

# A redetermination of the isotopic abundances of atmospheric Ar

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## Abstract

Atmospheric argon measured on a dynamically operated mass spectrometer with an ion source magnet, indicated systematically larger  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios compared to the generally accepted value of Nier [Nier A.O., 1950. A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium. *Phys. Rev.* **77**, 789–793],  $295.5 \pm 0.5$ , which has served as the standard for all isotopic measurements in geochemistry and cosmochemistry. Gravimetrically prepared mixtures of highly enriched  $^{36}\text{Ar}$  and  $^{40}\text{Ar}$  were utilized to redetermine the isotopic abundances of atmospheric Ar, using a dynamically operated isotope ratio mass spectrometer with minor modifications and special gas handling techniques to avoid fractionation. A new ratio  $^{40}\text{Ar}/^{36}\text{Ar} = 298.56 \pm 0.31$  was obtained with a precision of 0.1%, approximately 1% higher than the previously accepted value. Combined with the  $^{38}\text{Ar}/^{36}\text{Ar}$  ( $0.1885 \pm 0.0003$ ) measured with a VG5400 noble gas mass spectrometer in static operation, the percent abundances of  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{40}\text{Ar}$  were determined to be  $0.3336 \pm 0.0004$ ,  $0.0629 \pm 0.0001$ , and  $99.6035 \pm 0.0004$ , respectively. We calculate an atomic mass of Ar of  $39.9478 \pm 0.0002$ . Accurate Ar isotopic abundances are relevant in numerous applications, as the calibration of the mass spectrometer discrimination.

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## 1. Introduction

Argon has three stable isotopes,  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{40}\text{Ar}$ . The currently used atmospheric Ar isotopic ratios originated from Nier (1950),  $^{40}\text{Ar}/^{36}\text{Ar} = 296.0 \pm 0.5$  and  $^{38}\text{Ar}/^{36}\text{Ar} = 0.1880 \pm 0.0003$ . The measured value of  $0.003378 \pm 0.000006$  for  $^{36}\text{Ar}/^{40}\text{Ar}$  in Nier's paper actually corresponds to a value of  $296.0 \pm 0.5$ ; however the IUGS Subcommittee on Geochronology suggested that isotopic data be reported using the recommended value of  $^{40}\text{Ar}/^{36}\text{Ar} = 295.5$  (Steiger and Jäger, 1977). This value is derived from Nier's data, which used rounded percentage

abundances given as  $^{40}\text{Ar} = 99.600$ ,  $^{38}\text{Ar} = 0.063$ ,  $^{36}\text{Ar} = 0.337 \text{ atm}\%$ .

The isotopic ratios from Nier's (1950) have widely been used in geochemistry and cosmochemistry, and for studying the evolutionary history of the Earth's mantle and atmosphere (e.g., Kunz, 1999; Moreira et al., 1998; Pepin, 1998). Atmospheric argon ratios are generally used to monitor the mass discrimination of a mass spectrometer (McDougall et al., 2005).

We report a redetermination of the isotopic abundance of atmospheric argon as obtained by an isotope ratio mass spectrometer using Ar isotopic mixtures which were gravimetrically prepared with highly enriched  $^{36}\text{Ar}$  and  $^{40}\text{Ar}$ . The gravimetric method for preparation of calibration gas mixtures is very precise (ISO, 2001) and has significant advantages when compared to the volumetric preparation of mixtures as carried out by Nier (1950).

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## 2. Preparation of isotopic Ar gas mixtures

### 2.1. Gravimetric method

We used a gravimetric method to prepare the Ar mixtures according to ISO 6142 (2001), which utilizes two electronic mass-comparators; Mettler Toledo model PR10003 comparator, (capacity 10.1 kg, readability 1 mg) with an automated cylinder loading system (Park et al., 2004) and Mettler Toledo model AX1005 comparator (capacity 1109 g, readability 0.01 mg) in KRISS (Korea Research Institute of Standards and Science). The gravity difference on the mass-comparator between sample and tare cylinders is automatically recorded with a high level of accuracy. All cylinders were evacuated by a turbomolecular pumping system to less than  $1 \times 10^{-3}$  Pa at a temperature of 80 °C. To remove water from the cylinder, heat was applied by wrapping the cylinders with heating tape for two days. The gas-loaded cylinders were weighed in a balance room where temperature and humidity were controlled at  $22 \pm 1$  °C and  $50 \pm 5\%$ . The balance itself was installed in an isolated box mounted on a stone plate in order to eliminate fluctuations and vibrations from air flow. The gravimetric method uses a tare cylinder to automatically correct for buoyancy from ambient air pressure. This weighing system has an automated cylinder loading system and is registered in Korea (Patent No. 0495483, June, 2005). After each weighing, the cylinders were turned over to mix the gases for optimal homogeneity.

### 2.2. Ar isotopic mixtures

A synthetic Ar isotopic mixture (R2) was prepared by gravimetrically mixing pure Ar (99.999%, Deogyang Energen Co., Korea) commercially manufactured from air, and a highly enriched  $^{36}\text{Ar}$  spike ( $^{36}\text{Ar} > 99.5\%$ , Oak Ridge National Laboratory, USA). Another synthetic Ar isotopic mixture (R3) was prepared by mixing the highly enriched  $^{36}\text{Ar}$  spike ( $> 99.5\%$ ) and a pure  $^{40}\text{Ar}$  spike (99.95%), also purchased from Oak Ridge National Laboratory. An impurity analysis for the gases, nitrogen, oxygen, carbon dioxide, helium, methane, and hydrogen was carried out and the isotopic composition and elemental data are listed in Table 1. These data were determined mass spectrometrically on a Finnigan MAT 271 spectrometer and mole fractions of Ar in Table 1 were corrected for mass

discrimination as obtained from gravimetric isotopic mixture, R3. The errors in Table 1 represent overall uncertainties of experimental data obtained by mass spectrometry using known reference gas mixtures, for impurities excluding the principal Ar isotope component. The uncertainty of principal Ar isotope was calculated from equation ‘Purity of Ar =  $1 - \sum (\text{impurities})$ ’ written in ISO Standard 6142. The minor Ar isotopes were measured by precision mass spectrometer (Finnigan MAT 271) with molecular flow injection, which were calibrated by gravimetric mixtures prepared by this work. It is necessary to use an iteration process to obtain the isotope ratio of source by a prepared standard gas mixture. However, this iteration does not make any problem because the purity of source gases does not change much by uncertain correction of mass discrimination in the mass spectrometer. The resulting total pressure of the mixtures in each cylinder was  $\sim 8$  MPa for R2 and 0.34 MPa for R3. The gravimetrically determined  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are  $39.596 \pm 0.037$  and  $330.30 \pm 0.34$  for R2 and R3, respectively. The mole fractions for each isotope in the mixtures are listed in Table 2. The errors in Table 2 were obtained from uncertainties of the source gases and uncertainty from gravimetric preparation.

### 2.3. Sample preparation for mass spectrometry

The prepared Ar isotopic mixtures (R2 and R3) were filled into three stainless steel reservoirs (each 7 cm<sup>3</sup>) with welded stainless steel valves (Nupro) at  $\sim 93.3$  kPa pressure. The sample reservoir was connected to a 1/4 in. ultratorr adapter which connected to a mass spectrometer. Measurements were carried out on a dynamic isotope ratio mass spectrometer (Finnigan MAT 252 at UCSD). No further cleaning of the Ar mixture was necessary.

## 3. Mass spectrometry

Argon isotopic ratios ( $^{40}\text{Ar}/^{36}\text{Ar}$ )<sub>air</sub> and ( $^{38}\text{Ar}/^{36}\text{Ar}$ )<sub>air</sub>, were measured first in a sample of the gravimetrically prepared Ar mixture R3 ( $^{40}\text{Ar}/^{36}\text{Ar} = 330.30 \pm 0.34$ ;  $^{38}\text{Ar}/^{36}\text{Ar} = 0.0544 \pm 0.0010$ ) by cross-calibration on the dual viscous-inlet mass spectrometer equipped with Faraday cups in the appropriate positions for simultaneous collection of  $^{40}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{36}\text{Ar}$  beams (Severinghaus et al., 2003). Sample and laboratory standard gases were admit-

Table 1  
Composition of Ar source gases

Source gases	Mole fraction of Ar isotopes and impurities (mmol)									
	$^{36}\text{Ar}$	$^{38}\text{Ar}$	$^{40}\text{Ar}$	H <sub>2</sub>	He	CH <sub>4</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub> O
Normal Ar	3.291 (4)	0.634 (4)	995.947 (7)	<0.001	<0.001	<0.001	<0.001	<0.001	0.002 (1)	0.013 (4)
$^{36}\text{Ar}$ -enriched	998.15 (5)	0.775 (3)	0.112 (3)	0.32 (2)	0.40 (3)	<0.001	0.006 (2)	0.008 (2)	0.17 (1)	0.05 (2)
$^{40}\text{Ar}$ -enriched	0.273 (3)	0.163 (3)	999.486 (9)	0.009 (4)	<0.001	0.004 (2)	0.049 (5)	<0.001	0.013 (3)	0.003 (2)

An impurity mole fraction entry such as <0.001 mmol/mol indicates the detection limit of the method being used.

Other noble gas impurities were not detected by Finnigan MAT 271 for all source gases.

Numbers in parenthesis following the values indicate combined standard uncertainties in the last digit.

Table 2  
The gravimetric isotopic abundances of Ar in the two calibration gas mixtures

Cylinder	Mole fraction of Ar isotope/mmol			Isotopic ratio	
	$^{36}\text{Ar}$	$^{38}\text{Ar}$	$^{40}\text{Ar}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{38}\text{Ar}/^{36}\text{Ar}$
R2	6.057 (6)	0.1570 (10)	239.847 (6)	39.596 (37)	0.02587 (16)
R3	2.502 (3)	0.136 (3)	826.378 (51)	330.30 (34)	0.0544 (10)

R2:  $^{36}\text{Ar}$  enriched,  $0.18960 \text{ g} \pm 0.00020 \text{ g}$ ; normal Ar,  $9.61998 \text{ g} \pm 0.00020 \text{ g}$ .

R3:  $^{36}\text{Ar}$  enriched,  $0.08198 \text{ g} \pm 0.00003 \text{ g}$ ;  $^{40}\text{Ar}$  enriched,  $33.03944 \text{ g} \pm 0.00200 \text{ g}$ .

ted through capillaries and fed into the mass spectrometer or into a waste line at high vacuum, with rapid switching between sample and standard, minimizing the effect of instrument drift (McKinney et al., 1950). The uncertainty in the very low  $^{38}\text{Ar}$  abundance does not permit a calibration of the  $^{38}\text{Ar}/^{36}\text{Ar}$  ratio in atmospheric Ar. The laboratory standard gas, stored in a 2-L stainless steel canister, was prepared from commercial pure Ar (>99.995%) mixed with pure Ne, Kr, and Xe in approximately atmospheric proportions.

Aliquots of laboratory standard and sample gases were expanded with the inlet bellows of the mass spectrometer fully open. The bellows' volumes were then reduced to obtain equal pressures prior to the analysis. Balancing of  $^{40}\text{Ar}$  ion currents on the standard and sample sides was performed both manually or automatically throughout the run (Grachev and Severinghaus, 2003). The beam voltages of all these collectors were simultaneously integrated for 8 s on standard, sample, and then standard side, constituting one cycle. A delay of 10 s was allowed before data acquisition to stabilize the beam after switching between standard and sample. For the measurement of the mixture R3, beam current of  $2 \times 10^{-8}$  amps for  $^{40}\text{Ar}$  was used providing signal of  $\sim 6 \text{ V}$  on  $3 \times 10^8 \text{ ohm}$ . Resistors of  $3 \times 10^{11} \text{ ohm}$  and  $1 \times 10^{11} \text{ ohm}$  were used for  $^{38}\text{Ar}$  and  $^{36}\text{Ar}$ , respectively. For the measurement of the mixture R2, a resistor of  $3 \times 10^{10} \text{ ohm}$  was utilized for  $^{36}\text{Ar}$ . The isotopic composition was then calculated for each cycle using the conventional delta ( $\delta^*$ ) notation as follows:

$$\delta^* = \left[ \frac{([^{40}\text{Ar}]/[^{36}\text{Ar}])_{\text{sample}}}{([^{40}\text{Ar}]/[^{36}\text{Ar}])_{\text{std}}} - 1 \right] \times 10^3\text{‰} \quad (1)$$

where  $[^{40}\text{Ar}]$  and  $[^{36}\text{Ar}]$  are the voltages of  $^{40}\text{Ar}$  and  $^{36}\text{Ar}$  beams for a sample or a standard gas, which were corrected for an extremely small background voltage assigned to each Faraday cup.

The non-linearity of the detection system was tested by measuring the  $\delta^*$  for varying amounts of Ar pressure in the bellows (3–10 V for  $^{40}\text{Ar}$  on the Faraday cup) as depicted in Fig. 1, but the pressure does not significantly affect  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios.

#### 4. Preparation and analysis of atmospheric Ar

The atmosphere is the ultimate standard gas to which R2 and R3 mixtures are referred. The laboratory standard gas, however, is fractionated with respect to the atmosphere due to the commercial air reduction process. Thus,  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of the laboratory standard gas must be calibrated against the atmosphere. For this purpose, we measured isotopic ratios of atmospheric Ar against the laboratory standard gas on the MAT 252 with the same procedure applied for R2 and R3 gases. Atmospheric air samples were collected in three 2-L glass flasks (numbered 117, 118 and 300) on the pier of the Scripps Institution of Oceanography in March 2005 (hereafter La Jolla air), and in four flasks (numbered MGD01, MGD23, MGD103, MGD846) at a field site in a region of “Megadunes” near Vostok Station, Antarctica in January 2004 (80.78 °S, 124.5 °S; hereafter Megadunes surface air). The air sampling techniques were identical to those described by Severinghaus et al. (2001) and Severinghaus et al. (2003) for Megadunes air and La Jolla air, respectively, except an aspirated air intake was used for La Jolla air sampling to avoid possible diffusive fractionation (Blaine, 2005). The air in the 2-L glass flask was expanded into a single small volume (80 cc), and then Ar and other minor noble gases were extracted from the aliquot. The details are described elsewhere (Severinghaus et al., 2001), thus only the difference from the published procedure is given here. The air was exposed to a Zr/Al getter at 900 °C for 20 min to remove all reactive gases, and then  $\text{H}_2$  was absorbed by the getter at 300 °C for 3 min. The noble gases were then cryogenically transferred into a stainless steel tube at 4 K. The tube was warmed to room temperature and left for at least 2 h to allow homogenization. The delta value for

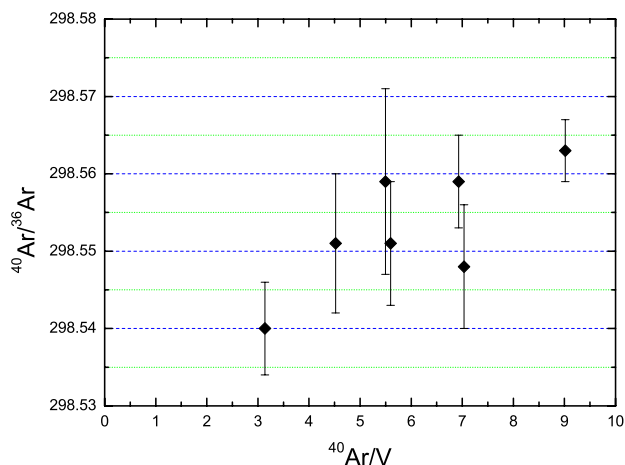


Fig. 1. Linearity of the detection system for  $^{40}\text{Ar}/^{36}\text{Ar}$  in mixture R3. Ratios vs. signal size (in V on Faraday) indicate good linearity because of the consistency of the measured  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio.

$^{40}\text{Ar}/^{36}\text{Ar}$  of the purified Ar was then measured with the same procedure as Ar isotopic mixtures. The delta values are slightly sensitive to imbalance between the standard and sample gas pressures in the ion source, thus the data were corrected for this effect (typically less than 0.005‰) (Severinghaus et al., 2003). Replicate measurements of the La Jolla air (six measurements for each flask) and Megadunes surface air (two measurements for each flask) vs. the laboratory standard were made over a month between March 6, 2005 and April 3, 2005 (Tables 3 and 4), together with 85 measurements of 42 air samples withdrawn from snowpack (firn) at Megadunes (hereafter Megadunes firn air). The pooled standard deviation from all replicate measurements of individual flasks of La Jolla air, Megadunes surface air, and Megadunes firn air samples was 0.006‰, which can be considered as the reproducibility of the atmospheric measurements including the gas handling procedures in the laboratory.

Table 3  
 $\delta^{40}\text{Ar}/^{36}\text{Ar}$  of La Jolla air samples against the laboratory standard gas

Flask number	Replicate number	Analysis date in 2005	$\delta^{40}\text{Ar}/^{36}\text{Ar}$ (‰)	$\delta^{40}\text{Ar}/^{36}\text{Ar}$ (‰), mean for each flask	$\delta^{40}\text{Ar}/^{36}\text{Ar}$ (‰), mean of all values
117	1	March 06	-0.628	-0.617 ± 0.010	-0.619 ± 0.007
117	2	March 06	-0.626		
117	3	March 07	-0.612		
117	4	March 07	-0.604		
117	5	March 07	-0.611		
117	6	March 07	-0.622		
118	1	March 08	-0.607	-0.618 ± 0.007	
118	2	March 08	-0.623		
118	3	March 08	-0.625		
118	4	March 08	-0.622		
118	5	March 09	-0.613		
118	6	March 09	-0.618		
300	1	March 15	-0.619	-0.621 ± 0.003	
300	2	March 16	-0.617		
300	3	March 23	-0.620		
300	4	March 23	-0.623		
300	5	April 3	-0.625		
300	6	April 3	-0.622		

Table 4  
 $\delta^{40}\text{Ar}/^{36}\text{Ar}$  of Megadunes surface air against the laboratory standard gas

Flask number	Replicate number	Analysis date in 2005	$\delta^{40}\text{Ar}/^{36}\text{Ar}$ (‰)	$\delta^{40}\text{Ar}/^{36}\text{Ar}$ (‰), mean of all values
MGD846	1	March 09	-0.620	-0.623 ± 0.005
MGD846	2	March 09	-0.624	
MGD01	1	March 11	-0.622	
MGD01	2	March 11	-0.624	
MGD23	1	March 25	-0.613	
MGD23	2	March 25	-0.628	
MGD103	1	March 28	-0.626	
MGD103	2	April 02	-0.624	

## 5. Results and discussion

### 5.1. Atmospheric Ar against the laboratory standard gas

The La Jolla air vs. our laboratory standard has a mean delta value of  $-0.619 \pm 0.007\text{‰}$  (one standard deviation,  $n=18$ ) for  $^{40}\text{Ar}/^{36}\text{Ar}$ , based on the replicate measurements of the three flask samples (Table 3). The standard deviation is consistent with the experimental uncertainty of 0.006‰, and the scatter within the six measurements of each flask is also consistent with the experimental uncertainty (Table 3). Also there are no appreciable differences between the mean values of the three flasks. The mean of all measurements (duplicate measurements of four flasks) of Megadunes surface air is  $-0.623 \pm 0.005\text{‰}$  ( $n = 8$ ), which agrees with the La Jolla air value within the uncertainty. This suggests that temporal and spatial variation of the present atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is not detectable with the current analytical precision, as expected, and that the La Jolla air has the typical atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio. The uncertainty of 0.007‰ of the atmospheric measurements vs. laboratory standard gas propagates to an uncertainty in the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the atmosphere of  $298 \times 0.000007 = \pm 0.002$ , which is negligibly small compared with other sources of uncertainty.

### 5.2. Calibration of the Ratio $^{40}\text{Ar}/^{36}\text{Ar}$ in atmospheric Ar

We analyzed two isotopic mixtures (R2, R3) where the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios differed by nearly one order of magnitude. The  $^{40}\text{Ar}/^{36}\text{Ar}$  in mixture R3 ( $^{40}\text{Ar}/^{36}\text{Ar} = 330.30 \pm 0.34$ ) is close to the atmospheric value and is expected to yield more accurate results by mass spectrometry. The Ar isotopic ratios were measured in two separated volumes of the mixture R3 and also measured on different days and with different pressures to check the reproducibility. The averaged delta values for the two volumes agree within  $1\sigma$  uncertainty (Table 5). Averages obtained in the mixtures are  $\delta^* = 105.61 \pm 0.04\text{‰}$  for  $^{40}\text{Ar}/^{36}\text{Ar}$  in mixture R3 and  $\delta^* = -867.53 \pm 0.02\text{‰}$  in R2 (Table 6). This corresponds to atmospheric abundance ratios,  $^{40}\text{Ar}/^{36}\text{Ar} = 298.56 \pm 0.31$  for mixture R3 and  $298.73 \pm 0.28$  for mixture R2. The uncertainty in the atmospheric Ar ratios were calculated from the uncertainty in the gravimetrically prepared Ar isotopic gas mixtures (Table 2) and the standard deviation of Ar ratios measured by a mass spectrometer (Table 5). The results obtained from R2 and R3 are in agreement within uncertainty and any difference may possibly be related to the significantly different isotopic composition of mixture R2 and atmospheric Ar. We adopt the data from mixture R3 as more reliable because the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is close to the atmospheric value.

### 5.3. Comparison with literature data

The present redetermination of the atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio yields a value which is larger than Nier's

Table 5  
Results of Ar isotopic ratios obtained from the Ar isotope mixture, R3, on Finigan MAT 252, are illustrated

Pressure/mbar	$\delta(^{40}\text{Ar}/^{36}\text{Ar})/\text{‰}$	$(^{40}\text{Ar}/^{36}\text{Ar})_{\text{La Jolla air}}$
Data from volume 1 of reservoir		
40	105.63	298.56
33	105.63	298.56
28	105.66	298.55
50	105.61	298.56
40	105.67	298.55
33	105.66	298.55
20	105.70	298.54
Average	105.65 ± 0.03	298.55 ± 0.01
Data from volume 2 of reservoir		
51	105.53	298.59
40	105.57	298.57
37	105.56	298.58
14	105.51	298.59
7	105.53	298.59
40	105.66	298.55
40*	105.65	298.55
Average	105.57 ± 0.06	298.57 ± 0.02

The ratios  $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{La Jolla air}}$  for the La Jolla air were calculated from the delta values from the R3 as well as from the La Jolla air against the laboratory standard. The standard deviation of each measured delta value is less than 0.04. The errors of the averaged  $^{40}\text{Ar}/^{36}\text{Ar}$  values represent the standard deviation, which does not include the uncertainty induced from the gravimetrically prepared Ar isotopic gas mixture ( $^{40}\text{Ar}/^{36}\text{Ar} = 330.30 \pm 0.34$ ). Idle time: 8 s. \*Idle time: 16 s.

Table 6  
Results of Ar isotopic ratios obtained from the Ar isotope mixture, R2, on Finigan MAT 252, are illustrated

Replicate number	$\delta(^{40}\text{Ar}/^{36}\text{Ar})/\text{‰}$	$\delta(^{40}\text{Ar}/^{36}\text{Ar})/\text{‰}$ , mean for measurements
1	-867.57	-867.56 ± 0.01
2	-867.56	
3	-867.55	
4	-867.55	
1	-867.53	-867.53 ± 0.01
2	-867.53	
3	-867.52	
4	-867.52	
1	-867.55	-867.54 ± 0.01
2	-867.55	
3	-867.54	
4	-867.53	
1	-867.51	-867.50 ± 0.01
2	-867.50	
3	-867.50	
4	-867.50	
Average		-867.53 ± 0.02
$(^{40}\text{Ar}/^{36}\text{Ar})_{\text{La Jolla air}}$		298.73 ± 0.05

The ratios  $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}}$  for the La Jolla air were calculated from the delta values from the R2 as well as from the La Jolla air against the laboratory standard. The errors of the  $^{40}\text{Ar}/^{36}\text{Ar}$  averaged values represent the standard deviation, which does not include the uncertainty induced from the gravimetrically prepared Ar isotopic gas mixture ( $^{40}\text{Ar}/^{36}\text{Ar} = 39.596 \pm 0.037$ ).

by approximately 1% outside the quoted error limits. The new calibration used is based on gravimetrically prepared isotopic mixtures and can be compared to the data obtained by the volumetric technique used by Nier (1950). The volumetric method is based on the ideal gas equation,  $PV = nRT$ , where pressure is measured by a McLeod gauge, and volumes were calibrated using mercury. In Nier's method, there are uncertain factors like microbubbles in vacuum grease of stopcocks and the possibility that grease may generate memory effects, that can adversely affect the accuracy of the results. This makes it difficult to evaluate possible systematic errors in the volumetric method. Nier (1950) used a system with stopcocks that required vacuum grease and incorporated two part valves for ease of measuring the volumes. Any hydrocarbons, hydrogen or nitrogen in the microbubbles could have introduced uncertainties in the measurement of the Ar concentrations. The gravimetric method eliminates most of these uncertainties, producing results of higher precision and accuracy. Furthermore, the ratio of  $^{36}\text{Ar}/^{40}\text{Ar}$  in the volumetrically prepared mixture of Nier (1950) was near to 0.01, considerably different from the isotopic composition of air Ar. It was assumed that effects due to mass discrimination do not depend on compositional differences.

#### 5.4. Atomic weight of atmospheric Ar

An air standard taken at UCSD was measured on a modified VG 5400 multi-collector instrument. The measurement of the isotopic composition of atmospheric argon gives an average ratio,  $^{40}\text{Ar}/^{36}\text{Ar} = 298.86 \pm 0.15$  and  $^{38}\text{Ar}/^{36}\text{Ar} = 0.1886 \pm 0.0002$ , which is close to the new value, although these ratios were not corrected for the mass discrimination. The mass discrimination of VG 5400 is calculated from the new ratio ( $^{40}\text{Ar}/^{36}\text{Ar} = 298.56 \pm 0.31$ ) and is 0.25‰ per atomic mass unit. The ratio  $^{38}\text{Ar}/^{36}\text{Ar}$  is calculated from an average measured on VG 5400 applying the 0.5‰ correction (Table 7). On the other hand, the low  $^{38}\text{Ar}$  abundance in the gravimetric mixture (see uncertainties in Table 2) prevents a determination of the atmospheric  $^{38}\text{Ar}/^{36}\text{Ar}$  ratio in mixtures R2, R3. Table 7 compares the new data on isotopic abundance ratios of argon with values given by Nier (1950). The ratios  $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}} = 298.56 \pm 0.31$ , and  $(^{38}\text{Ar}/^{36}\text{Ar})_{\text{air}} = 0.1885 \pm 0.0003$  correspond to percentage abundance of  $99.6035 \pm 0.0004$ ,  $0.0629 \pm 0.0001$ , and  $0.3336 \pm 0.0004$  for  $^{40}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{36}\text{Ar}$ , respectively. These abundances correspond to an atomic weight of  $39.9478 \pm 0.0002$  for atmospheric Ar.

Table 7  
Isotopic abundance ratios of atmospheric argon (1σ values)

Isotopic ratio	Nier (1950)	This work
$^{40}\text{Ar}/^{36}\text{Ar}$	295.5 ± 0.5	298.56 ± 0.31
$^{38}\text{Ar}/^{36}\text{Ar}$	0.1880 ± 0.0003	0.1885 ± 0.0003

## 6. Conclusions

Isotopic Ar mixtures were prepared by gravimetric techniques and measured on an isotope ratio mass spectrometer (IRMS). Two sets of reference gas mixtures were prepared at KRISS (Korea Research Institute of Standards and Science) and measured at UCSD for this work. The following results were obtained: (1) Averages obtained delta values compared with the laboratory standard Ar are  $\delta^* = 105.61 \pm 0.04\text{‰}$  for  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $-867.53 \pm 0.02\text{‰}$  in mixture R3, and R2, respectively. The  $\delta^*$  values correspond to atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios  $298.56 \pm 0.31$  for mixture R3 and  $298.73 \pm 0.28$  for mixture R2. Both ratios are in agreement within uncertainty and we adopt the value based on the mixture R3 as more reliable because it is close to the atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$ . (2) The mass discrimination for measurements on the mass spectrometer VG 5400 was calculated from the new  $^{40}\text{Ar}/^{36}\text{Ar}$  value and measured  $^{38}\text{Ar}/^{36}\text{Ar}$  data were recalculated using a mass discrimination of  $0.25\text{‰}$  per atomic mass unit resulting in a ratio of  $0.1885 \pm 0.0003$ . (3) The atmospheric Ar percentage abundances were calculated to be  $99.6035 \pm 0.0004$ ,  $0.0629 \pm 0.0001$ , and  $0.3336 \pm 0.0004$  for  $^{40}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{36}\text{Ar}$ , respectively. These abundances correspond to an atomic weight of  $39.9478 \pm 0.0002$  for atmospheric Ar.

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