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U.S. GEOLOGICAL SURVEY K_2O AND Ar ANALYSIS OF ZBH-25, LABORATORY STANDARD, ACADEMY OF GEOLOGICAL SCIENCES OF THE MINISTRY OF GEOLOGY AND MINERAL RESOURCES, BEIJING, P.R.C.

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As part of the United States-People's Republic of China Earth Sciences Protocol for Scientific and Technical Cooperation Project 4, potassium and argon analyses of rock and mineral samples from China were made by the U.S. Geological Survey. Some of these analyses were performed for comparison and calibration of laboratory standards. Other samples were analysed to use in K-Ar dating and geochronologic studies of various areas in China. This report presents the results of potassium and argon analysis of biotite ZBH-25, a laboratory standard used by the Chinese Academy of Geological Sciences of the Ministry of Geology and Mineral Resources, Beijing, People's Republic of China.

Potassium analyses by the U.S. Geological Survey were performed by a lithium metaborate flux fusion-flame photometry technique, using lithium as an internal standard (Ingamells, 1970). Argon analyses by the U.S. Geological Survey were performed by standard isotope-dilution procedures, using a 60°-sector, 15.2-cm-radius, Nier-type mass spectrometer operated in the static mode.

The results of the U.S. Geological Survey analyses (table 1) show a difference in age of 4.06%, compared to values reported by the Chinese Academy of Geological Sciences. The age difference is due to a difference in K_2O values of 1.01% and in Ar values of 3.11%. For comparison, Lanphere and Dalrymple (1976) found an average variation in K_2O values between labs of 1.2%, in argon measurement of 1.2%, and in calculated age of 1.2%, using standard muscovite P-207.

DISCUSSION

A rigorous statistical comparison between U.S. Geological Survey and Chinese Academy of Geological Sciences analytical values was not attempted because of the unavailability of information regarding the precision of the Chinese measurements. However, it is reasonable to assume that the Chinese Academy analyses on this standard are comparable to standards analyzed by other labs, which generally have a precision of better than 1.9% (Lanphere and Dalrymple, 1976). If it is also assumed that the Chinese Academy values are the result of 10 separate analyses (a reasonable number for a laboratory standard), then the significance of the difference in measurements can be compared in at least an approximate way.

The critical value equation,

$$\text{c.v.} = 1.960\left(\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}\right)^{1/2},$$

can be used to determine whether or not a difference in age reported by the two labs is significant at 95% confidence. In this equation, where σ_1 and σ_2 are the standard deviations reported by the respective laboratories, and n_1 and n_2 are the number of analyses made by each lab, c.v., or the critical value, must be exceeded in order to state that a real difference in age is detected. Using our assumptions about the Chinese Academy measurements, the equation is then

$$\text{c.v.} = 1.960\left(\frac{0.8^2}{4} + \frac{1.9^2}{10}\right)^{1/2} = 1.42\%.$$

The 4.06% difference in age as determined by the two labs therefore appears to be real and cannot be attributed to random analytical errors.

Unfortunately, a comparison between the analytical procedures and equipment used by the two laboratories is not feasible and may account, at least in part, for the difference in reported values. For example, the variation due

TABLE 1. Summary of analytical values for ZBH-25 by the U.S. Geological Survey and the Chinese Academy of Geological Sciences

	K_2O (wt %)	Ar ($\times 10^{-11}$ mol/g)	$^{40}Ar^*$ (%)	Age ($\times 10^6$ yr)[1]
U.S. Geological Survey	9.24	1.783	63.7	129.2
	9.25	1.760	92.7	127.6
		1.779	82.2	128.9
		1.753	84.5	127.1
Mean	9.245	1.769		128.2
Standard deviation	0.007	0.015		1.0
Coefficient of variation	0.1%	0.8%		0.8%
Chinese Academy (mean)	9.152	1.824		133.4
Difference between labs	0.093	0.055		5.2
% difference (relative to Chinese Academy values)	1.01%	3.11%		4.06%

[1] $\lambda_\epsilon = 0.581 \times 10^{-10}\ yr^{-1}$; $\lambda_\beta = 4.962 \times 10^{-10}\ yr^{-1}$; $^{40}K/K = 1.167 \times 10^{-4}$ mol/mol.

to different techniques and calibration of standards used in analyses for potassium could account for the 1% difference in K_2O values. This 1% difference is within expected variation for potassium analyses between labs (Lanphere and Dalrymple, 1976). Similarly, the type, design, and sensitivity of the spectrometer used by the Chinese Academy for argon analysis is unknown and could introduce small variations in the Ar values. The 3.11% difference in argon values reported by the two labs is higher than expected, and is most likely due to differences in spike calibration.

It should be noted, however, that the difference in reported ages is negligible with respect to application to normal geochronologic problems, for rocks older than a few million years. This is due to the fact that, for most geochronologic applications, only one or two age determinations are made for a given sample. With the resultant lack of information concerning analytical uncertainty, K-Ar ages are generally assigned errors based on such factors as K_2O uncertainty, errors in argon tracer calibration, uncertainty in measured peak ratios, and errors resulting from atmospheric argon contamination (Dalrymple and Lanphere, 1969). Based on multiple analyses of many different samples, this last factor, generally expressed in terms of the percentage of radiogenic ^{40}Ar ($^{40}Ar^*$), is by far the most important in assessing the uncertainty of a K-Ar age (McKee and Silberman, 1972; Tabor and others, 1985). In practice, these errors range from about 2.5–3.0% for samples with greater than about 30% $^{40}Ar^*$, to 50% or more for samples with very low percentages of $^{40}Ar^*$. Therefore, if single analyses on a rock are made by two labs, they must differ by at least 8.3% in order to state that a real difference in age is detected, according to the critical value equation. If each lab makes two analyses, they must differ by 5.9%. This fact would tend to mask the 4% bias between labs that is indicated by the U.S. Geological Survey measurements.

Therefore, within the normal realm of geochronologic applications, where only one or two age determinations are made on a rock, the difference detected between the U.S. Geological Survey and the Chinese Academy of Geological Sciences laboratories appears to be slight. This is not to say that a real difference was not detected in the age of ZBH-25 between the two labs. The 4.06% difference in age detected, however, is only apparent through a statistical treatment of multiple analyses.

SAMPLE DESCRIPTION

1. *ZBH-25* K-Ar

Laboratory standard biotite prepared by the Chinese Academy of Geological Sciences of the Ministry of Geology and Mineral Resources. *Analytical data:* Sample weight = 0.2884g, 0.2079g, 0.2796g, 0.2229g; K_2O = 9.24%, 9.25%; $^{40}Ar^*$ = 1.783 × 10^{-11} mol/g, 1.760 × 10^{-11} mol/g, 1.779 × 10^{-11} mol/g, 1.753 × 10^{-11} mol/g; $^{40}Ar^*/\Sigma^{40}Ar$ = 63.7%, 92.7%, 82.2%, 84.5%.

(biotite) 129.2 ± 3.2 m.y.
(biotite) 127.6 ± 3.2 m.y.
(biotite) 128.9 ± 3.2 m.y.
(biotite) 127.1 ± 3.2 m.y.

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