# Technical Papers

## Some Potassium-Argon Ages for Ontario

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Potassium contains the naturally radioactive isotope  $K^{40}$ , which decays by beta emission to calcium-40 and by orbital electron capture to argon-40. To measure the age of a potassium mineral, it is necessary to extract and measure either the radiogenic calcium-40 or the radiogenic argon-40 contained in the mineral. In addition a potash analysis must be made. All results (1) reported here were made by extracting the argon from a mineral, measuring the volume by means of a McLeod gage, and determining the radiogenic purity of the argon by a mass spectrometer.

Because of the dual decay process, it is necessary to stipulate two decay constants in order to describe the decay scheme of potassium-40 completely. The decay constants that we have used in all calculations are

Decay constant for beta emission =  $\lambda_{\beta} = 0.503 \times 10^{-9}$  yr<sup>-1</sup>, <u>Decay constant for orbital electron capture</u> <u>Decay constant for beta emission</u> = R = 0.089,

where R is the branching ratio. The decay constant for beta emission is the mean of 11 of the most recent counting experiments (2). The branching ratio used was determined by using results obtained by two different laboratories on potassium feldspars of known age (3). Using these decay constants, we have obtained many potassium-argon ages that are in agreement with lead-uranium and lead-lead ages from the same localities (2). The experimental procedure has been reported at length in a previous paper (2).

The formula used in calculating potassium-argon ages is

$$\frac{\mathbf{A}^{40}}{\mathbf{K}^{40}} = \frac{R}{(1+R)} \{ \mathrm{e}^{(1+R)\lambda\beta t} - 1 \},\$$

where  $A^{40}$  is the mass of radiogenic argon-40 present per gram of mineral sample,  $K^{40}$  is the mass of potassium-40 per gram of mineral sample, and t is the age of the mineral. With our decay constants and transposing, this becomes:

$$t = \frac{10^{\circ}}{0.548} \ln \left\{ 1 + 12 \cdot 18 \frac{A^{40}}{K^{40}} \right\} \times 10^{6} \text{ yr}$$

The results given in Table 1 are for a number of potassium minerals from Ontario, Canada.

Most of the potash determinations were made with a flame photometer at Toronto by K. Watson. The standard deviation of three individual determinations on each sample is given. The error in the ages is calculated for a possible 10-percent error in the  $A^{40}/K^{40}$ ratio.

The tests on associated minerals from the same pegmatite were made to determine whether consistent results would be obtained for minerals of entirely different lattice structure. It is obvious that each pair of associated minerals gives results that agree within the experimental error. Two separate samples of feldspar from MacDonald mine, Monteagle Township, were run. The first sample, 1019-A, had been ground to 200 mesh (0.01 cm) 2 yr prior to the runs, and the

Toronto No.	Location*	Mineral	Longitude, latitude	% by wt. radiogenic A <sup>40</sup> †	No. of runs	% by wt. K₂O	$A^{40}/K^{40}$	Age‡
1107-A	Dill Twp.	Perthite	80°50'W 46°24'N	$6.57 \pm 0.32  imes 10^{-5}$	8	12.56	0.052	$900 \pm 70$
1109-A	Dill Twp.	Mica		$5.11\pm0.47\times10^{\text{5}}$	3	$9.66 \pm 0.18$	.052	$900 \pm 70$
1223-A	Conger Twp. Lot 7, Con. X	Perthite	79°51'W 45°15'N	$7.26 \pm 0.14  imes 10^{-5}$	2	$13.0(5) \pm .05$	.055	<b>9</b> 30 ± 70
1224-A	Conger Twp. Lot 7, Con. X	Mica		$5.55 \pm 0.41 \times 10^{-5}$	2	$8.76 \pm 0.26$	.062	$1030\pm80$
1019-A	MacDonald mine, Monteagle Twp. Lot 19, Con. VII	Perthite	77°48'W 45°10'N	$6.20 \pm 0.10  imes 10^{-5}$	2	11.9(7) ± 0.12	.051	<b>89</b> 0 ± 70
1028-A	Second sample	Perthite		$6.29\pm0.10\times10^{\text{-5}}$	2	$11.8 \pm 0.24$	.053	$910\pm70$
1178-A	Besner mine, Henvey Twp. Lot 5, Con. B	Perthite	80°31′W <b>45°</b> 48′N	$6.87 \pm 0.16  imes 10^{-5}$	2	$13.2 \pm 0.2$	.052	900 ± 70

Table 1. Potassium-argon ages for some Ontario samples.

\* Samples 1223-A, 1224-A, 1019-A, 1028-A, and 1178-A were collected by R. D. Russell and R. M. Farquhar. Samples 1107-A and 1109-A were collected by H. A. Shillibeer.

<sup>4</sup> Uncertainty shown is standard deviation of individual measurements. <sup>‡</sup> Limits of uncertainty based on estimated mean probable error of  $\pm 10$  percent in  $A^{40}/K^{40}$  ratio.

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second sample, 1028-A, was freshly ground. The results agree within our experimental error.

An associated uraninite found with the Besner mine feldspar gave a lead-lead age of  $(940 \pm 50) \times 10^6$  yr in agreement with our potassium-argon age (4). A. O. Nier has published lead-lead and lead-uranium ages for a uraninite from Blackstone Lake, which is approximately 1/2 mi from the location of our Conger Township samples (5, 6). The mean age of this uraninite is  $1010 \times 10^6$  yr in good agreement with our potassium-argon ages. Similar results have been obtained by Wasserburg and Hayden (7).

These results provide additional support for potassium-argon ages and indicate that the age limits of 800 to 1100 million years assigned to the Grenville orogeny are reasonable (8).

#### **References and Notes**

- 1. This investigation was assisted by grants from the National Research Council of Canada and the Geological Survey of Canada.
- A. Shillibeer and R. D. Russell, Can. J. Phys. 32, 681 2. H. A. Shillibeer et al., Phys. Rev. 94, 1793 (1954).
  H. A. Shillibeer et al., Phys. Rev. 94, 1793 (1954).
  R. D. Russell et al., Phys. Rev. 91, 1223 (1953).
  A. O. Nier, ibid. 60, 112 (1941).

- 6.
- H. V. Ellsworth, Geol. Surv. (Canada) Econ. Geol. Ser., No. 11, 174 (1932). G. J. Wasserburg and R. J. Hayden, Geochim. et Cosmo-7.
- chim. Acta, in press. 8. C. B. Collins, R. M. Farquhar, and R. D. Russell, Bull.
- Geol. Soc. Am. 65, 1 (1954).

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## Critique of Extracellular Space Measurements with Small Ions; Na<sup>24</sup> and Br<sup>82</sup> Spaces

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Perhaps the most generally accepted reference substances for the measurement of extracellular fluid volume are inulin (1) and sucrose (2), which are thought to be incapable of entering cells, at least in normal circumstances. Since prolonged periods for complete equilibration in extracellular fluid are required, owing to the relatively large molecular size and slow diffusion rates of these substances in tissue, the search continues for other agents that might permit more rapid equilibration and simpler experimental procedure. Both sodium and bromide are known to penetrate cells to a certain extent, and the space of distribution of Na<sup>24</sup> 3 hr following intravenous administration (3) is significantly in excess of that now believed to represent the volume of the extracellular compartment. However, it was thought that intracellular permeation might be sufficiently slow compared with extracellular diffusion to permit evaluation of the extracellular compartment.

The concentration-time course of radioactivity in plasma, following intravenous administration of Na<sup>24</sup>

or Br<sup>82</sup> to human subjects, is a multicomponent curve. The concentration in terms of the fraction of the total radioactivity in the body per liter of plasma (Fig. 1A) becomes virtually constant after about 12 hr in



Fig. 1. Venous plasma curves. Phase I is related chiefly to mixing in extracellular fluids.

normal subjects. Between about 15 to 20 min and 1 hr (phase II), the concentration decreases almost exponentially (Fig. 1B) with a much shallower slope than during the initial period (phase I). It seemed reasonable to suppose that phase I may reflect, primarily, mixing in extracellular fluid and that phase II is chiefly attributable to penetration of cells and (in the case of Na<sup>24</sup>) bone apatite. Then the extracellular fluid volume would be given approximately by the reciprocal of the zero time extrapolation of phase II, assuming that intracellular penetration proceeded at the same rate throughout phase I as during phase II.

This assumption introduces at least slight errors into the calculations, since these ions cannot penetrate most tissue cells until they have diffused through some part of the extracellular compartment. In addition, errors of unknown magnitude may result from very rapid penetration of some cells during the period of extracellular diffusion. Entrance of Na<sup>24</sup> into erythrocytes is negligible at this time, but equilibration of Br<sup>82</sup> between erythrocytes and plasma occurs almost instantaneously and can be corrected for by simultaneous measurement of total red cell volume. Negligible amounts ( $\frac{1}{2}$  percent or less) of either ion are excreted during the first  $\frac{1}{2}$  hr.

The calculations just described have yielded values for extracellular space in nonedematous subjects which are reproducible (H.W., Fig. 1B) and are in good agreement with those obtained by inulin or sucrosethat is, about 13 to 19 percent of body weight (Table 1). It was further observed that simultaneous space measurements with Na<sup>24</sup> and Br<sup>82</sup> (Fig. 2) give almost identical values when correction is made for Br<sup>82</sup> in erythrocytes (Table 2). However, certain observations demonstrate the unreliability of these estimates of extracellular fluid in patients with large extracellular fluid collections such as edema, ascites, and pleural effusion. The specific activities in the abnormal fluid