Radiometric Dating for Geologists

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Preface

Radiometric dating of rocks, minerals and meteorites is becoming one of the most active fields in planetary science. The data of age determinations has accumulated mainly over the past two decades, and has had some profound effects, not only on our understanding of the *history* of our planet and the solar system, but on our ideas about the nature and extent of certain kinds of geological processes.

The rapidity with which geochronological techniques have been developed and applied has had other less desirable consequences. Research papers sometimes give confusing, apparently contradictory statements about the reliability with which various rock and mineral types may be dated; research groups cannot agree on the values of the constants to be used for computing ages; fragments of the chronologies of various areas appear from time to time scattered among a number of geophysical, geochemical or geological journals. All of these developments are typical of a young and expanding field—in fact they provide some of the challenge which attracts research workers to the subject. At the same time, these problems are particularly unsettling to the geologist or geophysicist who is not directly in touch with geochronology but who wishes to further his understanding or apply the methods of geochronology to specific problems.

Part of this difficulty can be overcome at this stage by providing texts in which the basic concepts are presented in a logical and well-defined way. Several of these are now available:

Hurley, P. M. (1959). *How Old is the Earth.* The Science Study Series. Heinemann, London.

Russell, R. D. and Farquhar, R. M. (1960). *Lead Isotopes in Geology.* Interscience, New York.

Starik, I. E. (1961). Yadernaya Geokhronologiya Akademiya Nauk, SSSR, Moscow.

Hamilton, E. I. (1965). *Applied Geochronology.* Academic Press, London.

Schaeffer, O. A. and Zähringer, J. (1966). *Potassium–Argon Dating.* Springer Verlag, Berlin.

Faul, H. (1966). *Ages of Rocks Planets and Stars.* Earth and Planetary Science Series (Consulting Editor, P. M. Hurley). McGraw-Hill, New York.

What still appears to be lacking is a volume in which 'case histories' are presented, so that the geologist or geophysicist has access to accounts of methods, results of age studies and related topics concerning the significance of some isotope ratios, in as full a geological and geophysical context as possible.

The present work is an attempt to fill this gap. Most of the papers are not based on unpublished data, but are attempts to interpret available data in as complete a way as is presently possible in the geological framework of the regions or geological settings concerned. It is the editors' hope that this volume will to some degree complement the basic texts of geochronology by illustrating the scope, applications and limitations of radiometric age studies in wider contexts in which the average geologist or geophysicist may feel more at ease.

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Potassium–argon dating of igneous and metamorphic rocks with applications to the Basin ranges of Arizona and Sonora

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I Introduction

It is the intent of this chapter to discuss in a systematic way the merits and inherent problems associated with the potassium–argon dating method as applied to igneous and metamorphic rocks. Perhaps there is no better way to illustrate for geologists the inherent power as well as the shortcomings of the method than to apply it to actual geologic problems. For this purpose, problems in the dating of igneous and metamorphic rocks within the Basin and Range Province of Arizona and Arizona's neighbor to the south, Sonora, have been chosen.

All of Sonora and approximately half of Arizona are included within the Basin and Range Province (figure 1). The remainder of Arizona is occupied by the Colorado Plateau and a mountainous transition zone between the Colorado Plateau and the Basin ranges.

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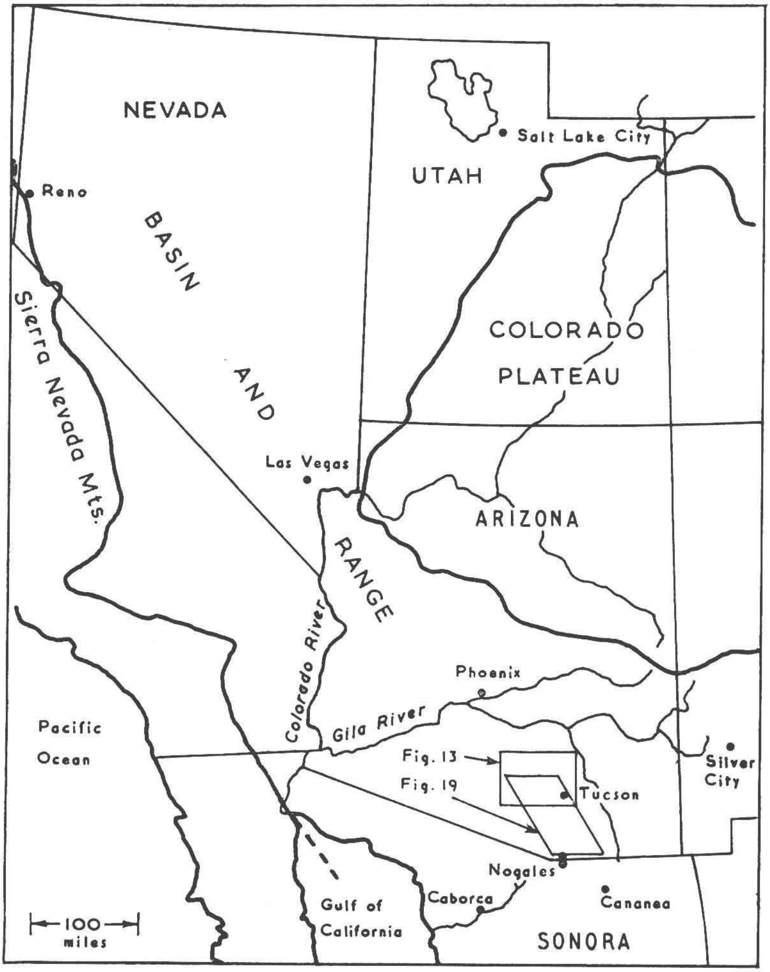

Figure 1 Location map outlining the Basin and Range Province and Colorado Plateau with pertinent reference points.

Magmatism within the Basin ranges of Arizona and Sonora has been essentially restricted to the Precambrian and Mesozoic eras. There is, as yet, no clear-cut evidence for the origin of any igneous rocks or metalliferous ore deposits within that area during the great expanse of time included within the Paleozoic era (Wilson, 1962). The Precambrian igneous rocks of the area, which have existed through a long and complex history, will serve to illustrate the limitations of the potassium–argon method, whereas the potassium–argon dating of late Mesozoic and Cenozoic rocks will serve to illustrate its virtues.

II The Potassium–Argon Method

A *Mode of decay and mathematical relationships*

There have been a number of excellent reviews of the potassium–argon method, most recently by Hamilton (1965) and Gerling (1961). The reader can refer to these works for a fuller account of the method and for references to the extensive literature. The intent here, as previously mentioned, is restricted to evaluating the method as applied to the dating of geologic events involving magmatic activity and thermal metamorphism.

There are three isotopes of potassium (^{39}K, ^{40}K, ^{41}K). The least abundant of these, potassium-40, is unstable with respect to both beta emission and electron capture. The eventual fate of each atom of potassium of atomic weight 40 is to be transmuted either by emission of a beta particle to become an atom of calcium (^{40}Ca) or by electron capture to become an atom of argon (^{40}Ar). As a result of this transmutation, the relative abundance of ^{40}K is continuously decreasing and that of ^{40}Ca and ^{40}Ar is continuously increasing with time. In 1290 m.y., the half-life ($t_{1/2}$) of ^{40}K, half of the atoms of ^{40}K in existence today will have decayed to either ^{40}Ca or ^{40}Ar. Approximately 11% of all transmutations will yield ^{40}Ar, the remainder will decay to ^{40}Ca. Thus in any mineral containing potassium, the ratios of ^{40}Ar and ^{40}Ca to ^{40}K will increase with time and be a measure of time. Naïvely, one might expect that the more frequent decay of ^{40}K to ^{40}Ca might be the most effective measure of time. Unfortunately, calcium is a major element in igneous rocks and the high abundance of nonradiogenic ^{40}Ca results in great uncertainty as to relative amounts of radiogenic to nonradiogenic ^{40}Ca. Isotopic and elemental abundances of potassium, argon and calcium are given in table 1. The abundance of calcium in igneous rocks is almost six orders of magnitude greater than the abundance of argon.

The mathematical relations governing the decay of ^{40}K are relatively simple. The probability, λ, that an atom of ^{40}K will decay in a unit of time, conveniently taken as one year, is the sum of the separate probabilities of decay to ^{40}Ca, λ_β, and ^{40}Ar, λ_K:

$$\lambda = \lambda_\beta + \lambda_K = \frac{0.693}{t_{1/2}} \tag{1}$$

Table 1 Crustal and isotopic abundances of potassium, calcium and argon

Element	Abundance of element in igneous rocks[a] (g/ton)	Isotope	Isotopic abundance[b] (atom %)
Potassium	25,900	^{39}K	93.08
		^{40}K	0.0119[c]
		^{41}K	6.91
Calcium	36,300	^{40}Ca	96.97
		^{42}Ca	0.64
		^{43}Ca	0.145
		^{44}Ca	2.06
		^{46}Ca	0.0033
		^{48}Ca	0.185
Argon	0.04	^{36}Ar	0.337[d]
		^{38}Ar	0.063[d]
		^{40}Ar	99.600[d]

[a] Rankama (1954, Table 9.1, p. 135).
[b] Rankama (1954, Table 1.3, p. 13).
[c] More recent determinations yield 0.0118; see text for discussion.
[d] This is the isotopic abundance of atmospheric argon, which is 0.93% by volume of total atmosphere. Lithospheric argon is almost pure argon-40.

The probability, P_d, that an atom in a sample will not decay in a time, t, measured in years is

$$P_d = \frac{^{40}\mathrm{K}}{^{40}\mathrm{K}_t} = \exp(-\lambda t) \tag{2}$$

where ^{40}K is the amount of that isotope measured now and $^{40}\mathrm{K}_t$ is the amount present t years ago. From equation (2), the amount of $^{40}\mathrm{K}_t$ at time t is

$$^{40}\mathrm{K}_t = {}^{40}\mathrm{K} \exp(+\lambda t) \tag{3}$$

The fraction of ^{40}K atoms that decay to ^{40}Ar is

$$\frac{^{40}\mathrm{Ar}}{^{40}\mathrm{Ar} + {}^{40}\mathrm{Ca}} = \frac{\lambda_K}{\lambda_K + \lambda_\beta} = \frac{\lambda_K}{\lambda} \tag{4}$$

The number of ^{40}Ar atoms produced within the sample in time t is equal to the original number of potassium-40 atoms (equation 3) minus the amount measured in the sample now, ^{40}K, times the fraction of potassium-40 atoms that decay to $^{40}\mathrm{Ar}$ (equation 4), which, factoring out $^{40}\mathrm{K}$, is

$$^{40}\mathrm{Ar} = \frac{\lambda_K}{\lambda}\, {}^{40}\mathrm{K}[\exp(\lambda t) - 1] \tag{5}$$

The age equation is then derived by solving this equation for time

$$t = \frac{1}{\lambda} \ln\left[1 + \frac{\lambda}{\lambda_K} \frac{^{40}\mathrm{Ar}}{^{40}\mathrm{K}}\right] \tag{6}$$

B *Radioactive clocks*

A mineral or rock containing a radioactive isotope such as $^{40}\mathrm{K}$ becomes, in a very real sense, a radioactive clock or geochronometer that can be used to date geologic events. Such a geologic event may consist of the crystallization of a mineral or solidification of a rock, or more rigorously, the cooling of the rock unit to a temperature at which loss by diffusion of the daughter decay product is negligible. If the clock is thermally, mechanically or chemically perturbed, the geologic event may correspond more or less closely to the perturbation rather than solidification.

The following conditions are a prerequisite to meaningful age determinations by the K–Ar method:

(1) The decay constants, λ_K and λ_β, must be known within sufficient limits of accuracy.

(2) The potassium-40 content of the mineral must be accurately and precisely determined either directly, such as by isotope dilution or neutron activation, or by chemical determination of the potassium content and accurate knowledge of the relative abundance of the isotope potassium-40. In this case, if K is the weight of potassium, as chemically determined, and ϕ is the relative abundance of $^{40}\mathrm{K}$ by weight, then the amount of potassium-40 by weight is

$$^{40}\mathrm{K} = \phi \mathrm{K} \tag{7}$$

and the quantity of potassium-40 in moles is obtained by dividing equation (7) by the isotopic weight of potassium-40 which is 39.964 gram per mole.

(3) The amount of $^{40}\mathrm{Ar}$ and the relative isotopic abundances of argon isotopes from the mineral must be determined precisely.

(4) An accurate estimate of atmospheric $^{40}\mathrm{Ar}$ contamination must be obtainable from the measured relative abundances of argon isotopes and subtracted from the measured $^{40}\mathrm{Ar}$.

(5) There must be negligible initial ^{40}Ar (excess ^{40}Ar) present at $t = 0$ or the experimenter must be able to estimate the amount of excess ^{40}Ar.

(6) The mineral or rock must constitute an essentially closed system following the geologic event, i.e. there must be essentially no gain or loss of ^{40}Ar and ^{40}K except by radioactive decay.

(7) By knowledge of mineralogic and petrologic factors and the geologic environment, the relationship between the K–Ar date and the geologic event must be established.

C *The decay constants*

Accurate knowledge of the decay constants for electron capture and beta disintegration (prerequisite 1) depends upon accurate determinations of the β-ray emission rate which results in transmutation to ^{40}Ca and the γ-ray emission rate. One gamma quantum is believed to accompany every electron capture that results in transmutation to ^{40}Ar. The relationship between these quantities is

$$\frac{\mathrm{d}N_\gamma}{\mathrm{d}t} = \frac{-\lambda_K \phi N_\mathrm{A}}{M_{40}} \ (\gamma \text{ dis. per sec per g K}) \tag{8a}$$

$$\frac{\mathrm{d}N_\beta}{\mathrm{d}t} = \frac{-\lambda_\beta \phi N_\mathrm{A}}{M_{40}} \ (\beta \text{ dis. per sec per g K}) \tag{8b}$$

where $\mathrm{d}N_\gamma/\mathrm{d}t$ and $\mathrm{d}N_\beta/\mathrm{d}t$ are the specific activities for γ-ray and β-ray emission, respectively; N_A is Avogadro's number (6.0226×10^{23}); and M_{40} is the isotopic mass of ^{40}K (39.964).

Nier (1950) measured a value of 1.22×10^{-4} g ^{40}K/g K (1.19×10^{-4} atoms of ^{40}K per atom of K) for ϕ. However, Strominger and others (1958) reviewed the isotopic abundance determinations for potassium. Three separate measurements in two different laboratories agree at a value of 1.21×10^{-4} g ^{40}K/g K for ϕ (1.18×10^{-4} atoms of ^{40}K per atom of K). Therefore, in this laboratory, we have always used the latter (smaller) value. The assumption of a constant value of ϕ implies that there is negligible fractionation of potassium isotopes during geologic processes. In general, this seems to be an acceptable assumption. However, it should be noted that Schreiner and Verbeek (1965) have reported up to several percent enrichment of ^{39}K relative to ^{41}K in altered xenoliths within a granite and at the contact of the granite with sedimentary country rock.

Aldrich and Wetherill (1958) reviewed the specific activity determinations and suggested values of 3.4 γ/g sec for the specific γ-activity and 27.6 β/g sec for the specific β-activity. There has been one new determination of the specific β-activity by Glendenin (1961) who obtained a value of 28.2 ± 0.3 β/g sec (errors quoted in this paper are standard deviations unless otherwise noted). However, most laboratories, including this one, have continued to use the specific activities recommended by Aldrich and Wetherill. Two sets of decay constants are commonly found in the literature, one based on $\phi = 1.21 \times 10^{-4}$, which includes this laboratory, and the other based on $\phi = 1.22 \times 10^{-4}$. Both sets of literature values are given in table 2 along with recalculated values.

Table 2 Physical constants for potassium-40

Source	ϕ ($\times 10^{-4}$ g ^{40}K/g K)	λ_K ($\times 10^{-10}$ yr^{-1})	λ_β ($\times 10^{-10}$ yr^{-1})	$t_{1/2}$ (m.y.)
Literature	1.21	0.589	4.76	1300[a]
Recalculated	1.21	0.588	4.78	1290[b]
Literature	1.22	0.584	4.72	1310[a]
Recalculated	1.22	0.584	4.74	1300

[a] See A. G. Smith (1964) for recent review.
[b] Values recommended by this author.

The small change in the recalculated value of λ_β is caused by an error which seems to have been repeated in the literature since the review paper of Endt and Kluyver (1954). Nier (1950) who determined the value of $\phi = 1.22 \times 10^{-4}$ g ^{40}K/g K (1.19×10^{-4} atomic abundance) has since accepted the more recent lower value of ϕ (Goldich and others, 1961). Smith (1964) has suggested that a slightly higher specific activity for λ_β might be appropriate. However, until further more definitive analyses are available, the author recommends the recalculated values in table 2 based on the lower value of ϕ accepted by most physicists including Professor Nier. The age equations calculated for natural logarithms and base 10 logarithms then become:

$$t = 4.29 \times 10^9 \log_{10} [9.12\ {}^{40}\mathrm{Ar}/{}^{40}\mathrm{K} + 1] \tag{9}$$

and

$$t = 1.86 \times 10^9 \ln[9.12\ {}^{40}\mathrm{Ar}/{}^{40}\mathrm{K} + 1] \tag{10}$$

To convert ages calculated with the higher value of ϕ (1.22×10^{-4}) to the recommended values, multiply the ^{40}Ar/^{40}K ratio by 1.0085 and recalculate, using either equation (9) or (10).

Wetherill and others (1956) and Smith (1964) have calculated the effect of errors in determining the parameters λ_β, and λ_K and ϕ on the calculated K–Ar dates. The effects of errors in determining these parameters and also the ^{40}Ar/^{40}K ratio are given in table 3.

Table 3 Effect on calculated K–Ar dates of errors in ϕ, λ_K, λ_β and the ^{40}Ar/^{40}K ratio

Date (m.y.)	$\delta\phi = +5\%$ (% error)[a]	$\delta\lambda_\beta = +5\%$ (% error)	$\delta\lambda_K = +5\%$ (% error)	$\delta[^{40}\mathrm{Ar}/^{40}\mathrm{K}] = +5\%$ (% error)
10	+0.0	−0.0	−5.0	5.0
100	+0.1	−0.1	−4.8	4.9
500	+0.6	−0.5	−4.2	4.4
1000	+1.1	−1.0	−3.8	3.9
2000	+1.9	−1.7	−3.2	3.0
3000	+2.5	−2.2	−2.7	2.4
4000	+2.8	−2.6	−2.4	2.0
5000	+3.0	−2.9	−2.1	1.7

[a] Assuming ϕ is constant, i.e. negligible natural isotopic fractionation. Fractionation of the sample is equivalent to an error in the ^{40}Ar/^{40}K ratio.

It becomes apparent that, for Cenozoic potassium–argon dating problems, ϕ and λ_β are not critical parameters and only λ_K and the ratio ^{40}Ar/^{40}K need be precisely and accurately determined. Errors in the parameters, ϕ and λ_β, become gradually more important and vice versa for λ_K and the 'daughter–parent' ratio until for dating work involving the oldest continental nuclei, all of the pertinent parameters become equally important.

For late Tertiary and Pleistocene K–Ar dating, the age equation (6) can be simplified with negligible error to

$$t = \frac{1}{\lambda_K} \frac{^{40}\mathrm{Ar}}{^{40}\mathrm{K}} \tag{11}$$

where $1/\lambda_K = 1.70 \times 10^{10}$ yr. The error introduced by use of this simplified equation is less than 0.1% for Pleistocene dating and becomes 1% at about 30 m.y.

It is important to evaluate the limits of the accuracy of K–Ar dating set by uncertainties in the determinations of the physical constants. There have been five determinations of the specific γ-emission and seven determinations of the specific β-emission of potassium-40 involving reported errors of less than 5%. The average of the γ-ray activities is 3.40 ± 0.03 γ/sec g ^{40}K and, rejecting one obviously discordant β-activity measurement, the remaining six average to 27.8 ± 0.4 β/sec g ^{40}K. The slight difference between this β-ray activity average and the currently used value of 27.6 β/sec g ^{40}K does not warrant a change that would involve laborious recalculations of many dates. The important point to be made is that, if the optimistic assumption is made that precision in determining ϕ, λ_K and λ_β is also a measure of accuracy, then the maximum uncertainty in K–Ar dating introduced by these parameters probably does not exceed ±2% at the 95% confidence level for rocks of any geologic age.

D *Determination of the* ^{40}Ar/^{40}K *ratio*

This brings the discussion to prerequisites (2), (3) and (4) which involve the precise and accurate determination of the ^{40}Ar/^{40}K ratio. For a full discussion of experimental details and for references the reader may refer to previously mentioned reviews (Hamilton, 1965; Gerling, 1961) and to Smales and Wager (1960).

In this laboratory we determine potassium by the flame photometric techniques described by Cooper (1963), Cooper and others (1966). The precision, as estimated by duplicate analyses of 27 samples ranging in potassium content from 0.01% to 1.83%, is ±0.40% of the amount present. The precision obtained for higher contents of potassium is, of course, better. The accuracy is ±1.54% estimated from replicate analyses of ten interlaboratory standards.

We determine argon by standard mass spectrometric isotope-dilution methods using a highly enriched ^{38}Ar (99.9% ^{38}Ar) diluent. ^{36}Ar is used as an indicator of atmospheric contamination. The precision for determining radiogenic ^{40}Ar as determined by ten duplicate analyses, with air corrections not exceeding 40%, is ±1.67%. The accuracy as indicated by analyses of four interlaboratory standards is ±0.86%.

For samples containing more than 0.1% potassium and with negligible air argon corrections, we report conservative errors of ±3% in determining the ^{40}Ar/^{40}K ratio. This corresponds to dating errors varying from 0.3 m.y. (3%) at 10 m.y. to 43 m.y. (1.44%) at 3000 m.y. The accuracy of potassium–argon dating of such samples, considering all measured parameters, is probably within ±7% at the 95% confidence level. This of course assumes negligible atmospheric argon correction, no excess ^{40}Ar or argon loss and, if the date is to be meaningful, that all pertinent mineralogic–geologic factors are known (prerequisites 4, 5, 6 and 7).

The graph used to estimate precision when the air argon correction becomes appreciable is given in figure 2. It is drawn on the assumption, based upon experience, that we routinely determine the atmospheric ^{40}Ar correction with ±2% precision. For corrections exceeding 50%, the air ^{40}Ar correction becomes the dominant error. Such large air corrections are usually restricted to very young samples or samples containing a very low content of potassium. Most of the air argon comes from the vacuum system in which the mineral or rock is fused to release its argon content, and from argon adsorbed during laboratory preparation of the sample. This argon has been derived directly from the present Earth's atmosphere and has the isotopic composition given in table 1. The amounts of ^{36}Ar and ^{40}Ar are measured relative to the known amount of isotopic diluent, ^{38}Ar. The ^{36}Ar content is multiplied by the ratio of ^{40}Ar/^{36}Ar in air (approximately 296) to obtain the amount of ^{40}Ar from the air, and this is subtracted, together with any ^{40}Ar from the isotopic diluent, to obtain the radiogenic ^{40}Ar content.

Undoubtedly, the isotopic composition of argon in the Earth's atmosphere has been gradually changing throughout geologic time as the result of degassing of radiogenic ^{40}Ar from the lithosphere. It is also possible that some of the air argon in a mineral or rock has been derived from the Earth's paleoatmosphere. However, any reasonable assumptions concerning the rate of argon degassing (Turekian, 1964; Wasserburg, 1964; Damon and Kulp, 1958a) indicate that the change in the isotopic composition of air argon during late Cenozoic and Pleistocene time would be quite negligible. Thus, for very young samples for which the air correction is highest and critically determines the precision, the constancy of the isotopic composition of air argon can be safely assumed. Air argon corrections for minerals in which potassium is a major constituent become progressively less with age, so that the assumption of air argon isotopic constancy is only in question for old minerals when the air correction is high as, for example, when attempting to date authigenic sedimentary minerals with low potassium content.

Evernden and Curtis (1965) have demonstrated that ^{40}Ar/^{40}K ratios can be measured with gratifying precision for potash feldspars less than 50,000 years old. For example, they have fused 12.6 g feldspar (9.48% K) from the Epomeo tuff (KA 1137) obtaining only 20.6×10^{-12} mole of atmospheric ^{40}Ar. Assuming an identical feldspar fused under identical conditions but only 30,000 years old, the results shown in table 4 would be obtained.

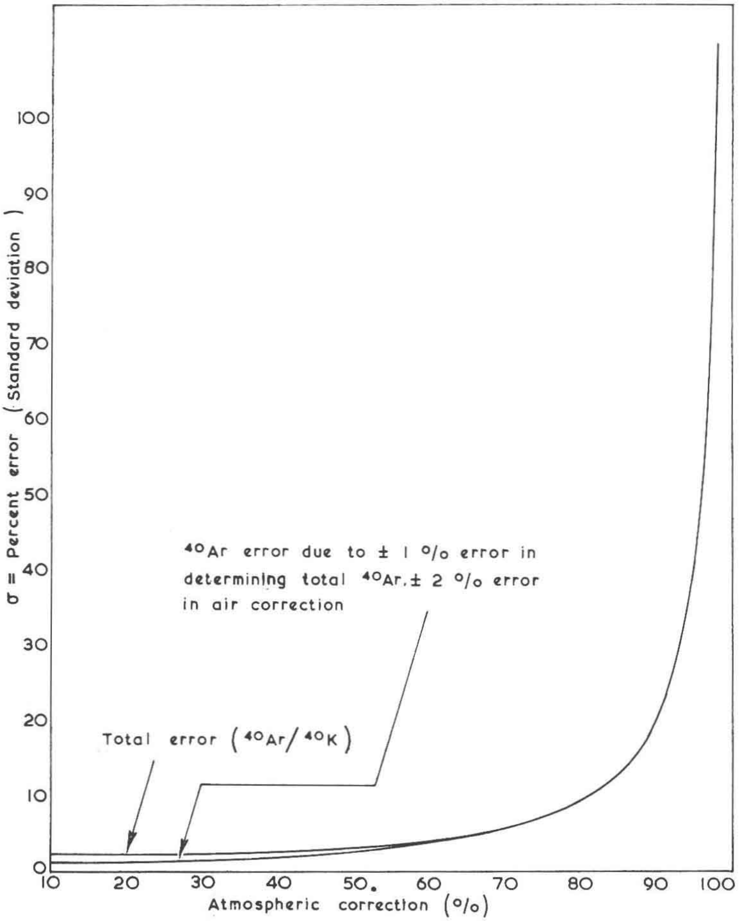

Figure 2 Estimated precision for determining the ^{40}Ar/^{40}K ratio as a function of the atmospheric correction.