Mass Spectrometric Trace Analysis of Rb and Sr by Isotope Dilution Method

Mass Spectrometric Trace Analysis of Rb and Sr by Isotope Dilution Method

Mitsutoshi UEDA*, Shigeru YAMASHITA*, and Teruo HAYAKAWA*

For the preliminary study of the age determination of minerals in rocks by Rb-Sr method, trace amounts of rubidium and strontium were determined by isotope dilution method using surface ionization mass spectrometer after the separating extraction of each element with ion-exchange resin column.

1. Introduction

Age determination of terrestrial rocks and meteorites from cosmic space, based on the measurement of decay products from radioactive nuclides contained in the rock-forming minerals of terrestrial rocks and meteorites, has been one of the most attractive problems for geochemists as studied by many workers[1~4] although the method is not so accessible. In our laboratory, age determination of rocks has been attempted using Rb-Sr method which is a kind of mass spectrometric investigation. In this paper, as a preliminary study of the age determination of rocks by Rb-Sr method[5~15], trace analysis of rubidium and strontium contained in biotites has been carried out as for granite samples found in the Tohoku districts.

The principle of the Rb-Sr method is based on the determination of the trace amount of ^{87}Sr produced from the β-decay of ^{87}Rb contained in the rock-forming minerals, and the following relation holds:

$$(^{87}Sr/^{86}Sr)_p = (^{87}Sr/^{86}Sr)_0 + (^{87}Rb/^{86}Sr)_p \{ \exp(\lambda t) - 1 \} \qquad (1)$$

where $(^{87}Sr/^{86}Sr)_p$ means the abundance ratio of the nuclides ^{87}Sr to ^{86}Sr at the present time, $(^{87}Sr/^{86}Sr)_0$ shows the initial abundance ratio of ^{87}Sr to ^{86}Sr at the time of rock-formation, $(^{87}Rb/^{86}Sr)_p$ denotes the abundance ratio of ^{87}Rb to ^{86}Sr at the present time respectively, and λ is the decay-constant of ^{87}Rb whose half-life has been known to be 5.0×10^{10} years[5,7,8,10], and t is the elapsed time from initial rock-formation to the present time, that is, the age of the sample minerals.

In order to estimate t from equation (1) by isochron plot, the contents of rubidium and strontium and the isotopic abundance ratio in each element must be determined for the sample minerals.

In this preliminary study of Rb-Sr method, because of the overlap of ^{87}Rb and ^{87}Sr peaks at mass number 87 in mass spectrometry, separation of rubidium and strontium has been carried out for the mixture solution extracted from the sample mineral biotite using ion-exchange column. The separated rubidium and strontium contained in each eluted fraction have been determined mass spectrometrically by isotope dilution method.

* Department of Chemistry, College of Integrated Arts and Sciences

2. Experimental

2.1 Treatment of the sample minerals

Sample minerals were weighed and digested in pure perchloric acid. Hydrofluoric acid was added repeatedly on water bath for complete dissolution of the sample[9, 12, 15, 16]. After the removal of excess acid from the solution, 3N hydrochloric acid was added and the 3N HCl solution of the minerals thus obtained was treated through ion-exchange column for the separation of rubidium and strontium.

2.2 Separation of rubidium and strontium

For the complete separation of rubidium and strontium each other from the 3N HCl solution of the sample minerals obtained as described before, the use of ion-exchange column seems to be the best way because of its high efficiency[15~19]. In this work ion-exchange resin Dowex 50W × 8 (200-400 mesh) was used and 3N HCl was used for elution. The apparatus were cleaned by acid-treatment and care was taken especially to avoid the contamination of water and chemicals by alkali-element impurities. The separation of rubidium and strontium was confirmed by flame spectrophotometric measurement of the fractions obtained from elution through ion-exchange column.

The rubidium-containing fraction and strontium-containing fraction were used for the mass spectrometric measurement as described in the following paragraph 2.4. In the case of isotope dilution experiment, known amount of isotopic spike was added to the 3N HCl solution before the preparation of samples for mass spectrometric measurement.

The chemicals and water used for the experiments were confirmed to be Rb- and Sr-free by mass spectrometry.

2.3 Determination of Rb and Sr by isotope dilution method

The isotope dilution method is a kind of mass spectrometric micro-analysis whose sensitivity is about 10^{-12} g at the best condition. Since so many works have been reported regarding to this method[20~25], short description will be given.

When we have a sample of X atoms of an element having n isotopes with the abundances $x_1, x_2, \ldots \ldots x_n$ ($\sum\limits_{i=1}^{n} x_i = 1$), we have $x_i X$ atoms of isotope i and $x_k X$ atoms from isotope k.

In a second sample of the same element with known quantity S atoms of different isotopic abundances $s_1, s_2, \ldots \ldots s_n$ ($\sum\limits_{i=1}^{n} s_i = 1$), we have $s_i S$ atoms from isotope i and $s_k S$ atoms from isotope k. The second sample is usually called isotopic "spike". Then the ratio m_{ik} of the isotope i and k in the mixture of the two samples is as following:

$$m_{ik} = \frac{x_i X + s_i S}{x_k X + s_k S} \tag{2}$$

Since quantity S is assumed to be known, we get for the unknown amount X as follows :

$$X = S \frac{s_{ik} - m_{ik}}{m_{ik} - x_{ik}} \frac{s_k}{x_k} \tag{3}$$

Here, $x_{ik} = \dfrac{x_i}{x_k}$, $s_{ik} = \dfrac{s_i}{s_k}$, and $m_{ik} = \dfrac{m_i}{m_k}$.

If the amount X and S are expressed in grams, X (g) is given from eq. (3) as follows :

$$X\,(g) = S\,(g) \frac{s_{ik} - m_{ik}}{m_{ik} - x_{ik}} \frac{s_k}{x_k} \frac{\sum\limits_{i=1}^{n} x_i A_i}{\sum\limits_{i=1}^{n} s_i A_i}$$

$$= S\,(g) \frac{s_{ik} - m_{ik}}{m_{ik} - x_{ik}} \frac{\sum\limits_{i=1}^{n} x_{ik} A_i}{\sum\limits_{i=1}^{n} s_{ik} A_i} \tag{4}$$

where A_i shows the masses of the isotopes in the atomic mass unit. Equations (3) and (4) mean that the excess abundance of the tracer isotope i in "spike" over its natural abundance in the probe is used to get the unknown amount X and X (g).

In the present work, for the determination of strontium content in biotite, isotope i has been ^{88}Sr and isotope k ^{86}Sr.

The ^{86}Sr-enriched spike prepared by Oak Ridge National Laboratory USA has been used in this work. The abundance ratio ^{88}Sr/^{86}Sr has been found 0.07907 ± 0.0001, which is two orders of magnitude less than the natural abundance ratio of ^{88}Sr/^{86}Sr.

The ^{87}Rb-enriched spike from Oak Ridge National Laboratory used in this work has the abundance ratio ^{85}Rb/^{87}Rb (= 0.00847 ± 0.0001) which is much less than the natural abundance ratio of 2.591.

2.4 Determination of isotopic abundance by surface ionization

For the mass spectrometric determination of isotopic abundance in Rb and Sr of the samples, surface ionization ion source of triple filament type has been used in this work. The triple filament ion source, developed by Inghram and Chupka[26], is useful in analyzing elements of low ionization potentials and is favoured for accurate measurement of isotopic ratios[9, 15, 24~27]. In this type of ion source, triple filament assembly consists of one center filament and two side filaments. In this work, tungsten ribbon was used for center filament and tantalum ribbon was used for side filament. These metal ribbons were cleaned by boiling in 1N HNO_3 and succeeding boiling in water before installation in the ion source. The material sample from Rb- or Sr-containing fraction described in paragraph 2.2, coated on side filaments, is evaporated at a controllable rate from the side filaments and then impinges on the hot center filament. Ionization then occurs dependent on the ionization potential I of the material and the work function Φ of the center filament. The proportion of the particles ionized on the hot center filament is given approximately by $\exp(-[I - \Phi])/kT$, where T means the temperature of the center filament.

The ions so produced are accelerated and collimated into an ion beam by means of electrode assembly of the ion source. The mass spectrometer used in this work was a single focusing type Hitachi RMU-6 instrument modified for surface ionization. Isotopic abundance ratio was obtained by measuring the ion current ratio of the corresponding isotopes averaged during the measurement lasting about 20 minutes in steady condition[27].

3.   Results

3.1 The abundance of ^{87}Sr and ^{87}Rb in the biotite samples

The isotopic abundance ratios ^{86}Sr/^{87}Sr obtained for the biotite samples found in the Kitakami- and Abukuma mountainland are shown in Table 1.

Table 1.   Isotope ratio ^{86}Sr/^{87}Sr and ^{85}Rb/^{87}Rb found in biotite samples by surface inonization

Sample number Isotope ratio	Biotite–I (Nakamura*)	Biotite-II (Yamadaya- matani*)	Biotite-III (Koide*)	Biotite-IV (Bohata-I*)	Biotite-V (Bohata-II*)	Biotite-VI (Furumichi*)
^{86}Sr/^{87}Sr	1.3434 ± 0.0040	1.3063 ± 0.0034	1.3153 ± 0.0053	1.2320 ± 0.0028	1.3376 ± 0.0057	1.2844 ± 0.0044
^{88}Sr/^{86}Sr	8.3731 ± 0.0010					
^{85}Rb/^{87}Rb	2.5906 ± 0.0032					

* The name of place in the parenthesis shows the spot where each biotite sample was found. The biotite samples I-III were found in the Kitakami mountainland, and IV-VI were found in Abukuma mountainland. Both of the mountainlands are placed in the Tohoku-district in Japan.
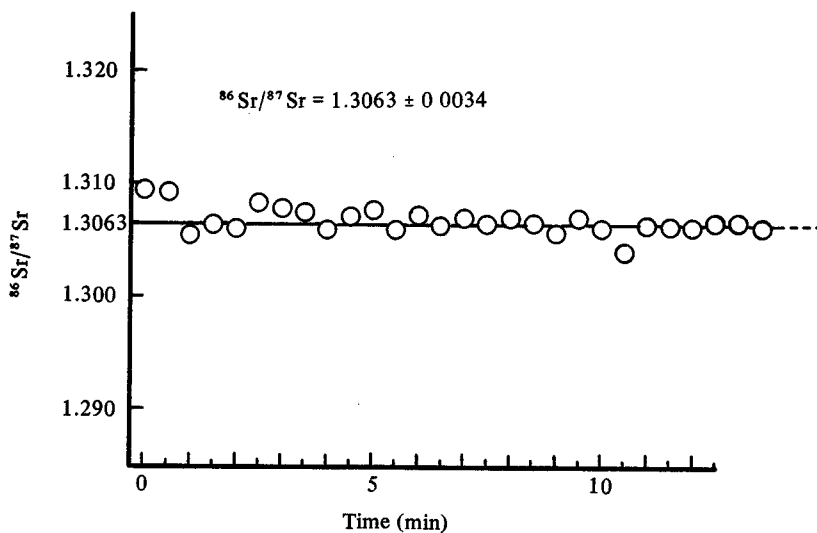

Fig. 1.   Time-variation of the isotope-ratio ^{86}Sr/^{87}Sr in the measurement by surface ionization of this work. The sample is the "Biotite-II" in Table 1.
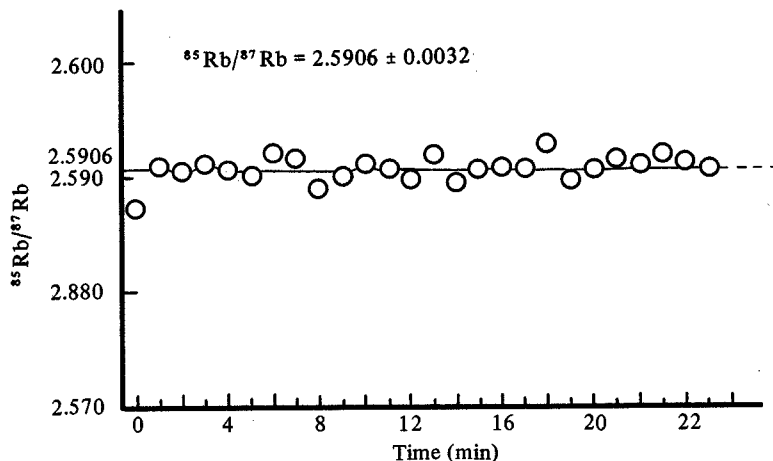
Fig. 2.   Time-variation of the isotope-ratio ^{85}Rb/^{87}Rb in the measurement by surface ionization of this work. The sample is the "Biotite-I" in Table 1.

Geochemical significance of the scattering of ^{86}Sr/^{87}Sr ratio in different samples found in Table 1 will be described in the next paper. The nuclides ^{87}Sr are composed of radiogenic species from ^{87}Rb decay and non-radiogenic species.

The abundance ratio ^{88}Sr/^{86}Sr, the abundance ratio of non-radiogenic isotopes ^{88}Sr and ^{86}Sr, was measured for the biotite sample I. The ratio ^{88}Sr/^{86}Sr was found 8.3731 ± 0.0010 as shown in Table 1 in good agreement with the well-known natural abundance ratio of ^{88}Sr/^{86}Sr. Therefore no further measurement of ^{88}Sr/^{86}Sr was carried out for other samples II ~ VI.

The abundance ratio ^{85}Rb/^{87}Rb was also measured for the biotite sample I, and the ratio observed (= 2.5906 ± 0.0032) is in accord with the natural abundance ratio ^{85}Rb/^{87}Rb (= 2.5906).

Fig. 1 and Fig. 2 show the time-variation of ^{86}Sr/^{87}Sr and ^{85}Rb/^{87}Rb values, respectively. Stability of the observed isotopic abundance ratio with time seems to be satisfactory.

3.2 Determination of Sr and Rb content in the biotite samples

The results of the determination of trace strontium content in biotites by isotope dilution method are shown in Table 2. Applying the values ^{88}Sr/^{86}Sr in spike, ^{88}Sr/^{86}Sr in biotite samples, and ^{88}Sr/^{86}Sr in the mixture to equation (4) of paragraph 2.2, the content of strontium in the biotite samples I ~ VI were obtained as shown in the last column of Table 2.

Similarly, the Rb-content values in the biotite samples I ~ VI were obtained as shown in Table 3.

Table 2.   The determination of the trace strontium contained in biotites by isotope dilution method. $^{88}Sr/^{86}Sr$ in ^{86}Sr-rich spike : 0.07907 ± 0.005, $^{88}Sr/^{86}Sr$ in biotite samples : 8.3731 ± 0.001

Sample number	Biotite-I (Nakamura*)	Biotite-II (Yamadaya-matani*)	Biotite-III (Koide*)	Biotite-IV (Bohata-I*)	Biotite-V (Bohata-II*)	Biotite-VI (Furumichi*)
Sample amount (g)	0.3160	0.2688	0.1800	0.2791	0.5560	0.2807
^{86}Sr-spike amount added (10^{-6}g)	15.52	119.07	5.97	5.32	12.10	7.93
Abundance ratio $^{88}Sr/^{86}Sr$ in mixture	0.6588	0.1296	0.9704	1.0085	0.9155	0.9984
Sr-content determined (ppm)	29.14	24.07	31.55	19.03	19.28	27.73

*   The name of place where each biotite was found. Detail is shown in the caption of Table 1.

Table 3.   The determination of the trace rubidium contained in biotites by isotope dilution method. $^{85}Rb/^{87}Rb$ in ^{87}Rb-rich spike : 0.00847 ± 0.001, $^{85}Rb/^{87}Rb$ in biotite samples : 2.5906 ± 0.0032

Sample number	Biotite-I (Nakamura*)	Biotite-II (Yamadaya-matani*)	Biotite-III (Koide*)	Biotite-IV (Bohata-I*)	Biotite-V (Bohata-II*)	Biotite-VI (Furumichi*)
Sample amount (g)	0.1705	0.1196	0.1235	0.1065	0.0895	0.0757
^{87}Rb-spike amount added (10^{-6}g)	177.7	161.95	152.78	152.00	122.54	102.94
Abundance ratio $^{85}Rb/^{87}Rb$ in mixture	0.1073	0.1569	0.2065	0.2330	0.1085	0.2343
Rb-content determined (ppm)	231.07	289.13	360.30	475.96	193.19	456.27

*   The name of place where each biotite was found. Detail is shown in the caption of Table 1.

Calibration using the samples of known concentration by isotope dilution method was not carried out. However, the results obtained in this work have been in good agreement with the results of other laboratory using the same biotite samples as ours, which suggests the reliability of the results in this work and will be reported in the next paper.

4. Conclusion

The separation of rubidium and strontium from the mixture solution, obtained by dissolving the biotite samples into hydrochloric acid, has been carried out using ion-exchange column. The separation of the two elements was confirmed by flame spectrophotometry. A single focusing mass spectrometer with triple filament type ion source for surface ionization has been used and the stability of the ion-currents showing the isotopic abundance has been found satisfactory. The trace amounts of rubidium and strontium have been determined by isotope dilution method and the results are available for the age determination of the biotite samples in the succeeding study.

Acknowledgment

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