

A MASS SPECTROMETRIC STUDY OF K^{39}/K^{41} ABUNDANCE VARIATIONS BY DUAL COLLECTION AND DIGITAL MEASUREMENT TECHNIQUE

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ABSTRACT

The status of K^{39}/K^{41} abundance ratios in rocks and minerals is reviewed and the errors and corrections required in such measurements pointed out. A double-collector mass spectrometer with digital recording has been used for K^{39}/K^{41} measurements in a number of granites, charnockites and zeolites. While the granites do not reveal fractionation effect, K^{39} deficiency has been observed in charnockites and zeolites. Possible reasons for such a fractionation are pointed out.

Key words : K-isotopes, isotope geology.

INTRODUCTION

Reports on the variation of K^{39}/K^{41} in natural samples started as early as 1936 through the work of Brewer.¹ Natural variations have been reported since then through to the present day. Many of the early results have been discredited and some workers concluded that no natural variations in the ratio have been observed.^{2, 3} It was suggested that observed variations may be due to impurity in the sample or fractionation due to difference in crystal structure of the sample.⁴ Nevertheless natural variations in the ratio K^{39}/K^{41} continue to be reported.⁵⁻⁷ Important results, viz., natural variations of K^{39}/K^{41} in contact zones have been reported by Schreiner *et al.*⁸ and natural fractionation at a granite/gabbro contact zone has been reported by Perminor *et al.*⁹ However, even these results are still not completely beyond controversy (Verbeck—personal communication).

From theoretical considerations, however, such variations are expected under conditions of extreme temperature/pressure fractionation as in deep-seated rocks like charnockites and in processes involving selective ion exchange/absorption as in zeolites.¹⁰ Practically all the above measurements have been made with a single collector and peak scanning. We have made

an attempt to investigate the existence of such variations by an improved mass spectrometric technique employing double collection and digital measurement.

Problems of Measurement

It is quite worthwhile to begin with a consideration of some of the difficulties and problems in the mass spectrometric measurement of K-isotopic abundances using a thermal ionisation source and how most of them can be avoided or minimised.

The problems of K-isotope studies with thermal ion source are the following:

(1) Variable efficiency of ion collection due to lack of perfect focusing of the ion beam.

(2) Poor resolution and poor line profiles. It has been calculated by Reutersward⁴ that the fraction of ions emitted from the source which is collected by the collector is $\sim 1\%$ for $V_{\text{accin.}} = 1000 \text{ V}$ and $T = 1000^\circ \text{K}$. These limitations pertain only to early studies and are overcome in modern instruments with better focusing and vacuum conditions.

(3) Space charge limitation was studied by Copley *et al.*¹¹ According to them, space charge has some influence on saturated emission. The effect is directly proportional to beam intensity and inversely proportional to beam width. But according to Becker and Walcher¹² the effect is negligible for ion currents smaller than 10^{-9} amp—a condition that holds in most isotope abundance measurements.

(4) Deflection of ion beam due to magnetic field of filament heating current. However, the effect was found to be much smaller than other experimental errors in abundance determination.⁴

(5) Scanning with electric field introduces some mass discrimination effect due to change of electrodynamic forces¹³ which causes different portions of the ion beam to pass through the entrance slit. However, this effect can be minimised to a great extent by properly centering the beam and can be avoided completely by scanning magnetic field or no scanning as in the case of double collection technique¹⁴ (with flat top peaks).

(6) (a) Beam translation across the entrance slit.

(b) Beam inclination in the median plane of magnetic field and

(c) Beam inclination in the median plane of collector system.

However, according to Reutersward⁴ the errors due to these causes can be reduced to less than other experimental errors by proper focusing of the beam resulting in flat-top peaks.

(7) Varying thickness of coating on filament. It has been observed by Reutersward⁴ that change in K^{39}/K^{41} ratio of as much as 2.5% could be caused by a thick coating of the sample on the filament. Mutual collision interaction of the atoms of different layers may be the cause for such discrepancies. This effect can be reduced to very low values by loading a very small amount of sample at the centre of the filament in the form of a thin coating.

(8) Memory effect can be eliminated as discussed by Kendall¹⁵ by heating the filament to a high temperature for complete evaporation of the sample, followed by chemical cleaning of the filament and ion source.

(9) A platinum filament contains a good amount of alkali atoms which interfere with the precise measurement of K^{39}/K^{41} . This effect can be eliminated by degassing the filament in vacuum for about an hour at white hot temperature before loading the sample.

(10) Temperature effect: Within a single analysis a discontinuous change in measured abundance ratios may result from a change of filament temperature.^{16, 17} This phenomenon clearly shows that there is a variable isotope discrimination or fractionation effect which depends on the dimensional changes of the filament or conditions of its surface. However, this effect can be minimised for measuring relative variation by measuring both the standard and sample under identical temperature conditions of the filament.

(11) Consumption of sample: It is observed that as the amount of sample gets consumed during analysis, a systematic variation of isotopic ratio takes place. This is due to the preferential evaporation of the lighter isotope. Reutersward⁴ has given an analysis of this by Rayleigh fractionation which shows a relation between the measured ratio at time t , $q(t)$ and the ratio at time $t=0$, $q(0)$, given by the expression

$$q(t) = q(0) [n(0)/n(t)]^{\alpha}; \quad \alpha = (N/M)^{1/2} - 1,$$

where $n(0)$ and $n(t)$ are the number of isotopic molecules of mass N remaining at $t=0$ and $t=t$ respectively and N and M are the mass numbers of the two isotopes. However, to a close approximation $n(0)/n(t) = i_0/i_t$ where i denotes the ion current corresponding to isotope N .

The measurement shows that the effect is negligible if the measurement is taken before an appreciable fraction of sample is consumed. A typical curve (Fig. 1) for standard K_2SO_4 (Merck) obtained with our instrument shows the variation of ratio with amount of K^{39} evaporated. The value of a calculated from the curve = -0.028 which is close to the theoretical value of $a = (39/41)^{1/2} - 1 = -0.025$. It is further observed that up to the evaporation of a small fraction of K^{39} , the error introduced in the measurement is less than the experimental error. This has been maintained in all the present measurements. The result supports the earlier result obtained by Reutersward.⁴

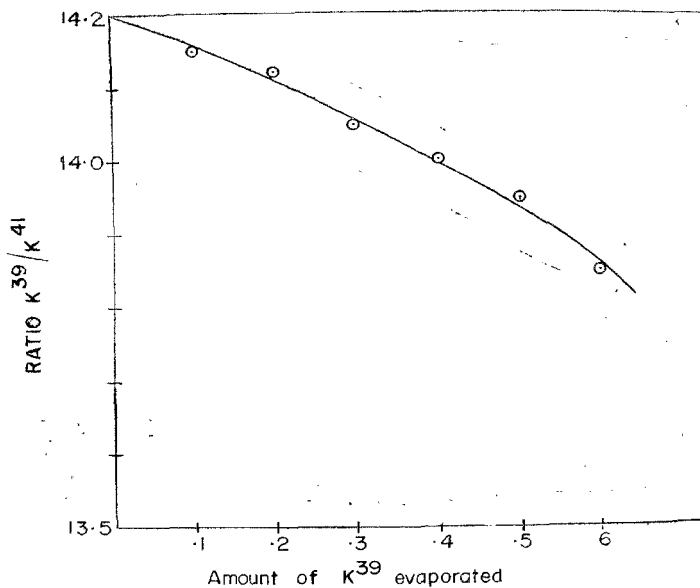


FIG. 1. Variation of K^{39}/K^{41} ratio with the amount of K^{39} evaporated.

Description of the Instrument

The mass spectrometer used for the present measurements is a Nier type, 90° sector magnetic field, $10''$ radius single focusing machine which

was previously used for the measurements of Rb and Sr and geochronological work in this laboratory.¹⁸

The collector end of the machine has been modified with a double-collector assembly mounted on a separate flange and inserted at the collector position. The double collector which facilitates the simultaneous collection of both the isotopes closely follows Nier's original design.¹⁹ In our case the separation between K^{39} and K^{41} is 12.5 mm. So the entrance collector slit is 13.5 mm and the slit on the first collector is about 1.2 mm wide. The advantages of dual collector are the following:²⁰

- (a) Elimination of errors due to variations in ion beam intensity since it is insensitive to variations in ion emission;
- (b) conservation of sample;
- (c) improved precision generally by cancellation of certain time dependent errors that are associated with the analysis;
- (d) no scanning is necessary and thereby the time for analysis is reduced.
- (e) due to static nature of simultaneous collection, the time constants can be increased and hence noise levels reduced.

There are a few disadvantages in dual collection system such as the following:

- (a) Beams follow slightly different paths and so the efficiency of ion collection is not the same in the two channels. Efficiency of collection can depend on voltage distribution at the source. However, for relative measurement the effect is negligibly small.
- (b) Tails of adjacent isotopic beams may overlap. With a single collector one can correct for this effect whereas in double collector the effect must be kept negligibly small.

All the measurements have been taken at a pressure of the order of 10^{-7} torr. The vacuum is obtained by two oil diffusion pumps with cold traps connected in parallel backed by a rotary pump.

Electronics

(1) For the acceleration of the ion beam a highly stabilised 2.5 kV constant voltage power supply has been used. The output voltage is smoothly variable from 400 V to 2.5 kV with a regulation of 0.01%.

(2) For the magnet, a highly stabilised constant current supply has been used. The current is smoothly variable from 50 to 500 mA. The current regulation is of the order of 0.01%.

(3) A highly stabilised constant current low voltage (6 V, 5 A) supply has been used for heating the filament. A Pt-Pt* Rh (10%) thermocouple been used for monitoring the filament temperature.

(4) For the detection set up, two identical electrometer amplifiers²¹ (using CK 5886, transistors and ICs) have been mounted very close to the collector end in shielded boxes. The amplifier linearity, stability and sensitivity have been tested to be satisfactory.

The analog output of the electrometer is converted to digital form. In the present set up, two identical voltage to frequency converters using op-amp and comparators²² have been used. The linearity of the units is $\sim 0.01\%$ and the stability is ~ 5 in 10^3 . The sensitivity of V.F.C. is 1500 c/s per volt. The isotopic signals are integrated for a known time and counted by frequency counters. Frequency counters using 7490 and 7441 with nixie display have been constructed for this purpose. To facilitate the integration of isotopic beams and counting of respective frequencies by the counters for equal time for both, a gate and a timer have been used. The ratio of counts in the counters gives directly the ratio of isotopic species. The block diagram of the collection technique is given in Fig. 2.

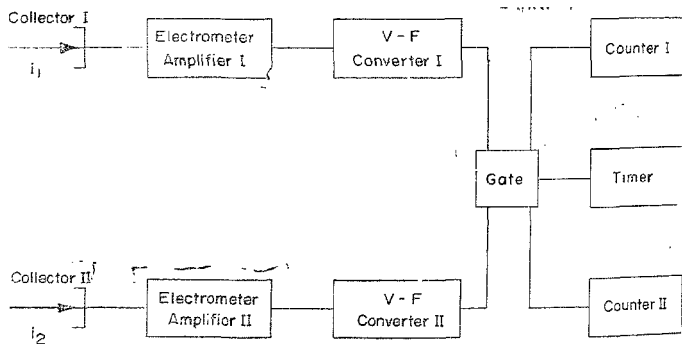


FIG. 2. Schematic diagram of the digital technique for dual collection.

Procedure of Measurements

Rock and mineral samples (charnockites and zeolites) have been used in the present measurement. Potassium has been separated by normal chemical treatment with HF, perchloric acid, etc., and the final solution containing K_2SO_4 is concentrated so that 1-2 drops at the centre of the filament yield a steady beam (5×10^{-11} A for K^{41}) for 1-2 hours.

The focusing of the instrument has been tested with standard K_2SO_4 (Merck) sample. For each sample the instrument is adjusted for flat-topped peaks with a chart recorder and after obtaining the best focusing condition, the chart recorder is replaced by the digital recording system. The contribution to K^{41} by the tail of the K^{39} peak is found to be less than 0.03%.

(a) Measurements with standard

In each run with the standard 3 sets of 20 measurements of isotopic ratios of K^{39}/K^{41} have been taken. The same standard has been repeated a number of times and alternately with the sample. No systematic variations have been observed. The ratio remained constant within an error of 0.35%.

The ratio of K^{39}/K^{41} (averaged over 25 runs) obtained is 14.20 ± 0.02 for the standard.

(b) Measurements with granite, zeolite, granite associated with charnockite and charnockite far away from granitic region have been carried out under conditions identical to those for standard (particularly temperature

TABLE I
Granite

Sample and locality	K^{39}/K^{41}
S (standard K_2SO_4)	14.20 ± 0.02 (= R_0)
G_1 [Prophyrite and homogeneous]	14.18 ± 0.02
G_2 [granite from Kolar District]	14.15 ± 0.02
G_3 [Grey granite from]	14.19 ± 0.02
G_4 [Chamundi Hill,]	14.16 ± 0.02
G_5 [Mysore]	14.17 ± 0.02
G_6 (Arsikere granite from Karnataka)	14.21 ± 0.02
G_7 (Homogeneous and pandeol granite, Patna area, Kolar District)	14.22 ± 0.02

and state of evaporation). Periodic repeats of standard and sample have been carried out to check the consistency of the results. The results obtained are shown in Tables I to III. S denotes standard K_2SO_4 ; Z_1 - Z_7 denote zeolites (natural); G_1 - G_7 are granites; GC_1 - GC_3 denote granites associated with charnockite and C-15 to C-17 are charnockites.

TABLE II

Charnockite and granite associated with charnockite

Sample and locality	K^{39}/K^{41}	$\frac{R - R_0}{R_0} \times 100$
C-15 (Discordant charnockite from Kabuldurga)	13.85 ± 0.02	2.47 ± 0.2
C-16 (Concordant charnockite from Kabuldurga)	13.89 ± 0.02	2.18 ± 0.2
C-17 (Charnockite, Bastipur Village, Karnataka)	13.82 ± 0.02	2.68 ± 0.2
GC-1 (Grey laistite gneiss from Kabuldurga)	14.01 ± 0.02	1.34 ± 0.2
GC ₂ [Pink gneiss from]	13.95 ± 0.02	1.76 ± 0.2
GC ₃ [Kabuldurga]	13.98 ± 0.02	1.55 ± 0.2

TABLE III

Zeolite (All from Gujarat)

Sample	K^{39}/K^{41}	$\frac{R - R_0}{R_0} \times 100$
Z ₁ (Lamontite)	13.85 ± 0.02	2.46 ± 0.2
Z ₂ (Stilbite)	14.06 ± 0.02	0.98 ± 0.2
Z ₃ (Natrolite)	13.91 ± 0.02	2.04 ± 0.2
Z ₄ (Scolecite)	13.89 ± 0.02	2.18 ± 0.2
Z ₅ (Heulandite)	13.82 ± 0.02	2.68 ± 0.2
Z ₆ (Gyrolite)	13.85 ± 0.02	2.47 ± 0.2
Z ₇ (Apophyllite)	13.90 ± 0.02	2.11 ± 0.2

Discussion of Results

The results on granites reveal a constancy of isotopic abundance ratios confirming the recent measurements available in literature.⁹ The granites cover a fairly wide range of mineralogical composition, texture and geological age (3000–1000 MY). The present results do not suggest large scale isotopic discrimination processes in the formation of large granitic bodies.

For charnockites K^{39}/K^{41} ratios 13.82–13.89 are obtained thus indicating a 2.68 to 2.18% depletion of K^{39} with respect to the standard. Charnockites are deep-seated crustal rocks belonging to the granulite facies of metamorphism. There is geochemical evidence that they have been subjected to repeated anatexis melting processes in the deeper crust, as indicated by their low K, Rb, U and Th contents and high K/Rb ratios. Isotopic fractionation is therefore conceivable²³ in such highly differentiated rocks. Here K^{39} may be expected to be concentrated in the anatexis melts that have been removed to the upper crustal regions resulting in lower (K^{39}/K^{41}) ratios for the residual granulitic rocks. Measurements in this laboratory²⁴ show abnormally large (K/Rb) ratios in these rock types. It is interesting that the granites associated with the charnockite (GC₁–GC₃, Table II) also show a depletion effect.

The results on a large number of zeolites also reveal a fractionation effect consisting of K^{39} depletion (1–2.7%). Taylor and Urey¹⁰ found as much as 10% change in K^{39}/K^{41} ratios in laboratory experiments involving cation exchange on zeolites. It is logical to expect a similarity of the process of preferential isotope effect in nature also. Cation exchange processes are expected to have played a role in the crystallization of the natural zeolites and their interactions with hydrothermal solutions.

REFERENCES

1. Brewer, A. K. The abundance of K-isotopes in mineral and plant sources, *J. Am. Chem. Society*, 1936, **58**, 365–370.
2. Cook, K. L. The relative abundance of K-isotopes in Pacific kelps and in rocks of different geological ages. *Phys. Rev.*, 1943, **64**, 278–293.
3. Kendall, B. R. F. Isotopic composition of potassium. *Nature*, 1960, **186**, 225–226.
4. Reuterswärd, C. Isotopic composition of potassium, *Ark. Fys.*, 1957, **11**, 1–54.
5. Letolle, R. Observation sur la composition isotopique de potassium de certaines roches. *Compt. Rend.*, 1962, **254**, 2205–2206.

6. Letolle, R. Sur l'abundance relative de d'isotope 41 du potassium suivant son origine geologique. *Compt. Rend.* 1963, **255**, 3996-3998.
7. Harms, G., Blanc, G., Espagno, L., and Blanc, D. Variations de la composition isotopique du potassium de differentes origin, *Compt. Rend.* 1962, **254**, 3203-3204.
8. Schreiner, G. D. L. and Verbeck, A. A. Variations of K^{39}/K^{41} ratio and movement of K in a granite-shak contact region. *Proc. Roy. Soc.*, 1965, **A 285**, 423-429.
9. Perminov, A. V. and Brandt, S. B. Natural fractionation of K-isotopes at a contact of granite and gabbro and in a paragenesis diopside-scapolite-pargasite. *U.S.S.R. Acad. Sci. Siberian Division Year Book*, 1969, pp. 205-208.
10. Taylor, T. I. and Urey, H. C. Fractionation of Li and K-isotopes by chemical exchange with zeolites. *J. Chem. Phys.*, 1938, **6**, 429-438.
11. Copley, M. J. and Phipps, T. D. The surface ionisation of potassium on Tungsten. *Phys. Rev.*, 1935, **48**, 960-968.
12. Becker, E. W. and Walcher, W. Abdeildungsfehler in Massenspektrometer infolge von raumladung und Magnetfeldsattigung. *Z. Physik*, 1952, **131**, 395-407.
13. Hintenberger, H. Precision determinations of isotope abundances. *Advances in Mass Spectrometry*, Vol. 3, Ed. by W. L. Head, pp. 517-546.
14. Wanless, R. K. and Thode, H. G. A mass spectrometer for high precision isotope ratio determinations. *J. Sci. Instr.* 1953, **30**, 395-398.
15. Kendall, B. R. F. Mass spectrometer ion source for solid samples. *Rev. Sci. Instr.*, 1958, **29**, 1089-1092.
16. Omura, I. and Morito, N. On the measurement of isotope abundance of Li with mass spectrometer. *J. Phys. Soc. Japan*, 1958, **13**, 659.
17. Dodson, M. H. A theoretical study of the use of internal standards for precise isotopic analysis by the surface ionisation technique. *J. Sci. Instr.*, 1963, **40**, 289-295.
18. Narayanswamy, R. *Ph.D. Thesis*, I.I.Sc. Physics, 1972.
19. Nier, A. O. A mass spectrometer for isotope and gas analysis. *Rev. Sci. Instr.*, 1947, **18** (6), 398-411.
20. White, F. A. *Mass Spectrometry in Science and Technology*, John Wiley and Sons, New York, 1968, Ch. 4, p. 90.
21. Rao, M. K. V. Electronics of surface instrumentation in *Proceedings of Symposium on Surface Instrumentation*, A.E.C., Government of India, Ed. by M. S. Murthy, 1975, p. 158.
22. A de Sa and Mitchell J. G. An inexpensive digital method for the measurement of isotopic ratios. *J. Sci. Instr.*, 1972, **5**, 138-140.
23. Heier, K. S. and Adams, J. A. S. *Geochemistry and Alkali Metals; Physics and Chemistry of Earth*, Pergamon Press, 1964, **5**, 237.
24. Venkatasubramanian, V. S., Iyer, S. S. and Pal, S. K/Rb and Ba/Rb ratio geochemistry of coexisting rock types in the shield complex of Mysore in *Proceedings of the 2nd Symposium on Upper Mantle Project (NGRI)*, 1970, pp. 455-462.