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Variation in the terrestrial isotopic composition and atomic weight of argon (IUPAC Technical Report)

Abstract: The isotopic composition and atomic weight of argon (Ar) are variable in terrestrial materials. Those variations are a source of uncertainty in the assignment of standard properties for Ar, but they provide useful information in many areas of science. Variations in the stable isotopic composition and atomic weight of Ar are caused by several different processes, including (1) isotope production from other elements by radioactive decay (radiogenic isotopes) or other nuclear transformations (e.g., nucleogenic isotopes), and (2) isotopic fractionation by physical-chemical processes such as diffusion or phase equilibria. Physical-chemical processes cause correlated mass-dependent variations in the Ar isotope-amount ratios ($^{40}Ar/^{36}Ar$, $^{38}Ar/^{36}Ar$), whereas nuclear transformation processes cause non-mass-dependent variations. While atmospheric Ar can serve as an abundant and homogeneous isotopic reference, deviations from the atmospheric isotopic ratios in other Ar occurrences limit the precision with which a standard atomic weight can be given for Ar. Published data indicate variation of Ar atomic weights in normal terrestrial materials between about 39.7931 and 39.9624. The upper bound of this interval is given by the atomic mass of ^{40}Ar, as some samples contain almost pure radiogenic ^{40}Ar. The lower bound is derived from analyses of pitchblende (uranium mineral) containing large amounts of nucleogenic ^{36}Ar and ^{38}Ar. Within this interval, measurements of different isotope ratios ($^{40}Ar/^{36}Ar$ or $^{38}Ar/^{36}Ar$) at various levels of precision are widely used for studies in geochronology, water–rock interaction, atmospheric evolution, and other fields.

Keywords: argon; atomic weight; atomic-weight interval; geochronology; isotopic composition; isotopic fractionation; IUPAC Inorganic Chemistry Division; noble gas; radioactive; radiogenic; standard atomic weight.

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1 Introduction

Argon (Ar) is the most abundant noble gas on Earth, with an atmospheric mixing ratio of $9.34\ (\pm\ 0.01) \times 10^{-3}$ in dry air [1, 2]. Argon separated from air (Table 1) is used primarily as an inert gaseous medium or carrier gas for various applications in chemistry and industry. Argon was used in acoustic experiments to determine the universal gas constant, for which the Ar atomic weight was an important parameter and a source of uncertainty [6]. Argon has three stable isotopes (^{36}Ar, ^{38}Ar, and ^{40}Ar), each of which has radio- or nucleogenic components that can be used in Earth sciences for dating and tracing rocks, gases, and water masses. Overviews of measurements and applications of the isotopes of Ar and other noble gases include [1, 7, 8].

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Table 1 Stable isotopic composition of argon in air.

Isotope	Atomic mass[a]	Mole ratio to ^{36}Ar[b]	Mole fraction[c]
^{36}Ar	35.967 545 105(29)	1	0.003 3361(35)
^{38}Ar	37.962 732 11(21)	0.1885(3)	0.000 6289(12)
^{40}Ar	39.962 383 1237(24)	298.56(31)	0.996 0350(42)

[a]Atomic masses are given in unified atomic mass units, *u*, with uncertainties in the last 2 digits in parentheses [3].
[b]Mole ratios are given with uncertainties (1σ) in the last 1 or 2 digits in parentheses [4].
[c]Mole fractions and uncertainties were derived from the mole ratio data by IUPAC [5]. Corresponding atomic weight = 39.947 7983 ± 0.000 0152 (CIAAW Minutes, 2009).

Whereas Ar produced by stellar nucleosynthesis consists mainly of ^{36}Ar, the major isotope of Ar on Earth is ^{40}Ar, which accumulated from radioactive decay of ^{40}K, which has a total half-life of approximately 1.25×10^9 a and produces both ^{40}Ca (approximately 89.5 % of decays) and ^{40}Ar (approximately 10.5 % of decays) [9] (Table 2). Atmospheric Ar is well mixed and has uniform Ar isotopic abundances, whereas the relative abundance of radiogenic ^{40}Ar is highly variable in many other terrestrial materials. Radio- and nucleogenic components of the minor stable isotopes (^{38}Ar and ^{36}Ar) also exist (Table 2) but commonly are not detectable because of the ubiquitous presence of atmospheric Ar. Nucleogenic ^{38}Ar is produced by cosmic ray reactions with elements such as Ca and can be detected in some types of rocks that have been exposed at the Earth's surface for long periods of time. Radiogenic ^{36}Ar is produced by decay of ^{36}Cl, which is produced by cosmic ray interactions with Ar and other elements in the atmosphere, and by neutron activation of ^{35}Cl in rocks, nuclear reactors, and nuclear explosions. Identifiable natural occurrences of radiogenic ^{36}Ar are relatively uncommon, generally being limited to environments where ^{36}Cl was produced and decayed over long periods of time in relative absence of radiogenic ^{40}Ar production. Anomalous sites of ^{38}Ar and ^{36}Ar enrichment include U ores, where high-energy particles from U decay interact with other elements including Cl in the minerals. The stable isotope ratios of Ar also can vary measurably as a result of mass-dependent isotopic fractionation by physical-chemical processes like diffusion and solution/exsolution. These variations are generally small, but they can be useful to science and have been explored in part using high-precision mass spectrometric techniques.

The standard atomic weight of Ar was assigned its current value of 39.948 ± 0.001 in 1979 by the International Union of Pure and Applied Chemistry (IUPAC) Commission on Atomic Weights and Isotopic Abundances, with annotations "r" and "g" indicating evidence for variability [11, 12]. The standard atomic-weight value was calculated from the isotopic composition of atmospheric Ar determined by mass spectrometry,

Table 2 Selected terrestrial production pathways for stable isotopes of argon.

Radioactive decay	
^{36}Cl (β-) ^{36}Ar	[$\lambda = 2.303 \times 10^{-6}$ a^{-1}; $t_{1/2} = 3.01 \times 10^5$ a]
^{40}K ($\varepsilon + \beta$) ^{40}Ar + ^{40}Ca	[$\lambda_T = 5.543 \times 10^{-10}$ a^{-1}; $t_{1/2} = 1.25 \times 10^9$ a]

Radioactive decay equation for ^{40}Ar production

^{40}Ar(rad) $= \lambda_\varepsilon/\lambda_T \cdot {}^{40}\mathrm{K} \cdot [e^{\lambda_T \cdot t} - 1]$

^{40}Ar(rad) is the amount (moles) of radiogenic ^{40}Ar produced in a closed system over time t, ^{40}K is the amount (moles) of ^{40}K remaining in the system after time t (where ^{40}K = 0.000 1167 × total K), and $\lambda_\varepsilon/\lambda_T$ (0.105) is the fraction of total ^{40}K decays that produced ^{40}Ar, where $\lambda_\varepsilon = 0.581 \times 10^{-10}$ a^{-1}. Decay constants are consensus values [9], subject to revision [10].

Selected other nuclear reactions yielding stable Ar isotopes

^{35}Cl (n, γ) ^{36}Cl (β-) ^{36}Ar
^{35}Cl (a, p) ^{38}Ar
^{37}Cl (n, γ) ^{38}Cl (β-) ^{38}Ar

then rounded and given an expanded uncertainty to reflect the fact that some common terrestrial sources of Ar have isotopic compositions and atomic weights that differ substantially from that of atmospheric Ar. The annotation “r” indicates the range in isotopic composition of normal terrestrial material prevents a more precise standard atomic weight being given, despite the fact that measurements on individual samples may be more precise. Even so, some sources of Ar with large concentrations of radiogenic ^{40}Ar, and some with large concentrations of nucleogenic ^{38}Ar and ^{36}Ar, were not included within the standard atomic-weight uncertainty limits. The annotation “g” indicates geological specimens are known in which the element has an isotopic composition not included within the expanded standard atomic-weight uncertainty. The current report summarizes some of the known variations in the isotopic composition and atomic weight of Ar in terrestrial materials and processes that cause those variations. Presented as an interval, using current IUPAC criteria adopted in 2009 and 2011 [13, 14], the standard atomic weight of Ar could have lower and upper bounds outside the current standard atomic-weight uncertainties, as described below.

The current study was done for the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW), as part of Project #2009-023-1-200: “Evaluation of radiogenic isotopic abundance variations in selected elements”. Previous Commission studies summarized variations in isotopic composition and atomic weight of elements exhibiting effects of natural isotopic fractionation [13–15]. Elements with substantial abundances of radiogenic (or nucleogenic) isotopes were excluded from those studies because ratios of radiogenic/nonradiogenic isotopes can be highly variable and do not conform to common mass-dependent isotopic fractionation relations used to estimate atomic weights from partial isotopic analyses of fractionated samples. The current study is the first from the radiogenic isotope project, and it highlights some of these general issues. Isotopic variations in extraterrestrial materials were excluded from this study, as they normally have been in the determination of standard atomic weights [12].

For simplicity in the text and tables, Ar isotope-amount (molar) ratios, $n(^{40}\mathrm{Ar})/n(^{36}\mathrm{Ar})$ and $n(^{38}\mathrm{Ar})/n(^{36}\mathrm{Ar})$, are referred to as “isotope ratios” and designated by ^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar, respectively. Relatively high-precision data commonly are expressed using delta notation, for example [16]: $\delta^{40}\mathrm{Ar} = \delta(^{40}\mathrm{Ar}/^{36}\mathrm{Ar}) = [n(^{40}\mathrm{Ar})/n(^{36}\mathrm{Ar})]_{\mathrm{sample}}/[n(^{40}\mathrm{Ar})/n(^{36}\mathrm{Ar})]_{\mathrm{AIR}} - 1$, or $\delta^{38}\mathrm{Ar} = \delta(^{38}\mathrm{Ar}/^{36}\mathrm{Ar}) = [n(^{38}\mathrm{Ar})/n(^{36}\mathrm{Ar})]_{\mathrm{sample}}/[n(^{38}\mathrm{Ar})/n(^{36}\mathrm{Ar})]_{\mathrm{AIR}} - 1$, with δ^{40}Ar or δ^{38}Ar typically given in parts per thousand (per mil or ‰) or parts per million (ppm or “per meg”). Conversions between isotope ratios, delta values, mole fractions, and atomic weights for selected materials are illustrated in the Appendix, Fig. A-1.

2 Reference materials and reporting of isotope ratios

The primary reference for measuring and reporting stable Ar isotope ratios is atmospheric Ar. The stable isotopic composition of atmospheric Ar is essentially constant spatially and has not changed substantially on human time scales. An increase in the ^{40}Ar/^{38}Ar ratio of around 0.07 ‰/Ma was estimated on the basis of trapped air in ice representing the last 800 000 years and attributed to radiogenic ^{40}Ar degassing from the Earth [17]. For over 60 years, the best-calibrated measurement of the Ar isotope ratios in air was attributed to Nier [18], who reported a ^{40}Ar/^{36}Ar ratio of 296.0 and ^{38}Ar/^{36}Ar ratio of 0.1880. Confusion resulted when Nier’s isotope ratios were converted to mole fractions, then reconverted to ratios, with the result that 295.5 was adopted as a conventional atmospheric ^{40}Ar/^{36}Ar ratio for geochronology [9]. In 2007 [19], IUPAC adopted new values for the isotope ratios of atmospheric Ar based on partially calibrated measurements by Lee et al. [4], as summarized in Table 1. It is emphasized that purified Ar gas separated from air for commercial purposes (i.e., “tank Ar”) may not have the same isotopic composition as atmospheric Ar because of isotopic fractionation during the processing of the gas. A subsequent study [20] demonstrated improved analytical precision is possible, supported the relatively high ^{40}Ar/^{36}Ar ratio for atmospheric Ar of Lee et al. [4], and confirmed isotopic variability among purified atmospheric Ar tank gases. Another subsequent study [21] supported the partially calibrated measurements of Lee et al. [4] for both ^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar.

Most Ar isotope ratio measurements in the literature were made by static gas-source magnetic-sector mass spectrometry [22] and are expressed as simple molar ratios (e.g., ^{40}Ar/^{36}Ar, ^{38}Ar/^{36}Ar). This method can be used with very small samples, and has precision suitable for quantifying most variations caused by radioactive decay and other nuclear processes (e.g., of the order of 1–10 parts per thousand uncertainty in the ratio). Relatively few Ar isotope ratio measurements have been made by dynamic dual-inlet mass spectrometry [23, 24], which can require larger amounts of gas, but can be done with superior precision (e.g., of the order of 0.01 parts per thousand uncertainty in the ratio in some cases). This method has been used in studies of small isotopic variations; for example, those related to mass-dependent isotopic fractionation caused by diffusion, dissolution, and other processes not involving nuclear transformations.

Reported Ar isotope-ratio measurements generally were calibrated by using atmospheric Ar or some other related secondary standard as a reference. In the current study, measurements calibrated using data from Nier [9, 18] and reported as isotope ratios were adjusted to be consistent with the data of Lee and others [4] only in selected cases (as noted in the text), generally where isotopic variations were relatively small, as analytical precision may not have been sufficient in other cases to warrant this adjustment. For air, the relative magnitude of this adjustment is equivalent to about 8.6 parts per thousand for $^{40}Ar/^{36}Ar$ and 2.6 parts per thousand for $^{38}Ar/^{36}Ar$. Measurements reported as delta values with respect to atmospheric Ar will not be affected by this change except when converted to isotope ratios, in which case the relative difference may be quite large. Uncertainties of the relative isotope-ratio differences (delta values) between samples may be smaller than the uncertainties of the actual isotope ratios of the atmospheric Ar reference. The relative uncertainty (1 sigma) of the isotope ratios reported by Lee and others [4] is approximately 1.0 part per thousand for $^{40}Ar/^{36}Ar$ and 1.6 parts per thousand for $^{38}Ar/^{36}Ar$; that is, 1–2 orders of magnitude larger than the relative uncertainties of the most precise delta measurements.

3 Overview of variation in the isotopic composition and atomic weight of argon

Naturally occurring Ar has widely varying $^{40}Ar/^{36}Ar$ ratios ranging from slightly less than that of atmospheric Ar to almost infinity (almost pure radiogenic ^{40}Ar) (Table 3; Fig. 1). Especially high $^{40}Ar/^{36}Ar$ ratios can be found in rocks and minerals devoid of primordial or atmospheric Ar in which radiogenic ^{40}Ar has accumulated from ^{40}K decay. $^{40}Ar/^{36}Ar$ ratios less than the atmospheric value can be found in young volcanic rocks, where Ar was fractionated isotopically during transport from air into the lava prior to cooling, and where ^{40}K decay to ^{40}Ar has not had sufficient time to augment the ^{40}Ar in the rocks since they cooled [25].

There is relatively little information about $^{38}Ar/^{36}Ar$ ratios, which commonly do not deviate substantially from the atmospheric value. Porcelli and Ballentine [26] conclude there is no reliable evidence for

Table 3 Overview of argon atomic-weight variation.[a]

	Low value	[c]	Representative value	High value	[c]
Standard atomic weight (1979–2013)	39.947		39.948	39.949	
Interval of reported natural variation	39.7931		39.9478	39.9624	
Atmospheric argon[b]			39.947 7983 ±0.000 0152		
Tank gas (cryogenic, from air)	39.947 66	F		39.947 94	F
Ocean water, shallow groundwater, snow, ice	39.947 80	F		39.947 83	F
Rocks and minerals	39.947 18	F		39.94780	F
	39.793 11	N		39.962 33	R
Natural gas, deep groundwater, geothermal fluid	39.947 80	F		39.962 29	R

[a]See Appendix and text for calculations and explanations.
[b]See Table 1.
[c]"F" indicates variation primarily related to isotopic fractionation; "N" indicates variation primarily related to nucleogenic ^{38}Ar and(or) ^{36}Ar production; "R" indicates variation primarily related to radiogenic ^{40}Ar production.

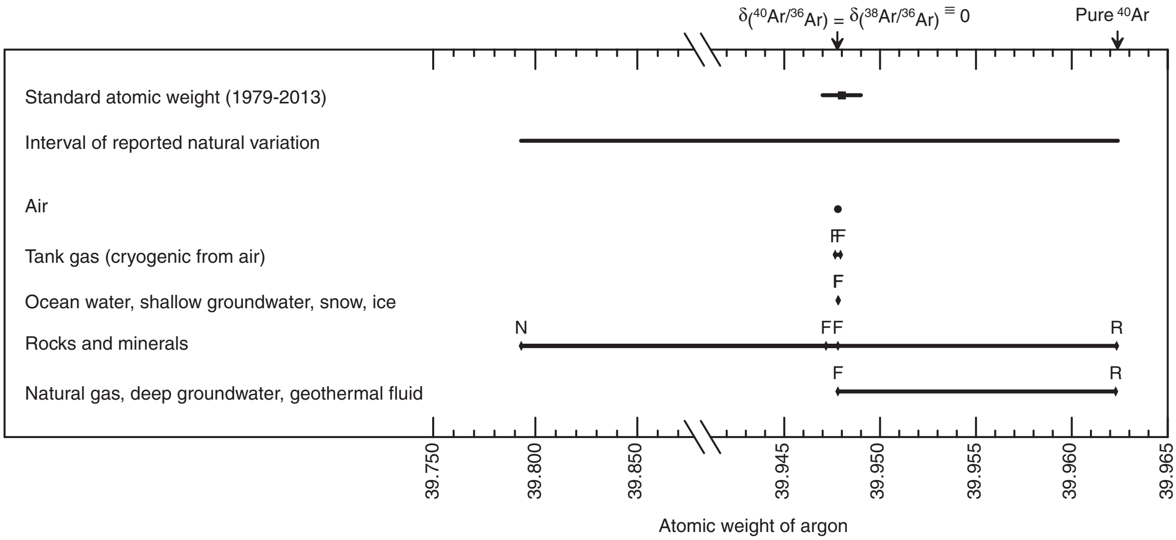

Fig. 1 Argon atomic weights in normal terrestrial materials compared with current standard atomic weight.[a]
[a]See Tables 1 and 3 for data.
"F" indicates variation primarily related to isotopic fractionation.
"N" indicates variation primarily related to nucleogenic ^{38}Ar and(or) ^{36}Ar production.
"R" indicates variation primarily related to radiogenic ^{40}Ar production.

non-atmospheric ^{38}Ar/^{36}Ar in rocks from the Earth's mantle. Small deviations can be produced by mass-dependent fractionation processes such as diffusion, dissolution, and degassing. In addition, some rocks and minerals exposed to cosmic rays at the Earth's surface for long periods of time have substantially elevated ^{38}Ar/^{36}Ar ratios from accumulation of cosmogenic ^{38}Ar [27]. This cosmogenic component is most likely to be measurable in materials with high Ca concentrations, low K concentrations, long exposure times to cosmic rays, and small atmospheric gas components. These conditions are met by certain Ca-rich minerals in old rocks exposed at the Earth's surface in areas with low erosion rates. Extreme enrichments of ^{38}Ar and ^{36}Ar can be found in U-bearing minerals where energetic particles released in the U decay series react with surrounding nuclei [28].

Naturally occurring radioactive isotopes of Ar (^{37}Ar, ^{39}Ar) have been measured because of their importance in geochronology and related fields of study [29, 30], but they do not affect the evaluation of Ar atomic weight because their concentrations are many orders of magnitude smaller than those of ^{36}Ar, ^{38}Ar, and ^{40}Ar. For example, ^{39}Ar (half-life 269 a) produced by cosmic ray interactions in the atmosphere can be traced throughout the world ocean and in some aquifers, providing information about relative ages and patterns of movement of water masses since they were isolated from exchange with air [31, 32]. The ratio of ^{39}Ar/∑Ar in air is of the order of 10^{-15}, which can be measured with useful precision but is too small to have a significant effect on the atomic weight of Ar.

Because the stable Ar isotopes can vary independently of each other, and because measurements typically are aimed at either geochronology related to ^{40}K decay (^{40}Ar accumulation) or geochronology related to cosmic ray exposure (^{38}Ar accumulation) or mass-dependent fractionation effects (small changes in δ^{40}Ar/^{36}Ar or δ^{38}Ar/^{36}Ar), there are relatively few published data that include all three of the stable Ar isotopes in the same samples. Therefore, although ranges can be given for each of the isotope ratios, it is more difficult to present ranges for the complete isotopic compositions and atomic weights of Ar in terrestrial materials. For atmospheric Ar, using the isotope-ratio measurements of Lee et al. [4] and the atomic mass data of Wang et al. [3], we obtain an atomic weight of 39.947 7983. Reported 1-sigma uncertainties in the isotope ratios correspond to atomic-weight uncertainty of ±0.000 0152 (Table 1) [5]. From reported data summarized below, it is estimated the lower and upper bounds of Ar atomic weights in natural terrestrial materials are approximately 39.7931 and 39.9624. The low atomic-weight value was derived from measurements of ^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar in pitchblende (U-rich mineral) from Saskatchewan, Canada [28]. High and variable abundances of the light isotopes ^{38}Ar and ^{36}Ar in this sample and other U minerals were attributed to nuclear reactions of Cl with neutrons and alpha particles derived from U and Th decay. The high atomic-weight value is approximately equal to the atomic mass of ^{40}Ar. Although no samples have been demonstrated to be completely free of ^{36}Ar and ^{38}Ar, $^{40}Ar/^{36}Ar$ ratios of the order of 10^5 and higher can be derived from analyses of K-rich silicate minerals [33], and it is considered likely that higher values exist. Therefore, it is concluded that the atomic weights of some terrestrial occurrences of Ar could be indistinguishable from the atomic mass of ^{40}Ar to within a reasonable number of significant digits that could be used to express an atomic-weight interval.

3.1 Snow and ice

Atmospheric gases including Ar are trapped in snow and ice, where they may be subject to minor fractionation of gas concentration ratios and isotope ratios by diffusion, advection, gravitational settling, and exchange with gas hydrate phases. For example, in a vertical profile of trapped air in snow and ice in Antarctica, $\delta^{40}Ar$ increased from 0.0 at the surface to +2.4 per mil at around 120 m depth [34]. Those values encompass the range reported in other similar studies in Arctic and Antarctic regions. Applying the Ar isotope ratios of Lee and others exactly, and assuming mass-dependent fractionation of ^{40}Ar, ^{38}Ar, and ^{36}Ar, $\delta^{40}Ar$ values of 0.0 and +2.4 per mil would correspond to $^{40}Ar/^{36}Ar$ ratios of 298.56 and 299.276 54, respectively, or Ar atomic weights of 39.947 7983 and 39.947 8316, respectively. The true values of these conversions are subject to the uncertainties of the atmospheric Ar isotope ratios, which are similar in magnitude to the range of $\delta^{40}Ar$ values. Studies relying on such small variations to investigate isotopic fractionation and gas transport processes are based on the relative difference (delta) values, which can be measured more precisely than the actual isotope ratios.

3.2 Surface water and shallow groundwater

Substantial amounts of atmospheric gases including Ar are dissolved in water when it is in contact with air. In groundwater and surface water bodies, concentrations of atmospheric Ar commonly are nearly in equilibrium with the partial pressure of Ar in air at the pressure (elevation) and temperature at which the water and air last were in contact. Dissolved Ar is slightly heavier than Ar in air at equilibrium. The equilibrium isotopic fractionation factor $\alpha[^{40}Ar/^{36}Ar]_{\text{aqueous/gas}}$ was determined experimentally and found to be 1.001 21 at 2 °C and 1.001 05 at 25 °C [35] (Note: These values were corrected by [36]; temperatures in the original publication were reversed). Thus, dissolved Ar in equilibrium with atmospheric Ar would have $\delta^{40}Ar$ values of +1.21 per mil and +1.05 per mil at 2 and 25 °C, respectively. Additional Ar may be present in water samples from incorporation of "excess air" by entrainment and dissolution of bubbles by wave action or by infiltration and groundwater recharge, and there may be additional kinetic isotopic fractionation during phase transfer [36]. Therefore, Ar dissolved in surface water and recharging groundwater is expected to have variable $^{40}Ar/^{36}Ar$ ratios averaging slightly higher than the atmospheric value. Accordingly, Nicholson et al. [35] measured $\delta(^{40}Ar/^{36}Ar)$ values from +0.67 to +1.33 ‰ for dissolved Ar in ocean water (lowest value from tropical Atlantic Ocean surface water; highest value from tropical Atlantic Ocean at 5000 m depth).

Because of the long half-life of ^{40}K, accumulation of non-atmospheric radiogenic ^{40}Ar occurs slowly in the subsurface. As a result, rivers, lakes, oceans, and most shallow groundwaters with residence times of the order of 10^3 years or less generally have $^{40}Ar/^{36}Ar$ ratios not much different from that of dissolved atmospheric Ar, even where K is present, although high-precision measurements in some such environments may be useful in the future. Deeper, older groundwaters may contain substantial radiogenic ^{40}Ar components released from aquifer minerals, providing useful information about groundwater movement and water–rock interaction [37, 38] (see below).

3.3 Rocks and minerals

Rocks and minerals, depending on their ages and K contents, can have widely varying amounts of radiogenic ^{40}Ar. Radiogenic ^{40}Ar may be diluted to varying degrees with more air-like Ar incorporated during crystallization or subsequently, such that bulk ^{40}Ar/^{36}Ar ratios are highly variable. In extreme cases, where K-bearing minerals or glasses solidified in the absence of environmental Ar and decayed subsequently, almost pure radiogenic ^{40}Ar can be found. In such situations, relative abundances of radioactive K and radiogenic ^{40}Ar can be used to estimate time since the rock or mineral formed.

The accuracy and precision of the highest measured terrestrial ^{40}Ar/^{36}Ar ratios are limited in part by small amounts of air contamination in samples and vacuum systems and by the difficulty of measuring very low abundances of ^{36}Ar. A ^{40}Ar/^{36}Ar ratio of >90 000 with unspecified uncertainty was reported for microcline (K-rich silicate mineral) by [39]. More recent data for K-rich silicate minerals and rocks ranging in age from 28 Ma to 1.1 Ga indicate ^{40}Ar/^{36}Ar ratios could be of the order of $1–2 \times 10^5$ [33, 40, 41]. A sample of 311 Ma sanidine with estimated ^{40}Ar/^{36}Ar of 165 000 [33], with trace amount of atmospheric Ar with ^{38}Ar/^{36}Ar = 0.1885, would have an Ar atomic weight of 39.962 3566, and it is possible that higher values exist locally. Therefore, it is concluded that Ar in some K-rich minerals could be indistinguishable from that of pure ^{40}Ar.

Burnard and others [42] report ^{40}Ar/^{36}Ar ratios up to about 40 000 ± 4000 (with a questionable outlier at 64 000) from gas-filled vesicles in mid-ocean-ridge basalt (MORB) that were opened with a laser and analyzed by static mass spectrometry. Marty and Humbert [43] report values as high as 42 366 ± 9713 from similar samples crushed under vacuum. Subsequent reviews indicate values of around 40 000 or slightly higher may be typical of the ^{40}Ar/^{36}Ar ratio in large regions of the Earth's mantle from which MORB magmas were derived [44–46]. ^{38}Ar/^{36}Ar ratios in such samples generally are similar to that of atmospheric Ar, although the uncertainties of these measurements are large compared to those used in mass-dependent fractionation studies. For a ^{40}Ar/^{36}Ar ratio of 40 000, and ^{38}Ar/^{36}Ar ratio of 0.1885 (atmospheric), the atomic-weight value of Ar would be 39.962 2738. Honda and others [47] report a ^{40}Ar/^{36}Ar ratio of 36 000 ± 5240 for bulk Ar extracted from polycrystalline diamond from Botswana, with a higher value (74 900 ± 9660) for the fraction of Ar extracted above 2000 °C, following release of less radiogenic Ar at 1000 °C.

In addition to the common occurrence of radiogenic ^{40}Ar, it is possible for the minor isotopes of Ar to be measurably enriched in samples of rocks and minerals. For example, cosmogenic ^{38}Ar can accumulate in minerals exposed to cosmic rays at the Earth's surface through spallation of K and Ca, thus potentially providing useful information about exposure ages of rocks and soils. ^{38}Ar/^{36}Ar ratios as high as 0.2894 were reported for total fusion analyses of apatite [27] and as high as 0.2245 for pyroxene [48] as a result of terrestrial cosmogenic ^{38}Ar accumulation. These Ca-rich, K-poor minerals were separated from granitic and diabasic rocks, respectively, from old exposed surfaces in Antarctica. Multiplied by (0.1885/0.1880) to adjust for the assumed ratio in atmospheric Ar in the original studies, these values are 0.2902 and 0.2251. If the higher ^{38}Ar/^{36}Ar ratio (0.2902) were combined with the atmospheric ^{40}Ar/^{36}Ar ratio (i.e., if there were negligible radiogenic ^{40}Ar or cosmogenic ^{36}Ar in the sample), the corresponding atomic weight would be 39.947 1251, which is only slightly higher than the atmospheric value. However, these assumptions are unlikely to be met in such situations [27, 48], so it is possible that larger atomic-weight variations would be revealed by more complete isotopic analyses of such samples.

Large variations in the isotopic composition of Ar have been observed in U-rich minerals, where radioactive U decay produces energetic particles that participate in reactions producing nucleogenic isotopes [28, 49]. Eikenberg and others [28] report ^{40}Ar/^{36}Ar ratios from 45.2 to 7527 and ^{38}Ar/^{36}Ar ratios from 0.182 to 14.74, indicating varying proportions of nucleogenic ^{38}Ar and ^{36}Ar attributed to n and α reactions with Cl (Table 2). In that study, the lowest atomic weight of Ar (39.793 1119) was in a sample of pitchblende from Saskatchewan, Canada, which had ^{40}Ar/^{36}Ar = 45.2 and ^{38}Ar/^{36}Ar = 2.09; whereas the highest atomic weight of Ar (39.959 3381) was in a sample of pitchblende from Switzerland, which had ^{40}Ar/^{36}Ar = 7527 and ^{38}Ar/^{36}Ar = 9.48. Uncertainties in those measurements were not reported; arbitrarily assigning uncertainty of 1 in the last digit of each reported ratio could yield a low atomic-weight value of 39.792 7606. It is possible data from other U-mineral samples could extend this range of variation to lower atomic-weight values. Such enrichments of ^{38}Ar and ^{36}Ar are not typical of other common rocks and minerals with lower in situ production rates of n and α particles. Irwin and Reynolds [50] report $^{38}Ar/^{36}Ar$ ratios from 0.14 to 0.38 (compared to an atmospheric ratio of 0.188) in microscopic fluid inclusions in old granitic rocks from Sweden, possibly as a result of similar processes.

Relatively low $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ ratios can occur in young volcanic rocks as a result of mass-dependent isotopic fractionation during transfer of atmospheric Ar into the lavas as they cooled [25, 51, 52]. Dalrymple [25] reports $^{40}Ar/^{36}Ar$ ratios as low as 283.5 in young volcanic glass (obsidian of age less than about 400 a). This could be interpreted as a result of mass-dependent fractionation of atmospheric Ar that entered the lava, where radiogenic ^{40}Ar production did not have sufficient time to obscure this effect. This effect can have important consequences for geochronology of young materials. In the current study, the low reported $^{40}Ar/^{36}Ar$ ratio (283.5) was multiplied by (298.56/296.1), the currently accepted atmospheric ratio divided by the reported atmospheric ratio [25], to obtain an adjusted $^{40}Ar/^{36}Ar$ ratio of 285.9 (corresponding to $\delta(^{40}Ar/^{36}Ar) = -34$ ‰). In addition, the $^{38}Ar/^{36}Ar$ ratio of the sample (0.1844) was estimated by assuming kinetic mass-dependent fractionation. These combined ratios correspond to an atomic weight of 39.947 1839. It is possible that lower values may exist in similar rocks with low concentrations of radiogenic ^{40}Ar.

3.4 Natural gas and deep groundwater

Argon is present in natural gas derived from various sources. Most commercial tank Ar is produced from air by cryogenic distillation, which can cause minor mass-dependent isotopic fractionation. Limited data indicate variations in the isotope ratios of commercial tank Ar produced from air can be of the order of ±1 % (10 ‰) or more, corresponding to atomic-weight variations of the order of 3 parts in 10^6 or more [20]. Argon in natural gas from the subsurface of the Earth typically has much higher relative abundance of radiogenic ^{40}Ar than does atmospheric Ar. Thus, Ar extracted from subsurface natural gas could have much higher $^{40}Ar/^{36}Ar$ and higher atomic weight than Ar extracted from air.

Some of the highest $^{40}Ar/^{36}Ar$ ratios are reported from natural CO_2 gas wells that apparently contained components of noble gases derived from the Earth's mantle. Holland and Ballentine [53] report a maximum $^{40}Ar/^{36}Ar$ ratio of 22 548 ± 730 from the Bravo Dome CO_2 gas well in New Mexico. This ratio is not much smaller than the highest values reported for vesicles in mantle-derived submarine volcanic rocks described above. The $^{38}Ar/^{36}Ar$ ratios in the CO_2 gas samples typically are similar to that of atmospheric Ar, although the uncertainties of these measurements are large compared to those used in mass-dependent fractionation studies. Slightly elevated $^{38}Ar/^{36}Ar$ ratios have been reported in some natural gas samples (e.g., up to around 0.207; [54]).

The highest $^{40}Ar/^{36}Ar$ ratios reported for "free-flowing" groundwater are from brine samples from Precambrian rocks in the Canadian Shield [55]. Water flowing into wells approximately 2 km below land surface had $^{40}Ar/^{36}Ar$ ranging from about 6600 to 44 400 with $^{38}Ar/^{36}Ar$ ratios (0.1871 to 0.1879) similar to that of atmospheric Ar. These data, along with He, Ne, Kr, and Xe isotope ratios, indicate the groundwater entered the subsurface more than 10^9 years ago and accumulated radiogenic noble gas isotopes from crustal rocks in which they were trapped [55]. The highest Ar atomic weight derived from data in that study is 39.962 2847.

3.5 Geothermal fluids

Fluids participating in active geothermal (hydrothermal) systems are derived from various sources including meteoric groundwater, seawater, volatiles released during metamorphism, and magmatic emissions. Hydrothermal fluids typically are modified extensively by water–rock interactions, through which radiogenic ^{40}Ar may be transferred from minerals to fluids. Therefore, hydrothermal groundwaters and hot springs can have $^{40}Ar/^{36}Ar$ ratios ranging from near the atmospheric ratio (298.6) up to much higher values. It is difficult to define an upper limit for such fluids. Reported values for well-known active geothermal fields are as high as 685 in the Yellowstone, Wyoming geothermal system [56] and 671 in the Valles, New Mexico geothermal system [57] (reported values, not adjusted to Lee ratios). These data are consistent with approximately equal amounts of atmospheric Ar dissolved during groundwater recharge and radiogenic ^{40}Ar acquired from magmas or rocks in the subsurface. Corresponding atomic weights, assuming atmospheric $^{38}Ar/^{36}Ar$ ratios, would be 39.956 0120 and 39.955 8841, respectively. Similar ratios of atmospheric and radiogenic Ar can be found in microscopic fluid inclusions in minerals deposited from extinct meteoric hydrothermal systems [58, 59]. Substantially higher and lower values exist in other geothermal fluids; for example, $^{40}Ar/^{36}Ar$ ratios as high as 2082 were reported for fumarole gas at Vulcano, Italy [60].

4 Summary

Ratios of Ar stable isotopes (e.g., $^{40}Ar/^{36}Ar$, $^{38}Ar/^{36}Ar$) have been measured with varying precision in many different terrestrial substances. In samples such as surface waters, shallow groundwaters, and some young volcanic rocks, Ar isotopic variations are relatively small and largely due to mass-dependent fractionation processes. In other samples such as old rocks and minerals, deep groundwaters, and natural gas deposits, Ar isotopic variations can be large and non-mass-dependent as a result of radioactivity and other nuclear processes. All three stable Ar isotopes can be enriched independently by radiogenic or nucleogenic sources. Because Ar isotope-ratio measurements typically target specific research objectives (e.g., geochronology, hydrologic processes), reported Ar isotopic compositions commonly are incomplete; that is, data commonly do not include all three isotopes used to determine an atomic weight. Compiled data indicate the maximum atomic weight of Ar in natural terrestrial materials is likely to be near that of the ^{40}Ar isotope, as a result of K decay in samples with little or no primordial, nucleogenic, or atmospheric Ar. The lowest atomic-weight value was derived from reported Ar isotope-ratio measurements in a U-bearing mineral in which nucleogenic ^{36}Ar and ^{38}Ar were substantial components of total Ar. Published data indicate variation of Ar atomic weights in normal materials between about 39.7931 and 39.9624. The upper bound corresponds to a theoretical limit, whereas the lower bound has unknown uncertainty and could change as additional data become available. Isotopic variations in Ar provide useful measures for many different processes in Earth science.

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Appendix

N (Ar)	delta i/36 ‰	Rsample/ Rstd	R i/36 sample	mole fraction	atomic weight	delta i/36 ‰	Rsample/ Rstd	R i/36 sample	mole fraction	atomic weight
	Air (Lee)					**Air (Nier)**				
36	0.00	1.00000	1.00000	0.003336	**39.9477983**	0.00	1.00000	1.00000	0.003365	39.9476760
38	0.00	1.00000	**0.18850**	0.000629		-2.65	0.99735	**0.18800**	0.000633	
40	0.00	1.00000	**298.56000**	0.996035		-8.57	0.99143	**296.00000**	0.996003	
	Air					Air				
	Lee 2006 (Complete analysis reported)					Nier 1950 (Complete analysis reported)				
	Tank Ar from air (low)					**Tank Ar from air (high)**				
36	0.00	1.00000	1.00000	0.003370	39.9476581	0.00	1.00000	1.00000	0.003303	39.9479358
38	-5.14	0.99486	0.18753	0.000632		5.12	1.00512	0.18946	0.000626	
40	**-10.00**	0.99000	295.57440	0.995998		**10.00**	1.01000	301.54560	0.996071	
	Estimated variation of commercial Ar separated from air					Estimated variation of commercial Ar separated from air				
	Valkiers 2010 (assuming mass-dependent 38/36)					Valkiers 2010 (assuming mass-dependent 38/36)				
	Snow, ice, surface water (low)					**Snow, ice, surface water (high)**				
36	0.00	1.00000	1.00000	0.003336	39.9477983	0.00	1.00000	1.00000	0.003328	39.9478316
38	0.00	1.00000	0.18850	0.000629		1.23	1.00123	0.18873	0.000628	
40	**0.00**	1.00000	298.56000	0.996035		**2.40**	1.00240	299.27654	0.996044	
	Air trapped in surface snow					Fractionated air in ice at 120 m depth, Antarctica				
	Severinghaus 2006 (assuming mass-dependent 38/36)					Severinghaus 2006 (assuming mass-dependent 38/36)				
	Rocks and minerals (low)					**Rocks and minerals (high)**				
36	0.00	1.00000	1.00000	0.020708	**39.7931119**	0.00	1.00000	1.00000	0.000006	**39.9623566**
38	10087.53	11.08753	**2.09000**	0.043280		0.00	1.00000	0.18850	0.000001	
40	-848.61	0.15139	**45.20000**	0.936012		551652.73	552.65273	**165000.00000**	0.999993	
	U mineral with nucleogenic 38 + 36					K-feldspar (sanidine)				
	Eikenberg 1993 (Complete analysis reported)					Kunk 1994 (assuming atmospheric 38/36)				
	Groundwater, geothermal fluid, natural gas (low)					**Groundwater, geothermal fluid, natural gas (high)**				
36	0.00	1.00000	1.00000	0.003333	39.9478129	0.00	1.00000	1.00000	0.000023	39.9622847
38	0.54	1.00054	0.18860	0.000629		-4.77	0.99523	**0.18760**	0.000004	
40	**1.05**	1.00105	298.87349	0.996039		147660.24	148.66024	**44384.00000**	0.999973	
	Air-saturated water at 25 °C					Canadian Shield brine				
	Nicholson 2010 (assuming mass dependent fractionation)					Holland 2013 (Complete analysis reported)				
	Rocks and minerals (other)					**Rocks and minerals (other)**				
36	0.00	1.00000	1.00000	0.003483	39.9471838	0.00	1.00000	1.00000	0.000025	39.9622738
38	-21.99	0.97801	0.18435	0.000642		0.00	1.00000	0.18850	0.000005	
40	-42.40	0.95760	**285.90000**	0.995875		132976.42	133.97642	**40000.00000**	0.999970	
	Young volcanic rock (fractionated air)					Vesicles in deep-sea volcanic rock (mantle volatiles)				
	Dalrymple 1969 (assuming mass-dependent 38/36)					Burnard 1997 (assuming atmospheric 38/36)				
	Groundwater, geothermal fluid, natural gas (other)					**Groundwater, geothermal fluid, natural gas (other)**				
36	0.00	1.00000	1.00000	0.001457	39.9560120	0.00	1.00000	1.00000	0.000044	39.9621892
38	0.00	1.00000	0.18850	0.000275		0.00	1.00000	0.18850	0.000008	
40	1294.35	2.29435	**685.00000**	0.998268		74522.51	75.52251	**22548.00000**	0.999947	
	Yellowstone geothermal water					CO2 gas well				
	Kennedy 1985 (assuming atmospheric 38/36)					Holland 2006 (assuming atmospheric 38/36)				

Fig. A-1 Argon isotope ratios, delta values, isotopic abundances, and atomic weights in selected materials, illustrating conversions from various reported values.[a]

[a]Blue cells indicate reported data; other values were derived from those, as indicated.

Orange cells highlight the primary argon isotopic reference material (atmospheric Ar) and samples yielding the highest and lowest atomic weights (see text for details).

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