Table 2. Data for aged NAS_{27-4} electrode. Activities and concentrations in milliequivalents per liter.

$(a_{K^+})_{std.}$	$[Na^+]$	$[K^+]$	$\frac{[Na^+]}{[Na^+]+[K^+]}$	γ_{NaKCl}	a_{Na^+}	a_{K^+}	$\Delta E/S$	k_{KNa}
77.0	100	—	1.00	0.778	77.8	—	−0.9829	0.103
77.0	200	5	0.98	0.732	146.4	3.7	−0.5985	0.107
77.0	50	5	0.91	0.812	40.6	4.1	−0.9671	0.103
77.0	200	20	0.91	0.728	145.6	14.6	−0.3984	0.111
77.0	50	20	0.71	0.796	39.8	15.9	−0.5870	0.108
77.0	20	20	0.50	0.828	16.6	16.6	−0.6218	0.105
77.0	50	30	0.62	0.787	39.4	23.6	−0.4437	0.102
77.0	200	30	0.87	0.724	144.8	21.7	−0.3162	0.107
77.0	200	50	0.80	0.718	143.6	35.9	−0.1778	0.106
77.0	50	50	0.50	0.774	38.7	38.7	−0.2596	0.094
77.0	25	50	0.33	0.789	19.7	39.4	−0.2741	0.090
77.0	200	200	0.50	0.669	133.8	133.8	+0.2917	0.104
77.0	50	200	0.20	0.702	35.1	140.4	+0.2696	0.087

bracketed by similar measurements in pure KCl solutions and were expressed as ΔE, the difference between the potential obtained in a mixed solution and that of a KCl standard (10 or 100 meq/liter). Possible errors resulting from electrode drift were thus minimized.

The value of the selectivity function, k_{KNa}, was calculated from the equation:

$$\Delta E = S \log \frac{[(a_{K^+}) + (k_{KNa})\,(a_{Na^+})]}{(a_{K^+})_{std}} \qquad (1)$$

where S is the Nernst slope factor $(2.3\ RT)/F$. Activities of sodium and potassium were calculated from their stoichiometric concentrations, $[Na^+]$ and $[K^+]$, with estimation of the ionic activity coefficients, γ_{NaKCl}, by methods described previously (*2*). All activities, although dimensionless quantities, are referred to the same concentration scale (meq/liter), which is also used for stoichiometric concentrations.

Data obtained with a relatively fresh (1-month old) $NAS_{27\text{-}4}$ electrode (Table 1) show that selectivity of this electrode for potassium, in preference to sodium, varied over a wide range as a function of the relative concentrations of sodium and potassium (columns 4 and 9, Table 1). Data similarly obtained with an electrode which had been in use for approximately 1 year are given in Table 2. Significantly, the variation in selectivity with solution composition was much less pronounced than with the unaged electrode. For both aged and unaged electrodes, there was a simple straight-line relationship between log k_{KNa} and $[Na^+]/[Na^+] + [K^+]$ (Fig. 1) which could be expressed by:

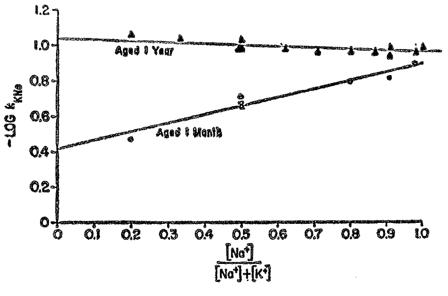

Fig. 1. Selectivity of NAS_{27-4} glass as a function of age and composition of the solution.

$$-\log k_{KNa} = \alpha + \beta\, q \qquad (2)$$

where $q = [Na^+]/[Na^+] + [K^+]$ and α and β are numbers whose values were independent of solution composition. For the fresh electrode, values for α and β were 0.41 and 0.49, respectively, whereas for the aged electrode the respective values were 1.03 and −0.06. There were small variations in α and β as a function of *p*H, but these were negligible over the limited range *p*H 6 to 8.

A practical modification of the equation developed by Eisenman, Rudin, and Casby (*3*) for measurement of potassium activities in mixed sodium and potassium solutions may therefore be represented by:

$$E = \text{constant} + S \log [(a_{K^+}) + (a_{Na^+}) \cdot 10^{-(\alpha + \beta q)}] \qquad (3)$$

An attempt was made to fit the experimental data to the equation of Eisenman, Rudin, and Casby (*3*):

$$E = \text{constant} + S \log [(a_{K^+})^{1/n} + (k_{KNa})^{1/n}\,(a_{Na^+})^{1/n}]^n \qquad (4)$$

where k_{KNa} and n are two adjustable parameters. If k_{KNa} is assumed to be independent of solution composition, our data for the unaged electrode offers values for n ranging from 1.29 to 1.14 over the range of q from 0.2 to 0.8. For the aged electrode, calculated values for n ranged from 0.98 at $q = 0.2$ to 0.995 at $q = 0.8$. At least for the unaged electrode, Eq. 3 corresponds more closely with the experimental data.

The mechanisms of aging in such electrodes are not understood, but the data indicate that electrodes intended for activity measurements of potassium in solutions containing significant sodium concentration should be carefully evaluated for selectivity in the concentration ranges under study and should have been in use for some period of time.

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Fission-Track Dating of Bed I, Olduvai Gorge

Abstract. *The discoveries of a series of hominid remains in the Olduvai Gorge, Tanganyika, has focused attention upon the age of the deposits of Bed I, in which both* Zinjanthropus *and* Homo habilis *were found. Because the age of 1.75 million years, as determined by the radioactive decay of potassium and argon, has been questioned several times, a fission-track age was measured for the pumice from Bed I. The result is 2.03 ± 0.28 million years, in good agreement with the result obtained by the potassium-argon decay method.*

Since a series of hominid remains were discovered in the Olduvai Gorge, Tanganyika (*1*), there has been considerable interest in the age of the deposits of Bed I, in which both *Zinjanthropus* and *Homo habilis* were found. The age of 1.75 million years found by Leakey *et al.* (*2*) using the K^{40}-Ar^{40} decay method has been questioned (*3*), not because of any lack of precision in the measurements, but on the basis of the possibility of the material being defective—for example, the material may have contained radiogenic argon at the time of crystallization or may have suffered atmospheric contamination. Although the results obtained by various dating methods do not allow us to answer stratigraphic questions such as have been discussed by Evernden and Curtis (*4*), the results can establish whether the ages found by Leakey *et al.* (*2*) apply to other materials in Bed I, and hence whether the K^{40}-Ar^{40} ages (*2*) for those materials are correct.

We have now determined the age of volcanic pumice from Bed I of Olduvai Gorge by means of fission-track dating (*5*), a method which has proved successful in dating glasses (*6*) and various minerals (*7, 8*) from 20 to 1.3×10^9 years of age.

Generally, the procedure for fission-track dating a crystal or glass is to count the number of tracks caused by spontaneous fission of uranium-238 during the lifetime of the sample. The age then depends only on the density of these tracks, ρ_s, and the number of uranium atoms, which is found from the increase in track density, ρ_i, produced by neutron irradiation and the resulting induced fission of uranium-235 (*9*). The age is then a simple function of the ratio (ρ_s/ρ_i).

For large single crystals or for homogeneous glass the experimental procedure is straightforward, but in some instances special problems must be overcome. The material used for the present study consisted of specimens from the volcanic deposit which extends over a wide area of the gorge and is particularly noticeable at sites DK I and MK I. This is the same deposit from which sample KA 847 was obtained in 1961 for dating by the K^{40}-Ar^{40} technique and which gave a date of 1.85 million years (*2*), and from which subsequently another part of the same material, KA 1043, gave a date of 1.76 million years. The procedure used was as follows. The tuff from Bed I was crumbled (resulting in crystals and glass pieces typically 200 μ in diameter), separated into compounds of like density, and found to include anorthoclase crystals, augite crystals, and a porous glass (density less than 2.5 and greater than 2.1).

The uranium content of the first of these materials was too low for it to be suitable for fission-track dating; and the second, though rich enough in uranium (1.4 parts per million by weight), presented great difficulty because of the need to section along specific crystal planes and at the same time to distinguish fission tracks from dislocations (*7*). Attention was therefore concentrated upon the glass, which also contains about 1 part per million by weight of uranium. Samples were mounted in glycol phthalate, sectioned, polished to an optical finish, etched for periods of 2 or 5 seconds in 48 percent hydrofluoric acid, and counted for fission tracks at a magnification of 550. The mounted samples were then wrapped in a plastic with a low uranium concentration, irradiated with thermal neutrons, re-etched for the same length of time, and counted again.

Under ideal circumstances the same area of glass should be counted first for spontaneous tracks and later for induced tracks. We found, however, that the combination of high porosity and small particle size caused the total exposed area of glass to change significantly as a result of etching. In our first series of experiments, we observed that the pumice is composed of nearly equal volumes of two different glasses; one glass is etched away after 10 seconds in 48 percent HF, and the other is etched sufficiently in 5 seconds for the tracks to be seen, but requires much longer to dissolve completely. The possible error in the correction for the decrease in area during etching leads to a 10-percent uncertainty in the final determination of age.

Using two separate groups of glass fragments from materials which had given a K-Ar age of 1.76 million years, we found a fission-track age of $2.0(^{+0.1}_{-0.3}) \pm 25$ percent million years. Here the range 1.7 to 2.1 results from the area correction, and the 25-percent error is the standard deviation from the statistics of the track count.

Because of these large errors due to the changes in area, we devised a quantitative procedure for measuring the area change caused by chemical etching. Some more glass fragments were mounted together in a group, polished, and etched for 500 seconds in 5 percent HF. The 79 tracks we

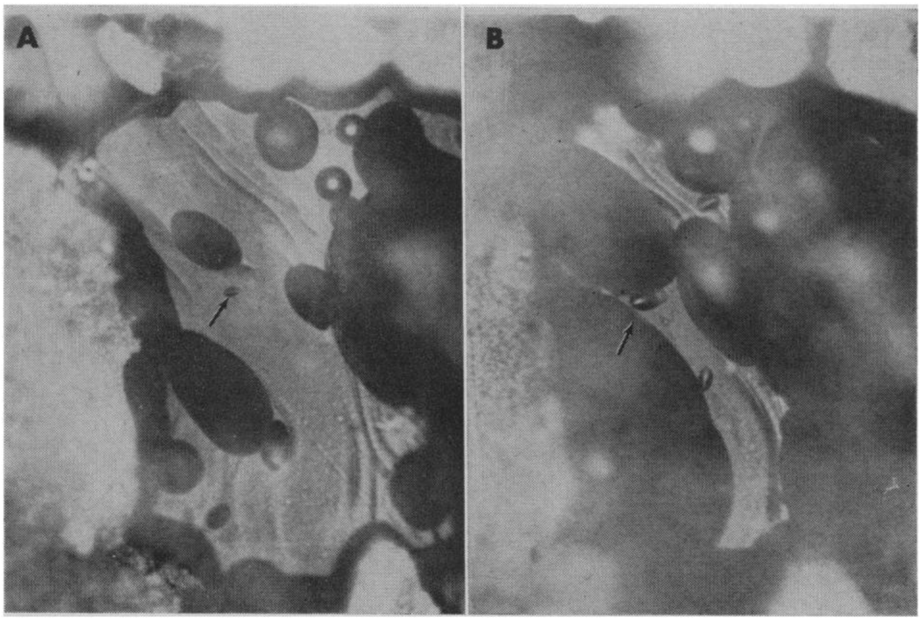

Fig. 1. Spontaneous and induced tracks in pumice from the Olduvai Gorge. (*A*) A single spontaneous fission track near the center of the photograph; (*B*) the same area after neutron irradiation and immersion in 5 percent HF for 500 seconds. The pit from the spontaneous fission track is now flat-bottomed and two new tracks have been induced by the irradiation. The ratio of the areas of exposed glass in (*A*) and (*B*) is roughly 7 to 1 (× 450). The arrows mark the site of the spontaneous fission track.

found which were caused by spontaneous fission were separately photographed and their positions recorded. After neutron irradiation the sample was re-etched for the same length of time, the total number of tracks was counted, and the locations of each of the original 79 tracks were photographed once again. Figure 1 shows one area after etching, before and after neutron irradiation. By point counts on the two groups of 79 photographs the ratio of the final glass area to that exposed during the spontaneous track count was found to be 0.416 ± 0.018.

Using this number along with the track counts, we obtained an age of 2.03 ± 0.30 million years. About 0.04 million years of the indicated standard deviation arose from the fact that the etching time used removed a slightly thinner layer of material than that crossed by a fission fragment. The need for this correction is discussed elsewhere (*7*).

If we now combine our two results, the final age is 2.03 ± 0.28 million years.

The possible sources of wrong ages in the K-Ar and fission-track methods are different. For example, the presence of "inherited" argon in the anorthoclase, which would lead to too high an age value by the K-Ar method, would not affect a fission-track age. On the other hand, fission tracks may be destroyed by heating—an effect which would lead to too low an apparent age. The fact that the two ages agree within the precision of the experimental procedures is therefore strong support for the validity of an age of nearly 2 million years. It would seem to be clear that if the age of the Upper Villafranchian is of the order of 1.75 to 2 million years then we must revise our ideas about the age of the beginning of the Pleistocene. The difference between the mammalian faunae of the Lower and Upper Villafranchian is such that we may reasonably expect that the former may have started no less than 3 million years ago.

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Lewis Acidity of Polar Organic Solvents from Thermodynamic Measurements

Abstract. *A quantitative measure of the Lewis acidity of common organic solvents is given by the equilibrium constant for complex formation between the solvent and a π-donor such as an aromatic hydrocarbon. Lewis acidities are reported for 12 solvents from new distribution and vapor-pressure measurements.*

A Lewis acid is a substance which has a tendency to attract electrons, and one direct measure of Lewis acidity is given by the electron affinity. Measurement of electron affinities of polyatomic molecules is at present essentially impossible and therefore, to characterize the strength of Lewis acids, indirect measurements must be employed.

In view of the potential importance of Lewis acidity in a variety of chemical and biological phenomena we have calculated Lewis acidities of several common polar organic solvents as obtained from our thermodynamic measurements. The use of thermodynamic data to give information on the formation of a complex between Lewis acid and Lewis base has been reviewed by Andrews (*1*) and by Briegleb (*2*), and our studies are in principle very similar to the technique used by Brown and Brady (*3*) to characterize the relative basicities of aromatic hydrocarbons.

We characterize the Lewis acidity of a polar solvent by comparing its volatility in a saturated hydrocarbon with that in an unsaturated hydrocarbon which is our reference Lewis base. We restrict ourselves to solutions which are very dilute in Lewis acid. If a 1:1 complex is formed in solution, the equilibrium constant for complex formation is

$$K_x \equiv x_C/x_1x_2 \qquad (1)$$

where x_C is the mole fraction of complex in solution and x_1 and x_2 are, respectively, the true (equilibrium) mole fractions of acid and base. We propose to use this equilibrium constant as our measure of Lewis acidity. If $x_1 \ll 1$, then $x_2 \approx 1$, and

$$K_x = \frac{x_C}{x_1{}^o - x_C}, \qquad (2)$$

where $x_1{}^o$ is the apparent mole fraction or the true mole fraction in the absence of complex formation. Let P_1 be the partial pressure of the polar species in the saturated hydrocarbon. If the complex is nonvolatile, then P_1', the partial pressure of the polar species in the unsaturated hydrocarbon, is less than P_1 by an amount of H_1x_C, that is,

$$P_1' = x_1{}^oH_1' = P_1 - H_1x_C = H_1(x_1{}^o - x_C) \qquad (3)$$

$$(H_1'/H_1) = 1 - (x_C/x_1{}^o) \qquad (4)$$

where H_1 is Henry's constant for the polar solvent in the saturated hydrocarbon and H_1' is Henry's constant in the unsaturated hydrocarbon. Combining Eqs. 2 and 4,

$$K_x = \frac{H_1}{H_1'} - 1 \qquad (5)$$

or, since the ratio of Henry's constants is identical to the ratio of the activity

Table 1. Lewis acidity constants for polar organic solvents at 25°C from *n*-hexane–*p*-xylene distribution coefficients.

Polar species	K_x (dimensionless)
Dimethyl carbonate	2.3 ± 0.7
Methoxyacetone	2.3 ± 1.4
2,3-Butanedione	2.5 ± 0.7
Acetone	2.6 ± 0.3
2,4-Pentanedione	3.3 ± 1.0
Nitrobenzene	4.2 ± 1.5
Propionitrile	4.5 ± 1.0
Nitroethane	5.1 ± 1.0
Methoxyacetonitrile	6.8 ± 1.0
Acetonitrile	8.0 ± 3.0
Triethyl phosphate	8.6 ± 2.4
Nitromethane	9.0 ± 1.0