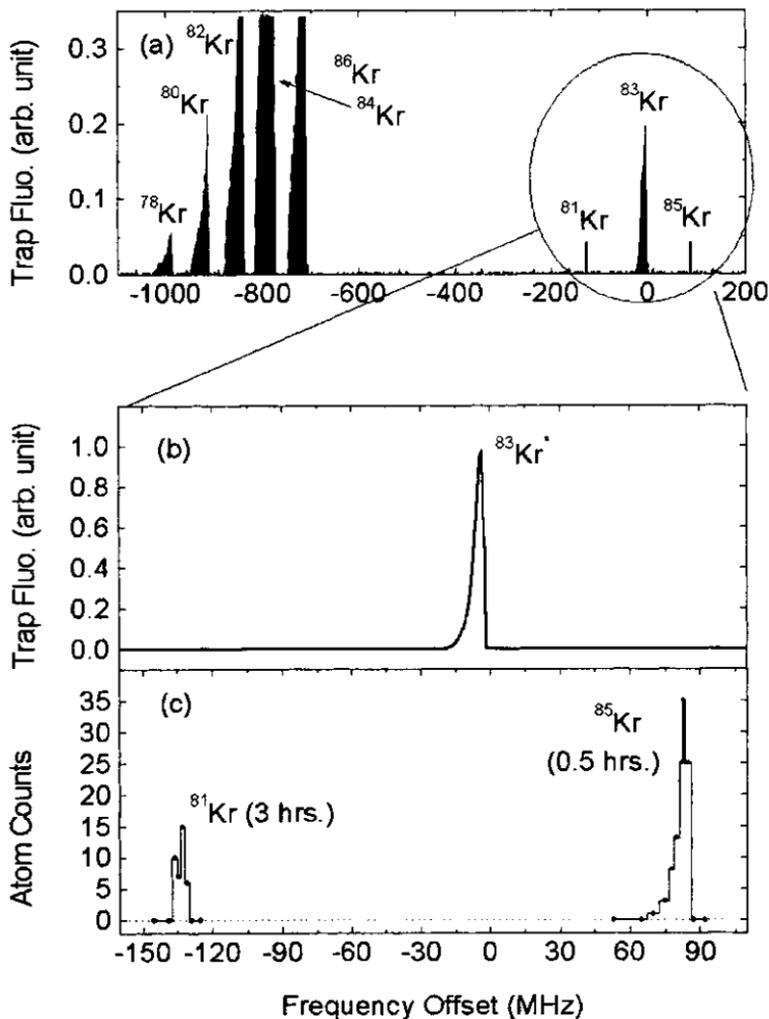
resulting fluorescence signal of a single atom is 16 kcps (kilo-counts per second) while the background level is 3.4 kcps (Fig. 2).



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

We have trapped and counted  $^{85}\text{Kr}$  and  $^{81}\text{Kr}$  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  $^{85}\text{Kr}$  gas and enriched  $^{81}\text{Kr}$  gas [37]. We have also mapped the atom capture rates versus laser frequency (Fig. 3). Furthermore, repeated tests were performed under conditions in which a  $^{85}\text{Kr}$  ( $^{81}\text{Kr}$ ) trap should not work, such as turning off repump sidebands and tuning the laser frequency above resonance. These tests always yielded zero atom counts, and showed that the recorded counts are solely due to laser-trapped  $^{85}\text{Kr}$  ( $^{81}\text{Kr}$ ) atoms.

Previous efforts to develop a laser-based technique have encountered serious problems as a result of contamination from nearby abundant isotopes or isobars. ATTA is immune from the contamination for several reasons: fluorescence is only collected in a small region ( $\phi 0.5$  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 ( $>100$  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



**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  $^{83}\text{Kr}$  atoms versus laser frequency. (c) Number of  $^{81}\text{Kr}$  and  $^{85}\text{Kr}$  atoms counted versus laser frequency. Each data point represents the number of  $^{81}\text{Kr}$  atoms counted in 3 hours, and  $^{85}\text{Kr}$  atoms counted in 0.5 hours.

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

$^{83}\text{Kr}$ ,  $^{85}\text{Kr}$ , and  $^{81}\text{Kr}$ , 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  $^{85}\text{Kr}$  and  $(1.0\pm 0.4)\times 10^{-12}$  for  $^{81}\text{Kr}$ , which are in good agreement with previous measurements performed using other methods [5, 6, 11]. 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  $^{81}\text{Kr}$ -dating, a known amount of  $^{85}\text{Kr}$  can be mixed into the sample, thus allowing the  $^{81}\text{Kr}$  abundance be extracted by measuring the ratio of  $^{81}\text{Kr}/^{85}\text{Kr}$ .

Our system has achieved an overall efficiency of  $1\times 10^{-7}$ . Use of this system to measure the abundance of  $^{85}\text{Kr}$  to within 10% would require 2 hours and a krypton sample of  $3 \text{ cm}^3$  STP while measurement of  $^{81}\text{Kr}$  to within 10% would require 2 days and a sample of  $60 \text{ cm}^3$  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 [38], 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  $\sim 10^{-4}$  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 inefficiencies. It should be noted that the laser excitation discussed here is different from what was used in RIMS. In ATTA, laser excitation is desirable only to boost efficiency, with selection being mainly accomplished by the atom-manipulation process.

## 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,  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$  [42]. Applications of this analysis are in environmental science [39] 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 [40] and detected by observing their fluorescence in the trap. With a sample where the isotopic abundances of  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$  were within the range of  $10^{-6}$ - $10^{-4}$  [41],  $\sim 10^4$  atoms of each isotope have been trapped and an ion-current normalized isotopic ratio of  $^{135}\text{Cs} / ^{137}\text{Cs} = 1.21 \pm 0.10^{\text{stat}} \pm 0.30^{\text{sys}}$  has been measured (a nominal value of 1 is expected) [42]. Since the time of this measurement they have improved the overall efficiency of their system to the  $10^{-3}$  level [41].

H 3(1)																	He
Li	Be 10(6)															Ne	
Na 22(0)	Mg															Ar 39(2) 42(1)	
K 40(9)	Ca 41(5)	Sc	Ti 44(1)	V 50(17)	Cr	Mn 53(6)	Fe 55(0) 60(6)	Co 60(0)	Ni 59(4) 63(2)	Cu	Zn	Ga	Ge	As	Se 79(5)	Br	Kr 81(5) 85(1)
Rb 87(10)	Sr 90(2)	Y	Zr 93(6)	Nb 91(2) 92(7) 93(1) 94(4)	Mo 93(3)	Tc 97(6) 98(6) 99(5)	Ru 101(0) 106(0)	Rh 101(0) 102(0)	Pd 107(6)	Ag 108(2)	Cd 109(0) 113(1)	In 115(14)	Sn 121(1) 126(5)	Sb 125(0)	Te 130(21)	I 129(7)	Xe
Cs 135(6) 137(1)	Ba 133(1)	La 138(11)	Hf 172(0) 174(15) 178(1) 182(0)	Ta 179(0) 180(15)	W	Re 186(5) 187(10)	Os 186(15) 194(0)	Ir 192(1)	Pt 190(11) 193(1)	Au	Hg 194(2)	Tl 204(0)	Pb 202(4) 205(7) 210(1)	Bi 207(1) 208(5) 210(6)	Po 209(2)	At	Rn
Fr	Ra 226(3) 228(0)	Ac 227(1)	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uuq					

Element ■ Laser manipulation demonstrated

Mass number Half-life:  
10<sup>1</sup> years

Kr
81(5)
85(1)

Ce	Pr	Nd 144(15)	Pm 145(1) 146(0) 147(0)	Sm 146(8) 147(11) 151(1)	Eu 150(1) 152(1) 154(0) 155(0)	Gd 148(1) 150(6) 152(12)	Tb 157(2) 158(2)	Dy 154(6)	Ho 163(3) 166(3)	Er	Tm 171(0)	Yb	Lu 173(0) 174(0)
Th 228(0) 229(3) 230(4) 232(10)	Pa 231(4)	U *	Np 235(0) 236(5) 237(6)	Pu *	Am 241(2) 242(3) 243(3)	Cm *	Bk 247(3) 248(0)	Cf 248(2) 250(1) 251(2) 252(0)	Es 252(0)	Fm	Md	No	Lr

\* U: 232(1), 233(5), 234(5), 235(8), 236(7), 237(6), 238(9).

\* Pu: 236(0), 238(1), 239(4), 240(3), 241(1), 242(5), 244(7).

\* Cm: 243(1), 244(1), 245(3), 246(3), 247(7), 248(5), 250(3).

**Figure 4.** A table of long-lived ( $t_{1/2} > 1$  year) radioisotopes [72]. The mass numbers and the exponents of the half-lives in years are tabulated. Elements upon which laser manipulation has been experimentally demonstrated are marked.

## OTHER POTENTIAL APPLICATIONS

Trace-isotope analysis has become an essential tool in modern science. In basic research, isotope tracers are used to detect solar neutrinos, study cosmic rays [43, 44], study rare  $\beta\beta$  decays [45], and search for exotic particles [46]. In environmental sciences, isotope tracers are used to track atmospheric, oceanic, and groundwater currents [9], and to help understand the earth climate. In archaeology [47] and geology [48], various long-lived isotopes are used to determine ages and to help understand the causality of historical events. Isotope tracing is also widely used in biology and medicine [49]. Furthermore, fission isotopes are monitored to assess the contamination of the environment either by the regular operation of a nuclear facility

or by a nuclear accident. It is also a means to verify compliance with nuclear nonproliferation treaties.

Laser manipulation of neutral atoms has been demonstrated on an increasing number of elements. Based on these demonstrated cases, there are already ~10 long-lived radioisotopes (Fig. 4) that can be analyzed with ATTA.

In the following text, some examples are discussed in more detail.

## Solar neutrinos

Solar neutrinos were first detected with a radioisotope tracer [50]. In this experiment,  $^{37}\text{Ar}$  ( $t_{1/2} = 35$  days) atoms were produced at the rate of 0.5 atoms/day in a sealed tank containing 615 tons of perchlorethylene via the  $^{37}\text{Cl}(\nu_e, e)^{37}\text{Ar}$  reaction (threshold = 0.814 MeV). These  $^{37}\text{Ar}$  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 because the source material is artificially maintained in a clean environment. The measured neutrino flux disagrees with the prediction of the Standard Solar Model [51]. Indeed the measured neutrino flux is  $2.56 \pm 0.22$  SNU while the theoretical prediction is  $7.7 \pm 1.2$  SNU, thus establishing the so-called solar neutrino puzzle. Later experiments as well as theoretical work continue to support this disagreement [52].

An analogous detector that counts  $^{81}\text{Kr}$  produced in the  $^{81}\text{Br}(\nu_e, e)^{81}\text{Kr}$  reaction (threshold = 0.471 MeV) has been proposed [53, 51]. Due to a lower reaction threshold, this detector would be more sensitive to the  $^7\text{Be}$ -branch neutrinos than the chlorine detector, and would help separate the contributions from the  $^8\text{B}$  and  $^7\text{Be}$  branches. For a detector containing 1000 tons of a Br-chemical,  $^{81}\text{Kr}$  is produced at a rate of 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, which would test the long-term constancy of the solar neutrino flux and the thermal stability of the solar core [54, 55]. In such a geochemical experiment, tracer atoms (for example,  $^{98}\text{Tc}$ ) are chemically extracted from an ancient mineral deposit (for example, molybdenite,  $\text{MoS}_2$ ), 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  $^{98}\text{Tc}$  and  $^{205}\text{Pb}$  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 [56], AMS [57], and RIMS [58] have been attempted, but none has succeeded so far.

**Table 2. Proposed radioisotope experiments to measure time-integrated solar neutrino fluxes.**

Tracer	Half-life (yr)	Target	Threshold (MeV)	Reference
Ca-41	1.0E5	K-41	2.36	[59]
Kr-81	2.3E5	Br-81	0.471	[53]
Tc-98	4.2E6	Mo-98	1.68	[60]
Pb-205	1.5E7	Tl-205	0.062	[61]

## Radiocalcium dating

$^{41}\text{Ca}$  ( $t_{1/2} = 100$  kyr) tracer could be used to date bones ranging from 50 thousand to 1 million years old [62, 63]. This period covers an important stage of early human development, and is beyond the reach of  $^{14}\text{C}$ -dating.  $^{41}\text{Ca}$  is produced by cosmic rays on the ground within 3 meters of depth from surface, therefore its isotopic abundance varies depending on the erosion rate of the ground. Early AMS work indicated that  $^{41}\text{Ca}/\text{Ca}$  in different bone samples vary in the range of  $10^{-15}$ - $10^{-14}$  [64]. However, the detection limit of AMS, a few  $\times 10^{-15}$ , is so close to the measured level that certain unaccounted systematic errors may contribute to some of the observed variation. Work aimed at improving the detection limit of AMS is in progress [65]. If ATTA can achieve a detection limit of  $1 \times 10^{-15}$  or lower, then dedicated setups can be used to investigate in detail on the feasibility of  $^{41}\text{Ca}$ -dating. Furthermore,  $^{41}\text{Ca}/\text{Ca}$  can be used to determine exposure age of geological samples.

## $^{39}\text{Ar}/^{40}\text{Ar}$ dating

$^{40}\text{K}/^{40}\text{Ar}$  dating is one of the most commonly used of all radiometric techniques [47]. 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  $^{39}\text{Ar}/^{40}\text{Ar}$ . Here  $^{39}\text{Ar}$  is artificially produced by irradiating the sample with neutrons via  $^{39}\text{K}(n,p)^{39}\text{Ar}$ , and its resulting abundance can be linked to the abundance of  $^{40}\text{K}$  with the known reaction rates and the  $^{39}\text{K}/^{40}\text{K}$  ratio. In this case the isotopic abundance of each argon isotope is quite high ( $>10\%$ ) and mass spectrometry, with a detection limit of  $\sim 10^7$  atoms, is the standard analysis tool. ATTA may be useful here due to its immunity to contamination [66]. With ATTA, steps of gas purification could be reduced or eliminated, thereby minimizing the contamination by environmental argon. By employing optical 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,  $^{14}\text{C}$  and  $^3\text{H}$  in particular, are widely used in biomedical research. With the advancements in AMS, other long-lived isotopes, such as  $^{41}\text{Ca}$  and  $^{26}\text{Al}$ , are also becoming available to the biomedical field. It is advantageous to use long-lived isotopes as tracers 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  $^{41}\text{Ca}$ -tracing to diagnose osteoporosis, a disease commonly found in women after menopause [67, 68]. A patient with osteoporosis loses bone mass, 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 provide a faster feedback in assessing treatments. In this proposal, a subject of the high-risk group would take a  $^{41}\text{Ca}$  pill.

$^{41}\text{Ca}$  in tissues would be depleted within a few weeks, but  $^{41}\text{Ca}$  in bones would last a lifetime.  $^{41}\text{Ca}$  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 (greater than a factor of 10).

Other biomedical applications are nutrition studies using isotopes such as  $^{22}\text{Na}$ ,  $^{40}\text{K}$  and  $^{41}\text{Ca}$ , and toxicology studies using  $^{10}\text{Be}$  and  $^{26}\text{Al}$  [49].

## Mapping ocean currents

Earth climate depends closely on the global ocean currents, which are mapped and modeled with the help of radioisotope tracers [69]. Radioisotopes are used to determine the "age" of water, defined as the time since the water was near the ocean surface and exchanged gas with the atmosphere. While the analyses of  $^3\text{H}$  and  $^{14}\text{C}$  have been successfully implemented,  $^{39}\text{Ar}$ -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  $^3\text{H}$  and  $^{14}\text{C}$ . Not to be confused with  $^{39}\text{Ar}/^{40}\text{Ar}$ -dating discussed earlier, the  $^{39}\text{Ar}$  discussed here is produced by cosmic rays, and its isotopic abundance in the atmosphere is  $8.1 \times 10^{-16}$ . Counting  $^{39}\text{Ar}$  atoms in water is difficult because 1 liter of surface water contains only  $\sim 1 \times 10^4$   $^{39}\text{Ar}$  atoms. At present, LLC is used to count  $^{39}\text{Ar}$ , but requires a large amount ( $\sim 1000$  liters) of water and several weeks of counting time [70]. AMS has succeeded in detecting  $^{39}\text{Ar}$  at the atmospheric level, but its efficiency needs to be improved [71]. A quick and efficient ( $\sim 1\%$ ) atom-counting method would make a global mapping possible.

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