**KRYPTON ISOTOPES IN NEUTRON–IRRADIATED MINERALS: USE IN EVALUATING SAMPLES FOR $^{87}$Rb/$^{87}$Sr DATING**

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**RESUMEN**

Durante la irradiación con neutrones rápidos, en preparación para estudios de determinación de edad por $^{40}$Ar - $^{39}$Ar, isótopos de criptón son producidos de rubidio y estroncio presentes en minerales silicatos naturales. Mediciones de la razón $^{84}$Kr/$^{86}$Kr en muestras irradiadas permite la determinación de su razón Sr/Rb que es un parámetro esencial al estimar lo adecuado de los minerales para su posible estudio de Rb-Sr. Interferencias por otros elementos que ocurren en la naturaleza son evaluadas y aparecen ser despreciables.

**ABSTRACT**

During fast-neutron irradiation in preparation for $^{40}$Ar-$^{39}$Ar age determination studies, krypton isotopes are formed from rubidium and strontium present in natural silicate minerals. Measurement of the $^{84}$Kr/$^{86}$Kr ratio in irradiated samples admits the determination of their Sr/Rb ratio which is a parameter essential in evaluating the minerals for possible Rb-Sr studies. Interferences from other naturally occurring elements are evaluated and appear to be negligible.

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This pilot investigation to assess the possibility of determining Rb/Sr ratios in natural silicate minerals was prompted by the interest shown by many geochronological laboratories in the $^{40}$Ar-$^{39}$Ar dating method (Mitchell, 1968; Dalrymple and Lanphere, 1971; Lanphere and Dalrymple, 1971). In the $^{40}$Ar-$^{39}$Ar dating method, mineral samples are subjected to a fast neutron dose of the order of $10^{18}$ to $10^{19}\text{cm}^{-2}$ (often accompanied by an almost equal thermal neutron flux in a proportion controlled by the particular reactor facility being utilised, and whether or not cadmium shielding of the samples is being employed). $^{39}$Ar is produced from $^{39}$K in a (n, p) reaction [of zero threshold and mean cross-section to fission neutrons of ca. 100 mb] and the potassium-argon age of a sample can be measured in terms of argon isotopic ratios using a gas-source mass spectrometer (Mitchell, 1968). Interfering reactions arising in such an irradiation, from other naturally occurring elements with atomic numbers around 19, have been discussed in detail by Berreton (1970) and Dalrymple and Lanphere (1971). Such a fast neutron irradiation will also produce isotopes of krypton from rubidium and strontium (as well as from other elements with neighbouring atomic numbers), and as will be demonstrated, krypton isotopic ratios may be utilised to establish the Rb/Sr ratio in an irradiated mineral. This parameter is essential in the evaluation of the suitability of a mineral for possible $^{87}$Rb/$^{87}$Sr dating studies, and in the procedure described here, could be determined on the same extracted gas sample used for the $^{40}$Ar-$^{39}$Ar age determination.

**PRINCIPLES OF TECHNIQUE**

Table 1 summarises the principal neutron-induced reactions in nuclides having atomic number between 35 and 39, and the table forms the basis of an account of the analytical procedure, and of a discussion of potential interfering reactions.

The six reactions giving rise to isotopes of krypton utilised in this procedure are as follows:

- $^{85}\text{Rb} (n, d)^{84}\text{Kr}$  \hspace{2cm} \text{Threshold 4.92 MeV}
- $^{87}\text{Rb} (n, d)^{86}\text{Kr}$  \hspace{2cm} \text{Threshold 6.47 MeV}
- $^{87}\text{Rb} (n, \alpha)^{84}\text{Br} \xrightarrow{\beta^-} \text{T}_1 = 33 \text{ min}^{84}\text{Kr}$  \hspace{2cm} \text{Threshold 1.22 MeV}
- $^{84}\text{Sr} (n, p)^{84}\text{Rb} \xrightarrow{\text{E.C.}} \text{34 day}^{84}\text{Kr}$  \hspace{2cm} \text{Threshold 0.13 MeV}
\[ ^{87}\text{Sr} (n, \alpha)^{84}\text{Kr} \]
\[ ^{38}\text{Sr} (n, n\alpha)^{37}\text{Kr} \]

Threshold zero

Threshold 8.00 MeV

in which the atomic yields of the krypton isotopes 84 and 86 can be expressed as:

\[ ^{84}\text{Kr} = \text{Rb} \left\{ I_{85R} \Delta t \int \phi(e)\sigma(n,d) \, de + I_{87R} \Delta t \int \phi(e)\sigma(n,\alpha) \, de \right\} \]
\[ + \text{Sr} \left\{ I_{84S} \Delta t \int \phi(e)\sigma(n,p) \, de + I_{87S} \Delta t \int \phi(e)\sigma(n,\alpha) \, de + I_{88S} \Delta t \int \phi(e)\sigma(n,n\alpha) \, de \right\} \]
and

\[ ^{86}\text{Kr} = \text{Rb} \, I_{87R} \Delta t \int \phi(e)\sigma(n,d) \, de \]

where Rb and Sr denote the atomic abundances of the respective elements and \( I_{85S}, I_{87R} \), etc., denote the isotopic abundances of the specified atomic number in strontium and rubidium respectively. \( \phi(e) \) is the neutron flux per unit time, \( \sigma(n, \alpha) \) etc., are the cross sections (functions of energy) of the respective reactions and \( \Delta t \) is the duration of the irradiation. Integration is performed over all neutron energies. In any given irradiation of a suite of samples in which the individual isotopic abundances are uniform, these last two equations may be written

\[ ^{84}\text{Kr} = C_1 \, \text{Rb} + C_2 \, \text{Sr} \]
\[ ^{86}\text{Kr} = C_3 \, \text{Rb} \]

where \( C_1, C_2, C_3 \) are constants peculiar to the irradiation.

Whence

\[ \frac{^{84}\text{Kr}}{^{86}\text{Kr}} = \frac{C_1}{C_3} + \frac{C_2}{C_3} \left\{ \frac{\text{Sr}}{\text{Rb}} \right\} \]

(1)

i.e. in a set of samples experiencing the same irradiation, a linear relation should, in principle, exist between the induced \(^{84}\text{Kr}/^{86}\text{Kr}\) ratio and the \( \text{Sr}/\text{Rb} \) ratio in any sample. It should be noted that the effect of a neutron flux gradient over a group of samples irradiated in this way does not affect the values of either the intercept or the gradient of the linear relationship, both of which are constants provided the shape of the neutron spectrum does not vary.
Table 1  Potential Interfering Reactions: Atomic Numbers 35 to 39

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(n,p)</th>
<th>(n,d)</th>
<th>(n,n)</th>
<th>(n,np)</th>
<th>(n,v)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nuclide</strong></td>
<td>74Br</td>
<td>79Se → 79Br</td>
<td>78Se</td>
<td>76As → 76Se</td>
<td>75As</td>
</tr>
<tr>
<td></td>
<td>81Br</td>
<td>81Se → 81Br</td>
<td>80Se</td>
<td>78As → 78Se</td>
<td>77As</td>
</tr>
<tr>
<td></td>
<td>80Kr</td>
<td>80Br → 80Kr</td>
<td>79Kr</td>
<td>77Se</td>
<td>76Se</td>
</tr>
<tr>
<td></td>
<td>82Kr</td>
<td>82Br → 82Kr</td>
<td>81Kr</td>
<td>79Se</td>
<td>78Se</td>
</tr>
<tr>
<td></td>
<td>83Kr</td>
<td>83Br → 83Kr</td>
<td>82Kr</td>
<td>80Se</td>
<td>80Se</td>
</tr>
<tr>
<td></td>
<td>84Kr</td>
<td>84Br → 84Kr</td>
<td>83Kr</td>
<td>81Se → 81Br</td>
<td>82Se</td>
</tr>
<tr>
<td></td>
<td>86Kr</td>
<td>86Br</td>
<td>85Kr</td>
<td>84Br → 84Kr</td>
<td>83Kr</td>
</tr>
<tr>
<td></td>
<td>85Rb</td>
<td>85Kr</td>
<td>84Kr</td>
<td>83Br → 83Kr</td>
<td>82Kr</td>
</tr>
<tr>
<td></td>
<td>87Rb</td>
<td>87Kr → 87Rb</td>
<td>86Kr</td>
<td>85Rb → 85Kr</td>
<td>84Kr</td>
</tr>
<tr>
<td></td>
<td>88Sr</td>
<td>88Br → 88Sr</td>
<td>87Sr</td>
<td>86Rb → 86Sr</td>
<td>85Sr</td>
</tr>
<tr>
<td></td>
<td>89Sr</td>
<td>89Br → 89Br</td>
<td>88Sr</td>
<td>87Rb</td>
<td>86Sr</td>
</tr>
</tbody>
</table>

Reactions utilized in technique. \( E_T \) = Threshold Energy (MeV).
Subsequent decay of induced isotope: \( \beta^+ \) = positron, E.C. = electron capture.

Potential Interferences.
\( ^{83}\text{Kr} \) from irradiated RbCl also signifies that atmospheric krypton does not contribute to any significant extent to the observed mass spectra at these levels of neutron-induced krypton.

**ANALYTICAL PROCEDURE**

Mixtures of spectroscopically pure RbCl and SrF\(_2\) in the proportions shown in Table 2 were irradiated with an integrated dose of \(10^{19}\) cm\(^{-2}\) "fast" and \(3 \times 10^{19}\) cm\(^{-2}\)

<table>
<thead>
<tr>
<th>Krypton isotopic abundances in irradiated Rb/Sr mixtures</th>
<th>( ^{83}\text{Kr} )</th>
<th>( ^{84}\text{Kr} )</th>
<th>( ^{85}\text{Kr} )</th>
<th>( ^{86}\text{Kr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{80}\text{Kr}^* )</td>
<td>1.000</td>
<td>0.336</td>
<td>0.711</td>
<td>n.d.</td>
</tr>
<tr>
<td>( ^{81}\text{Kr}^* )</td>
<td>0.158</td>
<td>0.443</td>
<td>0.770</td>
<td>n.d.</td>
</tr>
<tr>
<td>( ^{82}\text{Kr}^* )</td>
<td>0.311</td>
<td>0.468</td>
<td>0.494</td>
<td>1.419</td>
</tr>
<tr>
<td>( ^{83}\text{Kr} )</td>
<td>11.64</td>
<td>0.701</td>
<td>0.442</td>
<td>1.445</td>
</tr>
<tr>
<td>( ^{84}\text{Kr} )</td>
<td>1.502</td>
<td>0.749</td>
<td>0.471</td>
<td>1.518</td>
</tr>
<tr>
<td>( ^{85}\text{Kr} )</td>
<td>1.650</td>
<td>0.747</td>
<td>0.453</td>
<td>1.650</td>
</tr>
<tr>
<td>( ^{86}\text{Kr} )</td>
<td>1.752</td>
<td>0.817</td>
<td>0.487</td>
<td>1.752</td>
</tr>
</tbody>
</table>

*All isotopes normalised to \( ^{80}\text{Kr} \).

\( ^* \) n.d. = not detected.

Strontium Fluoride (\(\neq 0\))

<table>
<thead>
<tr>
<th>Rubidium Chloride ((\neq 0))</th>
<th>0.326</th>
<th>0.560</th>
<th>0.994</th>
<th>1.957</th>
<th>3.775</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium Fluoride ((\neq 0))</td>
<td>1.000</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Rubidium Chloride ((\neq 0))</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

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thermal neutrons using the "thermal column" facility of the "Herald" reactor at AWRE, Aldermaston, U. K. This fast neutron dose is typical of those used in the $^{40}$Ar/$^{39}$Ar dating method. While the Thermal/Fast neutron ratio is about a factor three higher than might be experienced during an in-core fast-neutron irradiation, it is not considered to be significant in determining the outcome of the experiment. Weights of sample mixtures were typically 0.2 gm and Sr/Rb ratios of between zero and four were studied. This range of values was selected by virtue of it representing the typical variation of this ratio in terrestrial rocks (excluding mafic and ultramafic rocks) (Faure and Powell, 1972), and, in addition, the analytically "acceptable" range of this ratio when dating rocks of lower Palaeozoic or Precambrian age, would be typically 0.1 to 1. Natural levels of rubidium and strontium in silicate whole rocks are commonly 50 to 500 ppm, and though no attempt has been made in this pilot investigation to reproduce these abundances, extrapolation of the measurements is valid, as will be demonstrated later in this report.

RESULTS AND DISCUSSION

Table 2 shows the isotopic yields of krypton for the range of Sr/Rb ratios used. The analyses were performed using an on-line gas extraction system similar to that described by Miller and Brown (1965) coupled to an MS10 mass spectrometer which incorporated a 0.45 T magnet (Rex and Dodson, 1970), and operated under static conditions. All the data are arbitrarily normalised to the (largest) $^{80}$Kr abundance. Estimates of the absolute yields of krypton isotopes were made based on calibration of the mass spectrometer sensitivity using break-seals of atmospheric krypton. About $10^{-6} \text{mm}^3$ (STP) of $^{84}$Kr and $^{86}$Kr were produced in each irradiated sample. Consideration of the atmospheric krypton isotopes, specifically $^{86}$Kr (17.37\% by volume of atmospheric krypton) and $^{86}$Kr (11.55\% by volume of atmospheric krypton), indicates that since $^{86}$Kr was not detected in the mass spectrum obtained from irradiated strontium fluoride, and $^{83}$Kr was not detected in the irradiated rubidium chloride, the contribution of atmospheric krypton to the mass spectra is negligible at these levels of neutron-induced krypton.

It is apparent from the spectra obtained that $^{86}$Kr is produced uniquely from rubidium, and hence may be used to characterise this element. $^{84}$Kr is, however, produced from both rubidium and strontium, though the very large yield from strontium through presumably low-threshold (n, p) and (n, $\alpha$) reactions, makes it particularly useful in characterising the element. The presence of $^{84}$Kr in irradiated rubidium chloride does not preclude the possibility of using this isotope to determine Sr/Rb ratios, but may impose a lower limit on the applicability of the proposed method when the $^{84}$Kr yield from strontium is small.
Fig. 1 shows the isotopic data from the group of irradiated samples with 1σ error bars attached. It is evident that at the 2σ confidence limit, all of the data would conform to the linear relationship predicted by eq.(1). The method would, in principle, therefore admit the determination of Sr/Rb ratios in any similar sample by determining their $^{84}\text{Kr}/^{86}\text{Kr}$ after irradiation, provided two suitable monitors of known Sr/Rb ratio (to define the “calibration” curve) are irradiated at the same time.

![Graph showing $^{84}\text{Kr}/^{86}\text{Kr}$ isotopic ratios in irradiated rubidium and strontium mixtures.]

The extrapolation of the method described here, to samples containing “natural” levels of rubidium and strontium (ca. 100 ppm, say) is evidently possible. In the samples analysed here, $10^{-1}$ gm of each element produced typically $10^6$ mm$^3$ (STP) of each isotope utilised. Thus in a 1 gm natural sample containing 100 ppm of rubidium or strontium (i.e. $10^4$ gm in absolute terms) krypton isotopic abundances of $10^{-9}$ mm$^3$ (STP) would be formed during irradiation, a level which can be conveniently measured on an MS10 instrument such as has been described [see for example, Mitchell and Terrell, (in press)]. Enhancement of the sensitivity of the method could naturally be achieved by increasing the neutron dose, thus providing a potentially valuable “spin-off” to the determination of $^{40}\text{Ar}/^{39}\text{Ar}$ ages.

**BIBLIOGRAPHY**


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