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Some Technical Aspects of the Rubidium-Strontium Geochronology

By

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Abstract

Some technical aspects of the Rb-Sr geochronology which is undertaken at our Department are briefly described. Attentions are paid to the isotopic fractionation of Rb and Sr in the mass spectrometric measurements. It has been confirmed that the main time variation in the isotope ratio principally follows the Rayleigh distillation mechanism. However, in the actual measurements, various types of fractionations were observed which probably include the simultaneous simple processes of fractionation such as exchange reaction, diffusion and Rayleigh distillation. Examples of Rb-Sr geochronology of some metamorphic rocks are also given.

Introduction

This paper deals some technical aspects of Rubidium-Strontium geochronology which is being carried out at Department of Geology, Faculty of Science, Kyushu University. The program on geochronology was started in 1960 under the heading of Prof. Jun YOSHIMURA, who was the Dean of the Faculty of Science, with the financial support by the Grant in Aid for Scientific Research from the Ministry of Education. The main part of the mass spectrometer was constructed in September 1961 and the additional equipment including the very high vacuum lines were gradually constructed in the succeeding years until the general *Rubidium-Strontium* analytical equipments were completed by adding the electron multiplier and solid ion sources with the funds supplied through Prof. Tatsuro MATSUMOTO to our Department in 1964. A suite of chemical facilities was completed in the period of 1965 to 1967.

Although the methods and technics carried out here essentially follow those of ALDRICH et al. (1956), performance of our machine is fairly different which we believe worth to record here.

Constant encouragements and supports of the many members of our Department, particularly of Professors T. MATSUMOTO and J. YOSHIMURA during the course of this investigation are greatly appreciated. Valuable suggestions were given from Prof. K. OGATA and J. OKANO of the Dept. of Physics, Osaka University in constructing the machines. We are indebted to Drs. L. T. ALDLICH, G. R. TILTON, S. R. HART, G. L. DAVIS and T. E. KROGH of the Dept. of Terrestrial Magnetism for their instructive advices and suggestions while YAMAGUCHI was the fellow of the Carnegie Institution. This study was financed by the Grants in Aid for Scientific Research from the Ministry of Education which is gratefully acknowledged.

Preparation of Materials

Separation of mineral is usually done with the Frantz isodynamic separator, by panning and tapping. Fine powders of the samples are studied first using the X-ray spectrometer. Rubidium and strontium contents in the sample are estimated by comparing respective intensities of Rb and Sr with those of appropriate minerals or rock standard previously determined on strontium and rubidium contents by the isotope dilution method. The estimated and determined values generally agree within 1 to 10 percent. Suitable samples for the rubidium-strontium isochron studies are selected on this stage.

Isotope dilution analyses

The chemical treatments are done in the air circulating laboratory. Care is taken to avoid the contamination of the dust from the air to a minimum. A slightly higher pressure than one atomosphere is maintained in the laboratory by controlling the size of the drawing of the circulating air, a part of which being discharged through fume hoods and the chinks. The air was filtered with mechanical filters previously. An electrostatic air filter recently installed now creating cleaner circumstances.

Generally about 0.2 to 0.5 g of the powdered sample is weighed into 100 ml. teflon beaker, decomposed with hydrofluoric and perchloric acids at low temperature on a hot plate, and then taken to dryness, the perchloric acid remained in the residue were eliminated by raising the temperature of the hot plate to about 204°C.

The residue is dissolved in 2.5 N hydrochrolic acid and diluted to about 80 ml with good water. To ensure complete mixing, this solution is warmed gently for several minutes, and then stored overnight with Parafilm cover.

The solution is weighed, and two aliquots weighed into 10 or 30 ml pyrex glass beakers containing appropriate amounts of tracer solutions of Sr^{86-84} mixture and Rb^{87} respectively. The rest of the solution in the teflon beaker is not spiked and used for the determination of the Sr isotope ratios. The tracer solutions contain 2.9 μg Sr^{86-84} and 3 μg Rb^{87} per gram (one pipette) of solution respectively. Usually, one to several pipettes of tracer solutions are weighed. The amounts of aliquot are chosen to contain about equal weight of Sr^{88} and Rb^{85} with the Sr and Rb tracers to be added.

The spiked and unspiked aliquots are then taken to dryness. The residue of Rb spiked sample, a drop of sulfuric acid was added and converted to sulphate on the hot plate. Free sulfuric acid remaining in the sample and on the wall of the beaker was eliminated by raising the temperature of the hot plate to about 340°C. This residue is wet with drops of water, the supernatant solution is skimmed using a pyrex glass pipette and applied to the mass-spectrometer filament for the measurement of Rb isotope ratios. When the original sample is low in alkali contents, much of the solution is used for the Rb aliquot resulting a larger amount of residues. This requires a larger amount of water to wet the residue, the alkalis may be diluted with other sulphate such as iron and aluminum soluble into the supernatant. In such cases, the residue is wet with drops of water, centrifuged, and the supernatant solution collected and evaporated again. Smaller amount of residue was obtained by this process.

The residues of spiked and unspiked aliquots for the strontium are dissolved in 1 to 2 ml. of 2.5 N hydrochloric acid, centrifuged, and the clear solution transferred to cation exchange columns. This is eluted with about 80 ml. of 2.5 N hydrochrolic acid added in several steps in the first stage, and then the Sr is eluted and collected with 20 to 25 ml. of the same acid added in the succeeding stage.

The ion-exchange columns are of pyrex glass, 33 cm × 1.3 cm i.d. with G-4 sintered glass filter at the bottom and with 100 ml. reservoir and standard tapered socket at the top. The resin used is Dowex 50W-X8, 200–400 mesh and the resin in each column is 180 mm in length in 2.5 N hydrochloric acid.

The columns are caliberated by using natural samples and Sr^{90} solutions. Each 5 ml. fraction is analysed by the flame photometry and radiation counting using Geiger counter. Sr peaks in the columns agrees well within 2–3 ml. of 2.5 N hydrochloric acid if tested using a same sample. However, considerable shift of the Sr peak is observed among samples of different chemical composition. This would probably due to the interference of major elements such as iron, calcium, magnesium and alkalies, the content of which greatly variable among the minerals.

The Sr fraction is evaporated to dryness, and converted to strontium-nitrate by adding several drops of good nitric acid and dried. This sample is transferred in drops of water or 3 per cent nitric acid to the mass-spectrometer filament using a cleaned pyrex glass pipette.

Measurements of Isotope Ratios

The mass-spectrometer used is a Hitachi RMU-5G type, made of stainless steel with alminum gaskets, major features are given below.

Analyser: mean ion beam radius 20 cm., 90 deflection, sector type magnet, stainless steel tubing.

Ion source: surface ionization, tripple filaments, max currents 5A., accelerating voltage 500–2400 V.

Magnet: 0.4–5 K gaus, manual and automatic magnetic scanning, and a manually operated peak hoping device.

Ion collector: single collector, the slit width is externally adjustable; secondary electron multiplier, Hitachi MD-1050A type, with 10 steps Ag-Mg dynodes, accelerating voltage 500–3000 V, gain ×300∼×10000. The first dynode can be used as Faraday collector.

Amplifier: Hitachi transistorized D.C. amplifier type MA-11B, response 0.2 sec., high input resistors are 10^{11}, 10^{10}, 10^{9}, 10^{8} ohms.

Recorder: Yamatake-Honeywell, ball pen chart recorder 10 mV, 0.25 sec. full scale.

The machine is evacuated with a rotary and an oil diffusion pumps on the ion source side and a getter ion pump (40 *l*/sec, Nippon Electric Co.) on the collector side. The solid ion source is evacuated separately with another rotary and oil diffusion pumps. The machine can be baked to about 400°C at the center of the analyser tube and to about 200°C at both ends of the analyser tube.

The surface ionization source is provided with a sample exchange turret with dual rods and vacuum lock which allow to replace a sample on one rod while the other sample on the other rod is in operation. The source is generally operated at 2 KV. The higher sensitivity, good resolution and flat topped peaks are maintained during the operation by the adjustment of each repellar potential given to the side filaments, each half plate potential of the ion source, the width of the receiving slit, and by the fine adjustments of the accelerating voltage. The width of exit slit is generally fixed to about 0.5 mm and the width of receiving slit is about 1 mm.

The machine is used with an electron-multiplier when the ion intensity is low. Fairly low accelerating potential (100 V per stage, total 1000 V) is used to reduce the noise level to about 10^{-14} A. When a high ion current is reached during the operation, the first dynode is switched directly to the D.C. amplifier and the dynode was used as the Faraday collector. This operation enabled the monitoring of the mass descrimination within the electron multiplier by comparing the isotope ratios determined with an electron multiplier and with Faraday collector. Linerlity of the D.C. amplifier is about 0.003 per cent in the range of 0~10 V.

The recorder reading is calibrated and used in the range of the reproducibility of 0.1 per cent. The calibrations are often made using the Shimazu PD type precise potentiometer and standard cell.

Contamination in the mass-spectrometer is eliminated by cleaning all parts of the ion source with mixed hydrofluoric and nitric acid solutions after about 15 runs, and often monitored on blank sample filament in the mass-spectrometer by raising the three filaments currents to about 3 A respectively.

Unit of filament stems is cleaned each time by dipping it into the mixture of hydrofluoric and nitric acid solutions for several seconds, washed with water and alcohol and then dried on hot plate.

Generally, rhenium ribbon with 0.001″×0.020″ in size is used as the center filament, and the tantalum ribbons of the same size are used as the side filaments. Each filament unit is outgassed in vacuum device designed for this purpose to eliminate the contaminated elements by raising the filaments temperature to about 2000°C for at least 20 minutes. The current temperature relation of each filament can be measured using the optical pyrometer through the glass window of this outgassing device.

Isotope ratio measurements are made with the single collector by changing the magnet current. Single filament techniques are usually used. The samples are loaded on rhenium center filaments, and the side filaments are used to give the repeller potentials. At the beginning of each measurement, pertinent effort was necessary to get flat topped peaks while using the electron multiplier. This was performed by the repeated adjustment of the ion source potentials and the repeated automatic sweep of the magnet current. However, when the ion intensity is enough, the first dynode is used as the Faraday collector and the flat topped peaks are easily maintained.

Different isotopes are collected by switching of the magnet current to four preset values of the magnet power supply. Each preset value is manually adjusted and the peak top is held and recorded for about ten seconds on each isotope. Peak tops of the two isotopes are recorded alternatively and repeated for at least 10 times on each isotope within four to five minutes. Intensity of each ion current is measured on each time coordinate by drawing lines along the peak tops of the respective isotopes on the chart. A value of a isotope ratio is thus a average of at least ten measurements of the respective isotopes within five minutes, and the mean deviation calculated generally falls within 0.1 to 0.3 per cent.

Isotope Fractionation in the Surface Ionization

The usual operating currents for Sr, loaded as strontium nitrate are about 1.6–2.0 A for sample filaments corresponding to about 1100–1300°C, and for rubidium and potassium sulphate are about 0.8–1.0 A which correspond to about 700–800°C. The temperature of the filament is generally raised slowly. The vacuum of the machine is maintained in the range of about $3\times10^{-6}\sim10^{-7}$ torr during the operation. Detectable strontium beam often appears at temperature as low as 900°C (1.2 A). However, suitable intensity is not attained until the Rb and K intensities are falling rapidly. Measurements of Sr^{87} are done after the confirmation of the Rb contributions to be less than 0.1 per cent.

The unspiked Sr 86/88 ratios were normalized to 0.11940. The normalized Sr 87/86 ratio of several sets of measurements of a single run agrees within 0.1–0.2 per cent. However, unnormalized Sr 86/88 ratio shows wide variation and deviates more than 3 per cent from the standard value of 0.11940.

The source of this variation depends largely on the isotopic fractionation of the sample which has been resulted from the evaporation process of the sample on the filaments. This is made clear during the process of repeated measurements of Sr^{86-84} double tracer which is used as an internal standard during the isotope dilution analyses.

Isotopic fractionation on rubidium and potassium compounds on a single filament thermal ion source was given by EBERHARDT et al. (1964) and by RIIK and SHUKOLIUKOV (1954). The similar isotopic fractionation is observed for the strontium tracer which indicates a time dependent variation of Sr 86/84 ratio during the runs. To confirm the type of this variation, experiments are performed in a limitted condition in comparison with the usual operating conditions as given in the following.

About one to twenty micrograms of strontium nitrate of the tracer are placed in V shaped indent at the center of a rhenium filament, a center filament of the triple filament unit. Single filament technique is used. Two side filaments are used to give the repeller potentials. The samples are heated in the air to dull red glow for several seconds. This is necessary to eliminate the gas which comes out in the mass-spectrometer to a minimum. Good vacuum is maintained before the operation. Measurements are made on these samples by immediately raising the temperature of the filaments to give a satisfactory ion current. The temperature of the filament is held constant at about 1300°C (2A) throughout the run. During the whole measurements, little focusing of the ion beam was necessary and the ion intensity and the peak shape did not changed very much. The ion intensity increased gradually reaching to a maximum and then decreased gradually. The measurements of the ratios and their intensities are followed over a period of 2 to 30 hours until the evaporation of the sample is completed. The end of the run is assured by raising the temperature of the filaments.

Investigations are carried out with single collector and an electron multiplier at the beginning of the measurement and with a Faraday collector when an appropriate intensity is reached.

The ion intensities are integrated with time, and the relation of the Sr 86/84 ratio to the per cent evaporated Sr^{86} is shown in Fig. 1. Within the experimental error, the measured isotope ratios fall on the Rayleigh distillation curve. The curve is calculated from the following equation (COHEN, 1951).

$$\left(\frac{[m_2]}{[m_1]}\right)_t=\frac{1}{\alpha}\left(\frac{[m_2]}{[m_1]}\right)_0\left(\frac{[m_2]_0}{[m_2]_t}\right)^{\alpha-1},\quad m_2>m_1$$

$([m_2]/[m_1])_t$ is the isotopic abundance ratio in the vapor at time t

$([m_2]/[m_1])_0$ is the ratio in the reservoir at the beginning of the distillation.

$[m_2]_0$ and $[m_2]_t$ are the amounts of the isotope m_2 in the reservoir at the beginning and at time t respectively. The fractionation factor α is equal to $\sqrt{m_2/m_1}$.

Another type of isotope fractionation as already demonstrated by EBERHARDT et al. (1964) is also observed. This is a sharp variation of the ratio appearing at the beginning of the measurement which is followed by the main variation of the Rayleigh distillation curve. This type of variation is obtained in sample loaded in different way. Instead of heating the sample on the filament to red glow in the air, the sample solution is gently dried. In the mass-spectrometer, the sample is heated very slowly. The ion intensity is increased gradually reaching to a maximum of moderate intensity and then gradually decreased once to a minimum, and then increased gradually to the maximum intensity and then decreased. The variation of isotope ratio is shown in Fig. 2.

From the strontium nitrate solution, a tetrahydrate strontium nitrate which is monoclinic would precipitate at low temperature. This tetrahydrate nitrate would dehydrate at 100°C. If the nitrate solution is higher than 32°C, anhydrate strontium nitrate would precipitate directly. Such a process is often observed during the loading of the sample to the mass-spectrometer filament. Slender crystals of tetrahydrate strontium nitrate are formed first from the drop of

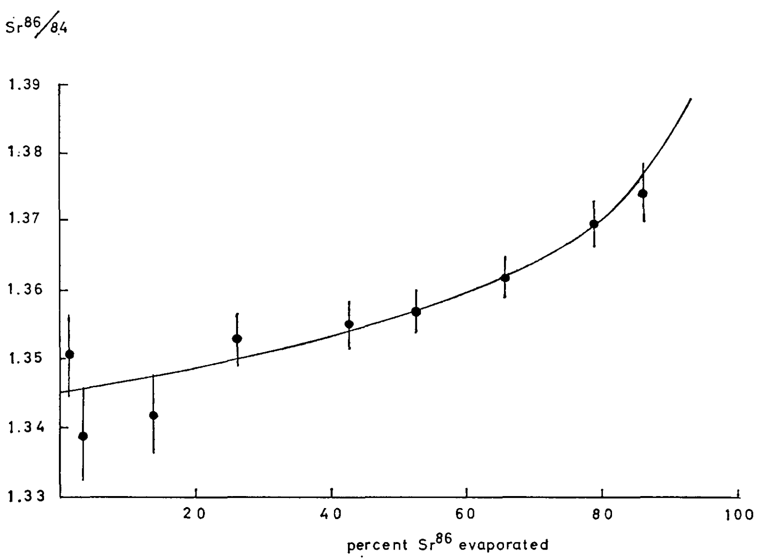

Fig. 1. Time variation of the observed Sr 86/84 ratio. The solid line represent the Rayleigh curve (Sr tracer ($Sr(NO_3)_2$) on rhenium filament).

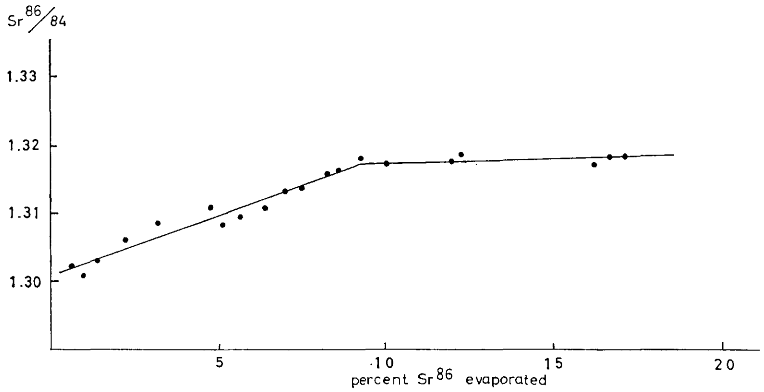

Fig. 2. Intial sharp increase of the Sr 86/84 ratio and subsequent Rayleigh Distillation (Sr tracer, on tantalum filament).

solution on the filament and these crystals are decomposed and converted to fine cubic crystals of strontium nitrate as the temperature of the filament is raised. The strontium nitrate would decompose to strontium oxide at about 1100°C, and the strontium oxide would dissociate to strontium metal in the presence of filament material followed by the evaporation and ionization of the strontium ions in the mass-spectrometer. These reactions are given below.

(1) $Sr(NO_3)_2 4H_2O \overset{100°C}{\rightleftarrows} Sr(NO_3)_2+4H_2O$ . . . loading in the air

(2) $Sr(NO_3)_2 \overset{1100°C}{\rightleftarrows} SrO+2NO_2+\frac{1}{2} O_2$ . . . in the source

(3) $SrO \overset{Re}{\rightleftarrows} \overset{\uparrow}{Sr}+\frac{1}{2} O_2$ . . . evaporation and ionization

The reactions mentioned above indicate the various chances of isotope fractionation involved in the isotope exchange reaction and evaporation.

In the usual operating procedure, the strontium sample is often contaminated with a fairly large amount of potassium and rubidium. In such a cases, the sample is kept around 800°C for a fairly long periods of time (12 to 24 hours) to eliminate the alkalis. After this procedure, strongly fractionated Sr ratio is obtained . It is also noted that the initial steep variation as shown in Fig. 2 is not observed when the temperature of the sample is raised very quickly (Fig. 1).

These observation indicates that the mass-spectrometric analyses are subjected to various type of isotope fractionation.

In the first stage, there is some possibility of the isotope fractionation which may occur during loading of the sample in the air. If the isotope exchange occurs during the reaction shown in equation (1), the $Sr(NO_3)_2$ molecule enriched with light Sr may be brought away along with the evaporation of H_2O molecule. Such a mechanism of fractionation was conceived from the experience that the strontium samples on the filaments were subject to red grow for a longer time in the air. It is often necessary to burn off the organic materials in the sample and to elimiate gas which might cause unfavourable effect to the vacuum and the ion intensity. This possible mechanism is, however, not confirmed in the present study.

The fractionation of the second stage may be understood in the reaction shown in the equation (2) which is shown by the initial steep variation of the isotope ratio shown in Fig. 2. The degree of this variation would depend on the size and the temperature of the sample which in turn, are related to the duration of reaction. If the temperature is fairly low and the amounts of sample is large, longer time would by necessary to convert the strontium nitrate to strontium oxide. The reaction rate would be controlled to the rate of removal of the NO_2 and O_2 in this equilibrium equation, the decrease of pressure of these gases by the evacuation in the source would increase the dissociation. The strontium oxide formed in the initial stage of the reaction would be enriched with light isotopes. This strontium oxide would immediately dissociate to strontium metal in the presence of rhenium or tuntalum filament followed by the ionization, the rate of which is also related to the decrease of the oxygen pressure in the equilibrium equation (3). The strontium metals and ions produced in the dissociation and evaporation of the strontium oxides and strontium metals would also be enriched with lighter isotopes. Dissociations of strontium nitrate to strontium oxide and that of the strontium oxide to strontium metal followed by the immediate evaporation of strontium would occur simultaneously until the dissociation of strontium nitrate to strontium oxide is completed. Combined effect of these two types of reaction would give a large fractionated isotope ratio.

If the size of the sample is small and the temperature is high, the dissociation of strontium nitrate to strontium oxide would be completed in a short duration and the initial steep variation of the isotope ratio can hardly be recognized.

The fractionation of the third stage is the Rayleigh distillation of the reaction (3). In principle, isotope fractionation by the Rayleigh distillation requires the continuous and complete mixing of the sample on the filament at a constant temperature during the evaporation. For this purpose, the sample should be carefully placed as a spot on the filament. However, the procedure is not always successful and the sample may often spread over the whole filament. In such a case, complete mixing can hardly be expected. The evaporation will begin from the center of the filament, migrating slowly outside. Even if the current of the filament is kept constant, temperatures along the filament would be uneven, and the evaporation rate of the sample would be different from the center to the outside of the filament. In such a condition, the time variation of the isotope ratio will be the average of the different rates of variation occurring on various points of the sample.

It is also observed that a change of isotope ratio occurs during the measurement when the temperature of the filament was changed. This change of time variation may be interpreted on one hand to the change of the rate of evaporation and on the other as the change of the area of mixing which means the change of the composition of the sample in the reservoir.

The foregoing discussion is mainly attempted to understand qualitatively the isotopic variation observed during the mass-spectrometric measurement. Quantitative aspects of the isotope exchange equilibrium and the rate of fractionation would remain to future study. In principle, fractionation of strontium on a single thermal ion source is a function of the square root of the mass. However, so far as we take the currently used procedure for normalization, the isotopic ratio of the common strontium can be determined within the accuracy of at least 0.05 per cent. If one plans to obtain more precise measurements, strictly controlled experiment would be necessary including the loading technique, measurement at constant temperature and the normalization procedure as a function of the square root of the mass. The difference of the normalized valeus between usual normalization and of Rayleigh distillation is shown in Table 1.

Table 1. Calculated Sr isotope variation on Rayleigh distillation and the Sr 87/86 ratios normalized to Sr 86/88=0.11940 assuming the degree of fractionation proportional to the difference between the masses (Sr $[86/88]_0=0.11940$, Sr $[87/86]_0=0.70840$).

Per cent Evaporated	Sr $[86/88]_t$	Sr $[87/86]_t$	Sr 87/86 Normalized
0	0.12078	0.70438	0.70840
10	0.12064	0.70480	0.70842
20	0.12047	0.70527	0.70840
30	0.12028	0.70581	0.70839
40	0.12007	0.70643	0.70840
50	0.11982	0.70717	0.70841
60	0.11951	0.70807	0.70839
70	0.11911	0.70924	0.70837
80	0.11856	0.71088	0.70836
90	0.11761	0.71371	0.70828
95	0.11666	0.71654	0.70813
98	0.11545	0.72030	0.70798

In practice, it should be noted that a large deviation would be expected if we take the ratio in the initial steep variation and that measured at the very end of the sample.

Determination of Rb and Sr isotope ratios

Isotope fractionation of Rb and Sr in the mass-spectrometric analyses is a serious problem in determining the true isotope ratios. Since the ratio of natural Sr 86/88 are believed constant, the Sr 87/86 ratio may be determined precisely by the usual normalizing procedure. Fairly good accuracy may also be maintained in determining the Sr content so far as we depend on the double normalization with double tracer Sr^{86-84} or Sr^{84}.

On the contrary, the determination of the Rb content involve no normalization and may be often subject to serious fractionation. In principle, we believe that the fractionation of Rb isotope should follow the Rayleigh distillation if the sample is pure in rubidium, as has already been discussed by EBERHARDT et al. (1964). However, in our practical measurements, the samples are contaminated

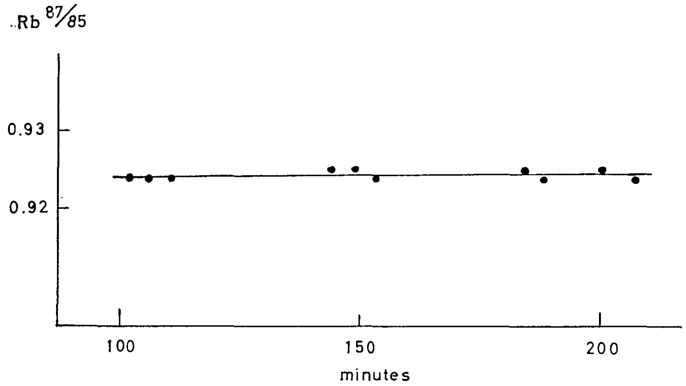

Fig. 3. Time Variation of Rb 87/85 ratio (HD 57-A, Muscovite in staurolite schist).

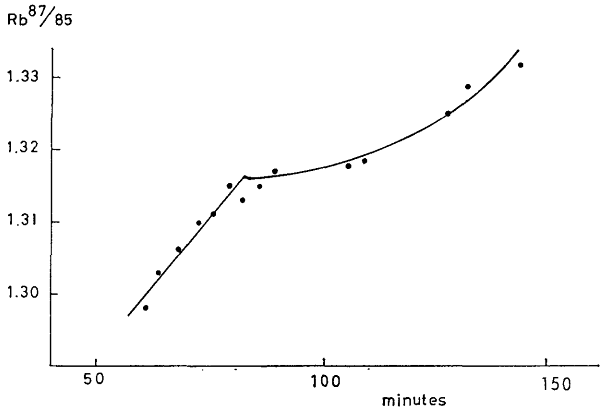

Fig. 4. Time variation of Rb 87/85 ratio (HD 56 Leptite, Whole rock, Rb spiked).

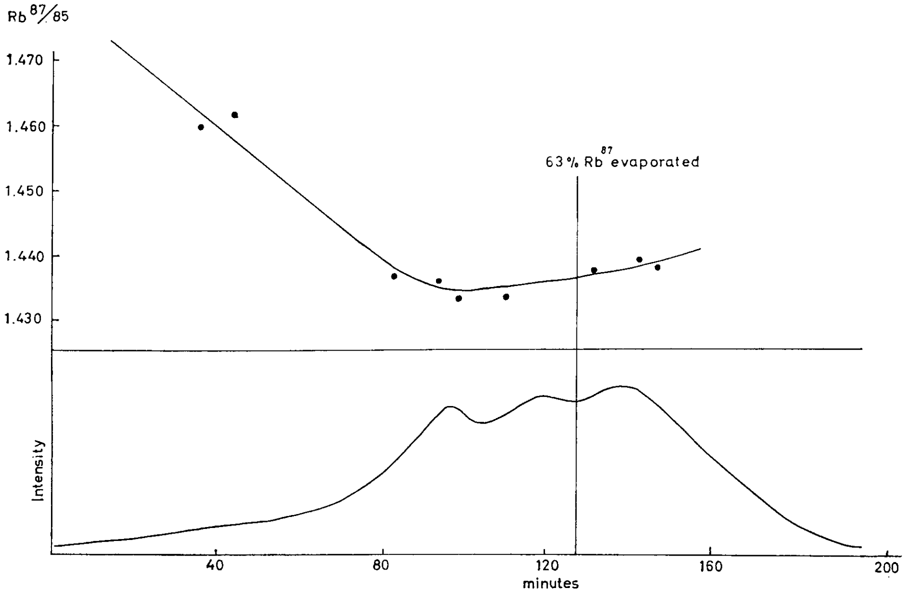

Fig. 5. Time variation of Rb 87/85 ratio and Rb 87 ion intensity (HD 52, Leptite, Whole rock, Rb spiked).

with elements other than rubidium to various extent, various types of time variation effect are observed, some of which are given in Figs. 3, 4 and 5. Fig. 3 indicates no appreciable time variation. Fig. 4 indicates the initial sharply increasing variation followed by the variation similar to the Rayleigh distillation. Fig. 5 indicates the initial sharply decreasing variation followed by the variation similar to the Rayleigh distillation. No attempt has been made to confirm these three types of variation by further experiment. Explanation of these types of variation would be complicated which includes simultaneous simple process such as diffusion, exchange reaction or distillation from the eutectic melting of rubidium and other elements.

It should be noted that in the usual operating condition, the maximum ion intensities are maintained in the region where the fractionated ratio becomes equal to the initial ratio of the sample in the variation of the Rayleigh distillation. For this reason, we are taking a fairly large number of isotopic measurements. A diagram showing the variation of isotope ratio with time is then constructed. If the whole ion intensity can be integrated, the ratio at the time when 63 per cent Rb^{87} evaporated would be equal to the initial composition of Rb. When the ion intensities are not integrated, the ratio of the initial steep variation, and the strongly fractionated values at the end of the run are generally ommitted. When the measurements at the beginning and at the end of a sample are not available, the ratios at the maximum intensities are usually averaged.

Similar types of time variation are also observed in the Sr isotopes. Isotopic composition of double tracer Sr^{86-84} are determined using the Rayleigh distillation formula. The initial sharp variation are found to continue until about 5 to 10 per cent of heavy isotope of sample are evaporated at the beginning. This variation is also taken into consideration in determining the isotopic composition of the tracer .

Integration of ion intensities of the Sr sample is no more necessary, if the composition of double Sr^{86-84} tracer is accurately known. After isotope ratio Sr 88/86 and Sr 86/84 and time variation diagram are constructed, the unfractionated ratio can be recalculated using the double normalizing procedure at any time coordinate. Examples are given in Fig. 6. Following the procedures above mentioned, the overall accuracy in the determination of Rb and Sr contents is believed better than 2 per cent and 1 per cent respectively. Common Sr 87/86 ratio measurement can be done with the accuracy of 0.2 to 0.1 per cent or better. The Sr 87/86 ratio of the commercial strontium carbonate (Eimer and Amend, Lot. No. 492327) normalized to Sr 86/88=0.11940 is Sr 87/86=0.7083.

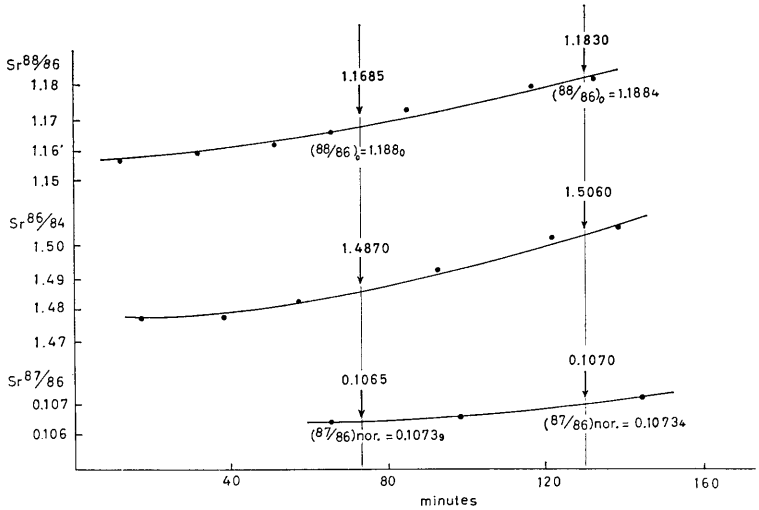

Fig. 6. Time variation of Sr isotope ratios (HD 57-A, Muscovite in staurolite schist. Sr spiked. rhenium filament).

Example of the Rb-Sr age determination

Results of isotope dilution analyses and the ages of some manganese minerals are given in Table 2 and in Fig. 7. The minerals were collected by F. HIROWATARI from the Taguchi managanese mine, about 50 kilometers north of the Toyohashi City, Central Japan (HIROWATARI et al. (1963)). Chemical separation of Rb and Sr of a manganophyllite (Sample No. 5) were done at the Department of Terrestrial Magnetism, Carnegie Institution of Washington. Minerals of Nos. 1, 2 and 3 were collected from the central portion of the quartz-feldspar-yoshimuraite-richterite-rhodonite gneissic rocks (50 cm thick), which are in contact with the ore bodies in the lower part, and the minerals of Nos. 4 and 5 were collected from potassium feldspar-manganophyllite-rhodonite gneissic rock, a transitional layer of yoshimuraite bearing rock to the hanging wall rock. The hanging wall rock is banded biotite gneiss of the Ryoke metamorphic rocks. Pegmatitic and aplitic

Table 2. Isotopic composition and concentration of Rb and Sr in the minerals from the Taguchi manganese mine.

Mineral Sample No.	Mineral	Rb ppm	Sr ppm	Rb 87/Sr 86	Sr 87/Sr 87*
1	Yoshimuraite	1.975	20242	0.000278	0.7092±0.0006
2	Rhodonite	1.191	261.4	0.0132	0.7090±0.0007
3	Manganophyllite	609.0	28.01	63.36	0.7720±0.0007
4	Rhodonite	1.0**	255**	0.0	0.7084±0.0007
5	Manganophyllite	397.1	63.9	18.03	0.7284±0.0007

* Unspike aliquot, normalized to 86/88=0.1194
** Estimated from X-ray spectrometry
Decay constant, Rb $\lambda=1.39\times10^{-11}$/year

veinlets derived probably from granitic rocks occur frequently in many parts of the ore deposit. It was reported that the Rb-Sr age of the Ryoke metamorphic rocks in the Kinki District ranges from 130 to 70 m.y. (YOSHIZAWA et al., 1966). The Sb-Sr age of granodiorites in this area is about 76 m.y. (OZIMA et al., 1967). Considering the geologic occurrence of the minerals and the previously determined Rb-Sr ages in this region, it may be concluded in the present study that the manganese minerals were formed at the age of about 70 m.y. after the intrusion of the granodiorites. The 80 m.y. age (Nos. 4–5) probably represents the intermediate age between the age of the Ryoke biotite gneiss and 70 m.y. due to the incomplete homogenization at the time of formation of manganese minerals.

The initial Sr 87/86 ratio of the manganese minerals is about 0.7090 which is practically equal to the Sr 87/86 ratio of rhodonite and yoshimuraite.

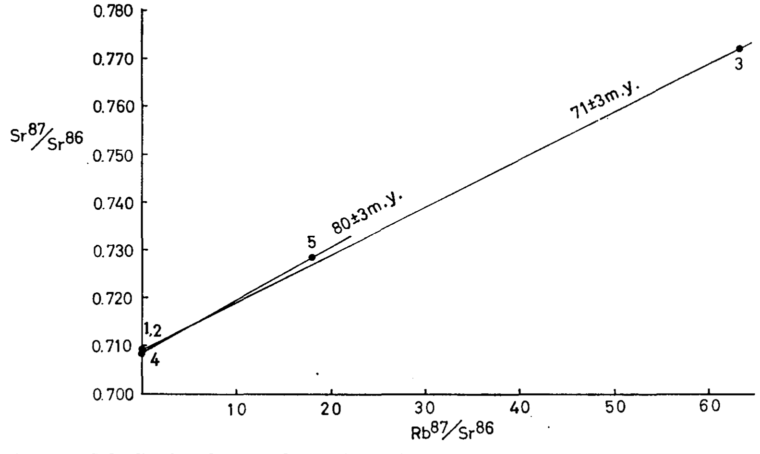

Fig. 7. Rb-Sr isochrons for minerals from the Taguchi manganese mine. Sample numbers refer to Table 2.

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Appendix

Chemicals Reagents

1. *Water.* City water is distilled first in a stainless container with automatic feed and stored in a polyethylene bottle. This is distilled again in 3 *l* pyrex glass until about a half of the volume is evaporated, and stored in a polyethylene bottle. The water is passed slowly through the anion and cation exchange resins in polyethylene tubings with teflon shavings as filter at the bottoms and stored in the polyethylene bottle. Stop cocks were installed under the tubings of the resin to adjust the flow rate of the water. No glass ware is used after the distillation in pyrex glass to avoid the contamination from the glass.
2. *Hydrofluoric acid.* Hydrofluoric acid of commercial special grade is distilled twice at constant boiling using all teflon line.
3. *Hydrochloric acid.* Hydrochloric acid of commercial first grade is distilled three times in pyrex glass at constant boiling.
4. *Perchloric acid and nitric acid.* Perchloric acid and nitric acid of commercial special grade are vacuum distilled twice at constant boiling in quartz glass.
5. *Sulfuric acid.* Sulfuric acid of commercial super special grade of Wako Pure Chemical Industries, Ltd. is used.

All pyrex glass wares are cleaned in hot sodium hydroxide solution and hot nitric acid solution respectively in the stainless steel containers. Contaminations in the analyses, estimated by the blank runs are less than 0.01 μg for strontium and 0.002 μg for rubidium per gram of sample respectively.