

there is a significant decrease in this ratio with increase in the degree of metamorphism/metasomatism. Whichever is correct it can scarcely be said that strontium isotope measurements offer a clear demonstration that carbonatites are not mobilized limestones.

We do not suggest that carbonatites are either limestone xenoliths or mobilized limestones but we doubt that the studies of strontium isotopic composition prove that they are not.

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<sup>1</sup> Powell, J. L., Hurley, P. M., and Fairbairn, H. W., *Nature*, **196**, 1085 (1962).

<sup>2</sup> Hamilton, E. L., and Deans, T., *Nature*, **198**, 776 (1963).

<sup>3</sup> Powell, J. L., *Proc. Intern. Min. Assoc., India*, 1964 (in the press).

**GEOCHEMISTRY**

**Estimation of Elapsed Time since a Certain Climatic Change for Lake Vanda**

WILSON<sup>1</sup> has considered the estimation of elapsed time since a climatic change for Lake Vanda (77° 35' S., 161° 39' E.), which is 5 miles long, 1 mile wide and occupies the lowest part of the Wright Valley, an ice-free valley in Victoria Land, Antarctica.

The estimation procedure makes use of the equation:

$$C = [M/(Dt)^{\frac{1}{2}}] \exp[-h^2/(4Dt)]$$

where *C* is the concentration of calcium chloride at distance *h* from bottom after an elapsed time *t*, *h* is the distance above bottom, *D* is the diffusion coefficient of calcium chloride (0.68 cm<sup>2</sup>/day at 10°—see ref. 2), and *M* is the total mass of calcium chloride per unit area.

Measurements were made on the concentration of calcium chloride at a distance *h* from bottom. Originally the data were presented by Wilson<sup>1</sup> in the form of a graph, but more recently he has presented them (personal communication) as in Table 1.

Table 1

<i>h</i> (ft.)	<i>C</i> (equiv./l.)
0	2.96
5	2.28
10	2.12
15	1.93
25	1.53
35	0.99
45	0.473
50	0.306
55	0.142
60	0.0604
65	0.0302
70	0.0230

*h* is the distance above bottom in feet, and *C* is the concentration of calcium chloride.

It should be noted that Wilson (personal communication) gives these data and points out that in Fig. 2 of ref. 1 there is an error in the concentration scale of about 0.5. This reduces the former good fit for approximately 1,200 years to the smaller value given in this communication.

It should be noted that the equation involved can be written:

$$\log C = -h^2/4Dt + \log[M/(Dt)^{\frac{1}{2}}]$$

where log refers to natural logarithm.

For the values  $0 = h_0 \leq h_1 \leq \dots \leq h_n$  we have associated  $C_0, C_1, \dots, C_n$ , respectively. We write:

$$W_i = \log(C_i/C_0) = -h_i^2/4Dt \text{ for } i = 1, 2, \dots, n$$

The value of *t*\* which minimizes the sum of squares  $\sum_{i=1}^n (W_i^* - W_i)^2$ , where *W*<sub>*i*</sub>\* is computed from the observed values *C*<sub>*i*</sub>\*, *C*<sub>*i*</sub>\*, . . . , *C*<sub>*n*</sub>\* of *C*<sub>*0*</sub>, *C*<sub>*1*</sub>, . . . , *C*<sub>*n*</sub>, is:

$$t^* = \frac{-\sum_{i=1}^n h_i^4}{4D \sum_{i=1}^n h_i^2 W_i^*}$$

If we assume that  $W_i = -h_i^2/4Dt + \epsilon_i$ , where  $\epsilon_i$  is normally distributed with mean 0 and variance  $\sigma^2$  for  $i = 1, 2, \dots, n$ , then  $1/t^*$  is normally distributed with mean  $1/t$  and variance  $16D^2\sigma^2 / \sum_{i=1}^n h_i^4$ . An unbiased estimate of  $\sigma^2$  is  $s^2$ , where:

$$(n-1)s^2 = \sum_{i=1}^n W_i^{*2} - \left( \sum_{i=1}^n h_i W_i^* \right)^2 / \sum_{i=1}^n h_i^4$$

It will follow that:

$$(1/t^* - 1/t) \left[ \left( \sum_{i=1}^n h_i^4 \right)^{\frac{1}{2}} / 4Ds \right] = T(n-1)$$

where *T*(*n* - 1) is the Student *t*-distribution with *n* - 1 degrees of freedom. Therefore, if *T* <sub>$\alpha$</sub> (*n* - 1) is such that Prob(*T*(*n* - 1)  $\geq T_{\alpha}$ (*n* - 1)) =  $\alpha/2$ , then a (1 -  $\alpha$ )100 per cent confidence interval for *t* has:

$$\frac{t^* \left( \sum_{i=1}^n h_i^4 \right)^{\frac{1}{2}}}{\left( \sum_{i=1}^n h_i^4 \right)^{\frac{1}{2}} + 4Dt^*sT_{\alpha}(n-1)} \leq t \leq \frac{t^* \left( \sum_{i=1}^n h_i^4 \right)^{\frac{1}{2}}}{\left( \sum_{i=1}^n h_i^4 \right)^{\frac{1}{2}} - 4Dt^*sT_{\alpha}(n-1)}$$

when  $0 < 4Dt^*sT_{\alpha}(n-1) < \left( \sum_{i=1}^n h_i^4 \right)^{\frac{1}{2}}$

The method of estimation used by Wilson<sup>1</sup> was simply trial and error. He observed graphically that the observed points fell between the graph for  $t = 1,000$  and  $t = 1,500$  and that  $t = 1,200$  looked like a good fit. By the described statistical estimation method one obtains  $t^* = 984$  years and 95 per cent confidence interval  $576 \leq t \leq 3,360$ . This is a much more satisfactory method of analysis since it gives an estimate with the optimal properties of least squares as well as a measure of the accuracy of the estimate.

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<sup>1</sup> Wilson, A. T., *Nature*, **201**, 176 (1964).

<sup>2</sup> *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1954).

DR. ROBERTS'S treatment of my data gives additional confirmation to my tenet that the chemical gradients found in Lake Vanda can be explained by chemical diffusion and that such chemical composition profiles in Antarctic lakes can provide valuable palaeoclimatic information<sup>1</sup>.

I would, however, like to make a few comments on the treatment used by Dr. Roberts. The model I used, and that adopted by Dr. Roberts, was diffusion from a planar source of negligible thickness on the bottom of a rectangular trough of infinite volume. This assumes the Lako has a flat bottom with vertical sides. As my Fig. 2 (ref. 1) and the mathematics of Dr. Roberts show, this is, in fact, a reasonable first approximation. Dr. Roberts is concerned with secondary refinements, and to do this one cannot give all