

$^{40}\text{Ar}/^{39}\text{Ar}$ TECHNIQUE OF K-Ar DATING: A COMPARISON WITH THE CONVENTIONAL TECHNIQUE*

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Received 10 June 1971
Revised version received 11 August 1971

K-Ar ages have been determined by the $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion technique on 19 terrestrial samples whose conventional K-Ar ages range from 3.4 my to nearly 1700 my. Sample materials included biotite, muscovite, sanidine, adularia, plagioclase, hornblende, actinolite, alunite, dacite, and basalt. For 18 samples there are no significant differences at the 95% confidence level between the K-Ar ages obtained by these two techniques; for one sample the difference is 4.3% and is statistically significant. For the neutron doses used in these experiments ($\approx 4 \times 10^{18}$ nvt) it appears that corrections for interfering Ca- and K-derived Ar isotopes can be made without significant loss of precision for samples with K/Ca > 1 as young as about 5×10^5 yr, and for samples with K/Ca < 1 as young as about 10^7 yr. For younger samples the combination of large atmospheric Ar corrections and large corrections for Ca- and K-derived Ar may make the precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique less than that of the conventional technique unless the irradiation parameters are adjusted to minimize these corrections.

1. Introduction

The new $^{40}\text{Ar}/^{39}\text{Ar}$ technique of K-Ar dating has generated considerable interest in geochronology and the possible applications of this approach are currently being explored in several laboratories. In this technique a known fraction of the ^{39}K in a rock or mineral sample is converted through an n,p reaction to ^{39}Ar by irradiation with fast neutrons and the age is calculated from the ratio $^{40}\text{Ar}/^{39}\text{Ar}$. The method has two variations, the *total fusion* technique, in which the sample is totally fused after irradiation and all of the Ar released is analyzed in a single experiment, and the *incremental heating* or *age spectrum* technique, in which the Ar is released by stepwise heating and which results in a series of apparent ages for one sample. This latter variation is useful in special cases, for example, where some Ar has been lost in a post-crystallization thermal event [1, 2]. This paper is concerned only with the total fusion approach. The prin-

cipal advantages of this new technique over the conventional technique are that only a very small sample is needed, problems of sample inhomogeneity are eliminated, and no elemental abundance measurements are required [3, 4].

The $^{40}\text{Ar}/^{39}\text{Ar}$ technique was first suggested by Sigurgeirsson [5], who not only described the basic technique for total fusion ages but predicted that undesirable Ar isotopes derived from neutron interaction with Ca and K would pose difficulties for dating young rocks. Sigurgeirsson's paper is in Icelandic, however, and a more readily available reference is that of Merrihue [6] to whom the method is generally attributed.

The total fusion $^{40}\text{Ar}/^{39}\text{Ar}$ technique has been used with considerable success on both meteorites [7] and on terrestrial materials [3, 8, 9]. One difficulty with this technique is the production of undesirable or interfering Ar isotopes (^{36}Ar , ^{39}Ar , and ^{40}Ar) by neutron reactions with calcium and potassium. Mitchell [3] found that $^{40}\text{Ar}/^{39}\text{Ar}$ technique K-Ar ages on high K, low Ca samples agreed well with those determined by the conventional technique and con-

* Publication authorized by the Director, U.S. Geological Survey.

cluded that the $^{40}\text{Ar}/^{39}\text{Ar}$ technique could be successfully applied to minerals as young as 1 my old provided their K/Ca ratio was greater than one. Berger and York [9] applied the technique to a 1 billion-year-old basalt and concluded that basaltic rocks more than 100 my old could be dated without appreciable interference from undesirable Ar isotopes. Brereton [10] suggested a way in which appropriate corrections could be made for these interfering Ar isotopes, but did not apply them to age data. Turner [4] has shown theoretically that these corrections can be minimized, if not eliminated, for samples of any age and K/Ca ratio by appropriate choice of irradiation parameters; this approach, while theoretically correct, may suffer from some practical difficulties that will be discussed later.

Although various authors have discussed the problems and methods of making corrections for undesirable Ar isotopes, all of the published total fusion $^{40}\text{Ar}/^{39}\text{Ar}$ ages known to us have been obtained on materials for which these corrections were either small or negligible and could be ignored (i.e., old samples and/or samples with high K/Ca ratios). Thus the actual range of applicability of this technique, the limitations imposed by the corrections for Ca- and K-derived Ar isotopes, and the precision with which these corrections can be made have not been demonstrated experimentally. The purpose of our experiment was to test the applicability of the total fusion $^{40}\text{Ar}/^{39}\text{Ar}$ technique of K-Ar dating to samples of various ages and K/Ca ratios for which conventional K-Ar ages were available. No attempt was made to minimize the corrections for interfering Ca- and K-derived Ar [4] because we were primarily interested in determining whether or not these corrections could be applied successfully to materials commonly used for conventional K-Ar dating without introducing an unacceptable loss of precision or accuracy. Throughout this paper we use the term *conventional technique* to indicate that Ar has been measured by isotope dilution and that K has been measured by one of the standard chemical or instrumental methods, such as isotope dilution, flame photometry, or X-ray fluorescence.

2. Techniques

Irradiations were made in the central thimble

(core) of the U.S. Geological Survey TRIGA reactor. The TRIGA is a light water-cooled and water-reflected reactor that uses U-ZrH fuel-moderator elements and is designed for continuous operation at 1 Mw. The cadmium ratio (total flux/fast flux for fast neutron energies greater than 0.4 eV) in the center of the core of the reactor is 9.24, and the fast/thermal flux ratio is 1.17 for fast neutron energies greater than 0.6 MeV.

The samples in this study were irradiated in four separate reactor experiments for 40 hr at 1 Mw and received a neutron dose of approximately 4×10^{18} nvt. During irradiation the maximum temperature to which the samples are subjected is less than 50°C .

Each sample was sealed in air in a fused silica vial and the vials were arranged on one to three levels in an aluminum tube, seven vials, arranged in hexagonal symmetry, to a level. The samples ranged in size from about 0.1 to 0.5 g. A 160.2-million-year-old biotite was used as the flux monitor. This biotite, separated from a quartz diorite (sample 62ALe-1) from the Aleutian Range, Alaska [11], has $8.84 \pm 0.03\%$ K_2O (13 analyses) and $(2.183 \pm 0.006) \times 10^{-9}$ mol $^{40}\text{Ar}_{\text{rad}}/\text{g}$ (14 analyses) where the analytical uncertainties are standard errors of the mean. Each level of samples contained at least one monitor, placed in the center of the surrounding six samples. On four occasions, two monitors were used, one in the center and one on the outside. The data from these duplicate monitors were averaged and agreed within 1.7% or better; the small differences observed may be due to horizontal gradients in the neutron flux.

The irradiated samples were fused in a conventional argon extraction system [12] and the purified argon was analyzed with either a 4½-inch radius Reynolds-type or a 6-inch radius Nier-type mass spectrometer. The measured isotope ratios were corrected for mass spectrometer discrimination, and the age of the unknown sample (t_u) was calculated using

$$t_u = \frac{1}{\lambda} \log_e (1 + F \cdot J) \quad (1)$$

where λ , the decay constant of ^{40}K , is $5.305 \times 10^{-10} \text{ yr}^{-1}$, and $F = (^{40}\text{Ar}_{\text{rad}}/^{39}\text{Ar}_{\text{K}})_u$, which is the ratio of radiogenic ^{40}Ar to K-derived ^{39}Ar in the unknown. J is a function of the age of the monitor (t_m) and of the integrated fast neutron flux and is given by

$$J = \frac{e^{\lambda t_m} - 1}{(^{40}\text{Ar}/^{39}\text{Ar})_{\text{rad}} / (^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}})_m} \quad (2)$$

[13]. For samples that are sufficiently old and have high K/Ca ratios, the measured ratio $^{40}\text{Ar}/^{39}\text{Ar}$ need be corrected only for atmospheric Ar contamination to obtain F . That is,

$$F = A - C_1 B \quad (3)$$

where A is the measured ratio $^{40}\text{Ar}/^{39}\text{Ar}$, B is the measured ratio $^{36}\text{Ar}/^{39}\text{Ar}$, and $C_1 = 295.5$, which is the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the atmosphere. A more generalized form of this expression, which takes into account the corrections for K-derived ^{40}Ar and Ca-derived ^{36}Ar and ^{39}Ar is

$$F = \frac{A - C_1 B + C_1 C_2 D - C_3}{1 - C_4 D} \quad (4)$$

where $D =$ the ratio $^{37}\text{Ar}/^{39}\text{Ar}$ in the unknown sample after correcting for the decay of ^{37}Ar , and the correction factors for interfering Ar isotopes are $C_2 = (^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$, $C_3 = (^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$, and $C_4 = (^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$. The subscripts K and Ca refer to the ratio of Ar isotopes that is produced by neutron interactions with potassium and calcium, respectively. Eq. (4) is similar to the one derived by Brereton [10] except for a term in the numerator, $C_4 C_3 D$, which is on the order of 10^{-6} and has been dropped because it is negligible.

3. Correction factors for Ca- and K-derived Ar isotopes

An inherent difficulty in applying the $^{40}\text{Ar}/^{39}\text{Ar}$ technique is the necessity of applying corrections for Ar isotopes produced or removed during irradiation by reactions other than the $^{39}\text{K}(n,p)^{39}\text{Ar}$ reaction. The major reactions that will produce Ar isotopes in irradiated samples have been tabulated and discussed by Turner [4] and Brereton [10]. Turner [4] has shown that there are only three principal sources of interference – K-derived ^{40}Ar and Ca-derived ^{36}Ar and ^{39}Ar .

Correction factors for Ca- and K-derived Ar produced in the U.S. Geological Survey TRIGA reactor

were determined by measuring the isotopic composition of Ar produced in samples of irradiated Ca and K salts. The samples were analyzed before irradiation and, within experimental error, yielded Ar of atmospheric composition. Four samples of CaF_2 optical-grade crystals and three samples of reagent-grade K_2SO_4 crystals were irradiated for 80 hr at 1 Mw in the core of the TRIGA ($\approx 8 \times 10^{18}$ nvt). The samples were then fused and the purified Ar was analyzed on the mass spectrometer. The values obtained (table 1) have been corrected for the decay of ^{37}Ar (half-life = 35.1 days) during and after irradiation and for atmospheric Ar contamination assuming that all of the ^{36}Ar in the irradiated K_2SO_4 and all of the ^{40}Ar in the irradiated CaF_2 were atmospheric. These assumptions may not be correct but were made in order to compare our data on irradiated salts with those of other workers (table 1). It is important to note, however, that the assumptions do not introduce any errors in the age calculations because their effect cancels out in eq. (4).

The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios obtained from the irradiated CaF_2 ranged from 15.8 to 58.8, indicating apparent percentages of atmospheric ^{36}Ar (relative to total ^{36}Ar) ranging from 5.4 to 19.9. These atmospheric corrections are much smaller than those indicated by the data of Mitchell [3] and Berger and York [9]. The standard errors of the mean of our values for $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ and $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ are 0.51% and 0.35%, respectively (table 1). For the irradiated K_2SO_4 the apparent atmospheric ^{40}Ar ranges from 65.8% to 79.2% and the standard error of the mean for $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$ is 7.1%. Again, these atmospheric Ar contributions are lower by about a factor of two or more than those indicated by the data of other workers [3, 9], but still further improvements would be desirable. We cannot compare our results with those of Brereton [10] because his data contain insufficient information.

Because of the relatively small contribution of atmospheric Ar to the CaF_2 and K_2SO_4 analyses, it is possible to place useful upper limits on the production ratios $(^{40}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ and $(^{36}\text{Ar}/^{39}\text{Ar})_{\text{K}}$ by neglecting the atmospheric Ar. ^{40}Ar can be produced from calcium by the $^{43}\text{Ca}(n,\alpha)^{40}\text{Ar}$ reaction. From nuclear systematics and natural isotope abundances Turner [4] has estimated a value of 3×10^{-3} for $(^{40}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$. The lowest value measured by us for

Table 1
Correction factors for Ca- and K-derived Ar.

Reference	Method	$(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ $\times 10^{-4}$	$(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ $\times 10^{-4}$	$(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$
This work	CaF ₂ , K ₂ SO ₄	2.72 ± 0.014	6.33 ± 0.043	0.0059 ± 0.00042
Brereton [10]	CaF ₂ , K ₂ SO ₄	2.47 ± 0.088	7.19 ± 0.24	0.0123 ± 0.0024
Berger and York [9]	CaCO ₃ , K ₂ SO ₄	2.7 ± 0.3	8.5 ± 0.4	0.031 ± 0.007
Mitchell [3]	CaCO ₃ , K ₂ SO ₄	2.1	30.1	0.0064
Turner [1]	Correlation diagram		8.0 ± 0.5	

$^{40}\text{Ar}/^{37}\text{Ar}$ from the CaF₂ is 4.6×10^{-3} which is in good agreement with Turner's estimate. ^{36}Ar may be produced from potassium by the $^{39}\text{K}(n, \alpha)^{36}\text{Cl}$ reaction and subsequent decay of ^{36}Cl to ^{36}Ar with a half life of 3×10^5 yr. Turner [4] has estimated

$$(^{36}\text{Ar}/^{39}\text{Ar})_{\text{K}} \lesssim 10^{-6} \Delta t$$

where Δt is the time in years since irradiation. Again neglecting atmospheric Ar contamination our lowest measured value of $^{36}\text{Ar}/^{39}\text{Ar}$ for the K₂SO₄ analyses is 3.4×10^{-5} which, when corrected for the time since irradiation, gives an upper limit of $6 \times 10^{-4} \Delta t$ for $(^{36}\text{Ar}/^{39}\text{Ar})_{\text{K}}$.

The values for Ca-derived Ar determined by us are in reasonable agreement with those of other workers (table 1) considering the differences in neutron energy spectra for the various reactors. An exception is the value of 30.1×10^{-4} reported by Mitchell [3] for $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$, which appears to be anomalous, especially since the experiments of both Brereton [10] and Turner [1], who found lower values (table 1), were done in the same reactor. Values for $^{40}\text{Ar}/^{39}\text{Ar}_{\text{K}}$ vary by a factor of 5, perhaps because of differences in the energy spectra of the reactors used by different workers, or difficulty in making large atmospheric Ar corrections, or both. The $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$ ratio appears to decrease with increasing flux spectrum hardness as expected from nuclear systematics [4].

The magnitude of the interference from K-derived ^{40}Ar on the calculated age is a function of integrated neutron flux and age [4]. For the 40-hr irradiation time used in this study, the interference produces an effect of approximately 0.1 my at all ages. Even a 10% error in the correction factor $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$ would contribute a negligible uncertainty to the calculated age.

The effect of Ca-derived ^{39}Ar is a function of the

K/Ca ratio of the material and is independent of integrated neutron flux and essentially independent of age [4]. In our experiments, this interference produces an effect less than 1% for materials having K/Ca ratios as low as 0.05, and the effect is negligible for materials having high K/Ca ratios. Even a 50% error in the correction factor $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ would contribute a negligible uncertainty to the calculated age.

The most serious interference is produced by Ca-derived ^{36}Ar . This interference is a function of integrated neutron flux, age, and K/Ca ratio. The effect of the interference becomes larger as the integrated neutron flux increases, as the age of material decreases, and as the K/Ca ratio of the material decreases [4]. For samples like those used in this study, the Ca-derived ^{36}Ar can produce errors of many hundred percent in the calculated age if a correction for the interference is not applied. Errors in the way in which this correction is applied may add significant uncertainties to the calculated ages and, as discussed later, may limit the precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique for young samples with low K/Ca ratios. Even so, the error in the correction factor $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ (table 1) is probably negligible compared with the error in measuring the relevant isotope ratios in a single unknown sample.

4. Estimates of analytical precision

Systematic methods for estimating the analytical precision of conventional K-Ar ages have been developed [14, 15] and have proved invaluable in assessing the quality of individual age data. We have developed a similar method for estimating the analytical error in K-Ar ages obtained by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique that takes into account the errors introduced by the at-

atmospheric Ar correction as well as the errors introduced by the corrections for interfering K- and Ca-derived Ar isotopes. If we neglect systematic errors in the correction factors (this is probably justified – see preceding section) and consider only the nonsystematic errors in the measured isotope ratios of the sample, then the estimated error in F may be obtained by differentiating eq. (4)

$$\Delta F \cong dF = \frac{\partial F}{\partial A} \Delta A + \frac{\partial F}{\partial B} \Delta B + \frac{\partial F}{\partial D} \Delta D \quad (5)$$

$$= \frac{(1-C_4D)\Delta A - C_1(1-C_4D)\Delta B + [C_4(A-C_1B-C_3) + C_1C_2] \Delta D}{(1-C_4D)^2} \quad (6)$$

The quantity $(1-C_4D) \cong 1$ and C_4C_3 is on the order of 10^{-6} and is negligible, so eq. (6) can be simplified to

$$\Delta F \cong dF \cong \Delta A - C_1 \Delta B + [C_4A - C_1C_4B + C_1C_2] \Delta D \quad (7)$$

The variance in ΔF may then be approximated by

$$\sigma_F^2 \cong \frac{A^2 \sigma_A^2 + C_1^2 B^2 \sigma_B^2 + [C_4A - C_1C_4B + C_1C_2]^2 D^2 \sigma_D^2}{F^2} \quad (8)$$

where σ_A^2 , σ_B^2 , and σ_D^2 are the estimated variances, in percent, of the isotope ratios A , B , and D , respectively [16]*. The estimated analytical error in the calculated age of the unknown can be obtained by using a similar approach on the $^{40}\text{Ar}/^{39}\text{Ar}$ technique age eq. (1) with the result

$$\sigma_{t_u} \cong \left[\frac{J^2 F^2 (\sigma_F^2 + \sigma_J^2)}{t_u^2 \lambda^2 (1 + FJ)^2} \right]^{1/2} \quad (9)$$

where the variances of $F(\sigma_F^2)$ and $J(\sigma_J^2)$ are expressed in percent. This equation is equivalent to the one of Berger and York [9].

The analytical precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ tech-

nique age data in this paper has been estimated using eqs. (8) and (9) and a figure of 1% for σ_J .

5. Results

The analytical data and the calculated ages for the samples studied are shown in tables 2 and 3, respectively. The ages obtained by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique have been calculated in two ways in order to show most easily the effect of interfering Ar isotopes derived from Ca and K (table 3). The ages in the column headed 'uncorrected' were calculated using eqs. (1) and (3), making the assumption that the only source of interfering isotopes was atmospheric Ar. The ages in the column headed 'corrected' were calculated using eqs. (1) and (4), which take into account Ca- and K-derived Ar isotopes as well as atmospheric Ar contamination. The last three columns in table 2 contain data that show the approximate contributions to the argon mass spectra of Ca- and K-derived isotopes. These percentages were calculated with the assumption that all of the ^{36}Ar in the irradiated K_2SO_4 and all of the ^{40}Ar in the irradiated CaF_2 were of atmospheric origin.

In most cases, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique ages were measured on the same mineral concentrate as the conventional K-Ar ages used for comparison (table 3). Six of the conventional K-Ar ages, however, require some explanation. The age of Bern 4M does not appear to be well known, as reported values for this standard vary from 10.19 to 10.63% for K_2O and from 2.115×10^{-10} to 2.901×10^{-10} mol $^{40}\text{Ar}_{\text{rad}}/\text{g}$. For the conventional K-Ar age we have used the means of the K_2O and Ar values compiled for the Colloquium on the Geochronology of Phanerozoic Orogenic Belts held in Bern, Switzerland in 1969, which yield a K-Ar age of 17.6 ± 1.4 my. Two Ar measurements (mean = 2.863×10^{-10} mol $^{40}\text{Ar}_{\text{rad}}/\text{g}$) and three K_2O (mean = 10.38%) measurements previously reported by us [17] gave a calculated age of 18.7 my. A more recent argon determination in our laboratory gives a value of 2.747×10^{-10} mol $^{40}\text{Ar}_{\text{rad}}/\text{g}$ and, using our earlier K_2O values, a calculated age of 17.8 my, which is in better agreement with the 'international' mean and with our $^{40}\text{Ar}/^{39}\text{Ar}$ age of 17.4 my. For B3203 we have calculated an age of 978 ± 11 my from the values reported in the most recent compilation [18], now

* Our colleague, J.D. Obradovich, has suggested the alternate form $\sigma_F^2 \cong [A^2 \sigma_A^2 + C_1^2 B^2 \sigma_B^2 + (C_1 C_2 + F C_4)^2 D^2 \sigma_D^2] / F^2 (1 - C_4 D)^2$, which, except for the simplifying assumptions discussed above (i.e., $C_4 C_3 \cong 0$, $1 - C_4 D \cong 1$), is equivalent.

Table 2
Analytical data for $^{40}\text{Ar}/^{39}\text{Ar}$ technique K-Ar ages.

No.	Measured ratios			J^*	% $^{40}\text{Ar}_{\text{rad}}^{**}$	% $^{40}\text{Ar}_{\text{K}}^{**}$	% $^{36}\text{Ar}_{\text{Ca}}^{**}$	% $^{39}\text{Ar}_{\text{Ca}}^{**}$
	$^{40}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}^{**}$	$^{36}\text{Ar}/^{39}\text{Ar}$					
P-207	5.56	0.00658	0.00485	0.01078	74.1	0.1	0	0
P-207	4.22	0.00320	0.00215	0.01224	84.8	0.1	0	0
Bern 4M	1.484	0.00466	0.00229	0.01155	54.0	0.4	0.1	0
ZL-3	61.8	0.0945	0.00322	0.01224	98.5	0	0.8	0
B3203	55.3	0.0575	0.00236	0.01224	98.7	0	0.7	0
W25	0.880	0.0220	0.00148	0.01078	49.7	0.7	0.4	0
JHGR-671	3.87	0.0166	0.00147	0.01106	88.7	0.2	0.3	0
W17	1.263	0.0602	0.00165	0.01078	61.3	0.5	1.0	0
RC-D1B	0.450	0.00259	0.000246	0.01155	82.6	1.3	0.3	0
8L-777	12.44	3.809	0.01069	0.01106	77.0	0	9.7	0.2
H64-148A	3.08	8.25	0.00738	0.01202	50.5	0.2	30.4	0.5
CAA-12	136.6	11.17	0.0607	0.01224	87.5	0	5.0	0.7
64AE-98	14.86	24.19	0.0274	0.01155	58.6	0	24.0	1.5
66CLE-18	8.79	4.12	0.00529	0.01155	85.9	0.1	21.2	0.3
70-7	26.06	41.1	0.0777	0.01202	24.5	0	14.4	2.6
199-127	3.43	0.00678	0.00852	0.01155	26.4	0.2	0	0
69ACy-163b	3.54	0.0695	0.00174	0.01106	85.5	0.2	1.1	0
W3	0.689	3.32	0.00207	0.01202	49.1	0.9	43.6	0.2
509-62-5-7	0.816	1.502	0.00259	0.01078	20.3	0.7	15.8	0.1

* Corrected for ^{37}Ar decay.

** % $^{40}\text{Ar}_{\text{rad}}$ = percent ^{40}Ar that is radiogenic, % $^{36}\text{Ar}_{\text{Ca}}$ = percent ^{36}Ar that is Ca-derived, and so forth; calculated using assumptions discussed in text.

nearly 10 years old. Four Ar and two K_2O analyses of this standard done in our laboratory give a calculated age of 995 ± 21 my [17], which still is not different from the $^{40}\text{Ar}/^{39}\text{Ar}$ age at the 95% level of confidence. For biotite W25 we have reported two conventional ages for comparison. These are on biotite concentrated from separate hand samples collected at the same outcrop [19]. The $^{40}\text{Ar}/^{39}\text{Ar}$ technique age was obtained using the same mineral concentrate that gave the conventional age of 9.35 my. For sample JHGR-671 we have obtained a $^{40}\text{Ar}/^{39}\text{Ar}$ age on a mixture of plagioclase and sanidine in addition to the sanidine age shown in table 3. From the K_2O values of this mixture and of the pure sanidine concentrate, we estimate that the plagioclase component comprises between 17 and 24 weight percent of the sample if we assume that the plagioclase contains between 0.2 and 1.0% of K_2O . The $^{40}\text{Ar}/^{39}\text{Ar}$ age on this mixture is 68.7 ± 1.2 my, which is in good agreement with the $^{40}\text{Ar}/^{39}\text{Ar}$ age of 70.3 ± 1.1 my for the pure sanidine concentrate. Conventional measurements on horn-

blende sample CAA-12 yielded a calculated K-Ar age of 1622 my. However, additional K-Ar and U-Pb zircon data from the same rock and from other localities within the same intrusive body indicate that the age of the pluton is about 1690 my [20] and it is this age that is used for comparison in table 3. The basalt sample 509-62-5-7 is from a hand specimen that was intensively studied by Dalrymple and Hirooka [21]. The conventional K-Ar age of 3.42 ± 0.06 is the mean of 12 conventional K-Ar ages on small pieces from this hand specimen. The mean K-Ar age of seven different hand specimens collected within a lateral distance of about 3 km from the same basalt is 3.32 ± 0.07 my.

Eleven of the samples studied have $\text{K}/\text{Ca} > 1$, and for these the corrections for Ca-derived Ar are either negligible or, for samples whose age is less than about 10 my, small. For samples with $\text{K}/\text{Ca} < 1$ the corrections for Ca-derived Ar varies in severity but are significant for all but hornblende CAA-12 whose age is 1690 my. Even for samples with ages of the order of

Table 3
Comparison of $^{40}\text{Ar}/^{39}\text{Ar}$ technique and conventional technique K-Ar ages.

No.	Material	K/Ca** (mol/mol)	$^{40}\text{Ar}/^{39}\text{Ar}$ ages* (10^6 years)		Conventional ages	
			Uncorrected	Corrected	10^6 years	Ref.
P-207	muscovite	136	82.1	82.0 ± 1.4	81.0 ± 2.1	[22]
P-207	muscovite	136	80.9	80.8 ± 0.9	81.0 ± 2.1	[22]
Bern 4M	muscovite	79	17.5	17.4 ± 0.3	17.6 ± 1.4	[23]
ZL-3	biotite	18.2	1049	1049 ± 10	1046 ± 7	[24]
B3203	biotite	56	964	964 ± 8	978 ± 11	[18]
W25	biotite	17.5	8.94	8.86 ± 0.18	{ 9.35 ± 0.37 9.01 ± 0.27 }	[19]
JHGR-671	sanidine	25.3	70.4	70.3 ± 1.1	72.8 ± 1.5	†
W17	sanidine	7.9	15.7	15.7 ± 0.2	15.8 ± 0.40	[19]
RC-D1B	adularia	159	8.19	8.07 ± 0.10	7.74 ± 0.09	††
8L777	plagioclase	0.137	184.2	190.3 ± 2.2	193 ± 6	†
H64-148A	plagioclase	0.063	20.2	35.1 ± 1.1	33.7 ± 1.3	†
CAA-12	hornblende	0.054	1691	1707 ± 15	1690	[20]
64AE-98	hornblende	0.026	141.8	183.2 ± 5.8	179 ± 5	[11]
66CLe-18	hornblende	0.149	151.1	158.0 ± 3.8	157 ± 5	[25]
70-7	actinolite	0.142	69.0	143.2 ± 7.9	153 ± 6	[26]
199-127	alunite	57.2	19.8	19.6 ± 0.6	20.7 ± 0.4	[27]
69ACy-163b	dacite	6.85	62.2	62.2 ± 0.7	62.5 ± 2	
W3	basalt	0.157	1.76	7.67 ± 0.30	7.43 ± 0.16	[19]
509-62-5-7	basalt	0.32	1.03	3.36 ± 0.48	3.42 ± 0.06	[21]

* 'Uncorrected' ages were calculated using formula (3) assuming that all of the ^{36}Ar was atmospheric Ar. 'Corrected' ages are corrected for K- and Ca-derived Ar isotopes and for atmospheric Ar using eqs. (1) and (4). The ± figures for $^{40}\text{Ar}/^{39}\text{Ar}$ ages are estimates of analytical precision at the 68% confidence level (see text). The ± figures for the conventional K-Ar ages were taken from the reference cited; where not specified, we have assumed that they were a standard deviation of precision; those for the unpublished data were estimated using the method of Cox and Dalrymple [14].

** K analyses by flame photometry, Ca analyses by atomic absorption.

† U.S. Geological Survey, unpublished data.

†† Miles Silberman, unpublished data.

10^8 yr, these corrections are essential. For example, for hornblende 64AE-98, the correction for Ca-derived ^{36}Ar increases the calculated age by more than 20% and brings the $^{40}\text{Ar}/^{39}\text{Ar}$ technique age into agreement with the conventional K-Ar age (table 3). Even in the most extreme example, basalt sample W3, where the corrections make a difference in the age of many hundred percent, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique age still is in satisfactory agreement with the conventional technique age.

With only one exception, there are no significant differences, at the 95% confidence level, between K-Ar ages obtained by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique and those obtained by the conventional technique. For adularia RC-D1B the two ages differ by 4.3% which is statistically significant.

Berger and York [9] and Turner [4] have claimed that the potential precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique is greater than the precision of the conventional method because the $^{40}\text{Ar}/^{39}\text{Ar}$ technique eliminates problems of sample inhomogeneity and relies upon measurements of isotope ratios rather than the measurement of isotope amounts. In view of this, it is worthwhile to consider the effect of the corrections for interfering Ca- and K-derived Ar on the precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique for our 40 hr irradiations in the U.S. Geological Survey TRIGA. Inspection of eqs. (4) and (8) indicates that uncertainties introduced by the corrections for K-derived ^{40}Ar and Ca-derived ^{39}Ar will be very small or negligible for all but very young samples ($< 5 \times 10^5$ yr). Uncertainties introduced by errors in the correction for Ca-derived ^{36}Ar

are far more serious. In the two most extreme cases examined by us, basalt samples W3 and 509-62-5-7, this correction contributes about the same uncertainty to the calculated age as would a 75% atmospheric Ar correction. For W3 the calculated standard deviation (table 3) is still only a few percent and is not unacceptably large compared with the calculated error for the conventional age measurement. For 509-62-5-7, however, the atmospheric Ar correction and the correction for Ca-derived ^{36}Ar combine to produce a calculated error that is significantly larger than the calculated error for a single age measurement by the conventional technique on the same material [21]. While the precision of this new technique is potentially better than the precision of the conventional method for samples with ages greater than about 10^8 yr or with high K/Ca ratios, this is probably not true for young samples (approximately $< 10^7$ yr) with low K/Ca ratios. Here, large atmospheric Ar corrections and large corrections for Ca-derived ^{36}Ar may sometimes combine to yield results that may have poorer precision than results obtained by the conventional K-Ar technique.

Turner [4] has suggested that the corrections for interfering Ar isotopes can be made very small or negligible by adjusting the irradiation parameters. For young rocks the integrated fast neutron flux must be decreased, which means that larger samples must be used in order to obtain ^{39}Ar in sufficient quantity. As Turner points out, however, it is essential that the monitor and all parts of the sample receive the same integrated fast neutron flux. For larger samples, flux gradients within the reactor make this condition more difficult to meet than with small samples [4]. Another practical difficulty is encountered when it is either more convenient or necessary to irradiate samples of different age and K/Ca ratio at the same time. The irradiation time cannot be adjusted to suit all of the samples, and this factor may be important for workers whose access to a reactor is limited. For most samples normally dated, we see no immediate difficulty or significant loss of precision in using a single, appropriate irradiation time for a variety of samples and simply applying the corrections for the interfering Ar isotopes. For samples with low K/Ca ratios and ages less than a few million years, however, careful adjustment of irradiation parameters [4] may be essential if the method is to yield satisfactory re-

sults. It is worth noting that had basalt samples W3 and 509-62-5-7 been irradiated a factor of 10 less, the effect of the corrections for Ca-derived isotopes on the precision of the analyses would have been greatly reduced and the precision of the calculated ages would have been comparable to the conventional analyses.

In conclusion, we feel that the total fusion $^{40}\text{Ar}/^{39}\text{Ar}$ technique can be applied successfully, without significant loss of precision, to all materials normally used for K-Ar dating and over nearly the entire age range encountered in most geochronologic studies. For older samples, the technique may be more precise than the conventional technique but this has yet to be demonstrated. The corrections for the interfering Ca- and K-derived Ar isotopes can be made easily and precisely once the appropriate correction factors are known. Provided that a reactor is readily available, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique is technically simpler than the conventional technique because the necessity for an ^{38}Ar tracer and for an independent potassium analysis is eliminated once an accurate monitor age has been determined by the conventional method. In our experience, the problems of handling the radioactive samples are minor. For very young rocks ($< 10^6$ yr) the applicability of this technique is less certain but the possibility, as yet untested, of significantly reducing the atmospheric argon contamination in such samples by incremental heating, as suggested by Merrihue and Turner [7], is promising.

Acknowledgements

We wish to thank G.P. Kraker and the operational staff of the U.S. Geological Survey reactor facility for supplying the large number of neutrons required for this study, S.J. Kover for assistance with the argon extractions, L.B. Schlocker and C.O. Ingamells for providing the K and Ca analyses for the ratios in table 3, and M.L. Silberman and R.E. Zartman for generously supplying some of the samples used for this study. We also would like to thank Derek York for reviewing the manuscript and for useful discussion concerning the $^{40}\text{Ar}/^{39}\text{Ar}$ technique prior to the initiation of this research, and J.D. Obradovich, M.L. Silberman, Grenville Turner, and two anonymous reviewers for their helpful comments.

References

- [1] G. Turner, Argon-40/argon-39 dating of lunar rock sample, *Geochim. Cosmochim. Acta, Lunar Sci. Conf. Supplement 2* (1970) 1665.
- [2] F.J. Fitch, J.A. Miller and J.G. Mitchell, A new approach to radio-isotopic dating in orogenic belts, in: *Time and Place in Orogeny*, P.E. Kent, G.E. Satterthwaite and A.M. Spencer, eds., *Geol. Soc. London Spec. Pub.* 3 (1969) 157.
- [3] J.G. Mitchell, The argon-40/argon-39 method for potassium-argon age determination, *Geochim. Cosmochim. Acta* 32 (1968) 781.
- [4] G. Turner, Argon 40-argon 39 dating: The optimization of irradiation parameters, *Earth Planet. Sci. Letters* 10 (1971) 227.
- [5] Thorbjörn Sigurgeirsson, Dating recent basalt by the potassium argon method (in Icelandic), Rept. Physical Laboratory of the Univ. Iceland (1962) 9p.
- [6] Craig Merrihue, Trace element determinations and potassium-argon dating by mass spectroscopy of neutron-irradiated samples (abs.), *Trans. Am. Geophys. Un.* 46 (1965) 125.
- [7] C. Merrihue and G. Turner, Potassium-argon dating by activation with fast neutrons, *J. Geophys. Res.* 71 (1966) 2852.
- [8] D. York and G.W. Berger, $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations on nepheline and basic whole rocks, *Earth Planet. Sci. Letters* 7 (1970) 333.
- [9] G.W. Berger and D. York, Precision of the $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique, *Earth Planet. Sci. Letters* 9 (1970) 39.
- [10] N.R. Brereton, Corrections for interfering isotopes in the $^{40}\text{Ar}/^{39}\text{Ar}$ dating method, *Earth Planet. Sci. Letters* 8 (1970) 427.
- [11] B.L. Reed and M.A. Lanphere, Age and chemistry of Mesozoic and Tertiary plutonic rocks in south-central Alaska, *Geol. Soc. Am. Bull.* 80 (1969) 23.
- [12] G.B. Dalrymple and M.A. Lanphere, *Potassium-Argon Dating: Principles, Techniques, and Applications to Geochronology* (Freeman and Company, San Francisco, 1969).
- [13] R.L. Grasty and J.G. Mitchell, Single sample potassium-argon ages using the omegatron, *Earth Planet. Sci. Letters* 1 (1966) 121.
- [14] A. Cox and G.B. Dalrymple, Statistical analysis of geomagnetic reversal data and the precision of potassium-argon dating, *J. Geophys. Res.* 72 (1967) 2603.
- [15] A.K. Baksi, D. York and N.D. Watkins, Age of the Steens Mountain geomagnetic polarity transition, *J. Geophys. Res.* 72 (1967) 6299.
- [16] E.L. Crow, F.A. Davis and M.W. Maxfield, *Statistics Manual* (Dover Publications, Inc., New York, 1960).
- [17] M.A. Lanphere and G.B. Dalrymple, P-207: An interlaboratory standard muscovite for argon and potassium analyses, *J. Geophys. Res.* 70 (1965) 3497.
- [18] P.M. Hurley, ed., Variations in isotopic abundance of strontium, calcium, and argon and related topics, M.I.T. Dept. Geol. and Geophys. Tenth Ann. Progress Report (1962) 153 p.
- [19] G.B. Dalrymple, A. Cox, R.R. Doell and C.S. Grommé, Pliocene geomagnetic polarity epochs, *Earth Planet. Sci. Letters* 2 (1967) 163.
- [20] M.A. Lanphere, Geochronology of the Yavapai Series of central Arizona, *Can. J. Earth Sci.* 5 (1968) 757.
- [21] G.B. Dalrymple and K. Hirooka, Variation of potassium, argon, and calculated age in a late Cenozoic basalt, *J. Geophys. Res.* 70 (1965) 5291.
- [22] M.A. Lanphere and G.B. Dalrymple, K-Ar and Rb-Sr measurements on P-207, the U.S. Geological Survey interlaboratory standard muscovite, *Geochim. Cosmochim. Acta* 31 (1967) 1091.
- [23] Anon., *Geochronology, Program of the Meeting; Colloquium on the Geochronology of Phanerozoic Orogenic Belts*, Bern-Zurich, Switzerland (1969).
- [24] R.E. Zartman, A geochronological study of the Lone Grove Pluton from the Llano Uplift, Texas, *J. Petrology* 5 (1964) 359.
- [25] M.A. Lanphere, W.P. Irwin and P.E. Hotz, Isotopic age of the Nevadan Orogeny and older plutonic and metamorphic events in the Klamath Mountains, California, *Geol. Soc. Am. Bull.* 79 (1968) 1027.
- [26] R.G. Coleman and M.A. Lanphere, Distribution and age of high-grade blueschists, associated eclogites, and amphibolites from Oregon and California, *Geol. Soc. Am. Bull.*, in press.
- [27] M.L. Silberman and R.P. Ashley, Age of ore deposition at Goldfield, Nevada from potassium-argon dating of alunite, *Econ. Geol.* 65 (1970) 352.