Reproducibility of the K-Ar Ages of Rocks and Minerals: An Empirical Approach

U.S. GEOLOGICAL SURVEY BULLETIN 1654

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By R.W. Tabor, R.K. Mark, *and* R.H. Wilson

Derivation of a model for estimating the statistical error in K-Ar ages

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Abstract

The error assigned to potassium-argon ages is important to geologists who need to place the ages within a stratigraphic or historical context. Errors in many single analyses reported in the past have been based on theoretical equations and commonly have been optimistically small. We have derived a model for predicting the reproducibility of single ages based on replicate age determinations on 362 separate samples of rocks and minerals analysed in the U.S. Geological Survey's K-Ar isotope laboratory in Menlo Park, Calif. This empirically derived model agrees well in form with the theoretical models but predicts larger errors than the theoretical model for samples contaminated by a significant fraction of atmospheric argon.

INTRODUCTION

The error assigned to potassium-argon ages—the "mysterious ±," as it was called by Dalrymple and Lanphere (1969, p. 100)—has always been difficult to assign and commonly is not fully appreciated or understood by the geologist who uses the ages. Generally, errors in K-Ar ages are expressed in years, a value calculated from the standard deviation expressed as a percent (the coefficient of variation or standard deviation/average), and represent an estimate of precision based on the formula of Cox and Dalrymple (1967):

$$\text{sdAge}=\{(\text{sdK}_2\text{O})^2+(\text{sdt})^2+(1/\underline{r})^2(\text{sd}^{40/38})^2 +(\text{sd}^{36/38})^2[(1-\underline{r})/\underline{r}]^2\}^{1/2}, \quad (1)$$

where sdAge is the standard deviation of the age determination, sdK_2O is the standard deviation of the potassium analysis, sdt is the standard deviation of the tracer calibration, $\text{sd}^{40/38}$ and $\text{sd}^{36/38}$ are the standard deviations of the measured $^{40}\text{Ar}/^{38}\text{Ar}$ and $^{36}\text{Ar}/^{38}\text{Ar}$ ratios, respectively, and $\underline{r}$ is the fraction of ^{40}Ar that is radiogenic.

As originally discussed by Lipson (1958, p. 144), the value of $\underline{r}$ is the overwhelming factor in determining the reported error because, as the proportion of contaminating atmospheric ^{40}Ar increases, accurate measurement of the radiogenic-^{40}Ar content becomes more difficult. K_2O-content errors are generally small. A large variation in the K_2O analyses probably reflects inhomogeneities in the sample, a condition that bodes ill for precision in the argon analysis. Other sources of error are generally even smaller (see below).

Although Cox and Dalrymple (1967, p. 2605) stressed that their formula is not exact and breaks down entirely for values of $\underline{r}$ approaching zero, it has been widely applied either in its original form or in a modified form for special needs (for example, Mahood, 1981, p. 220-243).

We have derived an empirical relation between the coefficient of variation in age (cvAge) of multiple analyzed samples and $\underline{r}$ which suggests that the error assigned to many single age determinations may be too small. Our model can be used to estimate the precision in ages based on single argon analyses when there is no reason to otherwise believe that the age is in error.

Acknowledgments

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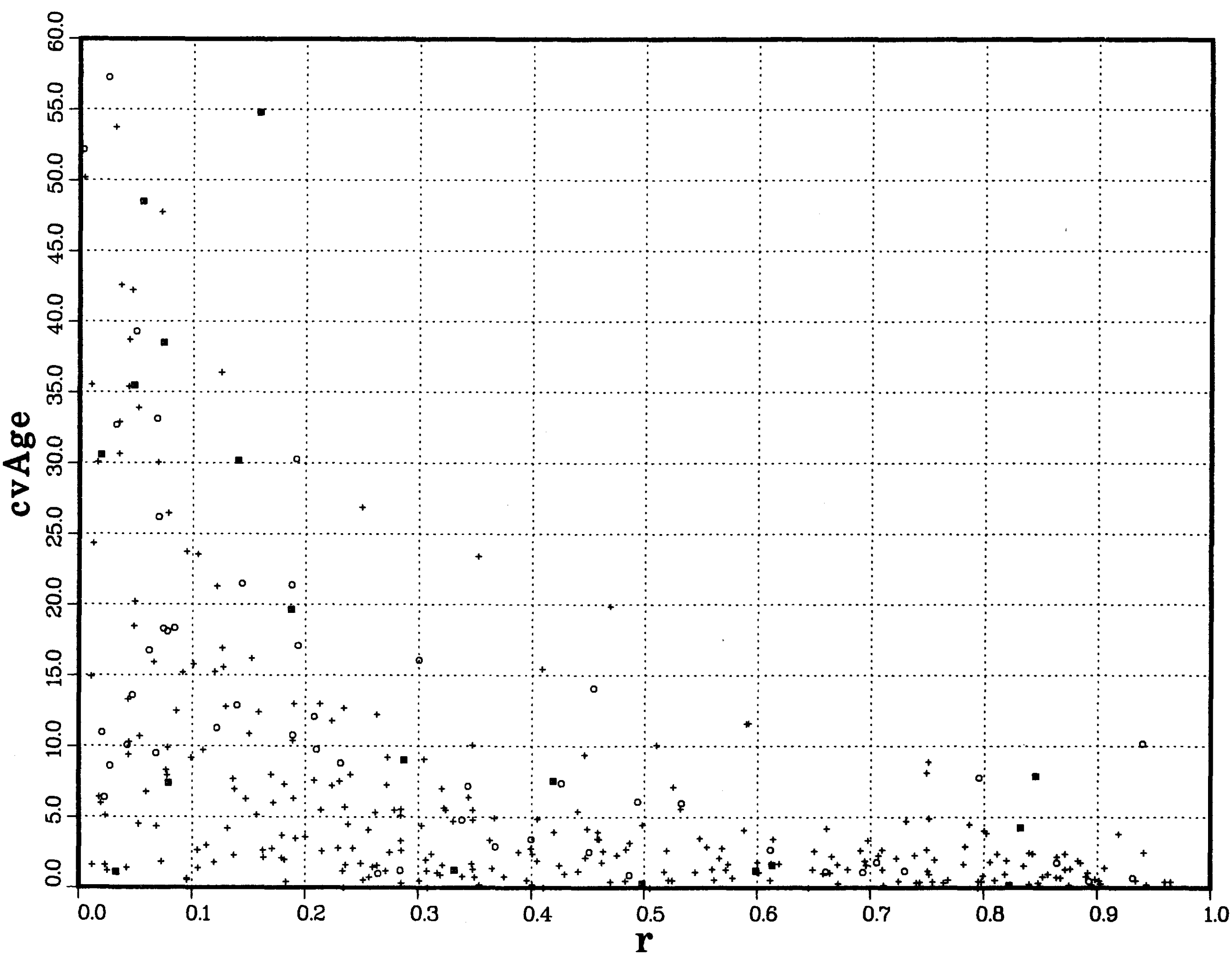

Figure 1. Coefficient of variation in age (cvAge) as a function of average fraction of radiogenic ^{40}Ar (r) in multiply analyzed samples. Crosses, two analyses; circles, three analyses; squares, more than three analyses. A total of 42 points with cvAge>60 and r<0.1 are not plotted but were used in the regressions.

DERIVING THE MODEL

For this study, we collected 829 replicate analyses of samples, including hornblende, biotite, feldspar, and whole rock, from workers in the K-Ar isotope laboratory of the U.S. Geological Survey in Menlo Park, Calif. The analyses were made between 1969 and 1983, using the isotope-dilution method of Dalrymple and Lanphere (1969). Argon-38 tracers were made by both batch and bulb methods.

We calculated the cvAge of 362 separate samples; 293 were analyzed twice, 50 three times, 13 four times, 3 five times, 1 six times, 1 seven times, and 1 ten times. Figure 1 plots the cvAge versus mean r. For 70 percent of these samples, the standard deviation from the mean of the r is less than 0.10, the maximum is 0.26, and the overall average is 0.05. Because we assumed that the cvAge of a sample analyzed many times is more reliable than that of one analyzed only twice, we weighted the data to give more influence to those sets of analyses derived from more than two extractions: a rock analyzed twice is treated as two datums, one analyzed three times as three datums, and so on. As we show below, this weighting becomes less influential because we use pooled means to derive the final equations.

We used the University of Pennsylvania Minitab program (Ryan and others, 1976) to investigate a various regression models for cvAge. The only variable that has a high correlation with cvAge is r. Surprisingly, cvK_2O does not appear to have any significant influence. We found little correlation between cvK_2O and cvAge even when we limited the data to analyses with greater than 80 percent radiogenic argon.

Figure 1 indicates that several points in each interval of r have a radically higher cvAge value than most of the data. We suspect that these points represent inhomogeneous rocks or minerals, or faulty analyses—clearly in the minority, although we have no objective reason to exclude them. Because these points unduly influence the averages in the pooled data

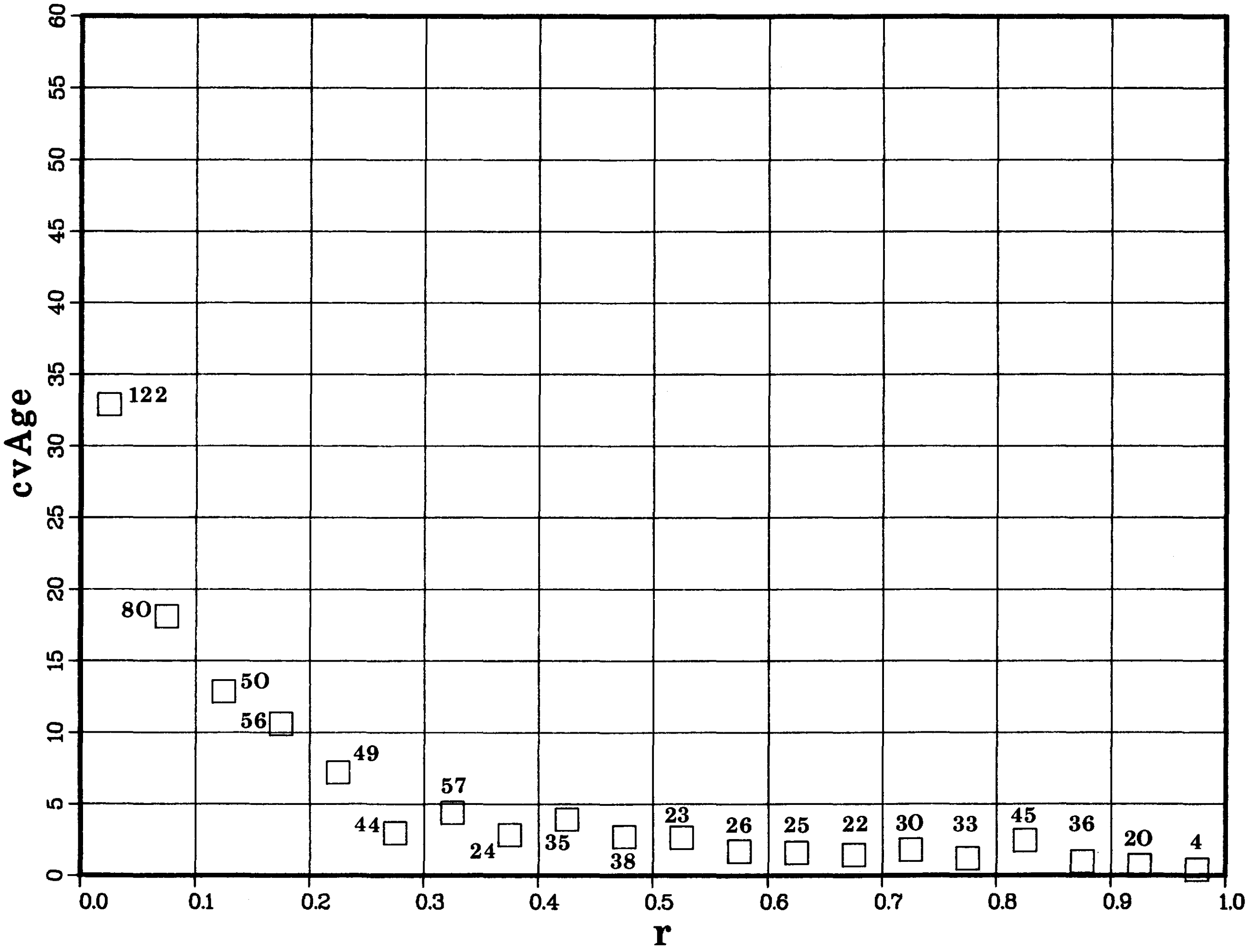

Figure 2. Medians of pooled data. Numbers indicate number of analyses in each interval.

sets, we used the medians, rather than the means, in the modeling. By using the medians, we have effectively decreased the influence of the outliers.

We attempted to fit a model in the form of equation 1 with terms $(K_2O)^2$, $(1/r)^2$, and $[(1-r)/r]^2$ to our data. The model fits the pooled data well, as might be expected, but analysis of the regression indicates that only the term $[(1-r)/r]^2$ is significant. Although the importance of this term was clearly emphasized by Lipson (1958, p. 144) and Cox and Dalrymple (1967, p. 2605), we were unable to produce a satisfactory curve based on that term alone. Thus, we adopted an empirical approach and looked for the simplest equation to fit the data illustrated in figure 1. We also tried constructing curves with selected data, such as less than 1 percent cvK_2O and greater than 1 percent cvK_2O, samples that yielded ages concordant with other phases of the same rock, and samples that did not. All these models gave approximately the same results.

Because r (and, thus, cvAge) is not entirely independent of the K_2O content of the samples, we separated low-K_2O samples—basalt, hornblende, plagioclase, and so on--from high-K_2O samples—rhyolite, biotite, muscovite, K-feldspar, and so on. The derived model, though nearly congruent at large values of r, predicts somewhat better reproducibility in low K_2O than in high-K_2O samples at low values of r. For example, when r=0.1, the difference in cvAge is about 2.5 percent, but considering the overall generalizations in the model, this difference is insignificant.

As might be expected from examination of the pooled median values (fig. 2), the model derived from them has a good fit:

$$cvAge=-2.42+3.38r^{-0.65}. \qquad (2)$$

DISCUSSION

Our model (eq. 2; fig. 3) corresponds in general shape to the error curves constructed by Cox and Dalrymple (1967, p. 2606). We selected this model to have a low positive value (approx 1 percent) for cvAge when r=1. This remnant error can be viewed as the sum of errors unrelated to the uncertainty in measuring radiogenic argon versus atmospheric argon. The average cvK_2O in our data set is 0.4

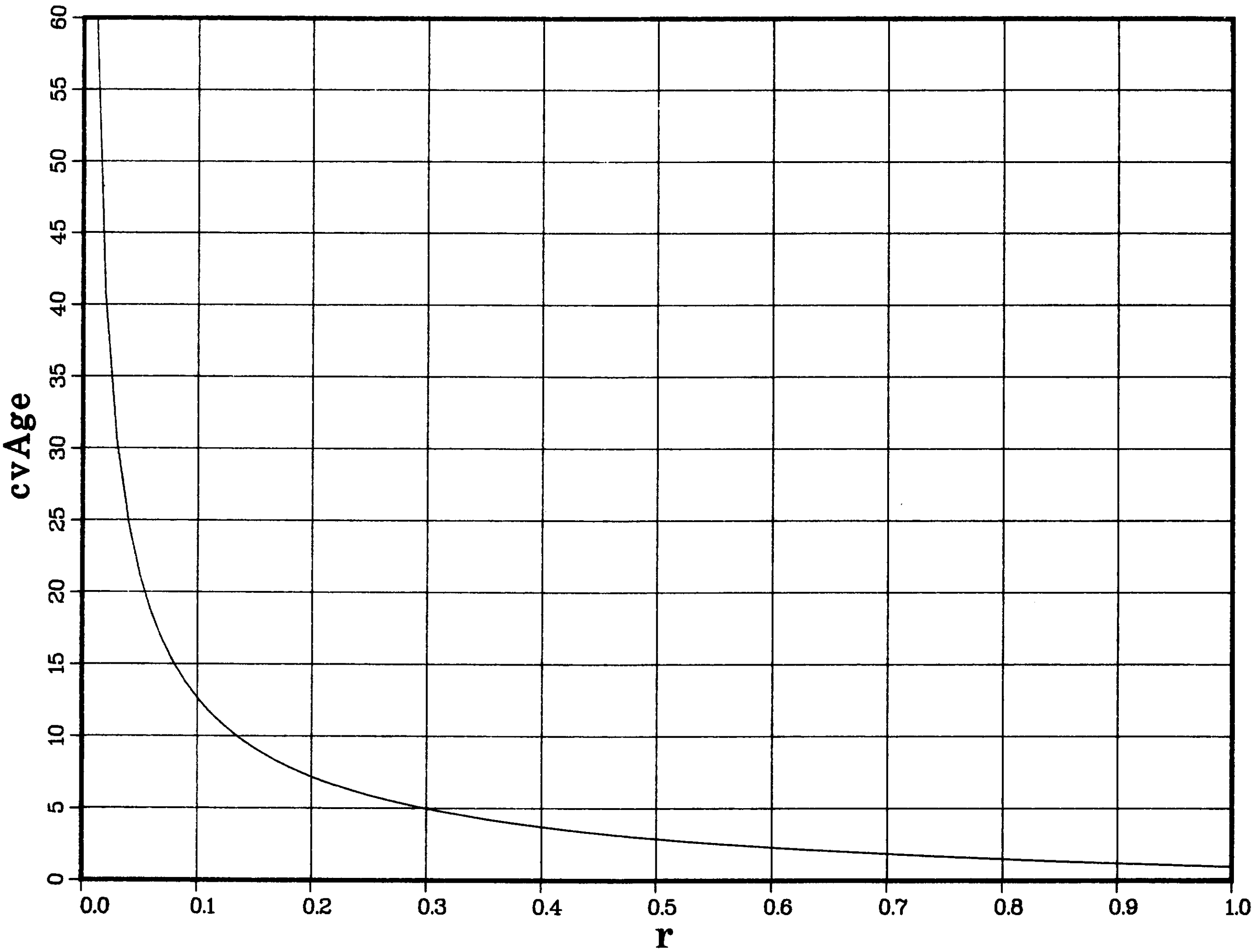

Figure 3. Model derived from regression equation, $cvAge=-2.43+3.38\underline{r}^{-0.65}$.

percent (s.d., 0.3), and the errors in tracer calibration range from about 0.40 to 1.65 percent, although most are less than 1.0 percent. The quadrature sum is about 1 percent. For comparison, Cox and Dalrymple (1967, p. 2605) estimated the error for K_2O at 0.5 percent, for tracer calibration at 0.3 percent, and for measurement of $^{40}Ar/^{38}Ar$ ratio at 0.2 percent. According to Cox and Dalrymple (1967, p. 2605), the error in measurement of the $^{36}Ar/^{38}Ar$ ratio is about 1.5 to 2 percent, but as little as 0.5 percent for small values of r. Our model most closely corresponds to Cox and Dalrymple's (1967, p. 2606) model that uses values of 1.5 percent for the $^{36}Ar/^{38}Ar$ ratio, of 0.5 percent for the K_2O content, and of 0.3 percent for tracer calibration. From our experience, $cv^{36}Ar/^{38}Ar$ is rarely greater than 1.0 percent, except for r approaching 1. Because this factor is the squared coefficient of the all-important term $(1-\underline{r})/\underline{r}$ in equation 1, it leads to predictions of small error.

The model in figure 3 predicts rather poor precision for samples with small r, though probably well within every geochronologist's experience. Our model predicts errors of the same magnitude, albeit somewhat more pessimistically than the estimates of error cited by Edwin McKee (written commun., 1982), based on a study of several hundred samples from the San Francisco volcanic field: "In general, the fraction of radiogenic ^{40}Ar is an index of the ± figure. Samples with 20 percent or more $^{40}ArRad$ have a possible error of 5 percent or less of the calculated date, those with 10 to 20 percent $^{40}ArRad$ about 10 percent, those with 5-10 percent $^{40}ArRad$ about 20 percent, and those with less than 5 percent $^{40}ArRad$ as much as, or more than, 100 percent of the age." Dalrymple and

Lanphere (1969, p. 119) suggest a precision of 2 to 5 percent for samples with r greater than 30 percent.

There are several weaknesses in the assumptions behind our error model. A primary one is that each sample analyzed is from a separate experiment with a separate set of circumstances; many procedures in the laboratory can increase the value of r, and they have little to do with the sample itself. Data in our set were not collected under uniform procedures to maximize r. Although averaging r makes the statistical approach a little neater, the averages only crudely reflect the actual air contamination of the dated material and, as such, can only crudely predict the reproducibility. As a result, the pooled data in the intervals of r close to zero (fig. 1) are of poor quality in comparison with those in the other intervals. For a few samples, we used average r values that included negative r values because they are mathematically viable, even if physically meaningless. There seems to be no reliable way to predict the error in this region where r approaches zero except in a gross statistical way. Thus, the errors predicted by the equation and the curves are probably unreliable at very low values of r. The cvAge of very young rocks probably will not be accurately predicted by our model. With considerable care, reproducible ages can be obtained from very young rocks, as indicated throughout the literature and by the large number of data points in the lower left-hand corner of figure 1. In estimating precision, there is no substitute for multiple runs; and for estimating accuracy, no statistics can replace good stratigraphic control and numerous ages determined by various methods.

All the data in our set came from one laboratory where procedures for extraction and spectometry are more or less uniform. Thus, our model might not be appropriate for data from other laboratories, although we expect that for a run-of-the-mill single analysis, this model will give a reasonable estimate of reproducibility.

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