Potassium-Argon Dating by Activation with Fast Neutrons

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When a potassium-bearing mineral is irradiated by a neutron flux containing a significant fraction of fast neutrons, 270-year Ar^{39} is produced by the K^{39} (n, p) reaction, and this may be used as a basis for measuring the potassium-argon age of the mineral. *Wänke and Konig* [1959] described such a method in which counting techniques were used to detect the Ar^{39}, as well as Ar^{41} produced by the Ar^{40} (n, γ) reaction. A calculation of the potassium content for a single sample would require a knowledge of the flux-energy distribution in the reactor and the excitation function of the K^{39} (n, p) reaction. The uncertainties of this calculation can be avoided, however, by comparing the (Ar^{40}/Ar^{39}) ratio in the unknown sample with that quantity in a sample of known age, given the same irradiation. In this case we may write down the following relationships.

$$\frac{(Ar^{40}/K^{40})}{(Ar^{40}/K^{40})_s} = \frac{(Ar^{40}/Ar^{39})}{(Ar^{40}/Ar^{39})_s} = \frac{(Ar^{41}/Ar^{39})}{(Ar^{41}/Ar^{39})_s} = \frac{(\exp(T/\tau) - 1)}{(\exp(T_s/\tau) - 1)} \quad (1)$$

T is the unknown potassium-argon age, τ is the mean life of K^{40}, and the subscript s refers to the sample of known age.

A correction for atmospheric contamination is not possible with this technique, and more recently *Merrihue* [1965] has suggested using mass spectrometric detection of the Ar^{39} and radiogenic Ar^{40}. The method has the advantage of allowing Ar^{36} to be measured, and, conse-

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TABLE 1. Potassium-Argon Ages from Irradiation 1[a]

Meteorite	Sample Weight, g	A^{40}/A^{39}	A^{40}/A^{36} This Paper	A^{40}/A^{36} Literature[a]	K-A Age, b. y. This Paper	K-A Age, b. y. Literature[b]
Richardton	0.910	4860 ± 200	1810 ± 60	1850	≡4.32	4.35
				1910		4.15[c]
				2050		4.47[d]
Abee	0.157	4660 ± 200	178 ± 5	185	4.25	4.71
Holbrook	0.942	4320 ± 150	3340 ± 80	4200	4.12	4.44
				5280		4.4[e]
St. Marks	0.354	4110 ± 170	127 ± 3	102	4.04	3.78
Indarch	0.379	4030 ± 150	967 ± 30	892	4.01	4.29
Murray	0.077	3190 ± 180	8.92 ± .25	4.63	3.62	1.58
				3.65		1.90[e]
				8.54		2.77[d]
Bruderheim (1)	0.223	742 ± 30	605 ± 20	740	1.61	1.85
(2) See Figure 5 and text.						

[a] Integrated thermal neutron flux, $1.7 \times 10^{19} n/cm^2$.
[b] *Kirsten et al.* [1963].
[c] *Geiss and Hess* [1958].
[d] *Reynolds* [1960].
[e] *Stauffer* [1961].

TABLE 2. Potassium-Argon Ages from Irradiation 2[a]

Meteorite	Sample Weight, g	A^{40}/A^{39}	A^{40}/A^{36} This Paper	A^{40}/A^{36} Literature[a]	K-A Age, b. y. This Paper	K-A Age, b. y. Literature[b]
Bjurböle	0.590	9850 ± 350	4230 ± 60	1830 9150 1310	≡4.33	4.34
Pantar light[c]	0.600	9700 ± 900	5600 ± 100		4.30	
Peseyanoe						
(900°C)	0.322	9110 ± 450	27.4 ± .5		4.20	
(1500°C)		9140 ± 450	16.6 ± .4		4.21	
Total		9130 ± 450	19.1 ± .5	18.2 28.0 26.8	4.21	4.50 4.2
Bruderheim[b] (1)	0.855	1850 ± 100	630 ± 50	740	1.86	1.85
(2)	0.88	2860 ± 150	407 ± 15		2.41	

[a] Integrated thermal neutron flux, $5.6 \times 10^{18} n/cm^2$.
[b] *Kirsten et al.* [1963].
[c] Temperature run—see graph.
[d] *Geiss and Hess* [1958].
[e] *Gerling and Levskii* [1956].
[f] *Stauffer* [1961].

quently, a correction for atmospheric contamination can be made in some circumstances. The correction is particularly simple for terrestrial samples under the assumption that all the Ar^{36} is of atmospheric origin, so that the Ar^{40} contamination is just 296 times the Ar^{36} value. In meteorites the situation is more complex because of two additional sources of argon: primordial, present in the material since its solidification, and cosmogenic, produced by cosmic-ray-induced nuclear reactions within the past 100 m.y. or so. For the sake of convenience we shall refer throughout the paper to all argon other than Ar^{39} and radiogenic Ar^{40} as contamination.

This technique offers two important advantages over conventional potassium-argon dating methods, in which argon abundance is measured by mass spectrometry and isotope dilution, and the potassium, by the flame photometry of a 'split' of the sample. First, both potassium and argon are determined simultaneously by a single measurement on the same sample. Secondly, neither potassium nor argon absolute abundances are required. The age is derived from the (Ar^{40}/Ar^{39}) isotope ratio, a quantity that can be measured more accurately than the absolute abundances of either potassium or argon. In principle, therefore, the technique is ideal for dating very small samples, such as single meteorite chondrules, or for particularly rare samples.

The purpose of this letter is to present some preliminary data and to show how the method may be usefully extended by observing variations in the isotopic ratio with temperature during gas release. This extension is similar to the technique of correlated release employed in I-Xe dating. [*Jeffery and Reynolds*, 1961; *Reynolds*, 1963].

The results of some argon measurements carried out routinely in the course of I-Xe dating experiments are shown in Tables 1 and 2, the two tables representing two distinct irradiations. In Table 1, the measurements refer to the total gas released from the meteorite in a single melting of one-hour duration. The K-Ar ages have been calculated relative to the meteorite Richardton, the age of which has been assumed to be 4.32 b.y. on the basis of three earlier determinations [*Kirsten et al.*, 1963]. In future experiments of this kind it might be preferable to include a terrestrial sample of more accurately known age. No correction for air contamination has been made in Table 1 because of the uncertainties already

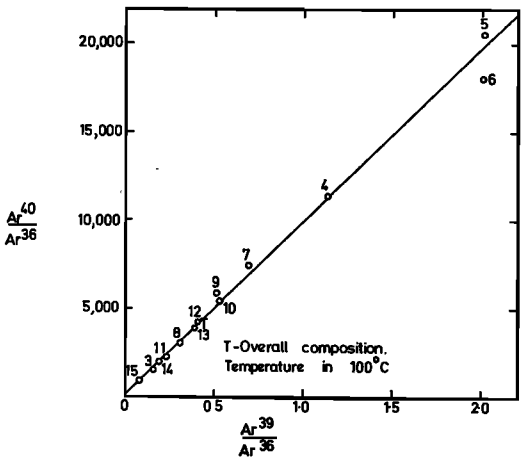

Fig. 1. Argon correlation in Bjurböle.

mentioned in attempting to do this for meteorites. However, (Ar^{40}/Ar^{36}) ratios were measured, and these are presented for comparison with other experimental determinations on unirradiated samples to see whether any systematic change in air contamination is brought about by the irradiation. Richardton, Holbrook, St. Marks, Murray, and Bruderheim show (Ar^{40}/Ar^{36}) ratios closer to the atmospheric value in the irradiated samples than in the unirradiated ones, whereas for Abee, Indarch, Bjurböle, and Peseyanoe the reverse is true. Consequently, no definite conclusions regarding contamination can be drawn. No information can be obtained from Ar^{38}, which is affected by Cl^{37} (n, γ) reactions. Nevertheless, the calculated K-Ar ages seem to be in reasonable agreement with earlier determinations except for the case of Murray. Air contamination is almost certainly the reason for this discrepancy.

Table 2 summarizes the results of more detailed experiments in which the irradiated sample was outgassed at a series of temperatures up to the melting point. For Bjurböle and Pantar (light) this was done in 100°C steps, heating for one hour at each temperature, and Figures 1 and 2 are graphs of (Ar^{40}/Ar^{36}) against (Ar^{39}/Ar^{36}) obtained. The measurement errors on the individual points are typically ±1–2% in the (Ar^{40}/Ar^{36}) ratio and ±5% in the (Ar^{39}/Ar^{36}) ratio.

If one makes the assumption that two types of gas of distinct composition are present, Ar^{40} and Ar^{39} derived from potassium (subscript k) and Ar^{40} and Ar^{36} present as contamination (subscript c), one may write

$$(Ar^{40}/Ar^{36}) = (Ar^{40}/Ar^{36})_c + (Ar^{40}/Ar^{39})_k(Ar^{39}/Ar^{36}) \quad (2)$$

Thus a plot of (Ar^{40}/Ar^{36}) against (Ar^{39}/Ar^{36}) would be a straight line. For meteorites $(Ar^{40}/Ar^{36})_c$ will not be constant, unfortunately, unless one of the three forms of contamination predominates. However, since this ratio in meteorites will in general lie somewhere between the atmospheric value of 296 and zero, the plot will be, for all practical purposes, a straight line if the observed values of (Ar^{40}/Ar^{36}) are much larger than 296 or than the variations in $(Ar^{40}/Ar^{36})_c$.

The first condition is fulfilled in Figures 1 and 2, and from the two slopes a K-Ar age of (4.30 ± 0.15) b.y. is calculated for Pantar (light) relative to an assumed 4.33 b.y. for Bjurböle [*Kirsten et al.*, 1963]. We should point out that in both cases the highest (Ar^{40}/Ar^{36}) ratio observed was a factor of 5 to 6 times the average or total meteorite value. Thus, even in the case of a meteorite for which the average (Ar^{40}/Ar^{36}) value is low and the contamination correction normally difficult to apply, we would expect that the separation of components brought about by a temperature run would reduce by almost an order of magnitude the uncertainty in this correction.

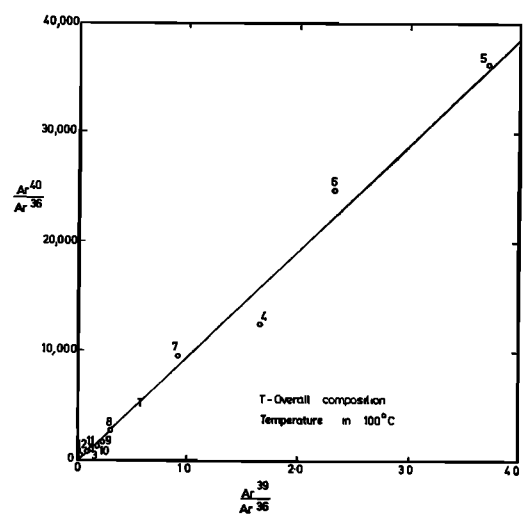

Fig. 2. Argon correlation in Pantar (light).

The possible presence of Ar^{39} from Ca^{42} (n, α) reactions has not been overlooked in these experiments. However, by comparing (Figure 3) the quite different release patterns of Ar^{39} and Ar^{37} (from the Ca^{40} (n, α) reaction), we are able to conclude that a negligible proportion of Ar^{39} has been produced in this way.

A less detailed experiment on Peseyanoe at just two temperatures yielded comparable (Ar^{40}/Ar^{39}) ratios corresponding to a K-Ar age, relative to Bjurböle, or 4.21 b.y. The agreement of the (Ar^{40}/Ar^{39}) ratios for different (Ar^{40}/Ar^{36}) ratios indicates that Ar^{40} air contamination was negligible and the Ar^{36} mainly primordial.

The results of outgassing experiments on Bruderheim are superficially less clear cut and indicate a further avenue for useful research. Diffusion loss of Ar^{40} has occurred in this meteorite whose K-Ar age based on total gas content is 1.85 b.y. according to *Kirsten et al.* [1963]. Because of this, the distribution within the meteorite of radiogenic Ar^{40} and K^{40} may not be the same and the $(Ar^{40}/Ar^{39})_k$ ratio observed in a temperature run would therefore be expected to vary. If the loss of Ar^{40} has been gradual or incomplete, one might intuitively expect the observed $(Ar^{40}/Ar^{39})_k$ ratio to increase monotonically from some value below the average to a value nearer to that corresponding to its 'true' age at higher temperatures. On the other hand, if the loss of Ar^{40} had occurred at a distinct time in the past and

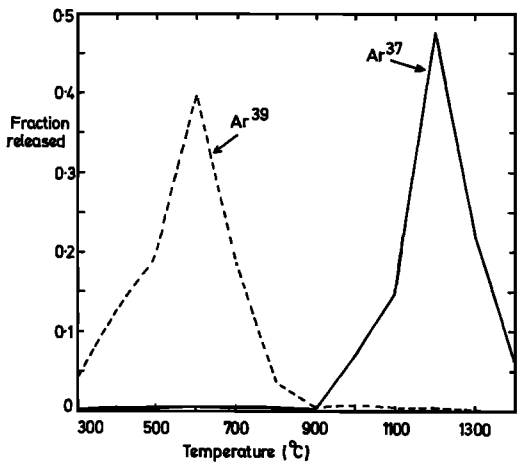

Fig. 3. Release of pile-produced argon from Bruderheim (irradiation 1, sample 2).

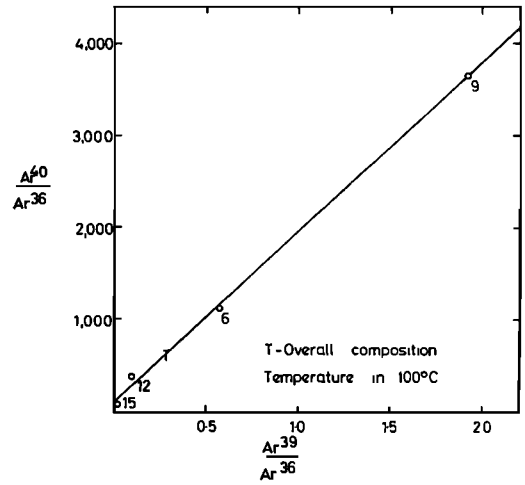

Fig. 4. Argon correlation in Bruderheim (irradiation 2, sample 1).

was complete, the observed $(Ar^{40}/Ar^{39})_k$ ratio would be expected to be constant and to indicate the time of outgassing.

In Figure 4 (Table 2, sample (1)) the results of a shortened outgassing of Bruderheim, with 300°C steps, lie on a straight line with a slope corresponding to 1.86 b.y. An attempt at a more detailed temperature run (Figure 5), however, indicates that this correlation is probably fortuitous, and, in fact, a variation of the (Ar^{40}/Ar^{39}) ratio is observed in a fashion consistent with incomplete degassing of the meteorite at some time in the past. While the overall (Ar^{40}/Ar^{39}) ratio in Figure 5 corresponds to 1.7 b.y., the 'age' of the various fractions rises from less than 1 b.y. at the low temperatures to more than 3 b.y. at higher temperatures. We can be more specific in an interpretation of this variation if we consider the possibility that partial outgassing occurred (or ended) at some definite time in the past. At this time the (Ar^{40}/K^{40}) ratio would be expected to be zero at the surface of mineral grains and practically zero for some depth into the grains. Subsequently, accumulation of Ar^{40} would lead to an (Ar^{40}/K^{40}) ratio in these surface regions corresponding to the time of outgassing, and the argon released at low temperatures in the present experiments should indicate this ratio. While stressing the preliminary nature of our results, we might point out that in Figure 5 the 200°C, 300°C, 400°C, and

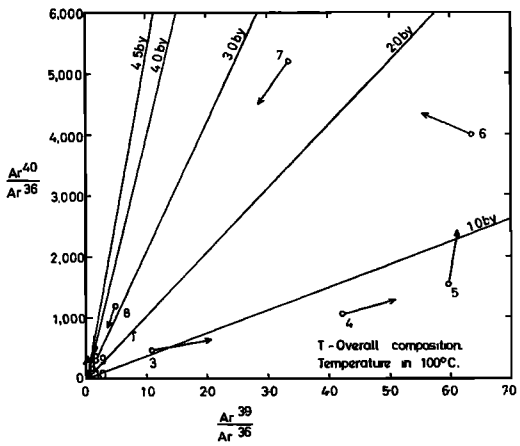

Fig. 5. Argon release from Bruderheim (irradiation 1, sample 2).

500°C points, together with the atmospheric point (A), lie on a line whose slope corresponds to 0.55 ± .05 b.y. This is particularly interesting in view of the observed tendency for (U, Th)—He ages of hypersthene chondrites to cluster close to 0.5 b.y. [*Anders,* 1964], possibly indicating a major parent body collision around this time. A similar interpretation of the present data is at this stage speculative, although one may certainly produce arguments to justify it. There is, for instance, a strong tendency for the loosely held atmospheric contamination to be released in the initial stages of an outgassing experiment, and we would therefore expect $(Ar^{40}/Ar^{36})_a$ to be 296 in the low temperature release, particularly in an ordinary chondrite with its very low primordial gas content. We may also set an upper limit of 0.7 b.y. on the age of the 400°C and 500°C gas, by drawing a line through these points and the origin, $(Ar^{40}/Ar^{36})_a = 0$. We expect $(Ar^{40}/Ar^{39})_a$ to increase monotonically with gas release so 0.7 b.y. is an upper limit for the 300°C point also. More detailed experiments on the hypersthene chondrites are in progress to check our initial findings.

In view of the above discussion, it is apparent that experiments of this kind could provide an extremely useful tool for investigating the thermal histories of both meteorites and terrestrial minerals. We are at present investigating the possibilities of a more detailed quantitative interpretation.

These preliminary experiments have indicated the potential usefulness of the correlated release method used in conjunction with neutron activation of potassium bearing minerals or groups of minerals. Very small samples may be used, and, in the case of meteorites, the uncertain effects of argon from other sources reduced by a large factor. There exists also the exciting possibility of deducing information of the past thermal history of the sample. For terrestrial materials with moderate or low air contamination simple one-shot ratio determinations on a small specimen would be sufficient to give the K-Ar age. The limit of detection of Ar^{39} in a mass spectrometer is set by the presence of the much larger adjacent Ar^{40} peak, the tail of which tends to obscure the Ar^{39}. The problem of producing sufficient Ar^{39} for detection in this way should therefore be much easier for terrestrial samples with lower K-Ar ages. For extremely young terrestrial samples with large air contamination, the separation of air and radiogenic argon in a many temperature outgassing experiment could be profitable in lowering by almost an order of magnitude the detectable (Ar^{40}/K^{40}) ratio.

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