VU Research Portal

A metrological approach to measuring ^{40}Ar * concentrations in K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ mineral standards

Morgan, L.E.; Postma, O.; Kuiper, K.F.; Mark, D.F.; van der Plas, W.; Davidson, S.; Perkin, M.; Villa, I.M.; Wijbrans, J.R.

published in

Geochemistry, Geophysics, Geosystems
2011

DOI (link to publisher)

[10.1029/2011GC003719](https://doi.org/10.1029/2011GC003719)

document version

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

citation for published version (APA)

Morgan, L. E., Postma, O., Kuiper, K. F., Mark, D. F., van der Plas, W., Davidson, S., Perkin, M., Villa, I. M., & Wijbrans, J. R. (2011). A metrological approach to measuring ^{40}Ar * concentrations in K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ mineral standards. *Geochemistry, Geophysics, Geosystems*. <https://doi.org/10.1029/2011GC003719>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:

vuresearchportal.ub@vu.nl

A metrological approach to measuring $^{40}\text{Ar}^*$ concentrations in K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ mineral standards

Leah E. Morgan, Onno Postma, and Klaudia F. Kuiper

Department of Petrology, Faculty of Earth and Life Science, Vrije Universiteit, De Boelelaan 1085, NL-1081 HV Amsterdam, Netherlands (leah.morgan@falw.vu.nl)

Darren F. Mark

NERC Argon Isotope Facility, Scottish Universities Environmental Research Centre, East Kilbride G75 0QF, UK

Wim van der Plas

Department of Petrology, Faculty of Earth and Life Science, Vrije Universiteit, De Boelelaan 1085, NL-1081 HV Amsterdam, Netherlands

Stuart Davidson

Engineering Measurement Division, National Physical Laboratory, Hampton Road, Teddington TW11 0LW, UK

Michael Perkin

Engineering Measurement Division, National Physical Laboratory, Hampton Road, Teddington TW11 0LW, UK

Igor M. Villa

Institut für Geologie, Universität Bern, Baltzerstrasse 3, CH-3012 Bern, Switzerland

Jan R. Wijbrans

Department of Petrology, Faculty of Earth and Life Science, Vrije Universiteit, De Boelelaan 1085, NL-1081 HV Amsterdam, Netherlands

[1] In geochronology, isotopic ages are determined from the ratio of parent and daughter nuclide concentrations in minerals. For dating of geological material using the K-Ar system, the simultaneous determination of ^{40}Ar and ^{40}K concentrations on the same aliquot is not possible. Therefore, a widely used variant, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique, involves the production of ^{39}Ar from ^{39}K by neutron bombardment and the reliance on indirect natural calibrators of the neutron flux, referred to as “mineral standards.” Many mineral standards still in use rely on decades-old determinations of ^{40}Ar concentrations; resulting uncertainties, both systematic and analytical, impede the determination of higher accuracy ages using the K-Ar decay system. We discuss the theoretical approach and technical design of a gas delivery system which emits metrologically traceable amounts of ^{40}Ar and will allow for the sensitivity calibration of noble gas mass spectrometers. The design of this system is based on a rigorous assessment of the uncertainty budget and detailed tests of a prototype system. A number of obstacles and proposed resolutions are discussed along with the selection of components and their integration into a pipette system.

Components: 9400 words, 6 figures, 1 table.

Keywords: $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology; international standards; isotope concentration measurements; metrology; noble gas mass spectrometry; pipette system.

Index Terms: 1115 Geochronology: Radioisotope geochronology; 1194 Geochronology: Instruments and techniques.

Received 18 May 2011; **Revised** 8 August 2011; **Accepted** 23 August 2011; **Published** 7 October 2011.

Morgan, L. E., O. Postma, K. F. Kuiper, D. F. Mark, W. van der Plas, S. Davidson, M. Perkin, I. M. Villa, and J. R. Wijbrans (2011), A metrological approach to measuring $^{40}\text{Ar}^*$ concentrations in K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ mineral standards, *Geochem. Geophys. Geosyst.*, 12, A0AA20, doi:10.1029/2011GC003719.

Theme: EarthTime: Advances in Geochronological Technique

Guest Editors: M. Heizler, G. Gehrels, D. Condon, and F. Hilgen

1. Introduction

[2] Isotope geochronology was initially suggested as a means to obtain formation ages of minerals and hence the timing of earth processes [Rutherford, 1906]. Numerous geochronometers have since been developed to record geological time in various minerals and rock types. Due to the prevalence of K-bearing rocks and minerals at the earth's surface, among the most widely applied geochronometers are the K-Ar system and its variant, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique.

[3] The K-Ar technique relies upon the natural radioactive decay of ^{40}K to ^{40}Ar ($t_{1/2}$: ca. 1250 Ma). Unfortunately, the determination of the daughter/parent ratio by means of a single analytical procedure is impossible; isotopic concentration determinations of both the parent and daughter nuclides are therefore required. Reliable determination of accurate ^{40}Ar concentrations in particular has proven to be a demanding, time-consuming, and low-precision endeavor [Dalrymple and Lanphere, 1969; Lanphere and Dalrymple, 1966, 2000; McDougall and Roksandic, 1974; McDougall and Wellman, 2011; Müller, 2006]. The $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique [Merrihue and Turner, 1966] removes the need for concentration measurements and resolves issues with sample size and heterogeneity by utilizing the neutron activation of ^{39}K to produce ^{39}Ar during irradiation. The attractive feature of this indirect approach is that the age of an unknown sample is not determined by directly measuring its ^{40}Ar and ^{40}K concentrations, but by comparing the sample's $^{40}\text{Ar}/^{39}\text{Ar}$ (where ^{39}Ar is a proxy for ^{40}K , via a naturally constant $^{40}\text{K}/^{39}\text{K}$ ratio) ratio with that of a mineral standard, which is co-irradiated with the sample of unknown age (fluence monitor). The previously determined $^{40}\text{Ar}^*/^{40}\text{K}$ (* indicates

radiogenic ^{40}Ar) ratio of the standard allows for characterization of the neutron flux, i.e., the production of ^{39}Ar from ^{39}K , during irradiation and the subsequent determination of ages for unknown samples based on measurements of Ar isotopes.

[4] A major limitation of the K-Ar decay system as it is used today is uncertainty in the *true* age (or more accurately the $^{40}\text{Ar}/^{40}\text{K}$ ratio) of $^{40}\text{Ar}/^{39}\text{Ar}$ mineral standards, which must be determined by some other means. Historically this has been achieved by dating of mineral standards using the conventional K-Ar method [Dalrymple and Lanphere, 1969; Lanphere and Dalrymple, 2000; McDougall and Roksandic, 1974; McDougall and Wellman, 2011]. The most commonly used K-Ar concentration measurements for biotite from the Mount Dromedary monzonite (GA1550) were measured in the 1960s [McDougall and Roksandic, 1974]; the complete data were only recently published [McDougall and Wellman, 2011]. These measurements were extraordinary for their time, but modern technology now allows for more accurate measurements. Further efforts in recent years include calibration with other mineral standards (which ultimately rely upon the accuracy of K-Ar ages) [Renne et al., 1998; Spell and McDougall, 2003], the tuning of radioisotopic ages with orbital timescales [e.g., Channell et al., 2010; Kuiper et al., 2008], intercalibration with other mineral phases and geochronometric systems [Schmitz and Bowring, 2001], and an optimization model using ^{40}K activity data, K-Ar isotopic data, and $^{40}\text{Ar}/^{39}\text{Ar}$ and U-Pb data pairs [Renne et al., 2010]. The aim here is to return to the K-Ar approach in order to improve the accuracy of the $^{40}\text{Ar}/^{39}\text{Ar}$ system independent of other chronometers.

[5] Here we focus on the theory and method for making the metrologically traceable measurements of ^{40}Ar concentrations in $^{40}\text{Ar}/^{39}\text{Ar}$ mineral stan-

dards with an aim of improving the accuracy of the ⁴⁰Ar/³⁹Ar technique. The construction of a pipette system for similar purposes was reported by Müller [2006]; many of the concepts discussed therein are also examined here. In the interest of full transparency and community involvement, here we report the methods and theory behind a series of forthcoming measurements, along with results from tests on a prototype system. It is the aim of this contribution to fuel scientific discussion regarding the optimal approach for making metrologically traceable concentration measurements of noble gases in geological materials.

2. Direct Approach

2.1. K-Ar Geochronology

[6] The K-Ar approach taken here is similar to that used by McDougall and Roksandic [1974] and McDougall and Wellman [2011], and compiled by Renne *et al.* [1998], in that concentrations of ⁴⁰Ar and ⁴⁰K are directly measured for a mineral, which then can be used as a calibrator (“mineral standard”). A K-Ar age is calculated [Smits and Gentner, 1950] as

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{\lambda}{\lambda_e} \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{K}} \right) \quad (1)$$

where t denotes the age, λ the total decay constant of ⁴⁰K, λ_e the ⁴⁰Ar branch of the ⁴⁰K decay constant, and ⁴⁰Ar* radiogenic ⁴⁰Ar. We should note that, for these purposes, ‘ t ’ need not represent a geologically meaningful age; more important is the homogeneity and reproducibility of ⁴⁰Ar/⁴⁰K in the standard. As discussed above the measurement of ⁴⁰Ar concentrations is one of the pre-requisites for determination of K-Ar ages.

2.2. Sensitivity Calibration

[7] Noble gas mass spectrometers are designed to measure isotopic ratios, or relative abundances, rather than absolute concentrations. At least two means exist for calibrating the sensitivity of a mass spectrometer, thereby facilitating measurement of concentration: isotope dilution and sample-standard bracketing. The system described here is primarily designed for use with the sample-standard bracketing method, but isotope dilution measurements will also be possible by use of a different isotope of Ar in the pipette system. The “standard” in sample-standard bracketing involves the expansion of a reference aliquot from a pipette (gas delivery sys-

tem) with a known amount of ⁴⁰Ar into an extraction line and subsequently a mass spectrometer. By measuring ion beams it becomes possible to determine the sensitivity of the mass spectrometer as well as to assess its long-term reproducibility. For simplicity, here we refer to the intensity I of a measured ion beam. The sensitivity calibration, then, can be made as follows:

$$n({}^{40}\text{Ar}^*)_s = \frac{\left[I({}^{40}\text{Ar})_s - I({}^{40}\text{Ar})_{bl} - \left(\frac{I({}^{36}\text{Ar})_s - I({}^{36}\text{Ar})_{bl}}{\left(\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}} \right)_{meas}} \cdot \left(\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}} \right)_{atm} \right)}{\left(\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}} \right)_{atm}} \right]}{I({}^{40}\text{Ar})_p - I({}^{40}\text{Ar})_{bl}} \quad (2)$$

where $n({}^{40}\text{Ar}^*)_s$ and $n({}^{40}\text{Ar}^*)_p$ are the concentrations (in mol/g) of ⁴⁰Ar* in a weighed sample and the reference pipette, respectively; $I({}^{40}\text{Ar})_s$, $I({}^{40}\text{Ar})_p$ and $I({}^{40}\text{Ar})_{bl}$ are the ⁴⁰Ar signal intensities from sample, reference pipette, and blank, respectively; and ‘atm’ and ‘meas’ denote the atmospheric and the measured ⁴⁰Ar/³⁶Ar ratio, respectively. The terms within the large square brackets of equation (2) are standard for ⁴⁰Ar/³⁹Ar measurements and involve the blank and mass fractionation corrections (assuming a power fractionation law [Renne *et al.*, 2009]). Displayed below but theoretically to the right of the large brackets is the sensitivity determination, whereby the number of moles in the reference pipette (“ n ”) is divided by the signal intensity on the mass 40 peak measured from the admitted pipette aliquot. This is all then divided by the mass of the sample. The resultant value will eventually be used in equation (1), along with the mass of the sample and concentration measurements of ⁴⁰K, to calculate an age for mineral standards. The derivation of this equation can be found in Appendix A. The uncertainty budget is addressed below.

2.3. Determination of $n({}^{40}\text{Ar}^*)_p$ and the Ideal Gas Law

[8] The application of equation (2) requires a determination of ‘ n ’ in each pipette aliquot. Here this is accomplished by employing the ideal gas law, commonly written as $PV = nRT$, where P indicates pressure, V denotes volume, n indicates the number of moles, R is the ideal gas constant, and T indicates temperature. Although the law is strictly valid only for ideal gases, deviations from the law are expected

to be negligible under the conditions represented here (calculated to, at most, ~ 1 part in 10^7 using the virial equation of state, where the 2nd virial coefficient $B = -11.7887 \text{ cm}^3 \text{ mol}^{-1}$ [Lemmon *et al.*, 2008]). We will isolate an amount of ^{40}Ar reasonable for expansion into an extraction line and mass spectrometer, under measured pressure, volume, and temperature conditions. This will subsequently allow for the calculation of $n(^{40}\text{Ar}^*)_{\text{p}}$, the amount-of-substance of ^{40}Ar in the pipette. Each successive pipette expansion will contain a slightly smaller amount of ^{40}Ar as the gas content of reservoir is depleted. This decrease follows an exponential pattern and is readily quantifiable. The lifetime for one reservoir fill is ca. 100 pipette aliquots, after which the system will be pumped down and the reservoir refilled to produce another batch of pipette aliquots. The design of a system to make these pressure, volume, and temperature measurements requires careful preparation. Considerable effort is involved in determining the optimum design for making metrologically appropriate measurements involving the lowest possible uncertainty and ensuring their traceability to international standards.

2.4. Constraints and Limitations

[9] A number of complicating factors require careful consideration. They center on the fact that noble gas mass spectrometers are designed to measure only extremely small amounts of Ar (usually ca. 10^{-11} to 10^{-17} mol, depending on detector type). Due to mechanical limitations on pipette sizes, the difficulty of determining the volumes of small cavities, and the lower limits of high accuracy pressure gauges (capacitance manometers), many simple approaches are not viable. Further complications include the potential for outgassing of Ar and other gases from stainless steel system components, the potential for valve seat deformation affecting measured volumes throughout the lifetime of the system, and problems with the quantitative extraction of Ar from minerals, particularly sanidine crystals. These complications have largely been addressed and limited, as discussed below.

3. System Design and Operation

[10] A schematic map and 3D model of the system can be found as Figures 1a and 1b. Numbers below indicate numbered components found in Figure 1. The heart of the system involves a reservoir (17) of ca. 350 mL, pressure gauge (19) of ca. 5 mL, and “pipette” (two valves (9, 10) with a small internal volume (12)) of ca. 2 mL. Eight spheres (18) with

well-known volumes (11.5 mL each) act as a volume standard and will be used to determine the volumes of the reservoir and pipette, as described below. A “sphere holder” of 108 mL (Figure 1c) allows for the precise placement and removal of these spheres in the reservoir without damage; this holder will reside in the reservoir at all times. The remainder of the system includes a leak valve (14) to control the filling pressure of the reservoir, along with a number of manual valves, a SAES vacuum getter (15), and cryotrap to be cooled with solid CO_2 (16) for ensuring gas purity, a bottle of high purity ^{40}Ar , and means for pumping the entire system to ultra-high vacuum ($<10^{-9}$ mbar) using a turbomolecular pump. Where possible electrosag refined (ESR) steel has been used to reduce outgassing of Ar and other gases [Geyari, 1976]. The use of all metal, bakeable, components (e.g., ConFlat® and VCR® seals; Varian, Swagelok®, and VAT valves) also helps in this regard.

3.1. Design Considerations

3.1.1. Materials

[11] The reservoir is designed to minimize outgassing from its components and thus ensure continued purity of the ^{40}Ar (e.g., other gases, hydrocarbons, atmospheric argon), and to ensure stable volumes over continued use during the lifetime of the system. This is achieved through minimizing TIG (tungsten inert gas) welding, which often uses argon as a shielding gas for the separation of the hot welding plasma from the corrosive influence of atmospheric gases on weld quality. Such TIG welds are present in the bellows of all Varian, Swagelok, and VAT valves used here. All but one valve on the reservoir is oriented so that gas in the reservoir is not exposed to the bellows (and thus is shielded from the welded region). The only exception is a Swagelok valve of the pipette (component 9 in Figure 1), due to our preference to form the small volume of the pipette from the seat side of two valves (as any volume instabilities in the bellows would have a significantly greater effect on the small volume of the pipette than the large reservoir volume). The three Swagelok valves (SS-4BG-VCRVD-5C; components 9, 10, 22 in Figure 1) have integral male VCR ports (and thus do not contain additional welds) and are attached to female VCR ports that have been vacuum-soldered onto the reservoir (to further minimize welds). The high temperatures required for vacuum soldering also act to heat the reservoir at high temperatures (ca. 900°C) under vacuum to minimize future outgassing [Elsey, 1975a, 1975b]. The VCR seal on a test piece displayed the ability to maintain

ultra-high vacuum following soldering, even under high heat conditions (300°C). Knife edges for ConFlat (CF) flanges on the reservoir will be machined following vacuum firing due to annealing effects on the stainless steel of the high temperature treatment.

[12] Swagelok valves were chosen for the valves that will be operated most often (components 9, 10) due to their small orifice diameter (4.1 mm). The potential is greater for these valves to experience valve seat deformation, which could result in volume changes in the reservoir, pipette, and pressure gauge. Any deformation that does occur will affect a smaller area due to the small orifice of the valve; any volume changes resulting from this deformation will thus be minimized. Manual VAT valves (Series 57, 16 mm orifice diameter; 7, 8, 11 in Figure 1) were chosen for the three remaining valves on the reservoir due to the CF flanges machined into the valve body, thus reducing the need for additional soldering of VCR ports. Manual Varian valves (Part # 9515014) are used for valves not attached directly to the reservoir.

3.1.2. Pressure Gauge

[13] The selected pressure gauge (or capacitance manometer) is the MKS Instruments 690A01TRA gauge and 670B electronic unit, with a full-scale reading of 133 Pa (1 Torr). This non-bakeable gauge was chosen for its better “accuracy” (defined by MKS as linearity, hysteresis, and reproducibility) of ca. 0.05% of the reading; the available 1 Torr bakeable gauge has an “accuracy” of ca. 0.25% of the reading. This gauge was selected over available resonant silica gauges (RSG) from Yokogawa due to the relatively high maximum leak rates of $10^{-5} \text{ cm}^3/\text{s}$ (10^{-5} mbar l/s at STP), as specified in Yokogawa literature. Although the selected gauge requires operation at 45°C (318.15 K), which could increase outgassing rates, the absolute temperature increase over room temperature (20°C, or 293.15 K) is only ca. 8.5% and should thus not have a major effect on outgassing. Furthermore, the selected MKS gauge contains an all-metal measurement section; Yokogawa gauges contain an O-ring composed of fluorubber, which is less than ideal in an ultra-high vacuum environment. However, as the MKS gauge calibration is less stable than RSGs, the potential still exists for inclusion of an RSG, either as a part of the system or for use as a local pressure standard.

[14] Initial uncertainty calculations (described in section 4) show that the lower uncertainties involved with the non-bakeable gauge superseded the potential for higher outgassing rates due to its non-bakeability.

It should be noted that this “accuracy” does not take into account the uncertainty in the calibration of the gauge (ie: the pressure metrologically traceable to international standards) by Deutscher Kalibrierdienst, which is significantly larger (ca. 0.16% between 1 Torr and 0.1 Torr). This calibration uncertainty will apply when making absolute pressure measurements for molar quantity determinations. Pressure measurements made for volume determinations rely only on the relative pressure measurements rather than the absolute calibration. In these cases, use of the uncertainty incorporating only the linearity, reproducibility, and hysteresis of the gauge (ca. 0.05%) is more appropriate.

3.1.3. Volumes

[15] The size of the reservoir, spheres, and sphere holder were also carefully considered. In order to minimize uncertainties in volume determinations, the spheres need to fill a large portion of the reservoir volume. The sphere holder (see Figure 1c) was carefully designed to meet this need while allowing for the placement and removal of the spheres in the reservoir without damage to the spheres, sphere holder, and reservoir. It is unfortunately necessary to expose the reservoir to atmospheric pressure in order to place or remove the spheres; adverse effects of this procedure are mitigated by first venting to a N_2 environment. Further, care was taken to maximize pumping capabilities of the system by designing the sphere holder so that it has three rounded points of contact with each sphere which allow for gas flow (and thus pumping ability) around each sphere. The three points of contact are used to define the positioning of the spheres without contact with the stainless steel interior of the reservoir. A linear guidance system is used to avoid damage while inserting and removing the sphere holder. It should be noted that although the sphere holder has an irregular shape, it occupies a constant part of the reservoir volume and thus does not require a separate volume determination. The volume change occurs solely by the addition or removal of the set of spheres; sphere volume determinations are described in section 3.4.1.

3.1.4. Vacuum

[16] The system is connected to a pumping system that will consist of a high compression turbomolecular drag pump (Pfeiffer Vacuum TMU 071P; compression ratio $>10^{-11}$ for N_2) connected to a diaphragm backing pump. If required, an ion pump or a secondary turbomolecular drag pump to maintain a lower forevacuum pressure may be added. The

connections are made with large diameter (CF40) components to improve conductance and consequently pumping rates.

3.2. Storage and Cleaning of ⁴⁰Ar

[17] The reservoir will be filled with high purity ⁴⁰Ar obtained from Oak Ridge National Laboratory (ORNL). This same batch (#66A2987) was analyzed by *Lee et al.* [2006] on a Finnegan MAT 271 in dynamic mode and found to contain $99.9486 \pm 0.0009\%$ ⁴⁰Ar. However, the ⁴⁰Ar and impurity content of pipette shots from this system, which may vary slightly from that measured by *Lee et al.* [2006] (e.g., by outgassing of metals during storage), will be measured by gas source mass spectrometry. The ⁴⁰Ar bottle has a CGA-580 valve welded to a CF16 flange and will be connected to a ca. 10 mL pipette (2, 3 in Figure 1) in the form of two manual Varian valves. This will allow for the transfer of a fraction of the gas to the system, while preventing isotopic fractionation (due to time allow for isotopic equilibration; the “pipette” concept). A blind flange allows for the attachment of another bottle of ⁴⁰Ar or other gas. The pipette leads to two six-way crosses (24, 25) designed for small volume. A SAES getter (15) with a ST-101 getter cartridge purifies the gas and will be operated at both high and low temperatures prior to the expansion of gas into the reservoir. Additionally, a cryotrap (16) containing a piece of sintered stainless steel will be cooled with a carbon dioxide slurry prior to such expansion, which will solidify and trap water and hydrocarbons while leaving noble gases (particularly Ar) in the gaseous state. One outlet (5) to the pumping system is through the first of these crosses. Blind flanges on many of the cross outlets will allow for flexibility if future additions are desired. This part of the system is designed to maximize the purity of the ⁴⁰Ar gas.

3.3. Filling the Reservoir

[18] A second 10 mL pipette, comprised of one manual Varian valve (on the cross side; 6 in Figure 1) and one manual VAT valve (on the reservoir side; 7 in Figure 1)), will allow for the partitioning of a small fraction of the gas in the storage and cleaning system for expansion into the reservoir. Calculations indicate that the pressure of gas in the reservoir at this point will be approximately 100 Pa (the full scale of the pressure gauge being 133 Pa), but adjustments can be made by using the leak valve (14) to remove some gas from the reservoir (section 3.5). It is likely that any fractionation occurring here will only

increase the fraction of ⁴⁰Ar in the reservoir, as the lighter isotopes with masses 36 and 38 should bleed from the reservoir preferentially. Evidence contradicting this has been published by *Gupalo* [1991]; the effects of fractionation by the leak valve will be examined prior to use of the system. At this point, the reservoir will be prepared for either volume determinations (section 3.4) or obtaining an optimum pressure for pipette aliquot measurements (sections 3.5 and 3.6).

3.4. Volume Determinations

3.4.1. Standard Spheres

[19] High accuracy volume determinations are critical in obtaining an accurate value for the amount-of-substance in the system. The standard volume, upon which all system volumes will be based, is a collection of 8 spheres made from 316L stainless steel (component 18 in Figure 1) with diameters ca. 28 mm. The volumes of ten such spheres have been determined by hydrostatic weighing [*International Organization of Legal Metrology*, 2004] at the National Physical Laboratory in Teddington, UK. These calibrations were performed at a nominal temperature of 293.15 K (20°C).

[20] Results are provided in Table 1. The mass values were determined by weighing in air against SI traceable standards; the densities were determined by weighing in air and in water using standards of known mass and density. Volumes were calculated using the following equation: $V_s = (M - W)/\rho_w$, where V_s is the volume of the sphere, M , is the actual mass of the sphere (based on weighing in air), W is the weight-in-water of the sphere, and ρ_w is the density of the water. The weighings in water were performed in deionised water purified by reverse osmosis at temperatures in the range 293.13–293.15 K (19.98–20.00°C). The density of water was calculated using the formula given by *Tanaka et al.* [2001]. Mass measurements are traceable via the UK National Standard of Mass to the International Prototype of the Kilogram; temperature measurements are traceable via NPL temperature standards to the International Temperature Scale of 1990.

[21] To allow determination of the volumes of the spheres at 318.15 K (45°C), the temperature at which the gas delivery system will be operated (see section 3.7), the thermal expansion of one of the spheres was determined. A value of $46.45 \times 10^{-6} \text{ K}^{-1}$ was determined for the coefficient of

Table 1. Results From Sphere Measurements Described in Section 3.4.1^a

Identification	Mass (g)	Estimated Uncertainty (± mg)	Volume at 20°C (cm ³)	Estimated Uncertainty (± cm ³)	Volume at 45°C (cm ³)	Estimated Uncertainty (± cm ³)
Sphere 1	91.47168	0.05	11.49342	0.00017	11.50677	0.00025
Sphere 2	91.46628	0.05	11.49401	0.00017	11.50736	0.00025
Sphere 3	91.47297	0.05	11.49313	0.00017	11.50648	0.00025
Sphere 4	91.47185	0.05	11.4936	0.00017	11.50695	0.00025
Sphere 5	91.58319	0.05	11.49327	0.00017	11.50662	0.00025
Sphere 6	91.47255	0.05	11.49323	0.00017	11.50658	0.00025
Sphere 7	91.46587	0.05	11.49287	0.00017	11.50622	0.00025
Sphere 8	91.47146	0.05	11.49338	0.00017	11.50673	0.00025
Sphere 9	91.46954	0.05	11.49306	0.00017	11.50641	0.00025
Sphere 10	91.47154	0.05	11.49293	0.00017	11.50628	0.00025

^aUncertainties are provided at the 1σ level.

cubic thermal expansion of the sphere with an uncertainty of $0.62 \times 10^{-6} \text{ K}^{-1}$. This value has been used to correct the volumes of the spheres to values at 318.15 K (45°C) (see Table 1).

3.4.2. Depletion Experiments

[22] Following the filling of the reservoir to a pressure of ca. 100 Pa (as described above, section 3.3), these determinations will be made via a series of pipette aliquots from the reservoir through the pipette. The pressure will be measured following each aliquot (which will be pumped away), and the measured data will be fit to an exponential curve. The coefficient of the exponential decrease in pressure ('a' in $y = y_0 e^{ax}$) can be used to calculate the volume ratio of the pipette and reservoir. By repeating this depletion both with and without the

standard spheres in the reservoir (Figure 2), the volumes of both pipette and reservoir (including the volume of the pressure gauge) can be calculated using the coefficients of the exponential functions as in equations (3) and (4):

$$V_{\text{res+gauge}} = \frac{V_{\text{add}} \cdot (e^{a2} - 1)}{\frac{e^{a2} \cdot (1 - e^{a1})}{e^{a1}} + e^{a2} - 1} \quad (3)$$

$$V_{\text{pip}} = \frac{V_{\text{add}} \cdot (1 - e^{a2})}{\frac{e^{a1} \cdot (1 - e^{a2})}{(1 - e^{a1})} - e^{a2}} \quad (4)$$

where $V_{\text{res+gauge}}$, V_{pip} , and V_{add} are the volumes of the combined reservoir and pressure gauge, the pipette, and the spheres, respectively, and $a1$ and $a2$ are the coefficients of the exponential functions

Figure 2. A model of the depletion curve occurring as pipette aliquots are removed from system. Data are synthetic. Uncertainties are smaller than markers. The coefficients of exponential pressure decrease (with and without spheres in the reservoir) are used to calculate reservoir and pipette volumes.

created without and with the spheres, respectively, as described above. Derivations of equations (3) and (4) are provided in Appendix B.

[23] Outgassing of the reservoir during these determinations is expected to be minimal due to component selection and vacuum firing treatment [Elsey, 1975a, 1975b; Geyari, 1976]. However, the effects of outgassing will be tested by filling the reservoir to a similar pressure and repeating the above procedure with the exception of opening the “pipette out” valve (component 10 in Figure 1). This will allow us to watch for increasing pressure, which can be subtracted from the expansion values as necessary. The outgassing contributes to the total pressure up to the moment just before expansions used in volume determination. The use of high purity Ar for these experiments will limit any non-equilibrium effects potentially arising from the presence of H_2O or non-inert gas phases.

3.4.3. Expansion Experiments

[24] As seen in Figures 1a and 1b, a pneumatically operated all metal valve (component 22 in Figure 1) is located between the pressure gauge (19) and reservoir (17). This is due to the non-bakeable nature of the pressure gauge and the ensuing higher rate of outgassing from its internal surface. To limit the effects of this outgassing, the valve will be closed when the reservoir is operated at the low pressures required for the sensitivity measurements described in section 3.6. The volume of the reservoir with valve 22 closed (ie: not including the volume of the pressure gauge) must therefore be determined. This will be accomplished by the expansion of gas trapped in the pressure gauge volume into an evacuated reservoir. Two ways exist of using the ratio of the resulting pressure difference to determine the separate pressure gauge and reservoir volumes. One option is to use the previously determined value of the combined reservoir and pressure gauge volumes. Combined with the ratio of the two separate volumes, we can calculate each separate volume. Alternatively, the expansion from the pressure gauge into the evacuated reservoir can be repeated both with and without the reference spheres in the reservoir; this is analogous to the determinations described above. These two methods should produce indistinguishable resulting volumes and will both be applied.

[25] Expansion ratios have been measured extensively on a prototype system and yield highly reproducible results using a number of different gases at a range of pressures, including Ar, He, N_2 , and CO_2 . Data for Ar are shown in Figure 3a; other

gases yielded similar results. Expansions at low pressures show more spurious behavior; the explanation for this is not yet determined but is discussed in section 3.4.4. Concern over a potential change in reservoir volume due to changing the copper gasket of the CF-40 flange during placement or removal of the reference spheres has been alleviated by testing of several gaskets (from the same manufacturing batch) on the prototype system and observing standard deviations of ca. 0.01%; this deviation is incorporated in the uncertainty calculations of section 4. Data collected using different gaskets is included in Figure 3a.

[26] Complicating this, a small pressure change is seen as valves open and close, due to a changing internal volume (seen in Figures 4c and 4d). The pressure ratio of this change has been determined on a prototype system with high precision (0.03%) and does not seem to be dependent on the pressure in the system. This pressure change is dependent, however, on the rate of valve closure, where high rates of closure (e.g., <40 s for closure) apparently result in differential pressure on the two sides of the valve. An appropriately slow closing rate has been determined in the prototype system and will be verified on the final system. Figure 3b shows the relationship between valve closing time and the pressure ratio; closing time was determined by measuring the time required for the pressure on the valve actuator to decrease from 3.5 to 2 bars. This pressure ratio will be used to calculate the pressure change in the reservoir upon valve closing.

3.4.4. Data Processing for Volume Determinations

[27] Measurements on a prototype system have been made to approximate situations that will be encountered during volume determinations for the reservoir, pressure gauge, and pipette. Specifically, this includes measurements of the pressure expansion ratio between the pressure gauge and entire system (Figure 4): an amount of gas is trapped in the pressure gauge volume, the remainder of the system is pumped to high vacuum, and then the gas within the pressure gauge volume is expanded into the rest of the system. The resulting pressure ratio (pressure in gauge before expansion: pressure in system after expansion) is equivalent to the ratio of the pressure gauge volume to the total system volume. As highlighted in the previous section, the closure of the intervening Swagelok valve causes a subtle increase in pressure (Figures 4c and 4d) which must be accounted for. Pressure rise due to outgassing within

Figure 3. (a) Expansion ratios from prototype system using Ar. Other gases (e.g., He, N₂, CO₂) yielded similar results. The expansions are made by trapping gas in the pressure gauge volume, evacuating the remainder of the system, and then expanding gas from the pressure gauge volume into the system. The expansion ratio is the ratio of pressures before and after expansion. Four different methods of calculating the expansion ratio are shown; see text for explanation. Measurements were made over several days by different users (LM and OP). Uncertainties are provided at 1σ and determined by Monte Carlo simulations for each method based on uncertainties specified by manufacturer; these account for reproducibility, linearity, and hysteresis effects, but not the absolute calibration of the gauge. See text for discussion. (b) Pressure ratio found as a pneumatic Swagelok 4BG valve (e.g., components 9, 10, 22 in Figure 1) moves from open to closed position on prototype system. The valve closing ratio is the ratio of pressures after and before the valve has closed; the valve closing time is determined by the time taken for the pressure on the pneumatic operator to decrease from 4×10^5 (4 bars) to 2×10^5 Pa (2 bars). The ratio changes depending on the rate of closing, but a valve closing time of >40 s results in reproducible pressures following closure. Uncertainties are provided at the 1σ level and are based on the precision of multiple measurements; these are not based on manufacturer's specifications or calibration of the gauge.

the system (seen in Figure 4d) and especially the non-bakeable pressure gauge, combined with the finite time required for the valve to open and close, further complicates these measurements. Fortunately, the time involved in opening and then slowly closing the valve can be sufficiently short, and outgassing rates even in the prototype system (which has not been extensively treated to minimize outgassing) are sufficiently small, that this should not affect measured ratios significantly. For example,

over the minimum of ca. 40 s between valve opening, pressure measurement, and subsequent valve closing, an outgassing rate of 1×10^{-5} Pa/sec (similar to rates measured in the prototype system) yields a difference of 3×10^{-4} Pa. When measuring a pressure of 10 Pa (0.1 of full scale of the gauge), the effect is negligible at the 0.003% level. As a result, although numerous methods exist for processing the pressure data produced by these measurements, outgassing of the system should not significantly

Figure 4. Example from an expansion experiment. At time = ca. 180 s, the gas retained in the pressure gauge volume is expanded to the entire line (which had been pumped down to $<10^{-6}$ Pa (10^{-8} mbar)). The intervening valve is then closed slowly. The ratio of pressures represents the volume ratio of the pressure gauge volume to the entire system volume. Error bars represent uncertainty based on manufacturer's specifications and do not include uncertainty in the calibration of the gauge. (a) Data from entire expansion experiment. Error bars are smaller than size of marker. Boxes labeled 'b' and 'c' correlate with Figures 4b and 4c, respectively. (b) Data from just after expansion, including valve closure. In this experiment, the valve was open for ca. 15 s (time = 185 to 200 s). (d) Data from just after expansion and including valve closure from a separate expansion experiment, illustrating a slight pressure rise over time, presumably due to outgassing of the system. This outgassing rate is higher than should be seen in actual system due to efforts made to limit outgassing, as described in text. The resolution of the pressure gauge is visible in the vertical spacing of some data points in Figure 4d.

affect measurements made when minimizing the time the valve to the pressure gauge is open.

[28] Data processing can be accomplished in several ways and involves two issues. The first issue involves data selection. One option is to carefully select and average data points in each time period of interest. If the outgassing rate is sufficiently low, it is often possible to select a time period where the pressure is particularly stable (and any change is thus within the resolution of the gauge). Alternatively, long-term

linear regressions (or nonlinear, depending on the characteristics of the data) can be fit to the data and assessed at particular (albeit somewhat arbitrary) points in time. This method has the ability to account for the slight rise in pressure due to outgassing during times in which it is not measurable (i.e., when the valve is opening or closing).

[29] The second issue involves the use of pressure measurements made during the time in which the valve (component 22) is open. One possibility is to

minimize the time the valve is open and simply ratio the pressures from before opening the valve and after closing it again (this may be done using either the data point averaging or regression techniques discussed above). A second option is to select data points (or make regressions) in three or four different time periods: (1) prior to opening the valve (Figure 4b), (2) while the valve is open (Figure 4c; if the valve is open for a long period of time, this may be divided into periods of just after opening and just prior to closing), (3) just following valve closure (Figure 4c).

[30] As shown in Figure 3a, the four resulting possibilities (E1–4; as described below) for processing data produce markedly similar pressure ratios. Values for E1 were determined by regressing data and using the pressure measurements from the time in which valve 9 was open; E2 by regressing data and not using such information; E3 by selecting points and using the valve open measurements; E4 by selecting points and not using the valve open measurements. Although the pressure ratios produced by these four methods are indistinguishable, the methods used in producing values for E1 are theoretically the most applicable and are the least reliant on user preferences; these will thus be used in the future.

[31] However, all four methods also display a somewhat irregular trend toward decreasing ratios at lower initial pressures. Although the cause of this trend is not yet definitively determined, it is likely due, at least in part, to desorption of gas from the internal surfaces of the system, which should have a larger effect at lower pressures. It is notable that by subtracting a constant factor (the “surface desorption factor”) of 5.65×10^{-5} from the denominator of this volume ratio (ie: to the pressure after expansion), resulting ratios (E5 in Figure 3a) are much more consistent regardless of the initial pressure in the system. This surface desorption, if it is indeed the culprit here, is apparently not accounted for through the use of linear regressions in data processing. As this solution is not particularly satisfying, this issue will be explored in detail in the actual system.

3.5. Obtaining an Optimum Pressure for Sensitivity Measurements

[32] As sensitivity and mass discrimination [Burnard and Farley, 2000] of the mass spectrometer vary with the amount of gas in the system (linearity), sensitivity will be determined across a range of gas quantities. To some degree, this can be done by measuring subsequent pipette aliquots, each of which will contain less

gas than the previous. To achieve a larger range, however, the initial amount of gas in the reservoir can be adjusted. This will be accomplished after filling the reservoir to ca. 100 Pa by carefully opening the leak valve (14) between the reservoir and pumping system (as in section 3.3).

[33] A series of two expansions will allow for the quantitative depletion of the Ar gas in the reservoir to a useable amount. Practically, each expansion will involve trapping gas in the pipette volume (using the slow valve closing rate described in section 3.4.3), baking and pumping out the reservoir through valves 7, 6, and 5, and then expanding the trapped pipette volume back into the reservoir. If the initial reservoir pressure is ca. 100 Pa, after two such expansions the pressure in the reservoir will be ca. 1 mPa. The first subsequent pipette aliquot expanded into the mass spectrometer will thus contain ca. 2×10^{-12} mol ⁴⁰Ar, appropriate for measurement on Faraday cup detectors on many mass spectrometers (see section 3.6 for reasoning behind the use of Faraday detectors). The highly accurate volume determinations described in section 3.4 will then allow for accurate calculation of the amount of ⁴⁰Ar in each subsequent pipette aliquot.

3.6. Pipette Sensitivity Measurements

[34] The calculated amount of ⁴⁰Ar in each pipette aliquot (“n” in equation (2)) will be used to calibrate the sensitivity of the mass spectrometer. This will be done taking a sample-standard bracketing approach, where these sensitivity calibrations will be scattered throughout a series of blank, air pipette aliquots (to correct for mass fractionation), and samples (in this case, mineral standards). As we attempt to limit uncertainties to every extent possible, the reproducibility of these measurements becomes important. Although secondary electron multipliers and similar detectors have high sensitivity, their stability over a number of hours is considerably lower than that of Faraday cup detectors. Thus we intend to make measurements primarily using Faraday detectors [e.g., Mark *et al.*, 2009].

3.7. Temperature Control and Measurement

[35] The control and measurement of temperature is a key component of gas abundance determinations. Uncertainty calculations suggest that knowledge of temperature with uncertainties of <0.1 K is required. The purchased pressure gauge is calibrated at 318.15 K (45°C); to prevent the need for significant thermal transpiration corrections, the system

will be contained and operated inside thermally controlled areas at this temperature. The innermost temperature controlled area will contain the heart of the system – the reservoir, pipette, and pressure gauge, and will be surrounded by a 0.5 mm thick stainless steel box. Although this box will be as airtight as possible, a surrounding outer box of 5 cm polystyrene will provide additional temperature regulation.

[36] Temperature will be maintained via a heater and fan system within the outer polystyrene box. The fan will serve to distribute heat as uniformly as possible throughout the outer box and prevent thermal stratification. Experiments indicate that temperature in the outer box will have a maximum deviation of ± 0.5 K. The inner box will also be equipped with a heater and fan, which will stabilize the temperature to within 0.1 K.

[37] Temperature will be measured via several thermistors calibrated to 0.01 K based on calibration by an ISO9001:2000 certified company (RS Technics, Roden, Holland). A Measurement ComputingTM temperature-to-USB box will record temperature readings and relay them to a computer. Calibration of the thermistors and temperature-to-USB box over the life of the system will be ensured via the use of an ultra-stable reference-resistor from the Vishay Sfernice[®] RCK series. This resistor has a stability of <50 ppm/3 years (0.0015K/3 years). After an initial calibration of the thermistors described above, the resistor will be used to periodically ensure the stability of the thermistors and temperature-to-USB box. Any instabilities can be readily corrected.

[38] Testing of a prototype system suggests that temperature can be controlled and measured using calibrated thermistors to within the desirable uncertainty of 0.1K. Any deviations from this will increase uncertainty in the measured pressure according to MKS temperature coefficient specifications. This increase is ca. 24 ppm/K when measuring pressures near the full scale of the gauge (13 to 133 Pa).

3.8. Quantitative Extraction of Ar From Sanidine

[39] Measurement of ^{40}Ar concentrations in minerals requires its quantitative extraction for measurement. Difficulties in achieving this for sanidine crystals have long been recognized [McDougall *et al.*, 1980; McDowell, 1983; Webb and McDougall, 1967] but have not been addressed using modern laser extraction techniques. This issue is currently being addressed; in the absence of strong evidence for the complete Ar

extraction from sanidine, other mineral standards such as the GA1550 biotite standard may be calibrated in its place. GA1550 has previously been intercalibrated to Fish Canyon sanidine at high precision [Renne *et al.*, 1998]; this intercalibration could be used if necessary. For this purpose, the “true” age of the primary standard is inconsequential, and thus any issues regarding excess ^{40}Ar or ^{40}Ar loss are negligible. However, homogeneity of the standard with respect to $^{40}\text{Ar}/^{40}\text{K}$ ratios is paramount; GA1550 has been shown to have homogeneous $^{40}\text{Ar}/^{40}\text{K}$ ratios [McDougall and Wellman, 2011].

3.9. Traceability to International Standards

[40] Recent work has resulted in the traceability of the U-Pb system to international standards [Condon *et al.*, 2010; Richter and Goldberg, 2003]. This traceability, along with the more precisely determined uranium decay constants, has resulted in attempts to calibrate the K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ system against the U-Pb system [Schmitz and Bowring, 2001; Smith *et al.*, 2010], leaving aside the problems highlighted by Begemann *et al.* [2001]. Here, however, we begin the attempt to establish traceability for the K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ system directly. This first step in this complex scheme (Figure 5) provides the determination of concentrations of ^{40}Ar in mineral standards. Using the methods presented here, traceability of the ^{40}Ar concentration in materials is established to five base international standards of the second, mole, Kelvin, meter, and kilogram (in part via the ideal gas constant R and a derived SI unit of pressure, the Pascal). Figure 5 visually shows the path of this traceability. Areas not addressed here that are involved in the calculation of a K-Ar age (K measurements and the decay constant) are shown schematically in dashed lines; this is not intended to imply that these factors are currently traceable to international standards.

4. Uncertainty Calculations

[41] Uncertainty estimations are based on manufacturer specifications (pressure gauge and its calibration, temperature measurements described above) and metrologically traceable calibrations. The estimated uncertainty in $n(^{40}\text{Ar}^*)_{\text{p}}$, the amount-of-substance of ^{40}Ar in each pipette aliquot, has been modeled using Mathcad[®] and MATLAB[®] software, using linear uncertainty propagation equations and Monte Carlo simulations, respectively. Due to the potentially significant effects of error correlation, which must be accounted for when using linear

Figure 5. A schematic showing the potential for traceability of ^{40}Ar measurements, and eventually $^{40}\text{Ar}/^{39}\text{Ar}$ ages, to international standards. The part of the figure shaded in gray (items used to determine concentrations of ^{40}Ar) is addressed herein.

uncertainty propagation, Monte Carlo simulations are more reliable in this case.

[42] The entire system has been designed to minimize uncertainties. Although Monte Carlo simulations do not allow for a quantitative sourcing of uncertainties, it is apparent that uncertainties associated with pressure measurements are by far the largest contributor. Uncertainties in reservoir, pressure gauge, and pipette volumes were modeled based on pressure gauge specifications. These will be determined experimentally in the final system. The absolute pressure measurement to be made prior to expansions is dependent on the calibration of the pressure gauge (ca. 0.16% from 10 to 100 Pa), which comprises a large part of the final uncertainty. This calibration may also be affected by transport and

other sources of vibration and instability and will have to be reassessed at regular intervals [Hyland and Shaffer, 1991; Müller, 1999]. Other sources of uncertainty, including sphere volumes, temperature, ^{40}Ar abundance in the source gas, the ideal gas constant ‘R,’ the potential for valve deformation, and dimensional variability in copper gaskets on the CF40 flange of the reservoir are expected to have negligible effect on the final uncertainty.

[43] Final uncertainties, based on a 10,000 trial Monte Carlo simulation, should be ca. 0.24%, as shown in the probability distribution in Figure 6. This is similar to the precision of measurements (0.52%) reported by McDougall and Wellman [2011], but more importantly incorporates uncertainties in

Figure 6. Probability distribution from Monte Carlo simulations of uncertainty in ‘n,’ the amount of gas admitted from a single pipette aliquot. The vertical line and gray band represents the optimal value and standard deviation for ‘n,’ respectively.

all measurements required for ⁴⁰Ar concentration calculations.

5. Summary

[44] This paper presents the theory for and design of a pipette system to measure molar quantities of ⁴⁰Ar. Many significant design considerations and issues are addressed herein. Following volume, pressure, and temperature calibrations, mass spectrometric measurements will allow for the determination of molar quantities of ⁴⁰Ar, and eventually other noble gases, in mineral standards and other materials. Such measurements using modern equipment and metrologically acceptable techniques are long overdue and will serve to improve the accuracy and precision of the ⁴⁰Ar/³⁹Ar technique.

Appendix A: Derivation of Equation (2)

[45] $n(^{40}\text{Ar}^*)_s$ = ⁴⁰Ar* amount of substance (in mol) in a weighed sample

$n(^{40}\text{Ar}*)_p$ = ⁴⁰Ar* amount-of-substance (in mol) in the reference pipette

$I(^{40}\text{Ar})_s$, $I(^{40}\text{Ar})_p$ and $I(^{40}\text{Ar})_{bl}$ = ⁴⁰Ar signal intensities from sample, reference pipette, and blank, respectively

‘atm’ and ‘meas’ denote the atmospheric and the measured ⁴⁰Ar/³⁶Ar ratio, respectively

[46] The signal intensity of ⁴⁰Ar during a mineral standard measurement is blank corrected:

$$I(^{40}\text{Ar})_s - I(^{40}\text{Ar})_{bl} \quad (\text{A1})$$

[47] The ³⁶Ar intensity is corrected for blank and discrimination:

$$\frac{I(^{36}\text{Ar})_s - I(^{36}\text{Ar})_{bl}}{\left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{meas}} \cdot \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{atm} \quad (\text{A2})$$

[48] The ⁴⁰Ar intensity is then corrected for atmospheric argon via the discrimination-corrected ³⁶Ar intensity and the known atmospheric ⁴⁰Ar/³⁶Ar ratio.

$$I(^{40}\text{Ar})_s - I(^{40}\text{Ar})_{bl} - \left(\frac{I(^{36}\text{Ar})_s - I(^{36}\text{Ar})_{bl}}{\left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{meas}} \cdot \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{atm} \right) \quad (\text{A3})$$

[49] The above steps are part of routine calculations in K-Ar and ⁴⁰Ar/³⁹Ar geochronology. The resulting ⁴⁰Ar intensity is then subjected to a sensitivity correction, whereby it is multiplied by the ratio of the known number of moles in a pipette aliquot to the measured (and blank-corrected) ⁴⁰Ar signal intensity resulting from said aliquot:

$$\frac{n(^{40}\text{Ar}*)_p}{I(^{40}\text{Ar})_p - I(^{40}\text{Ar})_{bl}} \quad (\text{A4})$$

Appendix B: Derivation of Equations (3) and (4)

[50] $P_{0(a,b)}$ = initial pressure in reservoir for experiments without and with spheres in reservoir, respectively, Pa

$P_{1(a,b)}$ = pressure in reservoir after one pipette aliquot has been removed for experiments without and with spheres in reservoir, respectively, Pa

$P_{(n,m)}$ = pressure in reservoir after ‘n’ pipette aliquots have been removed for experiments without and with spheres in reservoir, respectively, Pa

V_{res} = volume of reservoir, including pressure gauge, m³

V_{pip} = volume of pipette, m³

V_{add} = volume of spheres added to reservoir, m³

a_1 , a_2 = coefficients of the exponential for experiments without and with spheres in reservoir, respectively

[51] Following Boyle’s Law,

$$P_0 \cdot V_{res} = P_1 \cdot (V_{res} + V_{pip}) \quad (\text{B1})$$

and

$$P_{0b} \cdot (V_{res} - V_{add}) = P_{1b} \cdot (V_{res} - V_{add} + V_{pip}) \quad (B2)$$

Solving for P₁:

$$P_{1a} = \frac{P_{0a} \cdot V_{res}}{(V_{res} + V_{pip})} \quad (B3)$$

and

$$P_{1b} = \frac{P_{0b} \cdot (V_{res} - V_{add})}{(V_{res} - V_{add} + V_{pip})} \quad (B4)$$

Generalizing for P_n:

$$P_n = \frac{P_{n-1} \cdot V_{res}}{(V_{res} + V_{pip})} \quad (B5)$$

and

$$P_m = \frac{P_{m-1} \cdot (V_{res} - V_{add})}{(V_{res} - V_{add} + V_{pip})} \quad (B6)$$

Thus:

$$\frac{P_n}{P_0} = \left(\frac{V_{res}}{V_{res} + V_{pip}} \right)^n \quad (B7)$$

and

$$\frac{P_m}{P_0} = \left(\frac{V_{res} - V_{add}}{V_{res} - V_{add} + V_{pip}} \right)^m \quad (B8)$$

It is helpful to define *a1* and *a2* as:

$$e^{a1} = \frac{V_{res}}{V_{res} + V_{pip}} \quad (B9)$$

and

$$e^{a2} = \frac{V_{res} - V_{add}}{V_{res} - V_{add} + V_{pip}} \quad (B10)$$

Thereby:

$$e^{a1 \cdot n} = \left(\frac{V_{res}}{V_{res} + V_{pip}} \right)^n \quad (B11)$$

and

$$e^{a2 \cdot m} = \left(\frac{V_{res} - V_{add}}{V_{res} - V_{add} + V_{pip}} \right)^m \quad (B12)$$

As *a1* and *a2* are determinable from depletion experiments, and *V_{add}* is known from sphere volume measurements, we have two equations and two unknown variables (*V_{res}* and *V_{pip}*). Solving for

the unknown variables yields equations (3) and (4) in section 3.4.2:

$$V_{res+gauge} = \frac{V_{add} \cdot (e^{a2} - 1)}{\frac{e^{a2} \cdot (1 - e^{a1})}{e^{a1}} + e^{a2} - 1} \quad (B13)$$

and

$$V_{pip} = \frac{V_{add} \cdot (1 - e^{a2})}{\frac{e^{a1} \cdot (1 - e^{a2})}{(1 - e^{a1})} - e^{a2}} \quad (B14)$$

Acknowledgments

[52] The mechanical workshop team at the Vrije Universiteit, including Joost Rosier, Frans Hendriks, Rob Stoevelaar, Hans Bakker, Johan Kos, Niek van Harlingen, and Dick van Iperen are thanked for extensive technical support and design contributions. Tim Becker, Pete Burnard, Andy Calvert, Arnaud Dapigny, Jurgen Foeken, Hervé Guillou, Jay Hendricks, Ian McDougall, Noah McLean, Sébastien Nomade, Michael de Podesta, Xavier Quidelleur, Paul Renne, Thijs van Soest, Fin Stuart, and Gavin Sutton are thanked for specific advice and support. Ian McDougall and Andy Calvert are thanked for providing constructive reviews. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement 215458. K.K. is funded by grant 814.01.004 of the Netherlands Organisation for Scientific Research.

References

- Begemann, F., et al. (2001), Call for an improved set of decay constants for geochronological use, *Geochim. Cosmochim. Acta*, 65(1), 111–121.
- Burnard, P. G., and K. A. Farley (2000), Calibration of pressure-dependent sensitivity and discrimination in Nier-type noble gas ion sources, *Geochim. Geophys. Geosyst.*, 1(7), 1022, doi:10.1029/2000GC000038.
- Channell, J. E. T., et al. (2010), Reconciling astrochronological and ⁴⁰Ar/³⁹Ar ages for the Matuyama-Brunhes boundary and late Matuyama Chron, *Geochim. Geophys. Geosyst.*, 11, Q0AA12, doi:10.1029/2010GC003203.
- Condon, D. J., et al. (2010), Isotopic composition (²³⁸U/²³⁵U) of some commonly used uranium reference materials, *Geochim. Cosmochim. Acta*, 74(24), 7127–7143.
- Dalrymple, G. B., and M. A. Lanphere (1969), *Potassium-Argon Dating: Principles, Techniques, and Applications to Geochronology*, 258 pp., W. H. Freeman, San Francisco, Calif.
- Else, R. J. (1975a), Outgassing of vacuum materials-II, *Vacuum*, 25(8), 347–361.
- Else, R. J. (1975b), Outgassing of vacuum materials-I, *Vacuum*, 25(7), 299–306.
- Geyari, C. (1976), Design considerations in the use of stainless steel for vacuum and cryogenic equipment, *Vacuum*, 26(7), 287–297.

- Gupalo, L. K. (1991), Nonequilibrium partitioning of noble-gas isotopes between liquid and steam in reservoirs of hot springs, *Vestn. USSR Acad. Med. Sci., Engl. Transl.*, 311, 193–195.
- Hyland, R. W., and R. L. Shaffer (1991), Recommended practices for the calibration and use of capacitance diaphragm gages as transfer standards, *J. Vac. Sci. Technol. A*, 9(6), 2843–2863.
- International Organization of Legal Metrology (2004), Weights of classes E1, E2, F1, F2, M1, M1–2, M2, M2–3 and M3, Part 1: Metrological and technical requirements, *Int. Recomm. OIML R-R111*, Paris.
- Kuiper, K. F., et al. (2008), Synchronizing rock clocks of Earth history, *Science*, 320(5875), 500–504.
- Lanphere, M. A., and G. B. Dalrymple (1966), Simplified bulb tracer system for argon analyses, *Nature*, 209(5026), 902–903.
- Lanphere, M. A., and G. B. Dalrymple (2000), First-principles calibration of ^{38}Ar tracers: Implications for the ages of $^{40}\text{Ar}/^{39}\text{Ar}$ fluence monitors, *U.S. Geol. Surv. Prof. Pap.*, 1621, 10.
- Lee, J.-Y., et al. (2006), A redetermination of the isotopic abundances of atmospheric Ar, *Geochim. Cosmochim. Acta*, 70(17), 4507–4512.
- Lemmon, E. W., et al. (2008), NIST Standard Reference Database 23: Reference fluid thermodynamic and transport properties-REFPROP, version 8.0, Natl. Inst. of Stand. and Technol., Gaithersburg, Md.
- Mark, D. F., et al. (2009), The ARGUS multicollector noble gas mass spectrometer: Performance for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, *Geochem. Geophys. Geosyst.*, 10, Q0AA02, doi:10.1029/2009GC002643.
- McDougall, I., and Z. Roksandic (1974), Total fusion $^{40}\text{Ar}/^{39}\text{Ar}$ ages using Hifar reactor, *Aust. J. Earth Sci.*, 21(1), 81–89.
- McDougall, I., and P. Wellman (2011), Calibration of GA1550 biotite standard for K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating, *Chem. Geol.*, 280(1–2), 19–25.
- McDougall, I., et al. (1980), K-Ar age estimate for the KBS Tuff, East Turkana, Kenya, *Nature*, 284(5753), 230–234.
- McDowell, F. (1983), K-Ar dating: Incomplete extraction of radiogenic argon from alkali feldspar, *Chem. Geol.*, 41, 119–126.
- Merrihue, C., and G. Turner (1966), Potassium-argon dating by activation with fast neutrons, *J. Geophys. Res.*, 71(11), 2852–2857.
- Miiller, A. P. (1999), Measurement performance of high-accuracy low-pressure transducers, *Metrologia*, 36, 617–621.
- Miiller, A. P. (2006), Development of argon isotope reference standards for the U.S. Geological Survey, *J. Res. Natl. Inst. Stand. Technol.*, 111(5), 335–360.
- Renne, P. R., et al. (1998), Intercalibration of standards, absolute ages and uncertainties in $^{40}\text{Ar}/^{39}\text{Ar}$ dating, *Chem. Geol.*, 145(1–2), 117–152.
- Renne, P. R., et al. (2009), The isotopic composition of atmospheric argon and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology: Time for a change?, *Quat. Geochronol.*, 4, 288–298.
- Renne, P. R., et al. (2010), Joint determination of 40K decay constants and $^{40}\text{Ar}^*/^{40}\text{K}$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, *Geochim. Cosmochim. Acta*, 74(18), 5349–5367.
- Richter, S., and S. A. Goldberg (2003), Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry, *Int. J. Mass Spectrom.*, 229(3), 181–197.
- Rutherford, E. (1906), *Radioactive Transformations*, Charles Scribner, New York.
- Schmitz, M. D., and S. A. Bowring (2001), U-Pb zircon and titanite systematics of the Fish Canyon Tuff: An assessment of high-precision U-Pb geochronology and its application to young volcanic rocks, *Geochim. Cosmochim. Acta*, 65(15), 2571–2587.
- Smith, M. E., et al. (2010), Eocene clocks agree: Coeval $^{40}\text{Ar}/^{39}\text{Ar}$, U-Pb, and astronomical ages from the Green River Formation, *Geology*, 38(6), 527–530.
- Smits, F., and W. Gentner (1950), Argonbestimmungen an Kalium-Mineralien I. Bestimmungen an tertiären Kalisalzen, *Geochim. Cosmochim. Acta*, 1, 22–27.
- Spell, T. L., and I. McDougall (2003), Characterization and calibration of Ar- $^{40}\text{Ar}/^{39}\text{Ar}$ dating standards, *Chem. Geol.*, 198(3–4), 189–211.
- Steiger, R. H., and E. Jäger (1977), Subcommittee on geochronology: convention on the use of decay constants in geo- and cosmochronology, *Earth Planet. Sci. Lett.*, 6, 359–362.
- Tanaka, M., et al. (2001), Recommended table for the density of water between 0°C and 40°C based on recent experimental reports, *Metrologia*, 38(4), 301–309.
- Webb, A. W., and I. McDougall (1967), Isotopic dating evidence on age of Upper Permian and Middle Triassic, *Earth Planet. Sci. Lett.*, 2(5), 483–488.