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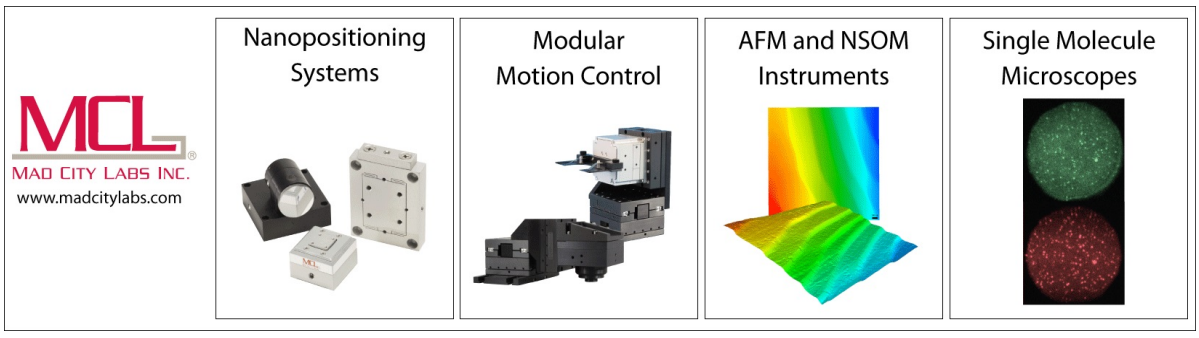

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ABSTRACT

Cosmogenic ^{39}Ar dating is an emerging technique in dating mountain glacier ice, mapping ocean circulation, and tracing groundwater flow. We have realized an atom-trap system for the analysis of the radioactive isotope ^{39}Ar (half-life = 269 years) in environmental samples. The system is capable of analyzing small (1–5 kg) environmental water or ice samples and achieves a count rate of 10 atoms/h for ^{39}Ar at the modern isotopic abundance level of 8×10^{-16}. By switching frequently between counting ^{39}Ar atoms and measuring the stable and abundant isotope ^{38}Ar, drift effects in the trapping efficiency are largely suppressed, leading to a more precise measurement of the isotope ratio ^{39}Ar/^{38}Ar. Moreover, cleaning techniques are developed to alleviate cross-sample contamination, reducing the background ^{39}Ar count rate down to <0.5 atoms/h. These advances allow us to determine the ^{39}Ar age in the range of 250–1300 years with precisions of <20%.

I. INTRODUCTION

The radioisotope ^{39}Ar in the atmosphere is primarily produced by cosmic-ray induced ^{40}Ar(n,2n)^{39}Ar reactions.[1] Once produced, ^{39}Ar stays in the atmosphere as an inert gas and is homogeneously distributed around the globe. It has long been considered an ideal tracer for the study of groundwater flow and ocean circulation and for dating mountain glacier ice. With a half-life of 269 years, ^{39}Ar uniquely covers the age range from 100 years to over one thousand years and bridges a gap between the age ranges of ^{14}C dating and young-age tracers, including ^{3}H, CFCs, SF_6, and ^{85}Kr.

Analysis of ^{39}Ar has been challenging due to its extremely low isotopic abundance in the environment at the level of 10^{-17}–10^{-16}. Three analysis methods based on different principles have been developed: Low-Level Counting (LLC), Accelerator Mass Spectrometry (AMS), and Atom Trap Trace Analysis (ATTA). LLC requires a large amount of sample (1–3 tons of water or ice), which practically limits its application.[1,2] Analyzing ^{39}Ar with AMS has been demonstrated with the use of the 200 MeV ATLAS accelerator facility,[3–5] whose beam time access has been a limiting factor.

A laser-based technique, ATTA, detects single atoms via their fluorescence in a magneto-optical trap (MOT). It has been developed for detecting rare krypton isotopes[6,7] and has enabled ^{81}Kr dating in the earth sciences at large.[8–11] The use of ATTA for ^{39}Ar analysis at the 10^{-16} level was first demonstrated at Argonne National Laboratory with an ^{39}Ar count rate of 0.2 atoms/h for atmospheric samples.[12] At Heidelberg University, ATTA was improved to allow applications of ^{39}Ar dating of groundwater,[13] ocean water,[14] and glacier ice.[15] The Heidelberg ATTA instrument has a count rate of 5 atoms/h for modern samples, a typical required sample size of 5 kg of water or ice, and a background count rate of 0.5–1.0 atoms/h. ^{39}Ar age errors are 20%–30% for samples younger than 600 years.[15] For older samples (600–1000 years), the relative age uncertainties vary from 30% to 100%. The background count rate constrains the detection limit to 8 pMAr (percent of the modern ^{39}Ar/Ar level), which corresponds to an upper age reach of 1000 years.[15]

We have developed an ATTA system for ^{39}Ar dating with improved performance at the University of Science and Technology of China. The system achieves an ^{39}Ar count rate of 10 atoms/h for 0.5 ml STP (Standard Temperature and Pressure) of modern Ar. The sample used for ^{39}Ar dating can be extracted from 1–5 kg of

water or ice. By switching frequently between counting ^{39}Ar and measuring the trap loading rate of the stable and abundant ^{38}Ar, drift effects in the trapping efficiency are largely suppressed, leading to a more precise measurement of the isotopic abundance of ^{39}Ar in the sample. These advances allow us to determine the ^{39}Ar age in the range of 250–1300 years with a precision of <20%. Moreover, cleaning techniques are developed to reduce the background ^{39}Ar counts to less than 10 in a 20-h measurement. We validate the system with calibration samples of known ^{39}Ar isotopic abundances.

II. METHODS

A. The ATTA system

The principle of ATTA has previously been described in detail.[8–12] Laser trapping of argon atoms in the ground state is not feasible due to the lack of suitable lasers at 107 nm. Instead, diode lasers at 812 nm are used to trap atoms in the metastable $1s_5$ state. The laser frequencies are tuned to the resonance of the cycling transition $1s_5$–$2p_9$. Various frequency modulators are used to provide additional laser frequencies needed to manipulate the atoms (Fig. 2). The required frequencies for laser cooling of ^{39}Ar have been measured in Refs. 16 and 17.

The atomic beamline is illustrated in Fig. 1. Atoms are first excited to the metastable state $1s_5$ in a liquid-nitrogen cooled and RF-driven gas discharge via electron–atom collisions. A helical-resonator type of discharge is used to ensure stable operations at low gas pressure and low RF driving power. The RF-discharge is driven by a RF amplifier with 30 W of power at 230 MHz. The typical working pressures in the transverse cooling chamber, the 2D-MOT chamber, and the MOT chamber are 5×10^{-6}, 7×10^{-7}, and 1×10^{-8} Torr, respectively. The metastable atoms then go through the following manipulation stages, including transverse cooling, transverse focusing, and Zeeman slowing, before they are trapped in a MOT at the end of the atomic beamline. The transverse cooling chamber is equipped with two 2000 l/s turbo-molecular pumps. The high pumping speed allows high throughput of the Ar gas while maintaining a working pressure that ensures a long mean free path for the metastable Ar atoms. A spin–flip type of Zeeman slower is used to slow the metastable Ar beam. Compared to the reversed field design in Ref. 13, the spin–flip design has a smaller B-field toward the end of the Zeeman slower and therefore produces less disturbance to the MOT B-field. All these measures work together to give a high atomic loading rate of the ATTA system.

Either ^{39}Ar or ^{38}Ar can been trapped depending on the frequency settings of the laser. For ^{39}Ar detection, a single-atom counting method is used in which the 812 nm fluorescence from a trapped atom is detected with an electron-multiplying charge-coupled device (EMCCD) camera. Based on the intensity of the fluorescence, the exact number of ^{39}Ar atoms inside the trap can be counted. The much more abundant ^{38}Ar, however, is measured with a different method.

B. Normalization of the loading rate

The trap loading rate of the stable reference isotope ^{38}Ar (isotope abundance = 0.063%) is monitored in the experiment for the purpose of normalization. By switching laser frequencies between the resonances of ^{38}Ar and ^{39}Ar, the trap loading rate of ^{38}Ar and the count rate of ^{39}Ar are measured alternately during the analysis period. The capture efficiency of the trap drifts and fluctuates under the influence of a multitude of laser and gas pressure parameters. By taking the ratio between the rates of ^{39}Ar and ^{38}Ar, the effects of the varying counting efficiency, common to both isotopes, can largely be canceled.

The loading rate of ^{38}Ar atoms into the trap is typically at 10^9 atoms/s, too high to use the single-atom counting method. Instead, it is measured with the "quench fluorescence" method.[8] A 10 μW laser beam at 802 nm is directed at the trapped ^{38}Ar atoms to resonantly excite the $1s_5$–$2p_8$ transition (Fig. 2). The atom excited to the $2p_8$ state decays to the ground state via the intermediate $1s_4$ state, emitting two photons at 843 and 107 nm, respectively. Once in the ground state, the atom no longer interacts resonantly with the trapping laser and is lost from the trap. The 843 nm fluorescence is collected with an EMCCD camera. Upon quenching, each trapped ^{38}Ar atom emits a single 843 nm photon. As discussed in Ref. 8,

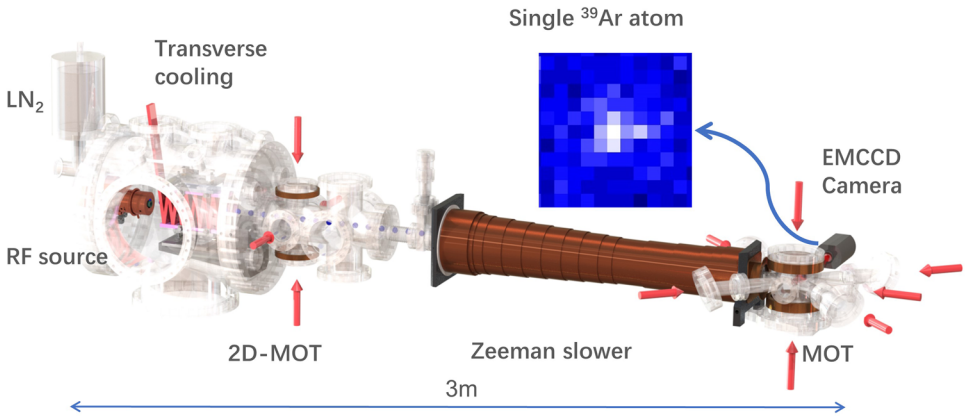

FIG. 1. Schematic of the ATTA apparatus. Metastable ^{39}Ar or ^{38}Ar atoms from a RF-driven discharge source are collimated by transverse cooling, focused by a 2D-MOT, and then decelerated in a Zeeman slower before they are captured into a MOT and detected by an EMCCD camera.

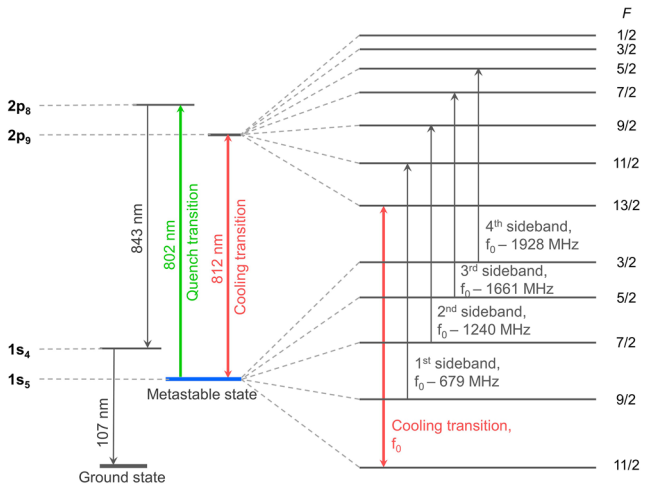

FIG. 2. Atomic level diagram of argon in Paschen notation. The cycling transition $1s_5$–$2p_9$ at 812 nm is used for trapping and cooling. The 812 nm fluorescence is detected for counting individual ^{39}Ar atoms. The transition $1s_5$–$2p_8$ is used to quench the metastable ^{38}Ar atoms back to the ground state. The 843 nm fluorescence on $1s_4$–$2p_8$ is detected when measuring the trap loading rate of the reference isotope ^{38}Ar. Hyperfine structures for the ^{39}Ar isotope and various laser frequencies used for laser trapping and manipulation are displayed on the right.

this method does not need fine controls of the quench laser. The direct linear relation between the loading rate and detected 843 nm photons provides an accurate measure for the loading rate. During the measurement, the system is switched back and forth between trapping ^{39}Ar and ^{38}Ar with a duty cycle of 20: 1–10 min for ^{39}Ar and 0.5 min for ^{38}Ar.

C. Sample measurement protocol

The measurement protocol for environmental samples is as follows: First, a discharge of pure xenon gas is used to clean the system. Then, the ^{39}Ar analysis is performed, spending 0.5–2 ml STP of Ar for each measurement. The measurement time ranges

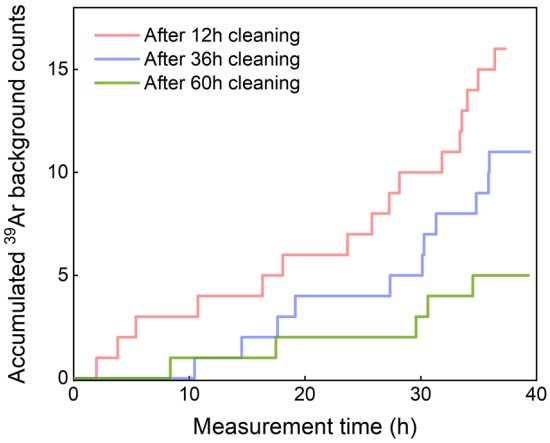

FIG. 3. Accumulated ^{39}Ar background counts after xenon discharge wash with different cleaning times.

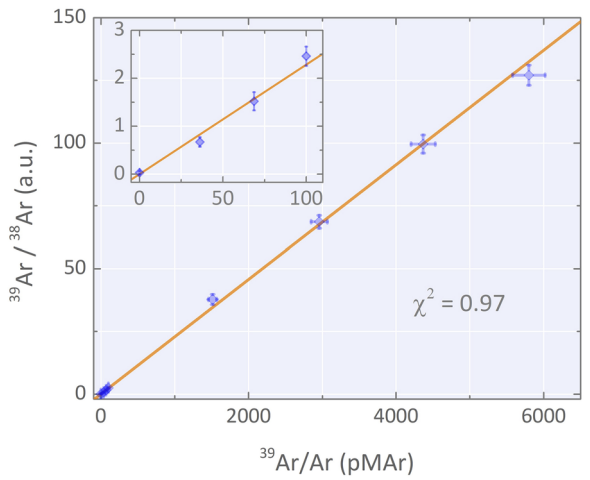

FIG. 4. Calibration result of the ATTA system. Comparison between ^{39}Ar/^{38}Ar ratios measured by ATTA and the ^{39}Ar/Ar ratios calculated from mixing ratios. The linear fit has $\chi^2 = 0.97$ and a slope uncertainty of 2.4%. Inset: zoomed-in view of the low concentration samples.

from 10 to 40 h depending on the ^{39}Ar isotopic abundance. Following each sample analysis, a reference sample enriched in ^{39}Ar (980 ± 50 pMAr) is measured.

Cross-sample contamination must be evaluated and corrected in the ATTA analysis.[8] Even at the liquid nitrogen temperature, neutral argon atoms do not stick to surfaces. However, the gas discharge employed to excite atoms into the metastable state also ionizes atoms and, unavoidably, accelerates ions into the surrounding surfaces, causing both sample loss and sample memory effects. The embedded argon atoms cannot come out spontaneously through diffusion with no active discharge. Their thermal energy is not high enough

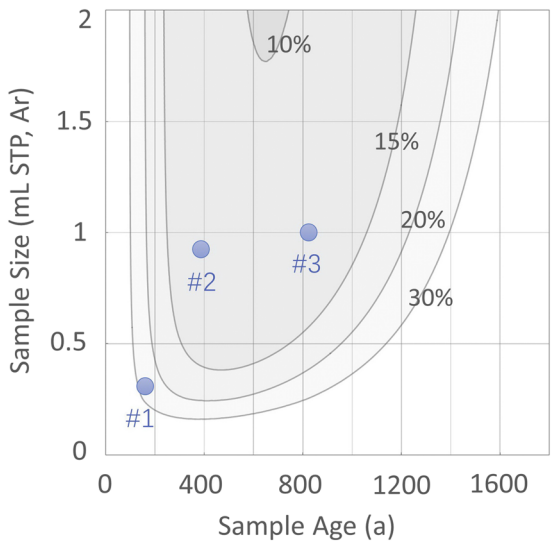

FIG. 5. ^{39}Ar dating performance plot. The contours are relative age uncertainties. The blue dots are artificial samples measured (see Table I).

TABLE I. Measurement results of Ar samples with different ^{39}Ar/Ar ratios.

Sample No.	Sample size (mL STP, Ar)	Measurement time (h)	^{39}Ar/Ar of the sample (pMAr)	^{39}Ar/Ar measured (pMAr)	Inferred ^{39}Ar age (a)
1	0.3	19	67.4 ± 0.7	$67.5^{+6.7}_{-6.3}$	153^{+38}_{-37}
2	0.9	17	33.1 ± 0.3	$37.2^{+5.5}_{-5.0}$	384^{+57}_{-54}
3	1.0	13	10.0 ± 0.1	$11.6^{+3.9}_{-3.3}$	840^{+130}_{-110}

for them to escape from the imbedded site. However, during each measurement, under bombardment of ions, the embedded argon atoms from previous measurements are gradually released, causing cross-sample contamination. In order to reduce contamination, we operate a pure xenon gas discharge to drive out the embedded argon prior to each measurement. We chose Xe for cleaning as it is more effective compared to other gases due to its high mass. Besides the embedded argon, leaks from constricted spaces inside the vacuum chamber also introduce argon during the measurement. The cross-sample contamination caused by both the embedded argon and the leaked argon becomes comparable after 30 h of xenon discharge cleaning. To characterize the cross-sample contamination effect, the background ^{39}Ar counts are measured experimentally after different xenon discharge wash periods. The ^{39}Ar depleted argon from the DarkSide dark matter experiments was used in these measurements.[20] The results are shown in Fig. 3. The accumulated ^{39}Ar counts show that, for a 20-h analysis, a xenon wash lasting 12 h reduces the background ^{39}Ar counts to less than 10. Even lower background counts can be achieved with a prolonged xenon wash if necessary. Based on these evaluations, the following measurement protocol is adopted in the sample analysis: prior to each measurement, a xenon-discharge cleaning overnight (~12 h) is performed to suppress the background ^{39}Ar counts; the analysis duration is 10–20 h.

III. RESULTS AND DISCUSSIONS

A. System calibration

To calibrate the ATTA system, a series of standard ^{39}Ar samples with different ^{39}Ar concentrations are measured. We have acquired two ^{39}Ar samples from the University of Bern: one is an enriched sample with an ^{39}Ar/Ar value of 5800 ± 200 pMAr[18,19] and the other is ^{39}Ar-free (0.07 ± 0.01 pMAr) argon extracted from underground for dark matter research.[20] By mixing these two samples and the modern atmospheric argon with precisely controlled mixing ratios (<1% uncertainty), a total of eight calibration samples are prepared. The calibration results are presented in Fig. 4. Each data point is the average of several independent measurements. The data show a good linear relationship between the ^{39}Ar/^{38}Ar ratios measured by the ATTA method and the ^{39}Ar/Ar ratio calculated from the mixing ratios. It is worth noting that this linear relationship is maintained over a large dynamic range.

B. Data analysis and age calculation

The raw data obtained in the ^{39}Ar analysis need to be corrected for the cross-sample contamination effect. The correction depends on the pre-determined background ^{39}Ar count rate, the measurement time, and the sample size. For a 1 ml STP atmospheric argon sample, a 10 h measurement typically records ~100 ^{39}Ar counts. The contribution from the background is about two atom counts, resulting in a 2% correction to the raw data. The corrected ^{39}Ar counts can then be used to calculate the ratio $[^{39}\mathrm{Ar}/^{38}\mathrm{Ar}]_{\mathrm{Sample}}$. The ^{39}Ar age of the sample is calculated as follows:

$$Age = -t_{1/2}\ \ln\left(\frac{C_{ref} \times \left[^{39}\mathrm{Ar}/^{38}\mathrm{Ar}\right]_{Sample}}{\left[^{39}\mathrm{Ar}/^{38}\mathrm{Ar}\right]_{Reference}}\right), \quad (1)$$

where $t_{1/2}$ = 269 ± 3 years is the half-life of ^{39}Ar[21] and C_{ref} = 980 pMAr is the ratio between the ^{39}Ar/Ar ratios of the reference and the modern air.

C. ^{39}Ar dating performance

The contour plots of the relative ^{39}Ar age uncertainty are displayed in Fig. 5. We measured three samples with known ^{39}Ar/Ar ratios to mimic different ^{39}Ar ages and sample sizes. Two different sizes are chosen, 0.3 ml STP and 1 ml STP, corresponding to typical ice and seawater samples, respectively. Between two sample measurements, an overnight xenon discharge wash is implemented to reduce the cross-sample contamination effect. The results are presented in Table I and Fig. 5. This shows that the measured uncertainties match the predicted performance. Samples as small as 0.3 ml STP Ar can be analyzed. For a 1 ml STP Ar sample, the age uncertainty is <20% between 250–1300 years.

Compared to the previous works, the atom trap system for ^{39}Ar reported in this paper has improved the atom counting rate by a factor of 2. This improvement means that the typical 20–40 h measurement time can be shortened by half. Moreover, it has a wider dating range and smaller dating uncertainties. The enlarged dating range covers some of the geological periods that are interesting to paleoclimate studies, including the little ice age (1300CE–1900CE) and the medieval warm period (900CE–1300CE).

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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