DOI: 10.1007/s12583-017-0948-9

Automatic $^{40}Ar/^{39}Ar$ dating techniques using multicollector ArgusVI MS with self-made apparatus

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Funding:

National Natural Science Foundation of China (No. 41503053,No. 41630315,No. 41688103& No. 91128203).

ABSTRACT

A new fully automatic $^{40}Ar/^{39}Ar$laboratory with a ThermoScientific©Argus VI mass spectrometer has been established in China University of Geoscience (Wuhan). We designed and developed a mini efficient preparation system (80 ml), a CO_2laser for heating samples, a crusher for extracting fluid inclusions within K-poor minerals and an air reservoir (31 L) and pipette (0.1 ml) system. The Argus VI mass spectrometeris operated by the Qtegra Noble Gas software, which can control the peripheral accessories, such as pneumatic valves, CO_2laser and crusher through a PeriCon (peripheral controller).The experimental procedures of atmospheric argon analyses, $^{40}Ar/^{39}Ar$ dating by laser stepwise heating and by progressive crushing in vacuo, can be fully automatically performed. Theweighted meanof atmospheric $^{40}Ar/^{36}Ar$ ratios is 302.22 ± 0.03 (1σ, MSWD = 0.74, n = 200), indicating that air reservoirand pipette system and the whole instrumentsystem areverystable. This laboratory is a successful pioneer example in China to establish a new noble gas laboratory with self-made peripheral accessories expect for the mass spectrometer.
Keys words:$^{40}Ar/^{39}Ar$ dating; fully automatic; CO_2 laser; Argus VI mass spectrometer; Qtegra noble gas software

INTRODUCTION

At the beginning of the 21stcentury, the English Nu Instrument Ltd released a new multi-collector noble gas mass spectrometry Noblesse, which provided impetus to the development of the multi-collector noble gas mass.Noble gas mass spectrometry is utilized to analysis the isotopic compositions of noble gas group elements that make up the rightmost group of the periodic table as usually arranged: helium (He), neon(Ne), argon(Ar), krypton(Kr), xenon(Xe), and radon(Rn). In the recent years, China has introduced many new generation noble gas mass spectrometer, such as Noblesse by the Nu Instruments and Argus VI, Helix SFT, Helix MC Plus produced by the Thermo Scientific.We have established a full automatic $^{40}Ar/^{39}Ar$ laboratory with Argus VI mass spectrometer in the China University of Geoscience

(Wuhan). In this paper, weintroduced our laboratory with the all self-madeperipheral accessories, such as a CO_2laser, crusher and air-pipette system, allowing fully automatic experimental procedures of atmospheric argon analyses, $^{40}Ar/^{39}Ar$ dating by laser stepwise heating and by progressive crushing *in vacuo*.

1. ARGUS MASS SPECTROMETER

The Argus noble gas mass spectrometer was built specifically for argon isotopes analyses (Figure 7)(Alexandre et al., 2006; Barfod et al., 2006; Mark et al., 2009; Pfänder et al., 2014), with very low internal volume of about 700 ml, resolution of >200, six collectors including five Faradays and one CDD(compact discrete dynode) ion counting multiplier. The ARGUS VI static vacuum mass spectrometer is a magnetic sector mass spectrometer designed for the isotopic analysis of small samples of the noble gases,it comprises a magnetic sector analyzer with 13 cm, 90° extended geometry ion optics. Given the sensitivity of a static vacuum mass spectrometer is directly proportional to its internal volume the Argus VI mass spectrometer is the most sensitive commercial instrument available.Coupled to its low volume the instrument utilizesa X and Z-focused Nier type bright source giving sensitivities in excessof 1×10^{-3}A/Torr at 200 μA trap current for argon.The flight tube is optimized for minimal volume and enables a remarkably low total instrument volume to be achieved. The internal design minimizes the possibility of ions scattering from the flight tube walls and reaching the collector.A chemical getter pump SAES NP10positioned at the sample inlet and the ion pump is located on the end of the flight tube close to the ion source. The ion pump (Varian Vaclon Plus 20 StarCell™) is the main vacuum pump of the instrument and its pumping speed is 20 L/s.

Figure 1ArgusVI noble gas mass spectrometer

The Argus VI collector array comprises a fixed five Faraday array. These Faraday cups are identified as H2, H1, Ax, L1 and L2. The design of these five detectors is such that the five isotopes of argon, masses 40, 39, 38, 37 and 36 can be measured simultaneously. These Faradays incorporate new high gain amplifier circuits that allow for gains of 10^{10}–10^{13}Ωmeasuring resistors to be used.Amplifier circuitswere installed on H2 with 10^{11}Ω and others with 10^{12}Ω in the factory.Amplifier circuit of 10^{13} Ω is a newly developed product. Considering the signals of most geological samples, we replaced the 10^{12} Ω amplifier circuits on Ax, L1 and L2 with 10^{13} Ω ones on April 27, 2016. In conjunction with these five Faradays there is also a CDD (compact discrete dynode) ion counting multiplier in the L3 position. This device is designed to be either utilized in a peak jumping mode or in conjunction with the H1 Faraday for simultaneous $^{40}Ar/^{36}Ar$measurements.

2. SELF-MADE ASSOCIATEDAPPARATUS

Our Argus VI mass spectrometersis connected to a low-volume samplepreparation system, which include an air tank (31 L) with a pipette (0.1 ml), a mini efficient purification system (80 ml),a laser sample chamber with a CO_2laser (50 W) and a crusher for extracting fluid inclusions.

2.1 SmallEfficient Purification System

We designed and developed an efficient preparation system of small volume, based on our experiment in $^{40}Ar/^{39}Ar$ dating. The purification system is composed of a Zr-Al purification pump anda cryotrapconnected with Swagelok pneumatic and manual valves, using a Pfeiffer HiCube 80 Eco turbo pumping station anda Varian StarCell 40L/s to obtain ultra-high vacuum.Theinternal volume of the purification system is 80 mL(Qiu et al., 2015), not including the crusher and laser sample chamber.

2.2 CO_2Laser

Ahomemade carbon dioxide infrared laser(10.6 μm, 50 W) is used for stepwise heating, which contains a CCD for sample location/observation and two micromotors to move the sample chamber.The laser software is based on the suggestions of H. N. Qiu for the ^{40}Ar/^{39}Ar stepwise heating experiment. The instrument control software Thermo Qtegra for the mass spectrometer can trigger the laser output through the PeriConby a “contact closure switch”.Therefore, the experiment of ^{40}Ar/^{39}Arlaser stepwise heating dating can be fully automatically performed. The laser heating software lists sequence number, laser energy (%), heating method (increasing output or constantoutput in a step), heating time (60s, usually), sample hole coordinates (*x, y*), diameter of the sample hole (mm). The list file (*.csv) can be edited by the Microsoft Excel.The laser spot size is 3mm in diameter.If the sample hole is bigger thanϕ3 mm, e.g. ϕ6 mm,the laser will heat the sample along a circular of ϕ3 mm covering the hole of ϕ6 mm, by moving the sample chamber in a circular of ϕ3 mm through two micromotors in *x* and *y* directions. Once receiving the trigger signal from Qtegra, the laser software willmarka tick in the front of sequence number, moving to the assigned sample hole of *x* and *y*, emitting laser to heat the sample for 60 s (heating time), then waiting for the next trigger signal from Qtegra. The laser software will execute in order and skip the marked steps.

ZnS crystals grown by Chemical Vapor Deposition process (CVD) are used as viewports and coverglasses of the sample chambers. The 50W CO_2 laser is strong enough to fuse all types of minerals and rocks. Many minerals release gases in low laser output. In order to reduce laser output heating samples, we also use a thick ZnS CVD as a filter in the laser path. The transmittance of a 7mm-thick uncoated polishedZnS CVD window is about 64%.

2.3 Crushing Apparatus

An online crusheris directly connected to the purification system to extract fluid inclusions(Qiu and Wijbrans, 2006; Qiu and Jiang, 2007; Qiu et al., 2011).

The crusher is made of a type 316L stainless steel tube (160 mm long,ϕ28 mm inner diameter and ϕ34 mm outer diameter) with a spherical curvature on the internal base. The pestle is made of 218 g of magnetic 3Cr13 type stainless steel (or S42030)(Qiu et al., 2011). Prior to experiments, the extraction and purification systems are baked out with heat tapes, and sample in the tube is heated to 150 ℃ with a furnace for ~10 h to reduce system blanks. The fluid inclusions in K-poor mineralsare extracted by repeatedly lifting and dropping the pestle using an external electromagnet with a frequency of 2 Hz. The pestle is freely falling from a height of 4~5 cm. The drop number of each step is set in the Qtegra Workflow and recorded on a digital counter. As the gas releases are decreased with progressive extraction steps, the number of pestle drops for each successive step is increased to maintain argon levels that can be measured precisely. In order to crush the sample as evenly as possible, we use two external electromagnets control the pestles stroke the tube in horizontal direction to make the sample grains gathered in the bottom of the tube. The crusher is very important for us to obtain good $^{40}Ar/^{39}Ar$ dating results. Inferior crusher may yield bad isochron lines corresponding to wrong age data.

2.4 Air Tank and Pipette

The atmosphere is used as a standard reference gas for mass spectrometric determinations of argon isotopes used principally in geochronology (Nier, 1950; Lee et al., 2006; Renne et al., 2009a; Valkiers et al., 2010; Mark et al., 2011).Air tank-pipette system is an indispensable branch for the noble gas mass spectrometer laboratory. It is used (1) to determine the mass discrimination of fractionation (MDF)during isotope ratio measurement (McDougall et al., 2005; Turrin et al., 2010).(2)to calibrate the Faraday cups and the CDD multiplier.

The air tankvolumeis ~ 31 L, connected to the purificationsystem byϕ6 mm tube anda 0.1 ml pipette defined by two Swagelok 1/4″VCR pneumatic valves(Figure 8). The volume ratio of the air tank topipette is as high as 310,000, therefore, thedetectors aredifficultto distinguish theargon signal differences between twoadjacent pipette extractions.The air tank-pipette system provides a stable argon reservoir for calibrations.

Figure 2 A sketch of the $^{40}Ar/^{39}Ar$ dating labortary in China University of Geosciences (Wuhan).

About 0.5ml airwas sealed with a Swagelok 1/4″VCR valve in the laboratory, purified by the Zr-Al getter for 8h, then spread to the tank as the air reservoir.

3. CORRECTION FACTORS FOR CMRR REACTOR

We have gotten four batchesof samples irradiated in the CMRR reactor since 2014.The *J* values are usually in straight lines with the positionsFigure 9, andhigh-precision $^{40}Ar/^{39}Ar$ages are obtained.

Figure 3 Diagram of the irradiation parameter *J* value *vs* position.

It was recognized from the earliest stages of development of the $^{40}Ar/^{39}Ar$ dating that isotopes of argon, apart from the ^{39}Ar produced in the key reaction on ^{39}K,may be formed by interaction of neutrons with isotopes of Ca, K, Ar, and Cl (Sigurgeirsson, 1962; Merrihue and Turner, 1966; Mitchell, 1968; Brereton, 1970; Turner, 1971).A wide variety of reactions may occur (Table 1).The most important nuclear reactions in relation to $^{40}Ar/^{39}Ar$ dating are highlighted by enclosing them in boxes, fortunately, many are of minor significance.Correction factors of argon isotopes derived from Ca and K are determined by measuring the relative production rates of these isotopes in pure calcium saltCaF_2 and potassium salt K_2SO_4 after neutron irradiation.The saltsirradiatedin the CMRR reactor were analyzed onthe Argus VI in CUG.The correction factors $(^{36}Ar/^{37}Ar)_{Ca}$ and $(^{39}Ar/^{37}Ar)_{Ca}$from the irradiated $CaF_2$are $2.3477\times10^{-4}$and 6.1748×10^{-4}, respectively, and the correction factors $(^{40}Ar/^{39}Ar)_K$ and $(^{38}Ar/^{39}Ar)_K$from the irradiated K_2SO_4 are $2.3228\times10^{-3}$and 9.4194×10^{-3}, respectively.

4. OPERATING THE SYSTEM

The Argus VI mass spectrometeris operated using the Qtegra Noble Gas for sample analysis, which is a true end-to-end solution for workflow-driven analysis.The main Qtegra Noble Gas contains Configurator, Instrument Control and Experiment Editor.

4.1 Qtegra Configurator

Within the Configurator, the Experiment Configurator enables the user to define the instrument and its associated peripherals. Therefore, drag and drop the required hardware components, such as Argus VI, ArgusControls, NGPrepOnArgusVI and PericonOnArgusVI, to create virtual instrument configure.Once the hardware components have been chosen, we can define the operating parameters of the system.

The Qtegra allows us to edit the hardware configuration. Hardware panels provide a graphical representation of technical equipment and are used to control all electrical and functions of the mass spectrometer as well as the peripheralapparatuses. Hardware panels can be customized to control different devices and can be added to control peripheral devices such as “PeriCon”. The peripheral accessories of pneumatic valves, CO_2 laser and crusher can be controlled by the Qtegra software through a PeriCon.Using the“Hardware panels configuration”, wecreate the sketch of our laboratory (Figure 8) in the“Graphics View” window and test in the “Preview” window.

PeriCon is a peripheral controller, it serves as a link between the Thermo Scientific mass spectrometer electronics and the user-made customized. With PeriCon, a specialized application such as a valve, an analog input or output or a trigger input can easily be added in a standardized way to the peripherals of Argus VI mass spectrometer.

4.2 Instrument Control

Instrument Control is used to switch on, optimize, and calibrate the instrument,it gives access to all the manual controls of the system. The main window of the

Instrument Control can be divided into several panes,we usually divided into three panes to facilitate operating and monitoring instrument and more convenient during the instrument leak detection. The left pane shows the Argus Control Panel, the upper right pane displays the “Argus VI Graph View”, the bottom right shows the sketch of our laboratory (Figure 8).

The Argus Control Panel is used to control various parameters of the mass spectrometer including the source electronics, filament, magnet field values and beam deflection supplies of the collectors.

The sketch of our laboratory (Figure 8, the PeriCon panel) can be shown in “Instrument Control” to facilitate operating and monitoring the instrument, leakingtest.We can open/close the pneumatic valves andion gauge on the PeriCon panel.Duringfully automatic experiments, the Instrument Control windows are locked (in gray)to prevent any manual operation,i.e., the mouse cannot be used to click any button.

4.3 Experiment Editor

The Experiment Editor is a main Qtegra module to design, start and stop the experiments.Experiment Editor is based on the Templates and LabBooks.

Templates contain all basic information on isotopes, for example, acquisition parameters of the Peak Centering, Baseline Correction, Cup Configurator, Method cycles, Integration time, Setting time, standards and sample definitions, and so on. Templates are generally created once by the Lab Manager for different types of applications. Once a Template is created and saved, it can serve as the basis for all analytical measurements based on the Template (LabBooks).

A LabBook is based on a Template. It contains the acquisition parameters defined in the Template used to create the LabBook, and the Sample List for the measurement generated from that Template’s Sample Definition.The LabBook corresponds to the actual analyticalmeasurement and upon completion of a scheduled LabBook. All rawintensities, concentrations and requested ratios are stored within theLabBook.

5. EXPERIMENTAL RESULTS

The $^{40}Ar/^{39}Ar$ results were calculated and plotted using the software ArArCALC (Version 2.52) (Koppers, 2002).The program ArArCALC provides an interactive interface to data reduction in $^{40}Ar/^{39}Ar$geochronologyand is coded within Visual Basic for the Microsoft Excelusing datasheets, charts, menus and dialogboxes.The program ArArCALC includes basicutilities within a single software program: (1) curved or linear data regression, (2) blank evolution analysis, (3) age calculation, (4) *J*-value calculation and (5) air shot calculation.

All $^{40}Ar/^{39}Ar$age calculations are reported in single Excel workbooks.Each Microsoft Excel workbook produced by ArArCALC includes five separate worksheets and contain all the necessary input and output data for the $^{40}Ar/^{39}Ar$ age calculations, which contain: (1) Multiple data tables (including the relative abundances table recommend by Renne et al. (2009b)); (2) Age and K/Ca plateau diagrams; (3)Normal and inverse isochron diagrams.The version 2.52 was releasedin 2012 (https://earthref.org/ArArCALC/). In this version, Argus VI multicollector input filter was added.

5.1 Isotopic analysis of atmospheric argon

The air tank-pipette systemprovides a stable argon reservoir for the laboratory.In order to obtain the MDF value and test the stability of the instrument, three atmospheric argon analyses were on March 11~12, April 7~9 in 2014 and July2~3, 2016.

Figure 4 Measurement of $^{40}Ar/^{36}Ar$ ratios of modern atmospheric argon in the laboratory.

The $^{40}Ar/^{36}Ar$ ratios and its error(1σ) of three times measurements were shown in Figure 10.The weighted mean $^{40}Ar/^{36}Ar$ ratios of three atmospheric argon analyses are 302.19 ± 0.04 (*n*= 94), 302.22 ± 0.03 (*n*= 200) and 302.24 ± 0.04 (*n*= 50), corresponding to the MDFvalues are0.996990 ± 0.000499, 0.996968 ± 0.000496 and 0.996951 ± 0.000498, respectively, according to the $^{40}Ar/^{36}Ar$ ratio of the atmospheric argon is 298.56 ± 0.31 (Lee et al., 2006). These well concordant $^{40}Ar/^{36}Ar$ ratios indicate that the Argus VI in our laboratory is quite stable, even though10^{12} Ω amplifier circuits were replaced with 10^{13} Ω ones on Ax, L1 and L2 on April 27, 2016.

$^{40}Ar/^{39}Ar$laser stepwise heating

In principle, any potassium-bearing mineral or rock can be used for $^{40}Ar/^{39}Ar$ dating, in practice, the range of samples that can be usefully dated is rather more restricted(McDougall and Harrison, 1999).The experimental sample for laser stepwise heating is a K-rich muscovitewhich was collected from the Xiangdong tungsten deposit inEastern Hunan Province, South China.The age spectrum and isochron plots based on the $^{40}Ar/^{39}Ar$ laser dating results are shown in Figure 11.The white dioctahedral mica, muscovite, has an ideal composition of $K_2Al_4Si_6Al_2O_{20}(OH, F)_4$, permitting up to about 9.7% potassium in its structure. The muscovites are used extensively for $^{40}Ar/^{39}Ar$ dating, because they show excellentargonretentivity.Muscovite dated by $^{40}Ar/^{39}Ar$ laser stepwise heating form a flat age spectrum (Figure 11a) with a plateau age of 147.3±0.9 Ma (2σ, MSWD = 0.37) and plateau segment ^{39}Ar = 98.3%. The plateau data points define concordant isochron line (Figure 11b) on the plot of $^{36}Ar/^{40}Ar$*vs*.$^{39}Ar/^{40}Ar$ with age of 147.3±0.9 Ma (2σ, MSWD = 0.33), corresponding to an initial $^{40}Ar/^{36}Ar$ ratio of 301.1± 11.9, which is concordant with the plateau age.

Figure 5$^{40}Ar/^{39}Ar$ age spectrum and inverse isochron for a muscovitefrom the Piaotang Tungsten Deposit.

5.2 $^{40}Ar/^{39}Ar$ progressive crushing

Inline crushing technique has been used to extract the fluid inclusions for $^{40}Ar/^{39}Ar$ dating. Many successful applications of the $^{40}Ar/^{39}Ar$ crushing method for different types of minerals have been reported, such as quartz (Turner and Bannon, 1992; Turner and Wang, 1992; Qiu, 1996; Kendrick et al., 2001; Qiu et al., 2002; Liu et al., 2015; Wang et al., 2016), pyrite(Phillips and Miller, 2006), sphalerite (Qiu and Jiang, 2007; Jiang et al., 2012), cassiterite (Bai et al., 2011; Bai et al., 2013; Wang et al., 2015)and wolframite (Bai et al., 2013).Figure 12 show the results of the fluid inclusions within non-potassium mineral of wolframite from the Piaotang tungsten deposit in Southern Jiangxi Province dating by the $^{40}Ar/^{39}Ar$ progressive crushing technique.This sample was crushed in 21 steps with a total number of pestle drops of 8530, and a gradually decreasing age spectrum is obtained from the experiment (Figure 12a).The dating of wolframite by stepwise crushing of sampleyields abnormally old apparent ages in the first four steps and forms an age plateau in the final steps from 10 to21, with an age of 153.3±1.0Ma (2σ, MSWD = 0.17) (Figure 12a) and plateau segment ^{39}Ar = 64.0%. The data points of the plateau definea concordant isochrone line(Figure 12b) with an age of 152.8 ± 2.0 Ma correspondingto an MSWD of 0.13 and initial $^{40}Ar/^{36}Ar$ ratio of296.5±2.8. This initial ratio is indistinguishable from the ratio of themodern atmosphere, the plateau age is concordantwith the isochron age.

Figure 6 $^{40}Ar/^{39}Ar$ age spectrum and inverse isochron for a wolframite from the Piaotang Tungsten Deposit.

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6. CONCLUSIONS

1) The self-made peripheral accessories of air tank-pipette system, CO_2 laser and crusher, can be completely integrated with Thermo Argus VI and controlled by the Qtegra Noble Gas software through a PeriCon. All the experimental procedures includingair argon isotopic analyses, $^{40}Ar/^{39}Ar$ laser

stepwise heating and progressive crushing *in vacuo* could be fully automatically performed.

2) The atmospheric $^{40}Ar/^{36}Ar$ ratios are well concordant in three analyses, indicating that the Argus VI mass spectrometer is very stable and the air tank-pipette system is well designed.
3) High-precision $^{40}Ar/^{39}Ar$ dating results of muscovite by laser stepwise heating and wolframite by progressive crushing indicatethat the small self-made purification system is very effective.
4) The 50W CO_2laser is specially designed for $^{40}Ar/^{39}Ar$ dating, with a CCD for searching and observing samples and two micromotors for moving sample chamber in *X* and *Y* directions. The laser software for stepwise heating can communicate with Qtegra through “contact closure”.
5) The $^{40}Ar/^{39}Ar$laboratory in the China University of Geosciences (Wuhan) is a state-of-the-art facility and capable to produce top quality data sets.

ACKNOWLEDGE

We thank two anonymous reviewersfor their valuable comments that improved this manuscript.This study was financially supported by the National Natural Science Foundation of China (No. 41503053,No. 41630315,No. 41688103& No. 91128203).

Figure Captions

Figure 7ArgusVI noble gas mass spectrometer.

Figure 8 A sketch of the ^{40}Ar/^{39}Ar dating labortary in China University of Geosciences (Wuhan).

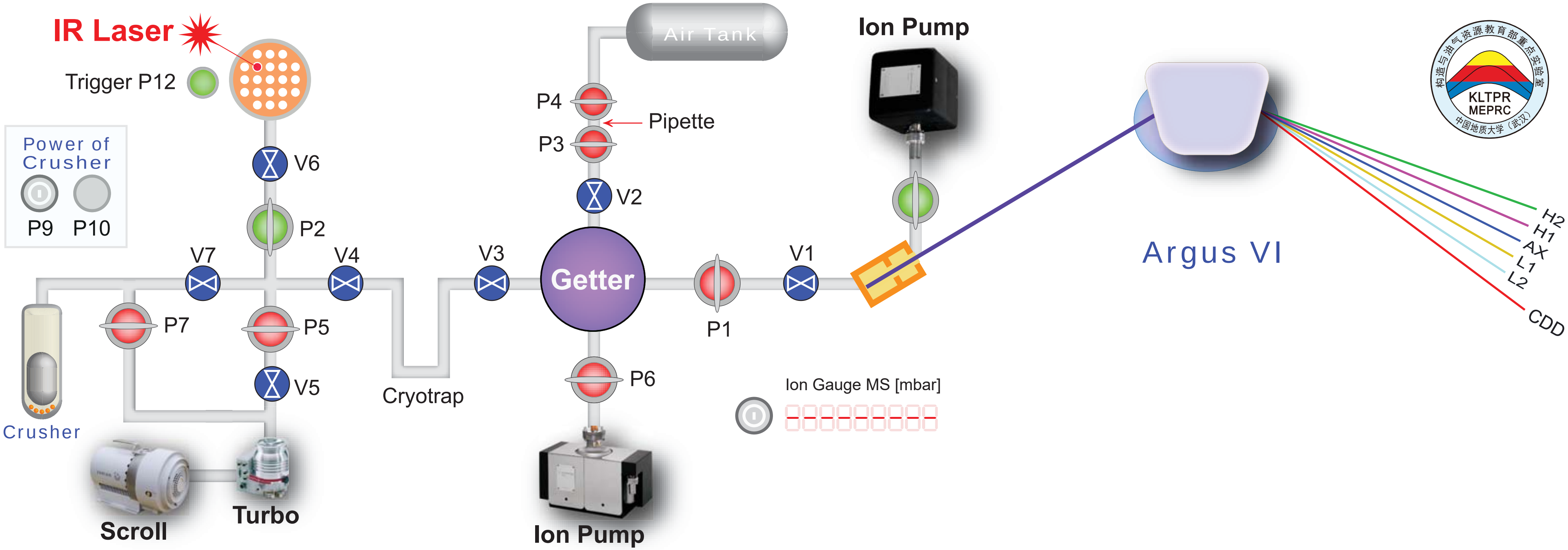
Figure 9Diagram of the irradiation parameter *J* value *vs*position.

Figure 10Measurement of ^{40}Ar/^{36}Ar ratios of modern atmospheric argon in the laboratory.

Figure 11^{40}Ar/^{39}Ar age spectrum and inverse isochron for a muscovitefrom the Piaotang Tungsten Deposit.

Figure 12^{40}Ar/^{39}Ar age spectrum and inverse isochron for a wolframite from the Piaotang Tungsten Deposit.

50W CO_2 Laser
Pipette
Sample
Chamber
Crusher
Purification System
Argus VI



IR Laser
Trigger P12
Power of Crusher
P9
P10
Crusher
V6
P2
V7
V4
P7
P5
V5
Scroll
Turbo
Cryotrap
V3
Air Tank
P4
P3
Pipette
V2
Getter
P6
Ion Pump
P1
V1
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Argus VI
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H1
AX
L1
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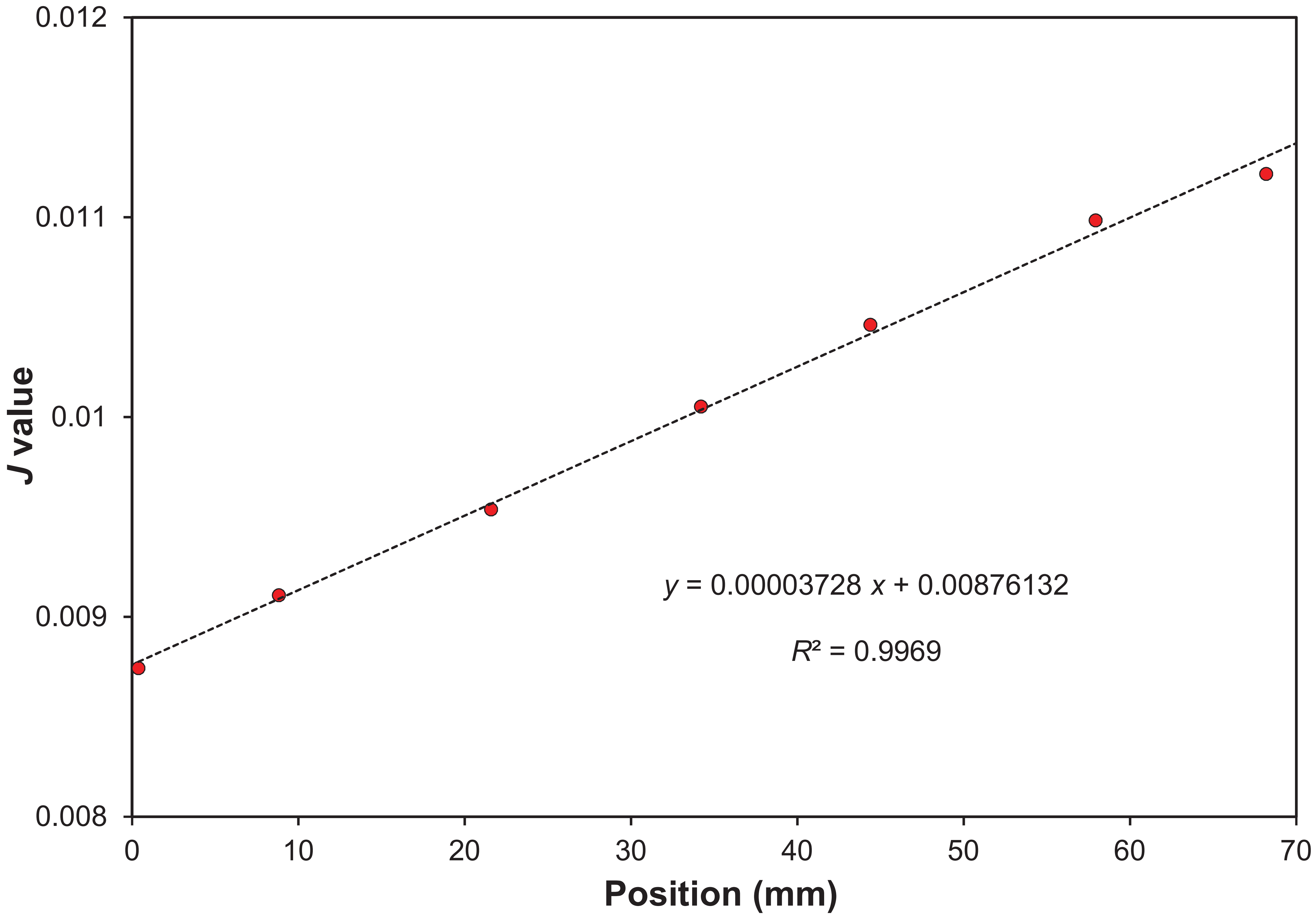
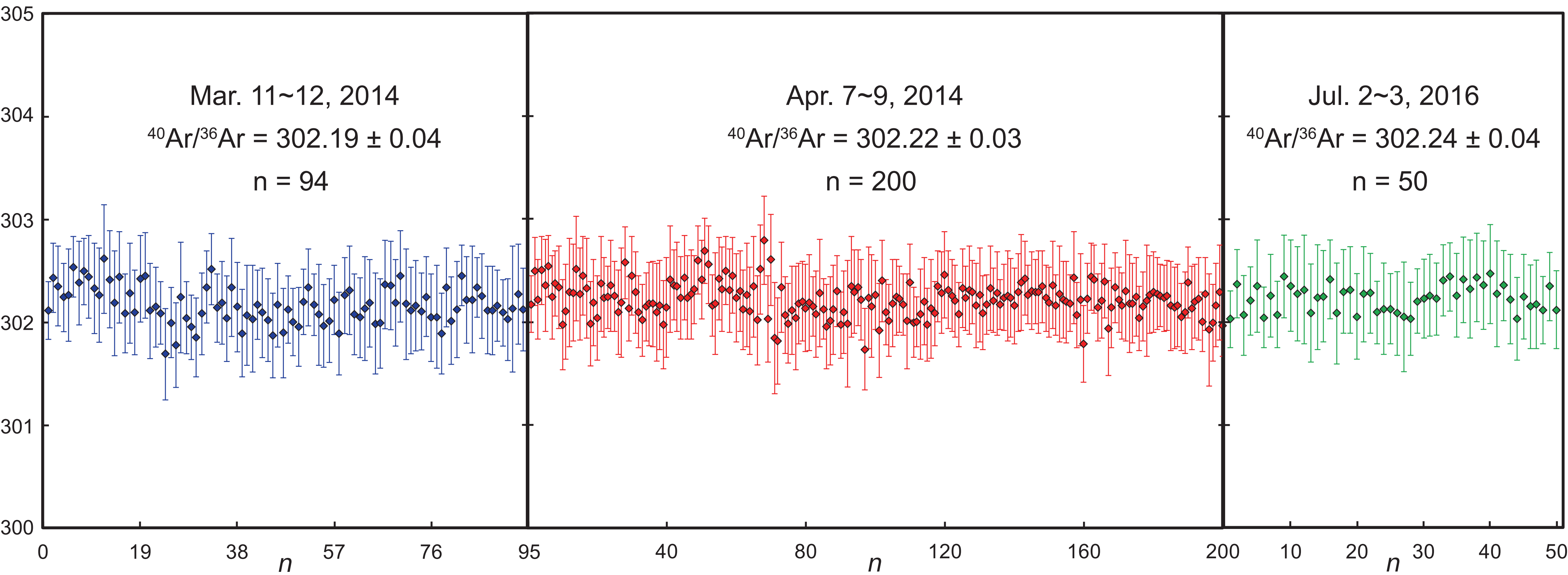
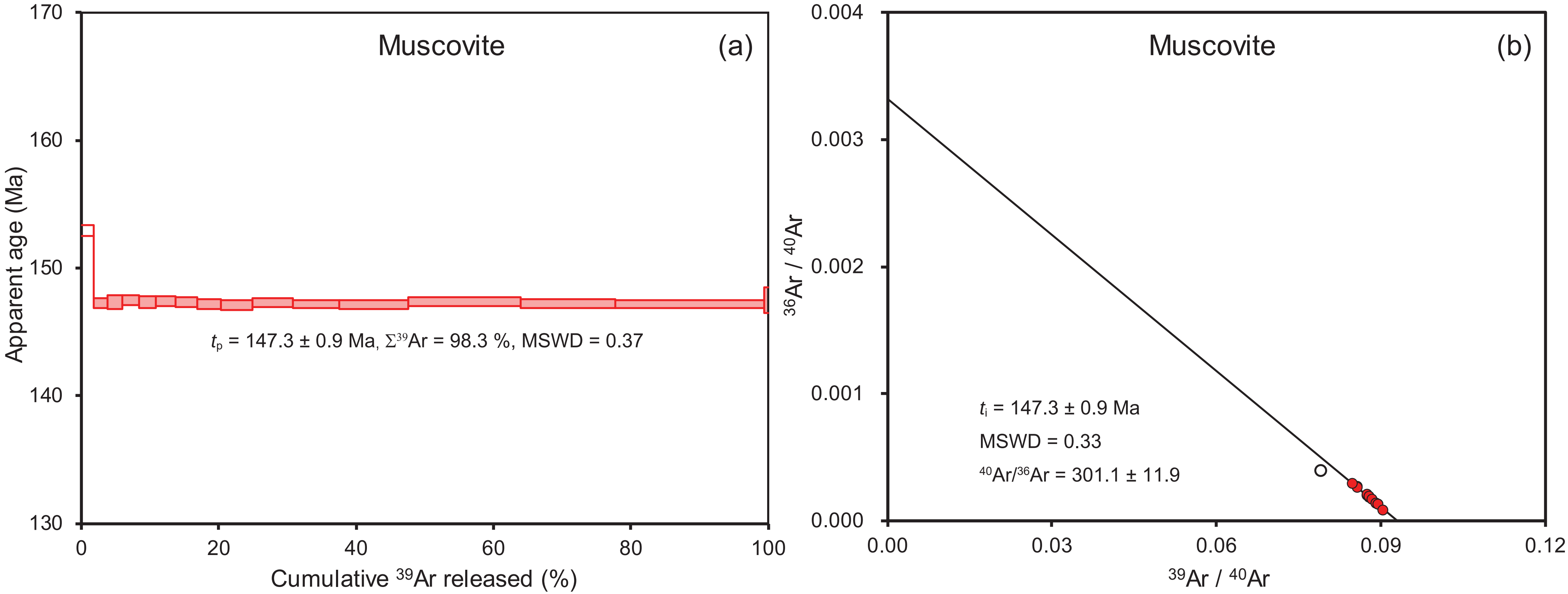
CDD
KLTPR
MEPRC

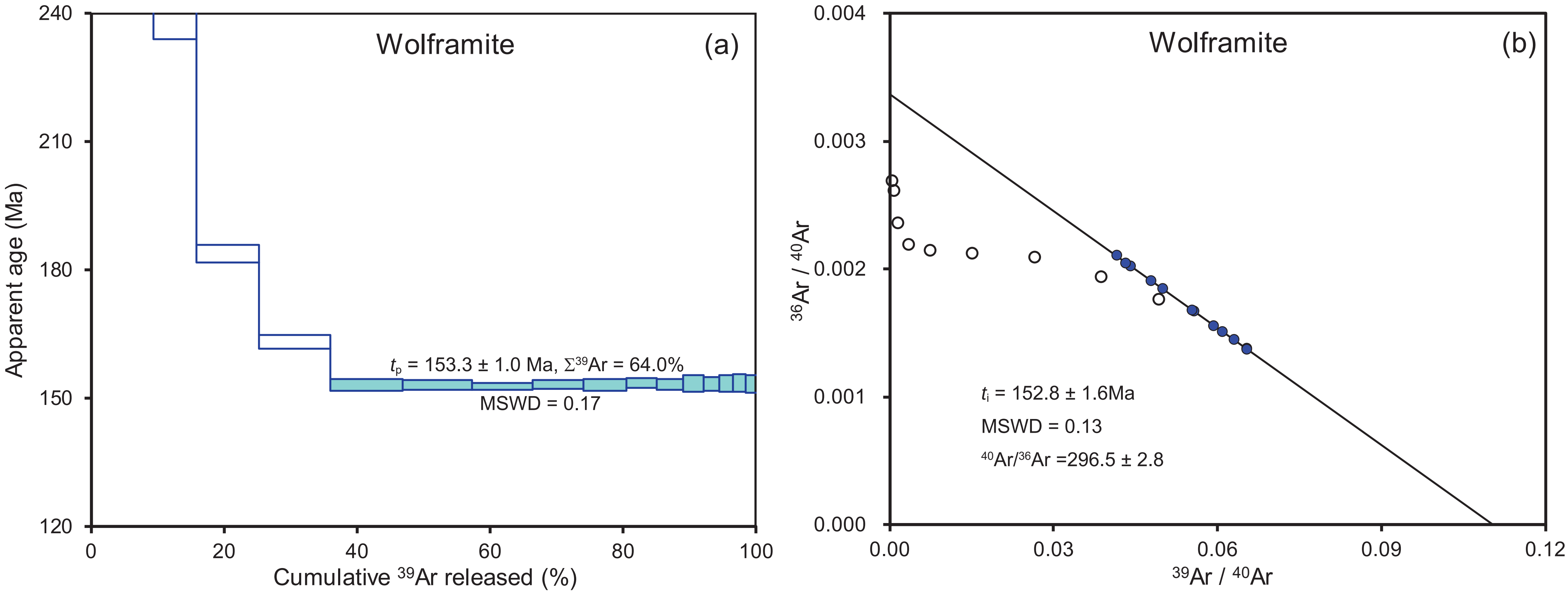

0.012
0.011
0.01
0.009
0.008
J value
0
10
20
30
40
50
60
70
Position (mm)
y = 0.00003728 x + 0.00876132
R² = 0.9969



Mar. 11~12, 2014
$^{40}Ar/^{36}Ar$ = 302.19 ± 0.04
n = 94
Apr. 7~9, 2014
$^{40}Ar/^{36}Ar$ = 302.22 ± 0.03
n = 200
Jul. 2~3, 2016
$^{40}Ar/^{36}Ar$ = 302.24 ± 0.04
n = 50
305
304
303
302
301
300
0
19
38
57
76
95
40
80
120
160
200
10
20
30
40
50
n
n
n



Muscovite
(a)
170
160
150
140
130
Apparent age (Ma)
0
20
40
60
80
100
Cumulative 39Ar released (%)
tp = 147.3 ± 0.9 Ma, Σ39Ar = 98.3 %, MSWD = 0.37
Muscovite
(b)
0.004
0.003
0.002
0.001
0.000
36Ar / 40Ar
0.00
0.03
0.06
0.09
0.12
39Ar / 40Ar
ti = 147.3 ± 0.9 Ma
MSWD = 0.33
40Ar/36Ar = 301.1 ± 11.9



Wolframite
(a)
240
210
180
150
120
Apparent age (Ma)
0
20
40
60
80
100
Cumulative ^{39}Ar released (%)
t_p = 153.3 ± 1.0 Ma, $\Sigma^{39}Ar$ = 64.0%
MSWD = 0.17
Wolframite
(b)
0.004
0.003
0.002
0.001
0.000
^{36}Ar / ^{40}Ar
0.00
0.03
0.06
0.09
0.12
^{39}Ar / ^{40}Ar
t_i = 152.8 ± 1.6Ma
MSWD = 0.13
$^{40}Ar/^{36}Ar$ =296.5 ± 2.8

Table 1Reactions producing argon isotopes in neutron irradiated samples[a,b]

Argon isotope produced	Target element			
	Ca	K	Ar	Cl
^{36}Ar	$^{40}Ca(n,n\alpha)^{36}Ar$ (−7.04, 96.94)			$^{35}Cl(n,\gamma)^{36}Cl$ (+8.58, 75.77) $\xrightarrow{\beta^-}{}^{36}Ar$
^{37}Ar	$^{40}Ca(n,\alpha)^{37}Ar$ (+1.75, 96.94)	$^{39}K(n,nd)^{37}Ar$ (−15.99, 93.26)	$^{36}Ar(n,\gamma)^{37}Ar$ (+8.79, 0.337)	
^{38}Ar	$^{42}Ca(n,n\alpha)^{38}Ar$ (−6.25, 0.75)	$^{39}K(n,d)^{38}Ar$ (−4.16, 93.26) $^{41}K(n,\alpha)^{38}Cl$ (−0.12, 6.73) $\xrightarrow{\beta^-}{}^{38}Ar$	$^{40}Ar(n,nd)^{38}Cl$ (-18.38, 99.60) $\xrightarrow{\beta^-}{}^{38}Ar$	$^{37}Cl(n,\gamma)^{38}Cl$ (+6.11, 24.23) $\xrightarrow{\beta^-}{}^{36}Ar$
^{39}Ar	$^{42}Ca(n,\alpha)^{39}Ar$ (+0.34, 0.65) $^{43}Ca(n,n\alpha)^{39}Ar$ (−7.59, 0.14)	$^{39}K(n,p)^{39}Ar$ (+0.22, 93.26) $^{40}K(n,d)^{39}Ar$ (−5.36, 0.01167)	$^{38}Ar(n,\gamma)^{39}Ar$ (+6.60, 0.063) $^{40}Ar(n,d)^{39}Cl$ (-10.30, 99.60) $\xrightarrow{\beta^-}{}^{39}Ar$	
^{40}Ar	$^{43}Ca(n,\alpha)^{40}Ar$ (+2.28, 0.14) $^{44}Ca(n,n\alpha)^{40}Ar$ (−8.85, 2.09)	$^{40}K(n,p)^{40}Ar$ (+2.29, 0.01167) $^{41}K(n,d)^{40}Ar$ (−5.58, 6.73)		

[a]Sources:Brereton (1970), Turner (1971), and (Dalrymple et al., 1981). Q values (MeV)， calculated from data in (Lederer and Shirley, 1978), and target isotope abundance (atom%) shown in parentheses below each reaction.

[b]Half lives:

$^{36}Cl \xrightarrow{\beta^-} {}^{36}Ar, 3.0\times10^5$ a; $^{38}Cl \xrightarrow{\beta^-} {}^{38}Ar$, 37.3min; $^{39}Cl \xrightarrow{\beta^-} {}^{39}Ar$, 55.5min;

$^{37}Ar \xrightarrow{ce} {}^{37}Cl$, 35.1 days; $^{39}Ar \xrightarrow{\beta^-} {}^{39}K$, 269 a; $^{40}K \rightarrow {}^{40}Ar$, $^{40}Ca, 1.25\times10^9$ a.

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