Argon-40–Argon-39 Dating of Apollo Sample 15555

Abstract. *An age of 3.33 ± 0.05 × 10⁹ years was obtained for Apollo 15 sample 15555 by argon-40–argon-39 dating. The age of rock 15555, a basalt from the rim of Hadley Rille, establishes an upper limit to the age of the rille. The basalt flows filling the Hadley Rille section of the Imbrium basin postdate the formation of the basin—as measured by the Apollo 14 samples of the Fra Mauro formation—by at least 500 × 10⁶ years. Therefore, the mare basalts cannot be simple impact melts but rather must result from some igneous activity on the moon.*

An ^{40}Ar-^{39}Ar age of $3.33 \pm 0.05 \times 10^9$ years, relative to a monitor age of $4.56 \pm 0.05 \times 10^9$ years, was obtained for Apollo sample 15555. Lunar sample 15555 is the largest moon rock yet returned to the earth. It is a 9.6-kg, brownish-gray, homogeneous, vuggy basalt (*1*). The rock was collected at the edge of Hadley Rille during the third period of extravehicular activity of Apollo 15 and "is believed to be a fragment of bedrock very locally derived" (*1*).

A 0.2361-g piece of sample 15555,22 and a standard were sealed under vacuum in quartz vials and irradiated in a rotating sample container. The irradiation was done in the shuttle tube of the General Electric test reactor (GETR) at the Vallecitos Nuclear Center and is designated Vallecitos 5. The container received a nominal thermal fluence of 3.2×10^{19} neutrons. Cobalt-doped aluminum flux wires were used to monitor flux variations within the irradiation container. The activity of the flux wires indicated that sample and monitor received the same fluence to within 0.5 percent. After the irradiation the sample and monitor were removed from the quartz vials, wrapped in aluminum foil, and placed in a gas extraction system.

The sample was heated by radio-frequency induction heating in a tungsten crucible. The temperature at each extraction step was monitored with a thermocouple [W, Re (3 percent)/W, Re (25 percent)] and is thought to be accurate to ± 10°C. Each temperature step was maintained for 30 minutes, and the gases were exposed to a Ti/Zr getter at 850°C during the heating. After the crucible and getter had cooled, the gases were collected on charcoal at −196°C (liquid nitrogen), the He and Ne were pumped away, and the crucible and getter were shut off from the system by valves. The gas on the charcoal was desorbed and cleaned by a second Ti/Zr getter at 850°C. After the second getter had cooled, the Kr and Xe were collected on the charcoal at −90°C, and the Ar was admitted to the mass spectrometer for analysis.

The argon was statically analyzed in a glass mass spectrometer with a radius of 11.43 cm (*2*), in the direct collector mode. The sensitivity and mass discrimination (a source magnet was used) of the spectrometer were calibrated by running samples (0.0130 cm^3 STP) of air through the complete sample procedure, without the crucible heating. An exponential interpolation of the ^{40}Ar reference peak was used to calculate the isotope ratios, which were then linearly extrapolated to the time the accelerating voltage was turned on.

The argon data from 15555,22 and the St. Severin monitor are shown in Table 1. The ^{37}Ar and ^{39}Ar data have been corrected for radioactive decay. The ^{36}Ar, ^{38}Ar, and ^{40}Ar data have been corrected for blanks. The errors listed in Table 1 are errors of 1 S.D. obtained as the quadratic sums of the statistical errors in the isotope ratios and the corrections listed above. The data for each extraction are subject to an additional error of ± 4 percent due to variations in the sensitivity between analyses.

Figure 1 is a plot of $^{40*}Ar/^{39}Ar$ against $^{37}Ar/^{39}Ar$ for sample 15555 and the St. Severin monitor. Argon-40* is ^{40}Ar corrected for either spallation

Table 1. Argon released during stepwise heating of pile-irradiated lunar sample 15555,22 and from the meteorite, St. Severin. The amounts for isotopes of mass number 37 and 39 have been corrected for decay with $\lambda^{37} = (1.974 \pm 0.0056) \times 10^{-2}$ per day and $\lambda^{39} = (7.05 \pm 0.079) \times 10^{-3}$ per day (*18*). The amounts for isotopes 36, 38, and 40 have been corrected for blank argon of atmospheric composition with $^{40}Ar_{blank} = 2.89 \pm 0.46 \times 10^{-8}$ cm^3 STP. The errors given are the quadratic sums of the errors of 1 S.D. in the corrections listed above with the statistical errors in the measured isotope ratios. The actual concentrations of the isotopes in a particular temperature fraction have an additional error of ± 4 percent due to the vriation of sensitivity between analyses. This sensitivity error does not affect the age calculation and therefore has not been tabulated.

Temperature (C°)	Specific volume (10^{-8} cm^3/g STP)				
	^{36}Ar	^{37}Ar	^{38}Ar	^{39}Ar	^{40}Ar
			St. Severin (0.1852 g)		
800	0.376 ± 0.031	9.387 ± 0.047	0.848 ± 0.075	7.703 ± 0.033	3018.9 ± 5.1
900	0.060 ± 0.031	6.205 ± 0.024	0.273 ± 0.017	3.443 ± 0.026	1447.8 ± 2.6
1000	0.043 ± 0.030	10.092 ± 0.063	0.477 ± 0.022	5.287 ± 0.022	2226.0 ± 3.1
1100	0.049 ± 0.013	17.420 ± 0.041	0.586 ± 0.023	6.383 ± 0.027	2730.3 ± 3.5
1200	0.318 ± 0.042	91.16 ± 0.16	1.885 ± 0.033	3.103 ± 0.032	1274.3 ± 3.0
1300	0.377 ± 0.026	66.63 ± 0.24	0.885 ± 0.015	0.499 ± 0.029	189.7 ± 2.5
1400	0.291 ± 0.019	27.52 ± 0.23	0.466 ± 0.014	0.264 ± 0.015	95.9 ± 2.7
1750	0.134 ± 0.016	5.766 ± 0.053	0.137 ± 0.035	0.071 ± 0.010	26.0 ± 2.5
			Lunar sample 15555,22 (0.2361 g)		
500	0.247 ± 0.015	2.042 ± 0.024	0.195 ± 0.027	0.901 ± 0.009	26.8 ± 2.0
700	1.372 ± 0.023	33.96 ± 0.19	0.747 ± 0.019	3.723 ± 0.040	373.5 ± 2.4
800	3.508 ± 0.014	89.29 ± 0.28	1.779 ± 0.025	2.579 ± 0.018	464.2 ± 2.3
900	4.127 ± 0.040	106.16 ± 0.34	2.093 ± 0.018	1.770 ± 0.010	344.3 ± 2.2
1000	1.724 ± 0.021	99.02 ± 0.36	1.592 ± 0.028	1.394 ± 0.010	265.5 ± 2.0
1100	2.172 ± 0.024	158.68 ± 0.75	2.998 ± 0.025	1.986 ± 0.014	360.0 ± 2.5
1200	4.879 ± 0.055	515.17 ± 4.19	7.565 ± 0.049	1.488 ± 0.011	226.5 ± 2.1
1300	2.672 ± 0.021	294.80 ± 0.49	4.159 ± 0.023	0.632 ± 0.018	85.0 ± 2.0
1400	2.093 ± 0.016	225.12 ± 1.27	3.183 ± 0.026	0.558 ± 0.015	76.7 ± 2.0
1750	0.346 ± 0.021	35.40 ± 0.10	0.4989 ± 0.0084	0.069 ± 0.018	10.3 ± 2.0

or solar-wind argon, or both, with the assumption that $^{40}Ar/^{36}Ar$ is 1.0 ± 0.5 in both spallation and solar wind. The actual equation used is

$$^{40*}Ar = {}^{40}Ar - (1.0 \pm 0.5) [{}^{36}Ar - ({}^{36}Ar/{}^{37}Ar)_{Ca}{}^{37}Ar] \quad (1)$$

The last term in Eq. 1 is introduced to correct for the ^{36}Ar produced from calcium. We used $(^{36}Ar/^{37}Ar)_{Ca} = 3.05 \times 10^{-4}$ from the work of Turner *et al.* (*3*) because their value is for a calcium salt irradiated in the shuttle tube of the GETR, as was our sample. Turner (*4*) has shown that for those temperature fractions in which the $^{40}Ar/K$ ratio is constant, a plot of the type given in Fig. 1 yields a straight line. The *x*- and *y*-intercepts are $(^{37}Ar/^{39}Ar)_{Ca}$ and $(^{40*}Ar/^{39}Ar)_K$, respectively. The ratio $(^{37}Ar/^{39}Ar)_{Ca}$ is for argon derived from calcium and is a function of the irradiation. The ratio $(^{40*}Ar/^{39}Ar)_K$ is for argon derived from potassium and is a function of the sample's age and of the irradiation.

The lower section of Fig. 1 shows the data for 15555,22. Data for 900°C and above were fitted to a straight line according to a modified version of the cubic-least-squares method of York (*5*). The modification consisted of including in the error estimate the uncertainty in the individual data as well as the scatter about the line. The value 1375 ± 132 for $(^{37}Ar/^{39}Ar)_{Ca}$ is in good agreement with the value 1366 ± 28 obtained by Turner *et al.* (*3*) and supports the use of their $(^{36}Ar/^{37}Ar)_{Ca}$ value in Eq. 1.

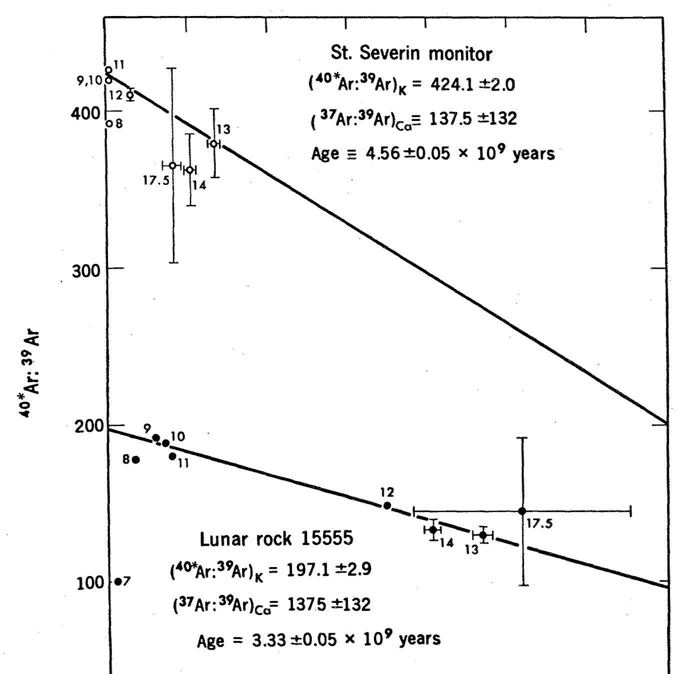
The data for the St. Severin monitor do not contain large enough $^{37}Ar/^{39}Ar$ ratios to define adequately an independent *x*-intercept. The *y*-intercept, which is the value we use in the age calculation, is essentially determined by the 900°, 1000°, and 1100°C points, and is not significantly changed by the choice of any reasonable *x*-intercept. Therefore, as the most reasonable estimate, we require the St. Severin line to pass through the *x*-intercept that was obtained from the 15555 data.

From Fig. 1 we calculate an age of $3.33 \pm 0.05 \times 10^9$ years for sample 15555,22 from the equation

$$T_s = (1/\lambda)\ln[1 + R(e^{\lambda T_m} - 1)] \quad (2)$$

where T_s is the age of the sample, λ is the probability of total decay of ^{40}K ($5.480 \pm 0.010 \times 10^{-10}$ per year) (*6*), T_m is the age of the monitor (taken to be $4.56 \pm 0.05 \times 10^9$ years; see below), and $R = (^{40*}Ar/^{39}Ar)_K$ sample/$(^{40*}Ar/^{39}Ar)_K$ monitor. The statistical errors in R and λ contribute $\pm 0.02 \times 10^9$ years to the error in T_s. The major source of error is the uncertainty in the age of the monitor.

The age of the monitor, the St. Severin meteorite, has not been determined by the ^{40}Ar-^{39}Ar method. A conventional K-Ar age of $4.38 \pm 0.06 \times 10^9$ years has been reported (*7*) for St. Severin. However, Gopalan and Wetherill (*8*) have measured a Rb-Sr age of $4.56 \pm 0.03 \times 10^9$ years (1 S.D. error) for the amphoterite chondrites, including St. Severin. The latter age is



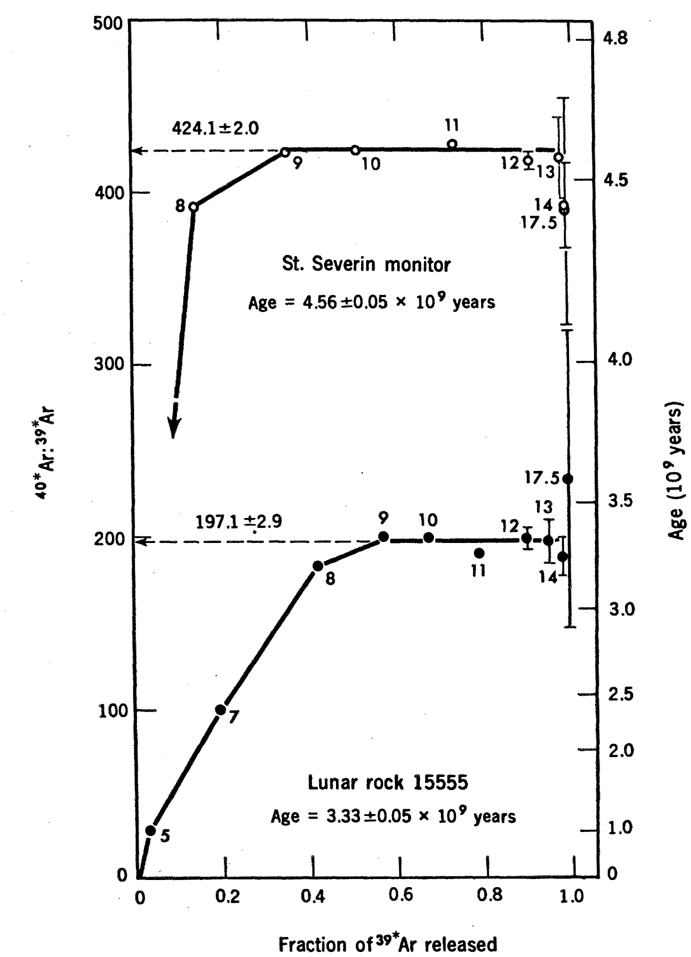


Fig. 1 (left). Argon from neutron-irradiated lunar rock 15555 and St. Severin, a meteorite. Errors of 1 S.D. are either indicated or are smaller than the points. The numbers by the points are the temperatures of those fractions in hundreds of degrees Celsius. The figure is discussed more fully in the text. Fig. 2 (right). Comparative release of ^{40}Ar from the spontaneous decay of ^{40}K and of $^{39*}Ar$ from an (n,p) reaction on ^{39}K for neutron-irradiated lunar rock 15555 and St. Severin, a meteorite. The quantity plotted as the abscissa of the nth extraction of the series of m extractions is given by $(\frac{1}{2}\,{}^{39*}Ar^n + \sum_{i=1}^{n-1}{}^{39*}Ar^i)/\sum_{i=1}^{m}{}^{39*}Ar^i$ (*14*), that is, the point is plotted at the middle of each segment. Errors of 1 S.D. are indicated or are smaller than the points. The numbers by the points are the temperatures of those fractions in hundreds of degrees Celsius. The figure is discussed more fully in the text.

supported by an age of $4.58 \pm 0.09 \times 10^9$ years for St. Severin, which is obtained by combining Podosek's (*9*) observation that St. Severin began to retain ^{129}Xe $7.5 \pm 1.0 \times 10^6$ years after the Bjurbole chondrite with Bjurbole's ^{40}Ar-^{39}Ar age of $4.59 \pm 0.09 \times 10^9$ years [calculated from the data for 580° through 1000°C given in Turner (*10*)]. Therefore, we have assumed the Rb-Sr age of 4.56×10^9 years (*8*) as the age of the monitor and assign an error of $\pm 0.05 \times 10^9$ years (1 S.D.) to allow for the uncertainties involved. Any change in the age assigned to the monitor will propagate to the sample age by a factor of $\delta T_s/\delta T_m = 0.914$.

Figure 2 is a plot of $^{40*}Ar/^{39*}Ar$ and apparent age against the fraction of $^{39*}Ar$ released. Argon-39* is the ^{39}Ar derived from potassium and is given by

$$^{39*}Ar = {}^{39}Ar - ({}^{39}Ar/{}^{37}Ar)_{Ca}\,{}^{37}Ar \quad (3)$$

Sample 15555 has lost 19.7 percent of its $^{40*}Ar$, and the St. Severin monitor has lost 2.2 percent. However, the temperature fractions ≥ 900°C define good "plateaus" in both cases.

Our age of $3.33 \pm 0.05 \times 10^9$ years (relative to an assumed monitor age of $4.56 \pm 0.05 \times 10^9$ years) for sample 15555 is in good agreement with an age of $3.30 \pm 0.05 \times 10^9$ years determined by the same method (*11*). A conventional K-Ar age of $3.32 \pm 0.05 \times 10^9$ years from a plagioclase separate and a Rb-Sr internal isochron age of $3.36 \pm 0.07 \times 10^9$ years also agree (*12*). It should be noted that the K-Ar ages were calculated with slightly different decay constants of ^{40}K, and part of the scatter may be due to this. For instance, when our data for sample 15555 are recalculated with $1/\lambda = 1.90 \times 10^9$ years [which is the value Husain *et al.* (*13*) used for their Apollo 14 work] the age of sample 15555 becomes $3.29 \pm 0.05 \times 10^9$ years, which is almost exactly the value obtained by Husain (*11*) for sample 15555.

If sample 15555 does represent the local bedrock at the edge of Hadley Rille, then $3.33 \pm 0.05 \times 10^9$ years represents an upper limit to the age of the rille. The age of sample 15555 overlaps the older ages reported (*14, 15*) for the Apollo 12 samples from Oceanus Procellarum. The result for sample 15555 tends to support the prediction and interpretation of Soderblom and Lebofsky (*16*), according to whom "the major mare unit at the Apollo 15 landing site is expected to have a crystallization age of $3.5 \pm .1$ billion years." They indicate that the major mare unit at the Apollo 15 site is part of the same spectroscopically "red" (*17*) formation as the Apollo 12 site but is slightly older by their crater-morphology dating technique. However, with only one sample dated the agreement may be coincidental.

If the Fra Mauro samples from Apollo 14 do date the formation of the Imbrium basin (*3, 13, 17*) and if sample 15555 is representative of the basalts filling the Imbrium basin, then the basalts postdate the formation of the basin by at least 500×10^6 years. Therefore, the mare basalts cannot be simple impact melts but must represent igneous activity that occurred long after basin formation.

The age of sample 15555 contrasts sharply with the value of $4.15 \pm 0.2 \times 10^9$ years reported (*11*) for the anorthosite rock 15415 from the mountain-front at the Apollo 15 site. With only two samples dated, it is already apparent that the Apollo 15 astronauts did an excellent job of obtaining samples with a wide range of ages at the Hadley site.

E. C. ALEXANDER, JR.
P. K. DAVIS, R. S. LEWIS
Department of Physics, University of California, Berkeley 94720

Notes and References

1. Lunar Sample Curator, written communication.
2. J. H. Reynolds, *Rev. Sci. Instrum.* **27**, 928 (1956).
3. G. Turner, J. C. Huneke, F. A. Podosek, G. J. Wasserburg, *Earth Planet. Sci. Lett.* **12**, 19 (1971).
4. G. Turner, in "Proceedings of the Apollo 11 Lunar Science Conference," *Geochim. Cosmochim. Acta* **2** (Suppl. 1), 1665 (1970).
5. D. York, *Can. J. Phys.* **44**, 1079 (1966).
6. R. D. Beckinsale and N. H. Gale, *Earth Planet Sci. Lett.* **6**, 289 (1969).
7. J. Funkhouser, T. Kirsten, O. A. Schaeffer, *ibid.* **2**, 185 (1967).
8. K. Gopalan and G. W. Wetherill, *J. Geophys. Res.* **74**, 4349 (1969).
9. F. A. Podosek, *Geochim. Cosmochim. Acta* **34**, 341 (1970).
10. G. Turner, in *Meteorite Research*, P. M. Millman, Ed. (Springer-Verlag, New York, 1969, p. 407.
11. L. Husain, personal communication.
12. G. J. Wasserburg, personal communication.
13. L. Husain, J. F. Sutter, O. A. Schaeffer, *Science* **173**, 1235 (1971).
14. G. Turner, *Earth Planet. Sci. Lett.* **11**, 169 (1971).
15. D. A. Papanastassiou and G. J. Wasserburg, *ibid.* **8**, 269 (1970).
16. L. A. Soderblom and L. A. Lebofsky, *J. Geophys. Res.*, in press.
17. G. J. Wasserburg, J. C. Huneke, D. A. Papanastassiou, F. A. Podosek, F. Tera, G. Turner, "Age determinations on samples from the Apollo 14 landing site," paper presented at the COSPAR meeting, Seattle, Wash., June 1971.
18. R. W. Stoenner, O. A. Schaeffer, S. Katcoff, *Science* **148**, 1325 (1965).
19. We thank Professor J. H. Reynolds for his support and encouragement in this work, Dr. W. A. Kaiser and M. C. Malin for helpful discussions, and G. A. McCrory for technical assistance. Supported by NASA contract NAS 9-9949.

15 November 1971

Rubidium-Strontium and Potassium-Argon Age of Lunar Sample 15555

Abstract. *The lunar mare basalt 15555 from the edge of Hadley Rille has been dated at 3.3 × 10⁹ years by both rubidium-strontium and potassium-argon techniques. Age and trace element abundances closely resemble those of the Apollo 12 mare basalts. Data from lunar basalts obtained thus far indicate that they cannot be derived by simple fractionation from a homogeneous source.*

We report here the age and the abundances of some trace elements for lunar sample 15555. As described in the Lunar Sample Preliminary Examination Team (LSPET) report (*1*), this 9.6-kg rock, collected from the edge of Hadley Rille, is a coarse-grained porphyritic olivine mare basalt and may be related to the layered sequence exposed in the wall of the rille. We received two chips of this sample, chips 15555,12 and 15555,15, weighing 1.04 and 0.52 g, respectively, as part of the early allocation scheme adopted for the distribution of Apollo 15 samples. The samples we received were coarse-grained rocks exhibiting the mineralogy reported by LPSET (*1*), but, contrary to their sample description, they were extremely friable and suffered considerable disintegration during shipment.

Analytical procedures related to sample handling, mineral separations, and mass-spectrometric procedures for Rb-Sr internal isochron age measurement have been described elsewhere (*2*). From sample 15555,12 a plagioclase fraction was handpicked from a fraction with a density $\rho < 2.89$ g/cm³ of $-100 + 125$ mesh size. Aliquots of this handpicked fraction were used both for the Rb-Sr and for the K-Ar dating described below. For the fraction with $\rho > 3.33$ g/cm³ magnetic separation methods were used to obtain moderately pure (~ 90 percent) olivine and pyroxene