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Determination of the half-life of ^{37}Ar by mass spectrometry

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The half-life of ^{37}Ar has been determined via mass spectrometry by measuring the ratio of ^{37}Ar to stable ^{36}Ar as a function of time in neutron-irradiated samples of CaF_2. The half-life we obtain is 34.95 ± 0.08 d (95% confidence level). This result is compared to previous experiments based on radioactivity measurements.

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^{37}Ar is produced in nature by cosmic-ray spallation and by neutron-capture processes, and decays by electron capture to ^{37}Cl. The half-life of this isotope is approximately 35 d. Knowledge of the half-life is important to ^{40}Ar/^{39}Ar dating [1] and various problems in cosmochemistry including neutrino detection [2]. Previous determinations [3–8] (Table I) of the ^{37}Ar half-life have been based on activity measurements. Here we report mass spectrometric data monitoring the ratio of ^{37}Ar to stable ^{36}Ar as a function of time after neutron activation. These data provide an independent corroboration of the activity-based results, and yield a more precise value for the half-life than all but the most recent of those experiments.

Optical grade fluorite (CaF_2), as 0.2–1.0-mg crystal fragments, was irradiated in 11 distinct neutron irradiation runs of 7–100-h duration (Table II). The samples were contained in aluminum disks [9] in the cadmium-lined in core irradiation tube (CLICIT) of the 1-MW TRIGA reactor at Oregon State University, Corvallis. ^{37}Ar and ^{36}Ar are produced by fast neutrons via the $^{40}\mathrm{Ca}(n,\alpha)^{37}\mathrm{Ar}$ and $^{40}\mathrm{Ca}(n,n\alpha)^{36}\mathrm{Ar}$ reactions, respectively. Normalizing radioactive ^{37}Ar to stable ^{36}Ar enables using decay of the ^{37}Ar/^{36}Ar ratio to constrain the ^{37}Ar half-life, obviating the need to determine absolute ^{37}Ar concentration. Measurement of isotope ratios, rather than determining absolute concentrations, is ideally suited to mass spectrometry.

Because atmospheric ^{36}Ar is present in variable concentrations, a correction using ^{40}Ar (based on $^{40}\mathrm{Ar}/^{36}\mathrm{Ar} = 296.0 \pm 0.5$; as determined by Nier [10]) is required. This correction, which assumes that all ^{40}Ar is of atmospheric origin, yields the reactor-produced ^{36}Ar ($^{36}\mathrm{Ar}_{\mathrm{Ca}}$). Analysis of unirradiated samples of the same fluorite confirms an atmospheric ^{40}Ar/^{36}Ar ratio. $^{36}\mathrm{Ar}_{\mathrm{Ca}}$ comprises 79–99 % (mean 94%) of all ^{36}Ar in the irradiated fluorite samples analyzed, and the atmospheric correction introduces small errors compared with those from mass spectrometry. The irradiated samples were baked to ca. 200 °C in ultrahigh vacuum ($<10^{-9}$ atm) overnight to a turbomolecular pump prior to analysis, and subsequently heated to ca. 800 °C for a few seconds with a laser, in order to remove adsorbed atmospheric argon. For each analysis, 0.2–3 mg of irradiated fluorite were degassed in ultrahigh vacuum ($<10^{-9}$ atm) with either an argon-ion or a Nd-yttrium aluminum garnet (YAG) laser, and purified gas was analyzed with either an MAP 215C or MAP 215-50 noble-gas mass spectrometer using facilities and procedures described by Renne *et al.* [9]. The amount of fluorite analyzed was adjusted to maintain ^{37}Ar yields at least 50 times background. The precision of individual ^{37}Ar/^{36}Ar measurements ranges from ±2% to ±35%, with a median of ±11%.

Argon-ion beam currents were measured on a single-electron multiplier (analog mode) on each mass spectrometer, using magnetic field switching to cycle sequentially between argon isotopes. Laser fusion, gas transfer and purification, and mass spectrometry were completely automated as described by Renne *et al.* [9] and references therein. All data reported herein are corrected for background (measured every 1–3 samples) and mass discrimination (1.00282 ± 0.00215 to 1.01133 ± 0.00200 per u) based on average values of ^{40}Ar/^{36}Ar from air pipettes interspersed with unknowns.

For each irradiation j, a differential time parameter $\tau_{i,j}$ is defined as the elapsed time between the beginning of a mass-spectrometric analysis of the first sample and that of the ith, sample from that irradiation. Thus by definition $\tau_{1,j}=0$. Uncertainties in $\tau_{i,j}$ are within 0.005 d, and we conservatively assign this uncertainty to all data. Cast in terms of variables appropriate to our data, the exponential decay law can be written as

$$\left(\frac{^{37}\mathrm{Ar}}{^{36}\mathrm{Ar}_{\mathrm{Ca}}}\right)_{i,j} = \left(\frac{^{37}\mathrm{Ar}}{^{36}\mathrm{Ar}_{\mathrm{Ca}}}\right)_{1,j} e^{-\lambda\tau_{i,j}}, \tag{1}$$

where λ is the decay constant. Rearranging,

TABLE I. Previous ^{37}Ar half-life determinations.

Reference (year)	$t_{1/2}$ (d)	Error[a] (d)
Weimer, Kurbatov, and Pool [3] (1944)	34.1	0.6
Miskel and Perlman [4] (1952)	35.0	0.8
Kiser and Johnston [5] (1959)	34.30	0.28
Stoenner, Schaeffer, and Katcoff [6] (1965)	35.1	0.2
Colomer and Gauvain [7] (1973)	35.06	0.18
Kishore *et al.* [8] (1975)	35.02	0.04

[a]95% confidence.

TABLE II. Schedule of irradiations and analyses.

Irrad. no.(j)	Duration (h)	Completion date	Analysis batch	Analysis no.(i)	Mean ^{37}Ar/^{36}Ar
1	25	4/13/93	7/10/93	1–8	599.6
			7/22/93	9–18	438.6
			8/30/93	19–23	212.1
2	14	7/16/93	9/9/93	1–5	762.4
3	14	2/28/94	4/11/95	1–2	1.184
4	21	4/7/94	8/9/94	1–5	312.2
			4/3/95	6–13	2.884
			4/9/95	14–20	2.574
5	60	12/15/94	3/19/95	1–5	532.1
			4/4/95	6–12	388.2
6	7	1/24/95	4/7/95	1–4	940.2
7	30	7/26/95	10/30/95	1–6	541.8
			4/16/96	7–14	18.56
			6/10/96	15–21	6.324
8	40	8/24/95	4/15/96	1–4	36.39
			6/10/96	5–11	11.46
9	100	10/20/95	3/13/96	1–7	179.9
			4/14/96	8–17	91.20
			6/10/96	18–24	30.56
			3/15/97	25–32	0.118
			7/28/97	33–34	0.009
10	60	6/17/96	7/10/97	1–5	1.516
			7/28/97	6–9	1.122
11	60	4/16/99	7/19/99	1–2	491.1
			9/11/99	3–12	169.9
			9/4/00	13–15	0.142
			11/13/00	16–17	0.034

$$\ln\left[\left(\frac{^{37}\mathrm{Ar}}{^{36}\mathrm{Ar}_{\mathrm{Ca}}}\right)_{i,j}\Big/\left(\frac{^{37}\mathrm{Ar}}{^{36}\mathrm{Ar}_{\mathrm{Ca}}}\right)_{1,j}\right]=-\lambda\,\tau_{i,j}. \tag{2}$$

For simplicity, we define

$$R_{i,j}\equiv\left(\frac{^{37}\mathrm{Ar}}{^{36}\mathrm{Ar}_{\mathrm{Ca}}}\right)_{i,j}, \tag{3}$$

so that Eq. (2) can be restated as

$$\ln\left[\frac{R_{i,j}}{R_{1,j}}\right]=-\lambda\,\tau_{i,j}. \tag{4}$$

Normalizing each value of $(^{37}\mathrm{Ar}/^{36}\mathrm{Ar})_{i,j}$ to $(^{37}\mathrm{Ar}/^{36}\mathrm{Ar})_{1,j}$ allows determination of *relative* changes in ^{37}Ar/^{36}Ar, enabling simultaneous comparison of all 158 data from all 11 irradiations without regard to possible variability in the nucleogenic ^{37}Ar/^{36}Ar production ratio. This approach also eliminates complications arising from protracted and episodic irradiation histories, which span a significant fraction of the half-life.

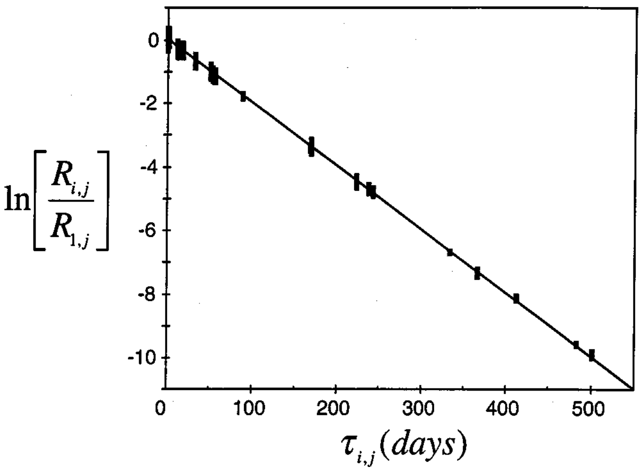

FIG. 1. Decay curve of ^{37}Ar based on 158 measurements of $(^{37}\mathrm{Ar}/^{36}\mathrm{Ar})_{\mathrm{Ca}}$ in CaF$_2$ from 11 different neutron irradiations. Error bars are at 95% confidence. Plot symbols (enlarged 10% vertically and 400% horizontally for legibility) correspond generally to analysis batches as shown in Table II, and include as many as ten replicate measurements (treated individually in the regression) too closely spaced in time to resolve visually at this scale. The regression shown yields a half-life of 34.95 ± 0.08 d (95% confidence).

Figure 1 shows all 158 data from the 11 irradiations. The data define a linear relationship whose slope according to Eq. (2) is equal to $-\lambda$, where λ is the ^{37}Ar decay constant. Regression of these data using the error-weighting method of York [11], as implemented by Ludwig [12], yields a value of $\lambda=0.019830\pm0.000043\,\mathrm{d}^{-1}$ (95% confidence), corresponding to a half-life of 34.954 ± 0.076 d. The regression line has an ordinate intercept of -0.009 ± 0.011, indistinguishable from zero as required by the definition of $\tau_{1,j}$. The mean-squared weighted deviates (MSWD) of the regression is 1.03 (probability = 0.37), indicating that the mean dispersion of data about the line is consistent with that expected due to analytical errors. These results are highly insensitive to the admittedly somewhat arbitrary choice of errors assigned to $\tau_{i,j}$; perturbing these errors by an order of magnitude produces no change in the results. Data from individual irradiations (i.e., for a given j) all yielded results indistinguishable from the pooled data set, but with variable precision resulting mainly from variable ranges (i.e., $\tau_{i\ \max,j}$) in $\tau_{i,j}$. The two subsets of data contributing most to the pooled result, with $\tau_{i\ \max,j}$ of 502 and 483 d, yielded half-life values of 34.951 ± 0.068 and 34.984 ± 0.077 d, respectively. We recommend the pooled regression value of 34.95 ± 0.08 d, based on all 158 individual data, as best representing our data.

Our mass spectrometric data yield a ^{37}Ar half-life value at least twice as precise as all but the most recent of the previous activity-based measurements shown in Table I. At 95% confidence, there is agreement between our data and all previous results except those of Weimer, Kurbatov, and Pool [3] and Kiser and Johnston [5], both of which yielded lower values. The utility of methods involving mass spectrometry for determining decay constants has been exploited for several decades by earth scientists searching for high-precision dating tools. To our knowledge, such experiments have always used ingrowth of a daughter nuclide rather than dimunition of the parent. In more difficult cases, e.g., low-energy β^- emitters such as ^{87}Rb, mass spectrometric methods offer clear advantages over counting experiments (i.e., as discussed by Begemann *et al.* [13]). In such cases, including that of ^{37}Ar, which involves experimentally challenging detection of soft x rays and/or Auger electrons, it would seem desirable for nuclear data evaluations such as ENSDF or NUBASE to expand their literature searches (e.g., Renne, Karner, and Ludwig [14]) and take account of all relevant data.

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[1] C. Merrihue and G. Turner, J. Geophys. Res. **71**, 2852 (1966).
[2] R. Davis, Jr., D. S. Harmer, and K. C. Hoffman, Phys. Rev. Lett. **20**, 1205 (1968).
[3] P. K. Weimer, J. D. Kurbatov, and M. L. Pool, Phys. Rev. **66**, 209 (1944).
[4] J. A. Miskel and M. L. Perlman, Phys. Rev. **87**, 543 (1952).
[5] R. W. Kiser and W. H. Johnston, J. Am. Chem. Soc. **81**, 1810 (1959).
[6] R. W. Stoenner, O. A. Schaeffer, and S. Katcoff, Science **148**, 1325 (1965).
[7] J. Colomer and D. Gauvain, Int. J. Appl. Radiat. Isot. **24**, 391 (1973).
[8] R. Kishore, R. Colle, S. Katcoff, and J. B. Cumming, Phys. Rev. C **12**, 21 (1975).
[9] P. R. Renne *et al.*, Chem. Geol. **145**, 117 (1998).
[10] A. O. Nier, Phys. Rev. **77**, 789 (1950).
[11] D. York, Earth Planet. Sci. Lett. **5**, 320 (1969).
[12] K. R. Ludwig, Berkeley Geochronology Center Special Publication No. 1a, 1999.
[13] F. Begemann *et al.*, Geochim. Cosmochim. Acta **65**, 111 (2001).
[14] P. R. Renne, D. B. Karner, and K. R. Ludwig, Science **282**, 1840 (1998).