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REPORT No. 227

GEOLOGICAL SURVEY OF JAPAN

K–Ar AGE DETERMINATIONS ON GRANITIC AND METAMORPHIC ROCKS IN JAPAN

By

Ken Shibata

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Konosuke SATO, Director

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K-Ar Age Determinations on Granitic and Metamorphic Rocks in Japan

By

Ken SHIBATA*

Abstract

The experimental methods of K-Ar age determination developed at the Goolegical Survey of Japan are described in full detail. Argon is extracted by fusion without flux using a radio-frequency heater and purified from other gases by hot titanium sponge and CuO furnace.

Radiogenic argon is determined by the isotope dilution technique using a mass spectrometer. Various performance data are obtained on the Mitsubishi MS-315G mass spectrometer, which is an all-glass, Reynolds-type instrument specially designed for micro-analysis of argon isotopes. Argon of less than 10^{-6}ml STP can be isotopically analyzed by the static operation. The error in radiogenic argon determination is estimated to be about ±3 %. Two getter ion pumps are successfully used for the maintenance of high vacuum. Potassium analysis is made by flame photometry or tetraphenylboron method, and the error is estimated to be within ±2 %.

The K-Ar age determinations were made on some sixty samples of granitic and metamorphic rocks from various regions of Japan. The results generally agree with geological evidence.

The K-Ar ages of granitic rocks indicate a zonal arrangement corresponding to the geotectonic provinces of Japanese Islands, and are generally divided into three groups: older, middle, and younger ages. The granitic rocks of older ages, around 170 m.y., are distributed mainly in the Hida belt, the innermost zone of Japanese Islands; those of middle ages, 60-120 m.y., are mainly in the medium and outer zones of the Honshu belt; and those of younger ages, 10-20 m.y., are in the Shimanto and Hidaka belt, the outermost zone.

The K-Ar ages of the metamorphic rocks are similar to those of the associated granitic rocks in most of the major metamorphic belts of Japan. This probably indicates that the metamorphic rocks have been formed in close connection with the intrusion of granitic rocks nearly in the same period, although there remains the possibility of the recrystallization of biotites caused by the granitic intrusion.

Altered biotites from the Amami-oshima granites and from the Hida and Maizuru metamorphic rocks gave apparently concordant K-Ar ages. The X-ray analyses indicate that these samples consist mainly of biotite and chlorite. It is supposed that these biotites were altered to chlorite not by recent weathering, but by the hydrothermal alteration which followed the main plutonism or metamorphism, therefore their K-Ar ages are thought to be reliable.

I. Introduction

The absolute age determination of a rock is an important subject to geological sciences, as the time dimension is essential to the geological phenomena. Relative ages of rocks can be known through the aid of paleontology

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and stratigraphy, but the measurement of the absolute ages can only be made by the use of disintegration of natural radioisotopes. During the last ten years methods of isotopic age determination have been greatly developed with the advance of the techniques of mass spectrometric isotope dilution, and are widely used for dating various types of geological materials.

The K-Ar method of age determination utilizes the decay of K^{40} to Ar^{40}. This method has the advantages as described in the following. Potassium is a common element in some important rock-forming minerals such as mica and feldspar, K^{40} has a proper length of half-life for dating a wide range of geological time, and Ar^{40} is not a normal constituent of rocks.

The radioactivity of potassium was discovered by Cambell and Wood early in the century. The radioactive isotope was identified as K^{40} by Smythe and Hemmedinger in 1937, and in the same year von Weizäcker pointed out that K^{40} should decay to Ar^{40} by electron capture and predicted that old minerals containing potassium should contain radiogenic argon. The existence of radiogenic argon in potassium minerals was first proved by Aldrich and Nier (1948). Smits and Gentner (1950) first applied the K-Ar method to a potassium mineral of unknown age. Since then many studies on fundamental problems and experimental techniques have been made. Some of the important works are cited in the following.

The geological branching ratio of K^{40} was estimated by Wasserburg and Hayden (1955) and Aldrich et al. (1956). Accurate measurements of K^{40} decay constants by the physical method were made by McNair et al. (1956), Wetherill (1957), and others. Reynolds (1956) constructed a high sensitivity mass spectrometer for noble gas analysis. Wetherill et al. (1955) found the mica-feldspar effect. Lipson (1958) successfully measured the K-Ar ages of glauconites from sedimentary rocks. Although mica has been the most suitable and common mineral group for K-Ar dating, the usefulness of amphiboles and pyroxenes was shown by Hart (1961). More recently, the K-Ar method has been applied to date volcanic rocks of less than several million years by the total rock method (Evernden et al., 1964; McDougall, 1964).

In Japan, the study of the K-Ar age determination was initiated at a few institutions in the late 1950's. Okano (1961) and Saito et al. (1961) first reported the preliminary results, although some Japanese rocks had already been dated in foreign institutions.

Recently Kawano and Ueda (1964, 1965a, 1965b, 1966a, 1966b) made an extensive study on the method and dated a few hundred granitic rocks from various regions in Japan.

The author had the chance to study K-Ar age determination in 1960-61 at the Department of Geodesy and Geophysics at Cambridge, England, and some of K-Ar ages of granitic rocks from Japan were determined by the author at the Department.

He started the work at the Geological Survey of Japan in late 1961. Much effort was directed for establishing the experimental techniques of argon extraction and mass spectrometry with a commercial instrument. The actual determination on rocks became possible towards the end of 1962. In 1965 the all-glass mass spectrometer specially designed for the determination of a small amount of argon was installed, and dating of young samples became possible. Since the study was initiated, K-Ar age determinations on more than sixty samples from Japanese granitic and metamorphic rocks have been carried out by the author, and most of the results have already been published.

The details of the experimental methods are described in the first part of this paper, and compilation of all the results obtained by the author on the granitic and metamorphic rocks of Japan and discussion on the geological meaning of the results are made in the latter part.

II. Acknowledgments

The author wishes to thank Professor S. Oana of Nagoya University for his constant guidance and encouragement throughout this study. Professor E. C. Bullard of the Department of Geodesy and Geophysics at Cambridge directed the work while the author was there, and the assistance given by Dr. J. A. Miller of the Department is gratefully acknowledged.

Thanks are due to Dr. H. Nagasawa of Gakushuin University and Dr. M. Ozima of Tokyo University for the kind assistance in preparing the spike Ar^{38}. The author is also indebted to Dr. H. Sakai of Institute for Thermal Spring Research of Okayama University for his help in constructing the apparatus during the early part of the study.

Valuable suggestions on sampling and geology were given by a number of colleagues in the Geology Department of the Geological Survey of Japan, especially the author is indebted to Dr. T. Nozawa for his kind co-operation. Thanks are also due to colleagues of the Geochemical Research Section, for their help and advice during the study. In particular Dr. K. Motojima, chief of the Section, kindly assisted in facilitating the study, and Mr. N. Ando offered many useful suggestions on technical problems.

The author is grateful to Assistant Professor K. Nagasawa of Nagoya University for his helpful suggestions on X-ray analysis.

III. Experimental Methods

III. 1 Sample preparation

The mineral used in this study is mostly biotite, a few samples of total rocks are also used.

The rock is first broken into pieces of about 5 cm cube, crushed to grains less than 5 mm diameter with a jaw crusher, then ground with a disc grinder. The ground materials are sieved with an automatic siever, and those which remain on a 40-mesh sieve are ground again. Normally the size fraction of $-40+80$ mesh is used for mineral separation. When biotite is fine-grained, the size fraction of $-100+150$ mesh is used.

Minerals are roughly separated in a 7-pole electromagnetic separator. Highly magnetic minerals and iron pieces from the grinder are collected in the least magnetic portion, biotite, amphibole, and pyroxene in the moderately to weakly magnetic portion, and non-magnetic minerals such as quartz, feldspar, and muscovite pass through all poles and are collected in the final portion. In a few cases minerals are washed after the rough separation to make the final purification easier.

Biotite is finally purified with a Frantz-type isodynamic separator. By setting the inclination and tilt of the chute at 25° and 15° respectively and applying a magnet current of about 0.4 A, biotite can be separated from less magnetic minerals, although repeated runs are necessary in many cases. Separation of biotite from hornblende by the magnetic method is not easy as their magnetic characters are similar. In this case tapping the paper on which the mixture is placed is a simple and rapid way to separate two minerals.

The biotite in the granitic rocks usually is more easily separated, while the magnetic separation of biotite in some metamorphic and volcanic rocks is rather difficult owing to the fine-grained highly magnetic minerals scattered in the rocks. In such a case biotite is separated using a heavy liquid. Methylene iodide or bromoform, both diluted with acetone, is normally used. Purity of biotite is mostly over 95 %. At least 10g of biotite are separated from a rock and kept for analysis.

The total rock method is carried out when a rock does not contain a suitable mineral or separation of mineral is extremely difficult. Careful examination of the sample for alteration and mineral composition should be made when using this method. The rock sample is crushed, ground, sieved and the size fraction of $-40+80$ mesh is kept for analysis.

III. 2 Potassium analysis

III. 2. 1 Flame photometry

Most of the potassium analyses in the study were made by flame photometry.

About 0.2 g of the sample is accurately weighed into a platinum dish and then 10 ml of concentrated hydrochloric acid and 5 ml of 46 % hydrofluoric acid are added. The mixture is warmed on a sand bath to digest the mineral and finally evaporated to dryness. The residue is moistened with 1 ml of concentrated hydrochloric acid and evaporated again to dryness. Heating should be made very carefully at this time as the material tends to scatter. After cooling the residue is dissolved by warming in 2 ml of (1:1) hydrochloric acid and about 20 ml of distilled water. The solution is warmed gently on a heater at least for 20 minutes, distilled water is added occasionally, then transferred to a 200 ml volumetric flask and diluted to the volume.

The standard solution of 1000 ppm K is made from potassium chloride, and the working standards of 100, 80, 60, 40, and 20 ppm K are made by diluting the 1000 ppm solution. Each working standard solution contains the same quantity of concentrated hydrochloric acid as the sample solution. The depression effect of hydrochloric acid on potassium emission appears when its concentration exceeds the level of 4 ml per 200 ml solution, which is twice the level of the sample solution. So the concentration of hydrochloric acid in the solution is not critical for the present determination.

The Hitachi EPU-2 type spectrophotometer with flame attachment is used for potassium determination. The potassium emission at 768 mμ is measured. The instrument is operated with an oxy-hydrogen flame fed with oxygen at 0.8 kg/cm^2 and hydrogen at 0.1 kg/cm^2, and adjusted to maximum emission just before measurement.

The calibration curve is first made using a set of working standard solutions. The 100 ppm solution is fed into the flame at first and the reading is

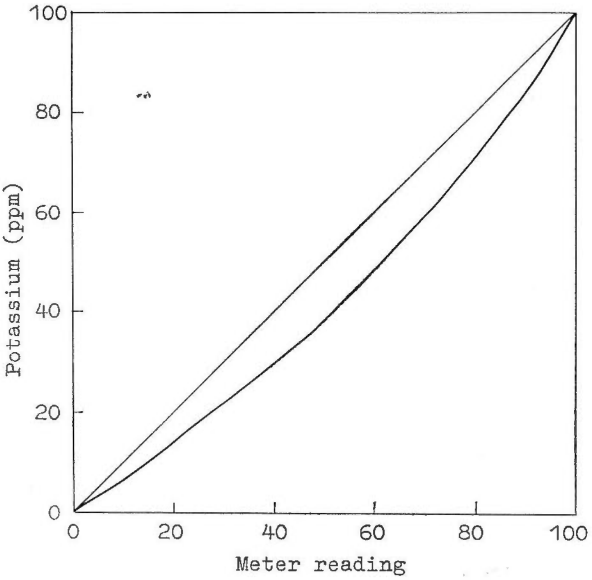


Fig. 1 Calibrations curve for potassium determination

set at 100 scale divisions, then solutions of lower concentrations are successively fed without changing the instrument setting. An example of the calibration curve is shown in Figure 1. The curve is always concave to the abscissa due to the phenomenon of self-absorption. During the measurement of the sample solutions the 100 ppm solution is fed at intervals to adjust the galvanometer reading. Usually three readings are taken on a sample, averaged, and the potassium concentration is determined on the calibration curve. At least two separate determinations are made on each sample. If the difference of the two exceeds 2 % of the average, another determination is carried out.

Potassium analyses on some biotites were made at Cambridge University by flame photometry. The method is somewhat different from the above-mentioned one, and is briefly described in the following.

About 0.1 g of biotite is accurately weighed into a platinum crucible and 1 ml of 50 % sulphuric acid and 2 ml of hydrofluoric acid are added. The mixture is warmed gently on a sand bath until fuming ceases, then heated strongly to dryness. After cooling, 1 drop of 50 % sulphuric acid is added to the residue and the crucible is half filled with distilled water, and heated on a water bath till the residue is completely dissolved. The solution is transferred to a liter flask which is then half filled with distilled water. Ten ml of ammonium carbonate solution are added and the flask is shaken, then made up to the mark. This is allowed to stand for some hours to precipitate heavy metals. The solution is filtered, and collected into a polyethylene bottle. Potassium content is estimated using the 'EEL' flame photometer. Usually six separate determinations are made on each sample, and the average and the error are calculated from them.

III. 2. 2 Tetraphenylboron method

Some of the latest analyses in this study were made by gravimetric tetraphenylboron method.

Among several methods for the gravimetric determination of potassium, the tetraphenylboron method is considered to be most promising. The solubility of potassium tetraphenylboron is sufficiently low for quantitative precipitation, the precipitate is said to be of constant composition and easily dried, and the conversion factor $K_2O/KB(C_6H_5)_4=0.1314$ is very favorable for the determination. Although ammonium, rubidium, and cesium ions are quantitatively precipitated, many ions including magnesium, calcium, aluminum, iron, and manganese do not interfere with the potassium analysis. These characteristics are especially suitable for potassium determination of silicates.

The method used here is essentially the same as that described by Cluley (1955), slight modification was made for biotite analysis.

About 0.2 g of biotite is accurately weighed into a platinum dish and 5 to 10 ml of 46 % hydrofluoric acid and 1 ml of 60 % perchloric acid are added. The mixture is warmed gently on a sand bath and finally evaporated to dryness. After cooling 1 ml of perchloric acid is added and again evaporated just to dryness. The residue is dissolved in 1 ml of N hydrochloric acid, about 40 ml of distilled water and a few drops of BTB indicator are added, and then N sodium hydroxide is added dropwise until color of the indicator turns blue. This will precipitate iron, aluminum, calcium, magnesium, etc. The material is warmed, filtered, and then N hydrochloric acid is added dropwise to the solution until the color begins to turn yellow. The solution is finally made up to 90 ml. To the solution 8 ml of sodium tetraphenylboron solution are added dropwise, continuously stirring and taking 3 minutes. After 30 minutes the precipitate is filtered on a No. 4 glass filter, washed ten times with about 3 ml of wash solution, and finally with 2 ml of water, and dried for one hour at 120°C and weighed. The blank run is carried out exactly as above in the absence of the sample, but in the presence of a known quantity of the standard potassium solution.

III. 2. 3 Accuracy and reproducibility

In order to estimate the accuracy and reproducibility of the potassium determination, Plastic Clay No. 98 (U.S. Bureau of Standards), P-207: interlaboratory standard muscovite (Lanphere and Dalrymple, 1965), and GS 1: Geological Survey standard biotite, were repeatedly analyzed. The results are given in Table 1. The value of 3.17 % K_2O for Plastic Clay No. 98 is given by the supplier; U.S. Bureau of Standards. The value of 3.12 % determined at our laboratory by flame photometry, is about 2 % lower. P-207 was prepared by the U.S. Geological Survey as the interlaboratory standard muscovite for K-Ar dating, and its value of 10.34 % for K_2O is the average of results from 10 laboratories. The slightly higher value obtained by the tetraphenylboron method is due probably to addition of rubidium, of which the content is known to be 0.08 %. GS 1 is the biotite separated from the Sori granodiorite, Gumma Prefecture, which was selected by the Geological Survey of Japan as a standard rock for chemical analysis and also as a laboratory standard for K-Ar dating. Its potassium content has been analyzed intermittently, and

Table 1. Potassium analyses of standard samples

Sample	K_2O (%) Other laboratories	K_2O (%) This study	Average
Plastic Clay No. 98	3.17 *	3.09, 3.11, 3.17, 3.12(F)	3.12
P-207	10.34 **	10.28, 10.15(F)	10.22
		10.37, 10.50, 10.57 (T)	10.48
GS 1		8.37, 8.43, 8.34 (F)	8.38
		8.15, 8.43, 8.20, 8.34(T)	8.28

* U. S. Bureau of Standards
** Lanphere and Dalrymple (1965)

F : flame photometry
T : tetraphenylboron method

the average value for K_2O content is 8.32 %.

From these results it is estimated that the potassium analyses are accurate and reproducible to within ±2 %.

III. 3 Argon extraction and purification

Argon is extracted from a mineral by fusion without flux using a radio-frequency induction heater, purified with titanium sponge and copper oxide furnace, and the amount of radiogenic argon is estimated by the isotope dilution method, in which a known amount of argon-38 spike is mixed with gases evolved by fusion of the mineral, and argon isotopic ratios are measured with a mass spectrometer.

The schematic diagram and the photograph of the extraction and purification system are shown in Figures 2 and 3, respectively. A few modifications have been made during the work; a mercury manometer and a grease stopcock were replaced by a Pirani gauge and a metal valve respectively, and an oven was adopted to bake the main part of the system. The system shown in

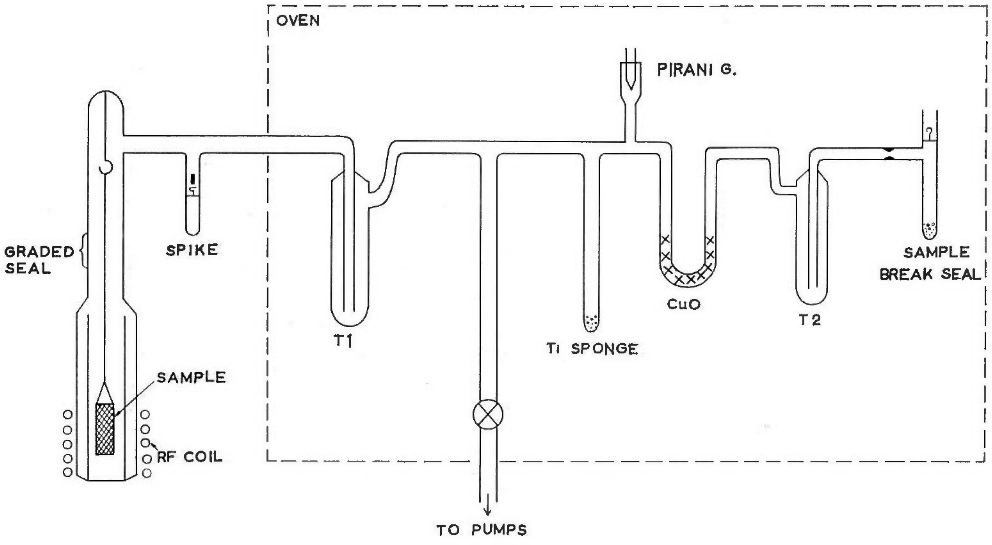
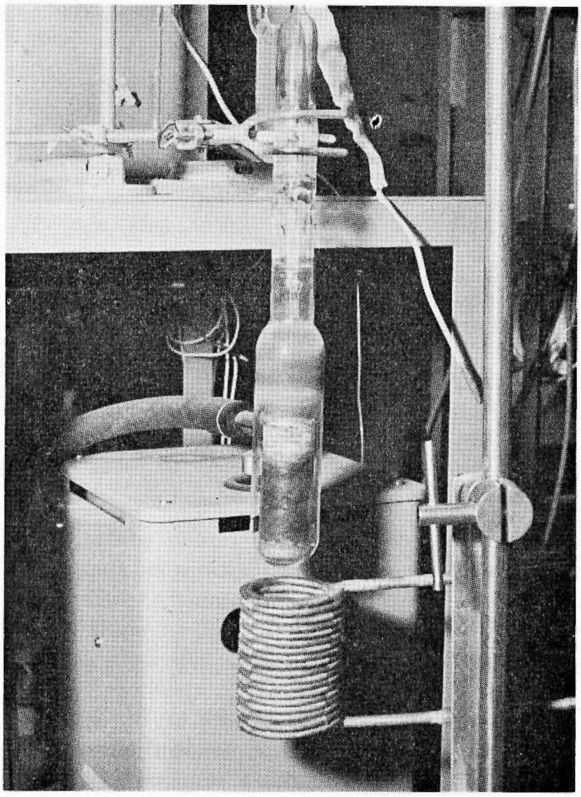
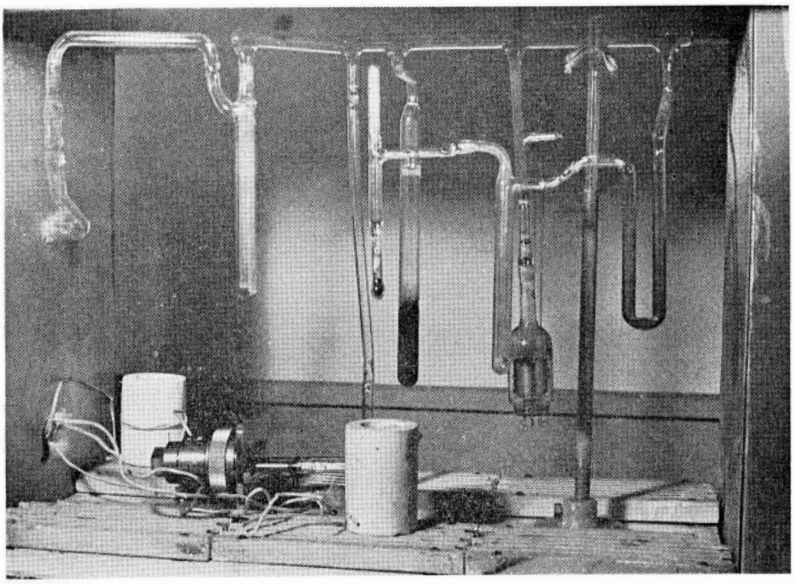


Fig. 2 Schematic diagram of argon extraction system at the Geological Survey of Japan



a.



b.

Fig. 3 Photograph of argon extraction system
a. Fusion furnace b. Purification line

the Figures is the latest one.

The furnace for fusion is made of a quartz tube 5 cm in diameter, 20 cm in length, and 3 mm in thickness, a quartz-pyrex graded glass is used at the top of the tube. Inside this tube is placed another quartz tube 3.8 cm in diameter and 13 cm in length as a radiation shield. The crucible is made of molybdenum foil with a thickness of 0.05 mm. The cylindrical part is made of a rectangular sheet by folding back both ends. The top and the bottom caps are formed by stamping out a round sheet and fitted tightly to the cylindrical part. The crucible has a length of 5 cm and a diameter of 2 cm.

About 10 g each of titanium sponge and CuO are contained in a quartz tube and a quartz U tube, respectively, and ends of both tubes are grade-sealed to pyrex glass. Other parts of the system are made mostly of pyrex glass.

The vacuum system consists of a rotary and a mercury diffusion pump and a liquid nitrogen trap, all of which are placed under the extraction system. The valve used to separate the vacuum system from the extraction system is the VMH-10 type all-metal valve made by the Nippon Vacuum Engineering Co. It is said that the valve can be baked at 450°C for a long period, and that its conductance is 1 l/sec when it is open, and less than 1×10^{-10} l/sec when closed.

The main part of the system is baked by the oven 30 × 45 × 60 cm in size, the upper half of which is movable over the main part. Heating is done with a 2 kw heater controlled by the temperature regulator. The sample furnace is heated with a tape-heater. Each of the charcoal, the CuO furnace, and the titanium songe is heated with a 500 w nicrome wire mounted in a ceramic cylinder, and the temperature of each heater is controlled by a variac.

Argon extraction and purification are carried out as follows. The pyrex glass tube is cut at a point 5 cm above the graded glass of the furnace for sample replacement. An appropriate amount of the sample is weighed into a molybdenum crucible, which is then suspended with molybdenum wires inside the quartz tube. The cut part is then sealed with an oxygen torch. The amount of the sample loaded depends on its potassium content and age. In the first stage of this study 5-10 g of biotite were used, but in the recent determination with the new mass spectrometer 2 g are enough for an analysis of a biotite about 10^7 years old.

The break seal containing a known amount of Ar^{38} spike and the sample break seal with about 1 g of activated charcoal are sealed on to the system, and then the evacuation is started. The main part of the system is baked at 200°C, the sample furnace is baked at 150°C, and the sample break seal and the CuO furnace are baked at 450°C. Bakeout is continued for a few hours. The outgassing of the titanium sponge is made by heating at about 1000°C for half an hour. The pressure in the system during and after bakeout is watched with the Mitsubishi IG-305A ionization gauge, which is also used as a leak monitor. After bakeout the pressure falls to about 10^{-6} mmHg within two hours and the system is ready for sample fusion. The metal valve is closed with a torque wrench.

Liquid nitrogen is put on trap T1, and heating of the sample is started using the 3 kw radio-frequency induction heater, of which the coil, made of water-cooled copper tubing 1 cm in diameter and having a length of

10 cm and an internal diameter of 6 cm, is placed around the quartz tube. Just before the crucible grows red, biotite tends to scatter about and very slow increase in temperature is necessary at this time. When the crucible grows red the spike Ar^{38} is released to the system by dropping an iron piece on the break seal. The maximum temperature of about 1300°C is reached within 40 minutes, and this temperature is maintained for half an hour. The pressure in the system, whose volume is about one liter, reaches a few cmHg when biotite is fused.

The temperature was measured at first with an optical pyrometer, and the relationship between the meter reading of the power applied to the radio-frequency heater and the temperature was obtained. As the inner wall of the quartz tube blackens by repeated heating, the direct measurement of the temperature becomes difficult, hence the temperature usually is not directly measured but controlled only by the power of the heater.

The pressure in the system during extraction procedure was measured at first by a mercury manometer, which was useless below 1 mmHg. Later the specially designed Pirani gauge was used, and the purification procedure was more easily controlled. The filament of the gauge tube is made of platinum wire 0.016 mm in diameter and 40 mm in length, and the tube is attached to the system and can be baked.

The gases evolved from a mineral upon fusion are rare gases including argon, plenty of water vapor, nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen, hydrocarbons, and others. Almost all of these gases except rare gases should be removed. The titanium sponge plays a very important part in the purification process. It is said that the hot titanium sponge reacts with oxygen and nitrogen to make TiO_2 and TiN respectively, whereas its reactions with hydrogen, carbon monoxide, and carbon dioxide are reversible, having equilibria depending upon temperatures. In this particular case of argon purification, nitrogen, oxygen, carbon monoxide, carbon dioxide would be removed by heating the titanium sponge at about 900°C. The absorption of hydrogen by the titanium sponge, however is a different process, and it is believed that heating of the titanium at a lower temperature of about 600°C is most efficient for hydrogen absorption. In this procedure of purification the hydrogen absorption would be accomplished while the titanium sponge is allowed to cool after heating at 900°C, although hydrogen is not completely removed by this process. The CuO furnace is used for further purification.

Most of gases absorbed on the titanium sponge can be removed by heating at about 1000°C in vacuum, although nitrogen and oxygen probably are not removed at this temperature. The absorption character of the titanium sponge does not apparently change by repeated use. During this work the titanium sponge has been replaced only a few times.

In reference again to the purification procedure, heating of the titanium sponge is begun when the temperature of the crucible reaches the maximum. In a few minutes the temperature of the titanium sponge is raised to about 900°C, and the pressure in the system rapidly falls to 1-2 mmHg as the sponge absorbs gases. Water drops which have condensed at the upper part of the furnace suddenly disappear. The titanium sponge is heated at 900°C until fusion finishes although the pressure does not fall below about 1 mmHg during this period.

After the fusion has been completed, heating of the titanium sponge is stopped and it is allowed to cool for 20 minutes. During this time most of remaining impurities are absorbed on the sponge. Then the CuO furnace is heated at about 450°C and liquid nitrogen is put on the trap T2 and on the charcoal of the sample break seal. The gases pass over the CuO and remaining impurities consisting mainly of hydrogen are removed. Then liquid nitrogen is removed from the charcoal and the gases are again released in the system. The CuO furnace is turned off, and finally liquid nitrogen is put on the charcoal trap of the sample break seal in order to collect the purified argon. After 20 minutes the sample break seal is sealed off at the narrow portion with an oxygen torch.

Argon extraction and purification on some biotites were made at Cambridge University by a similar method: argon is extracted from biotite by direct fusion using a radio-frequency heater, and purified with titanium sponge. Two methods are used for the measurement of argon volume. In the total volume method the amount of argon is directly measured using an accurately calibrated McLeod gauge. In the isotope dilution method a known volume of argon-38 spike is mixed with the gases evolved upon fusion of the mineral, and volume of argon is estimated from the isotopic ratios of the mixture.

The argon extraction and purification system used at Cambridge University is shown in Figure 4. The spike argon portion in the system was attached in the later stage of the research when the isotope dilution method was adopted.

The furnace units are mounted on 3/8-inch thick, 3-¾-inch diameter stainless steel flanges. A 2-inch diameter Kovar-Kodial glass seal is welded at the center and graded to hard glass. The unit is cooled by an external water jacket. Vapor traps are made of stainless steel and copper, connecting pipes

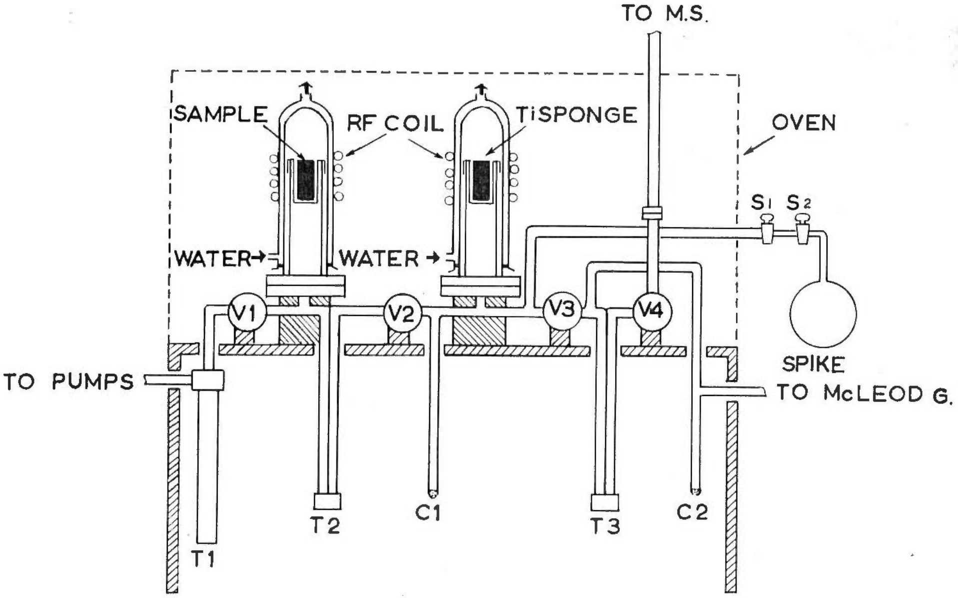


Fig. 4 Argon extraction system at Cambridge University

are made of copper and glass. The high vacuum valves used in the system are constructed of stainless steel, copper and phosphor bronze.

The sample is weighed in a molybdenum crucible, which is slung by a molybdenum strap inside the quartz tube. The furnace unit is replaced and the system is evacuated with an oil diffusion pump backed by a rotary pump. Usually traps and connecting pipes are baked by a torch. After the pressure in the system has fallen to about 10^{-6} mmHg, liquid nitrogen is put on vapor traps T1 and T2. Valve V1 is closed and fusion is started. The sample is heated gently then strongly for one hour to a final temperature of 1300°C. This temperature is maintained for 15 minutes. During these periods the gases evolved are absorbed on charcoal trap C1 in liquid nitrogen. When the isotope dilution method is used, the spike argon-38 is admitted from the reservoir using the double tap S_1 and S_2.

After the fusion, the coil of the radio-frequency heater is transferred to the titanium furnace and used to heat the titanium sponge at about 900°C. Charcoal trap C1 is allowed to warm up. After 10 minutes the temperature of the sponge is reduced slowly to about 600°C, then heating is stopped and the crucible is allowed to cool.

The remaining gases are collected on charcoal trap C2 using liquid nitrogen for 20 minutes, then valve V1 is opened to the pumps. Hydrogen is pumped off for 20 minutes. Valve V3 is closed and liquid nitrogen is removed from charcoal trap C2, while the titanium sponge is outgassed by heating to a temperature of about 1000°C. Towards the end of outgassing, the pressure between valves V3 and V4 is measured with the McLeod gauge. Valve V2 is closed, V3 is opened and the purification cycle is repeated. At least three purification cycles are carried out in the total volume method, while in the isotope dilution method two cycles are done and the pressure measurement on the McLeod gauge is unnecessary. The pure argon sample is introduced to the mass spectrometer through valve V4.

III. 4 Analysis by use of the Hitachi RMU-5BR mass spectrometer

III. 4. 1 Mass spectrometer

The instrument was designed originally for the precise measurement of isotope abundance ratios. It was installed in 1960, and was used during the first half of the study. Its main parts were modelled after the RMU-5 type, details of which were described by Higo et al. (1957). The schematic diagram and the general view of the mass spectrometer are shown in Figures 5 and 6, respectively.

The mass spectrometer consists of 4 units: sample inlet, analyzer, power source, and automatic voltage regulator. Most parts of the analyzer tube and the evacuating system are made of stainless steel and connected with each other through teflon gaskets. The analyzer tube is a 90° sector-type with 200 mm radius of curvature, and is made of stainless steel. The width and thickness of the flattened part is 60 mm and 10 mm, respectively. The ion source and the collector blocks are each 70 mm square and about 170 mm long, and are welded to the tube. The ion source is of a T-2 type, composed of 3-slit system. The filament is made of 0.2 mm diameter tungsten wire, and behind the filament are set 2 spiral heaters, by which the temperature of the ion source

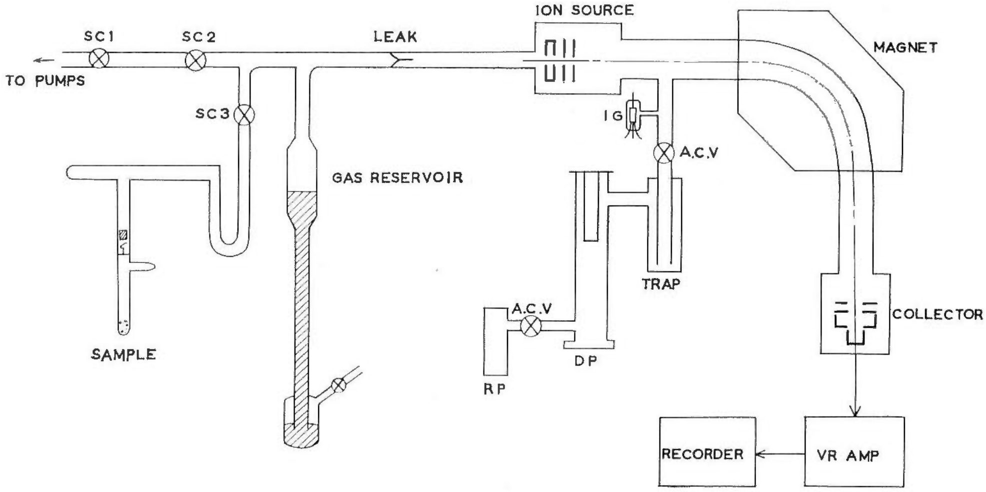


Fig. 5 Schematic diagram of Hitachi RMU-5BR mass spectrometer

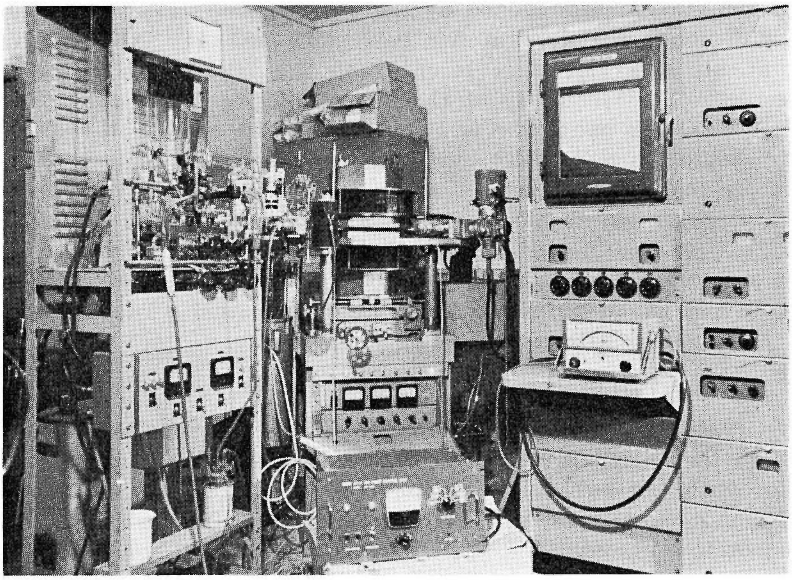


Fig. 6 General view of Hitachi RMU-5BR mass spectrometer

is controlled at 250°C. A source magnet for the collimation of the electron beam is set on the ion source block, and a magnetic field of about 200 G is applied by it. The collector is of a double-type, which is designed for isotopic ratio measurement. The inner collector, which is of the Faraday cage type is used for argon isotope measurement. The width of the collector slit is variable from 0 to 2 mm and adjusted by a gauge set outside the vacuum system.

The analyzer tube can be baked at 300°C by passing an electric current through it, and the ion source and the collector blocks are baked at 120°C. The main magnet consists of two hexagonal pieces at a 15 mm gap, and is mounted on the movable stand. The magnetic field is variable between 400 and 5000 G.

The evacuating system is composed of a mechanical fore pump, an oil diffusion pump, a dry ice and a liquid nitrogen trap, the last two are placed between the diffusion pump and the analyzer tube, and are efficiently worked for 18 hours once the containers are filled with coolants. Two automatic closing valves protect the vacuum system against the lowering of vacuum and the stoppage of power supply. The pressure in the analyzer part is measured with an ionization gauge, the tube of which is attached near the ion source block.

The power supply unit consists of various supplies and regulators together with amplifiers and a recorder. The ion accelerator supplies the D.C. voltage of 500-2000 v to the ion source, regulated to 0.1 %. The emission current is regulated to 0.5 % between 0 and 300 μA by the emission regulator. The electron accelerator supplies the D. C. voltage of 0-130 v, regulated to 0.2 %. The magnetic current can be set at any value between 10 and 250 mA. The scanning is made by increasing the magnetic current, and the scanning speed is changed by 7 steps.

The ion current is amplified by the Takeda TR-81 vibrating reed electrometer with input registors of 5×10^{10} ohms and 1×10^{12} ohms, and the output of the electrometer is recorded on the Hitachi TVK type pen and ink recorder. The sensitivity of the electrometer is changed by 5 ranges of 1:3:10:30:100. The noise level is about 0.1 mv with the 5×10^{10}-ohm resistor.

The original sample inlet system for normal gas analysis was greatly modified for the micro-analysis of argon isotopes. The new one has a sample reservoir of about 100 ml, the volume of which can be reduced by filling it with mercury. A sample gas is introduced from the reservoir to the ion source through a glass capillary tube. The evacuating system consists of a mechanical fore pump and an oil diffusion pump, no trap is used. The pressure of the system is measured with a thermocouple gauge.

III. 4. 2 Performance

The evacuation of the mass spectrometer from atmospheric pressure is made in the following way. The analyzer part of the spectrometer is first evacuated with the mechanical pump. The dry ice is put on the trap and the diffusion pump is turned on. When the pressure falls to about 10^{-5} mmHg, the bakeout is initiated. The analyzer part is baked at about 300°C, and the ion source and collector blocks are baked at 120°C, the bakeout is continued for several hours. Liquid nitrogen is put on the trap when the pressure falls to 10^{-6} mmHg. The sample inlet system is also evacuated and the gas reservoir and the capillary tube are baked with tape heaters. After bakeout the pressure decreases gradually to about 2×10^{-7} mmHg in ten hours. Continuous evacuation and another bakeout considerably reduce backgrounds, specially at hydrocarbon positions including mass 36, although the pressure remains at about 2×10^{-7} mmHg. The evacuation is stopped only during week end.

The background characteristics are of critical importance in the measurement of a small amount of argon. Since this mass spectrometer was not originally designed for micro-analysis, it was very difficult to keep the background

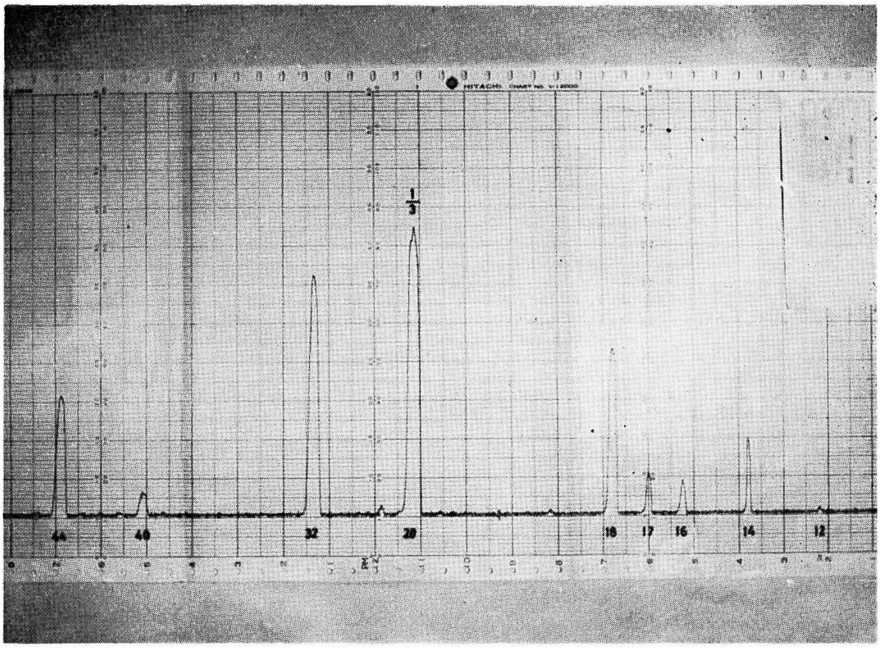


Fig. 7 Background mass spectrum between masses 12 and 44. Recorded with 3×10^{10} –ohm resistor on the Hitachi mass spectrometer.

low enough for the analysis. As shown in Figure 7 the background peaks appear at masses 12, 14, 16, 17, 18, 28, 29, 32, 40, 44 when a 5×10^{10}-ohm resistor is used. In some cases small peaks also appear at masses 27, 39, 41, and 43. Relative heights of the main peaks in the particular case shown in Figure 7 are: mass 44:6, 40:1, 32:11, 28:44, and 18:8. The relative peak heights of masses 40, 32, and 28 are nearly the same in most instances, whereas peaks of masses 44 and 18 decrease more rapidly than others by the continuous evacuation. The peak ratios of N_2/Ar and O_2/Ar for air determined on this instrument are about 50 and 12, respectively, which are nearly the same as those of background peaks. It is thought therefore that residual gases of this mass spectrometer consist mainly of water vapor, carbon dioxide, nitrogen, oxygen, and argon, most of the last three are probably derived from air introduced through small leaks.

Another important factor besides background characteristics is the sensitivity of the instrument. In K-Ar dating the amount of atmospheric argon contamination is estimated by a small amount of Ar^{36} in the argon isotope mixture, and the instrument should have a sensitivity high enough for Ar^{36} determination. In the case of this mass spectrometer, all possible procedures were attempted in order to produce a high sensitivity, among them adopting a smaller gas reservoir, raising emission current, adjusting the high voltage applied to the lens system of the ion source, were considerably effective. In spite of these improvements, however, it was impossible to get a sensitivity high enough for the Ar^{36} determination as long as an input resistor of 5×10^{10} ohms was used. So a 10^{12}-ohm resistor was adotped to measure the Ar^{36} peak. The problem in using this resistor, however, is that the time constant of the electro-

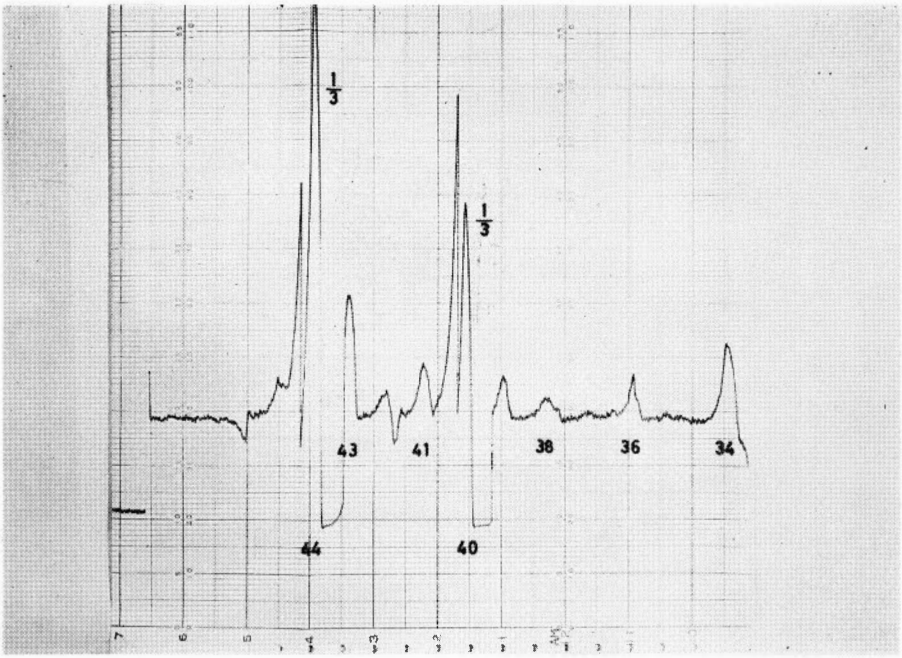


Fig. 8 Background mass spectrum between masses 34 and 44.
Recorded with 10^{12}-ohm resistor on the Hitachi mass spectrometer.

meter becomes fairly large, i.e., over ten seconds, and full peak heights can not be obtained by a normal magnetic scanning. A relatively small difference in the peak height at mass 36 between the sample and the background also makes the measurement inaccurate. Therefore a different method was used for Ar^{36} determination, details of which will be described in the next section.

Figure 8 shows an example of background peaks between masses 34 and 44 recorded with a 10^{12}-ohm resistor. Besides masses 40 and 44, which already appear when a 5×10^{10}-ohm resistor is used, a small peak exists at every mass. The background peak height at mass 36 is usually 2-10 divisions depending on the evacuation condition, and it corresponds to $(2\text{-}10) \times 10^{-16}$ A. The noise level in this case is about 1×10^{-16} A for a short period, although a long period noise often exceeds 3×10^{-16} A.

The sensitivity for argon of this mass spectrometer is defined as the ratio of the ion current of an argon isotope to the amount of this isotope in the gas reservoir. Using the calibrated Ar^{40} the ratio is known to be about 10^{-13} A/10^{-5} ml Ar^{40} at the maximum. If the minimum detectable ion current is assumed to be 2×10^{-16} A, about 2×10^{-8} ml of argon can theoretically be detected. In the actual analysis of a biotite sample, the amount of Ar^{40} collected in the sample tube is normally 10^{-4} ml or less, and the Ar^{40}/Ar^{36} ratio varies from about 500 to 5000 depending on the percentage of atmospheric argon contamination. Therefore it is rather difficult to determine the Ar^{36} amount when the Ar^{40}/Ar^{36} is high. A low sensitivity is the main disadvantage in using this instrument.

Table 2. Operational conditions for Hitachi RMU-5 BR mass spectrometer

Ion accelerating voltage	2,000 v
Electron accelerating voltage	120 v
Target potential	70 v
Grid potential	−25 v
Repeller potential (in)	10 v
〃 (out)	5 v
Filament current	3.5 A
Emission current	200 μA
Trap current	30 μA
Pressure	2×10^{-7} mmHg

III. 4. 3 Isotopic analysis of argon sample

The sample break seal is attached to the inlet system as shown in Figure 5, and the system is evacuated. After about 30 minutes the background mass spectrum is recorded in the following way under the same condition as for a sample run. The conventional flow method is used, wherein the gas is introduced to the spectrometer through a leak and continuously removed by the pumps. Normal operational conditions are given in Table 2. Repeller voltages are adjusted to give the highest sensitivity. At first the peaks of masses 35-44 are scanned using the 5×10^{10}-ohm resistor. The background peak height at mass 40 is 5-20 divisions, which is usually less than 1/10 of the sample peak at mass 40. Then peaks of masses 35-40 are scanned using the 10^{12}-ohm resistor. This time the scanning speed is set to the slowest. The peak height at mass 36 is at least a few divisions at the highest sensitivity of the electrometer.

As described before the full peak height can not be obtained by the normal scanning method owing to a large time constant, hence in the argon analysis the mass 36 peak is not magnetically scanned but another method is used. Magnetic current is adjusted so as to get the top of the 36 peak immediately before the introduction of a sample gas to the analyzer and its background level is recorded on the chart. Once the background is satisfactory and the background level of the mass 36 is being recorded, liquid nitrogen is put on the U tube trap and the break seal of the sample tube is broken with an iron piece. The mercury in the reservoir is lowered to the bottom of the reservoir. After about one minute the argon sample is introduced to the reservoir by opening stopcock 3. The sample gas now flows into the analyzer tube through the capillary. Stopcock 3 is closed and the mercury is raised to the top of reservoir, thus the sample pressure is increased by about five times. The mass 36 peak now increases from the background level and reaches the maximum in a minute. The difference of the two levels is the net height of the mass 36 peak in the sample gas. Then the input resistor is changed to 5×10^{10} -ohm and 38 and 40 peaks are scanned at least five times by changing the magnetic current automatically. After this scanning the resistor is changed again to 10^{12}-ohm and the top of the 36 peak is recorded as before, then stopcock 1 is opened and the sample is pumped off. Now the 36 peak decreases to the background level, and the net peak height at mass 36 is determined again.

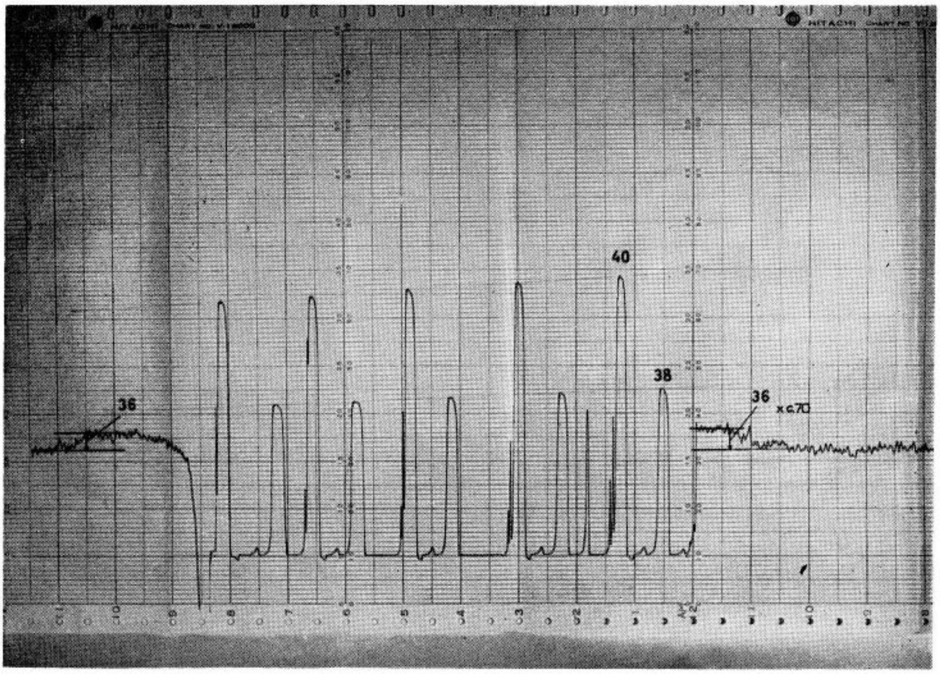


Fig. 9 Record of mass spectrometric analysis of argon sample

It takes about 15 minutes to make the above analysis, during which peak heights decrease by 5-10 per cent. However, measurable change in the isotope ratios does not occur. Figure 9 shows a result of the mass spectrometric analysis of an argon sample.

In measuring the peak heights of masses 38 and 40, a line is drawn connecting tops of mass 40 peaks. The line should theoretically be exponential, but in practice a straight line is drawn in most cases because of a slow decrease of the peak height. The peak heights of mass 40 are measured at time positions of mass 38, and at least five pairs of masses 38 and 40 are obtained. The base line is straight and no drift is observed in most cases. The mass 40 line is extraporated to the mass 36 positions, and two peak heights are measured, thus two pairs of masses 36 and 40 are obtained. These peak heights are tabulated, the background heights are subtracted, and 40/38 and 40/36 ratios and their averages are calculated.

The standard deviation of the 40/38 ratio is always less than 1 %. However the estimation of error in the 40/36 ratio is rather difficult as only two values are obtained. In the measurement of the mass 36 peak, the difference of two levels, namely the net peak height of mass 36 in the sample, is between 2 and 15 divisions at the highest sensitivity. Using the above-mentioned method of measurement the measurable minimum difference is about 0.3 division, although the noise level is larger than this; about 1 division. Therefore, if the rough error is defined to be the percentage ratio of this minimum difference to the difference due to the sample, it is about 15 % at the maximum. Accordingly, the error in the 40/36 ratio also is estimated to be about 15 %

at the maximum. The effect of the error in the 40/36 ratio on the radiogenic argon determination increases with the percentage of atmospheric argon. For instance, if the percentage atmospheric argon in the sample is 10 %, the error in the radiogenic argon due to the error in the 40/36 ratio decreases to 1/9 of the error in the 40/36 ratio. Since the mass 36 peak is attributed to the Ar^{36} in the atmospheric argon, it is roughly said that the error in the radiogenic argon determination decreases as the mass 36 peak does. This fact fortunately compensates the fact that the error in the 40/36 ratio increases as the mass 36 peak decreases. The overall error in radiogenic argon determination, therefore, is in most cases considerably smaller than that in the 40/36 ratio.

In order to examine the mass discrimination of this instrument, the abundance ratios of atmospheric argon were determined occasionally. The Ar^{40}/Ar^{36} raito determined always agreed with that of Nier (1950) to within 3 % in spite of rather inaccurate determination of mass 36.

III. 5 Analysis by use of the Mitsubishi MS-315G mass spectrometer

As noted previously it is essential for a mass spectrometer designed for micro-analysis of argon isotopes to have high sensitivity and precision, and low background. Reynolds (1956) first made an all-pyrex high sensitivity mass spectrometer for noble gas analysis. It was shown that his mass spectrometer has many advantages over a metal one; it is leak-free if carefully fabricated, less outgassing and of low background, totally bakable, easy to make and handle, and of low price. An instrument of this type was later called "Reynolds-type", and is now widely used in many laboratories of the world.

In Japan the Reynolds-type mass spectrometer was first developed by the Central Research Laboratory of the Mitsubishi Electric Co. Ltd. The first commercial instrument, model MS-315G, was installed at the Geophysical Institute of Tokyo University in 1964, and its operational data was very satisfactory. The second one was installed at the Geological Survey of Japan in the spring of 1965. Studies on the fundamental characteristics and establishment of operational procedure of the instrument had been carried out for the first few months, and it has been used without any great trouble for the argon isotope analysis of K-Ar age samples.

As very few performance data have been reported on the MS-315G mass spectrometer (Goto et al., 1965, Ozima et al., 1966), the details of the performance together with construction and method of analysis are described in the following.

III. 5. 1 Mass spectrometer

General design. The mass spectrometer consists of two nuits: analyzer and sample inlet unit and power source unit, the photograph and the schematic diagram of the main part are shown in Figures 10 and 11, respectively. The analyzer is of 15 cm radius, 60° sector, first-order focusing system. The analyzer and inlet systems are made mostly of pyrex glass, and are baked by ovens at high temperature. Four all-metal bakeout valves and two greaseless valves are used in the instrument for the separation of the systems. By the employment of two getter ion pumps in the evacuating system together with normal diffusion and rotary pumps, the vacuum maintenance is very satisfactory.

Analyzer tube. The tube is made of pyrex glass, about 1 m in length along the curvature, and each of the ion source and collector parts on the end of

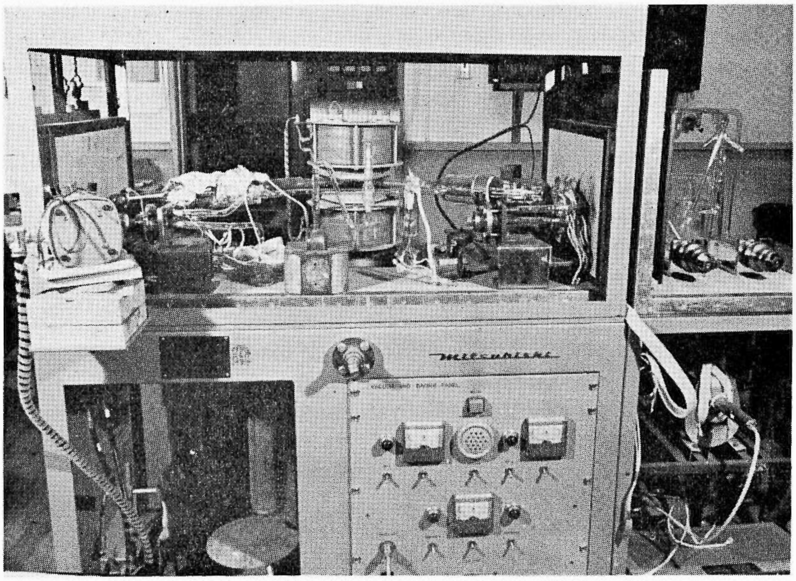


Fig. 10 Photograph of Mitsubishi MS-315G mass spectrometer

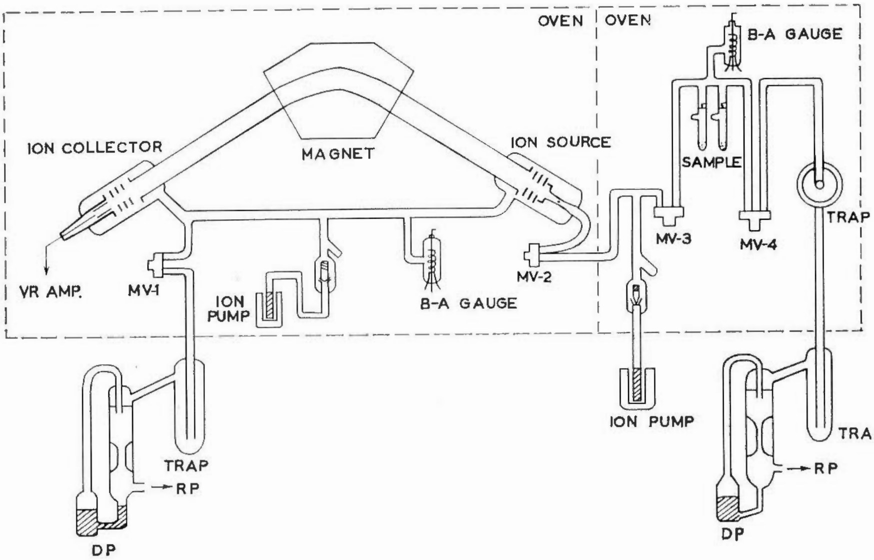


Fig. 11 Schematic diagram of Mitsubishi MS-315G mass spectrometer

the tube is 60 mm in diameter and about 150 mm in length. The central part of the 30 mm diameter tube is flattened to 18 mm so as to enter the 20 mm magnet gap. A 10 mm tubing is attached to the ion source part and a 25 mm tubing to the collector part as evacuation leads, both are connected together and led to a metal valve. Another 12 mm tubing connects the ion source with the sample inlet system through a metal valve. This tubing is made to narrow to 8 mm in the ion source part, and near the ionization chamber it has a ball valve, which consists of an iron ball and a small hole. The valve is closed by placing the iron ball on the hole using a magnet outside the vacuum envelope. When the static method is used the valve is opened in order to make the gas sample more easily diffused within the analyzer tube. In the flow method the valve is closed.

The inside wall of the analyzer tube is coated with the electrically conductive film made from "Nesacoat", which is composed mainly of tin tetrachloride. The resistance of the analyzer between two ends is about 300 ohms. The analyzer tube is horizontally placed and supported at two positions over the oven base, the ion source part is tightly clamped and the collector part is only placed on the support.

Ion source. The ion source is of the Nier type (Nier, 1947). The ionization chamber block is made of stainless steel, the plates of the slit system are of tantalum. The exit slit is 0.1 mm wide and 12 mm long. Quartz ball spacers are used to separate the ionization chamber from earth-slit plates and base plates. The filament is made of tungsten ribbon, 0.8 mm wide and 0.025 mm thick, and about 15 mm long. The molybdenum wires from the electrodes and the nickel wires from the filament are connected to the 14 tungsten leads which are arranged in a ring and are glass-sealed at the end of the analyzer tube.

The source magnet of about 100 G is used for the collimation of the electron beam. The ion intensity is thus increased by about 10 times. The setting of this magnet is very critical; a few millimeters of movement changes the ion intensity by a factor of 5.

Ion collector and amplifier. The collector is of the Faraday cage type, made mostly of stainless steel. At the end of the collector part 14 tungsten leads are arranged in a ring, and connected to molybdenum wires from the plates including 4 slits. No potentials are applied to the collector slits.

The central lead for the electrometer is made of 1.5 mm diameter molybdenum wire. The connection of this lead with the electrometer is made by a sleeve and a cable with connectors. The sleeve is a stainless steel tube with a connector on one side, 17 mm in diameter and 7 cm in length. The cable is of 3C-2V type, 10 cm long, the BNC type connector is attached on each end. There was a little trouble in the ion detection while a 35 cm-long cable was used in the beginning of the adjustment. The noise was relatively large: about 1 mv with a 10^{11}-ohm resistor, and it was difficult to measure peaks of small intensity. Upon using the 10 cm cable the noise level decreased to 0.1 mv, there has been no trouble since then.

The ion current is amplified by the Takeda TR-84B vibrating reed electrometer, which consists of a pre-amplifier and a main amplifier. One of 4 input resistors: 10^8, 10^{10}, 10^{11}, 10^{12}-ohms, can be selected by rotating a switch bar on the pre-amplifier. When a 10^{12}-ohm resistor is used, the response time can be changed by 3 ranges: 10, 20, 60 seconds. With other resistors the response time is less than 2 seconds. The sensitivity of the electrometer is changed by 9 ranges: from 1 mv to 30 v full scale.

The output of the electrometer is recorded with a Yamatake-Honeywell J-153X16 pen recorder, having a 1/4 second pen speed and a 30 cm chart width. The normal chart speed is 50 mm/min. The main amplifier of the electrometer and the recorder are set in the power source unit of the spectrometer. The pre-amplifier of the electrometer is placed just outside the oven base.

Magnet. The magnet is made of carbon-free iron, 22 × 29 × 38 cm in size, and 101 kg in total weight. The pole pieces are hexagonal, 20 mm gapped, and the length of the sides perpendicular to the ion beam is 10 cm. The magnet is mounted on a steel platform which can be slided back and forth on a steel frame. The frame can be moved up and down by 4 screw rods. The horizontal adjustment of the magnet is made by 4 screws attached to the platform. During the period of bakeout the magnet is moved backward outside of the oven shell.

Vacuum system. The evacuating system of the analyzer consists of a rotary and a mercury diffusion pump, a trap and a getter ion pump. The rotary pump is of a DAIA CRP-50 type, having a pumping speed of 50 l/min. The mercury diffusion pump is a pyrex glass, 8 l/sec one, and about 100 ml of mercury are used. A non-bakeout metal valve exists between these two pumps. The trap is also of pyrex glass, 30 cm in length and 8 cm in external diameter. The diffusion pump and the trap are assembled within a frame 55 × 76 × 100 cm in size, on which the oven base is placed A 2 l/sec getter ion pump made by the Mitsubishi Electric Co. is used as another evacuating system. The pump unit is located at the front center of the oven base. The magnet is made of Alnico metal. Usually the ion pump only is used for the evacuation of sample gas and for vacuum maintenance between sample analyses. The ordinary pump system is used only at bakeout, which is done intermittently.

At first it was feared that argon would be accumulated in the analyzer tube owing to the low pumping speed of the ion pump for rare gases. However, experiment showed that there was no trouble with this problem. This may be because the amount of argon introduced to the analyzer tube by leaks is extremely small and that introduced as sample also is so small as to be easily pumped off by the ion pump. In order to isolate the analyzer tube from the ion pump, a 1 cm diameter greaseless valve is attached just before the ion pump. The leakage conductance of this valve is rather large as its closure is made only by a tapered greaseless ground joint. However, this valve proved to be satisfactory at the low pressure maintained for this mass spectrometer.

Two type C all-metal bakeout valves made by the Granville-Phillips Co. are used in the system. One is to separate the ion source from the sample inlet system. The other is to separate the analyzer tube from the trap and the pumps. They are rigidly mounted on brackets of about 10 cm square. According to the manufacturer's data, the valve has an extremely low leakage conductance: less than 10^{-11} l/sec if closed by applying torques of 35 to 45 ft-lbs. There seems to be no leakage trouble even when the outer side is opened to atmospheric pressure, although it is usually maintained at the rotary pump vacuum. The valve is designed to withstand repeated bakeout at 450°C when the driver is removed, and flexible monel bellows on each tube eliminate possible glass breaking during bakeout.

The bakeout oven of the analyzer consists of the oven base with side walls and the oven shell which is lowered over the analyzer, the internal size is 31 × 46 × 100 cm. It is shown in Figure 11 by dotted lines. The oven is made of asbestos board 3 cm in thickness, outer sides of which are covered by aluminum plates. Heating is done with nine 500-watt strip heaters which are placed in three groups on the oven base. With these the temperature of 450°C can be obtained in three hours. The bakeout of the ion pump is done with a 500-watt tape heater.

The pressure in the analyzer is measured by the Mitsubishi 1G-BA3 type ionization gauge which is attached to the tubing connecting the ion source with the collector part. It is of a Bayard-Alpert type, and a pressure as low as 10^{-11} mmHg can be measured. The operational conditions of the gauge are as follows: ion collector potential, -30 v against the filament; anode potential, $+180$ v against the ion collector; emission current, 0.1, 1 and 2 mA. The filament is turned off when the ion current reaches about twice the full scale of each meter range. The outgassing of the gauge is done by applying A.C. 900 v between the anode and the filament. The Mitsubishi TG-R2 type thermister gauge, which is mounted near the rotary pump, is used for the measurement of lower vacuum. Upon lowering of the vacuum, the heater of the diffusion pump is turned off by the relay action of this gauge. The control circuits of both gauges are mounted in the power source unit.

Sample inlet system. The system is constructed next to the analyzer. Two VMH-10 type metal bakeout valves, made by the Nippon Vacuum Engineering Co., are mounted on the oven base which is placed on a frame of about 70 cm square. These valves are said to have a leakage conductance of 10^{-10} l/sec or less, which is a little larger than that of the Granville-Phillips valves. In practice the performance of the VMH-10 valve is satisfactory. One valve is used to separate the main part of the inlet system from the evacuating system, and the other is to separate the inlet system from the analyzer. Between the two valves the sample tubes and an ionization gauge are attached. The ionization gauge is of the same type as that of the analyzer, and one control circuit is used in common for both gauges. The thermister gauge, which is also of the same type as that of the analyzer, is mounted near the rotary pump for the measurement of lower vacuum.

The evacuating system of the inlet system is nearly the same as for the analyzer. The same types of rotary and diffusion pumps are used. A double trap is attached between the main trap and the metal valve for the purpose of rapid lowering of the pressure. A NEC 8 l/sec getter ion pump was added to the system in the later stage of this of this study. This machine is specially designed to raise the pumping speed for rare gases. The pump unit is located under the frame, and the pump lead is connected between MV2 and MV3 as shown in Figure 11. A greaseless valve separates the ion pump from the inlet system. The bakeout oven of the inlet system is of similar type to that of the analyzer, the internal size being 42 × 42 × 60 cm. The heating is done with six 500-watt strip heaters mounted on the sidewall. The temperature within this oven can be controlled by the thermo-switch.

Power source unit. The unit contains control circuits of various parts of the

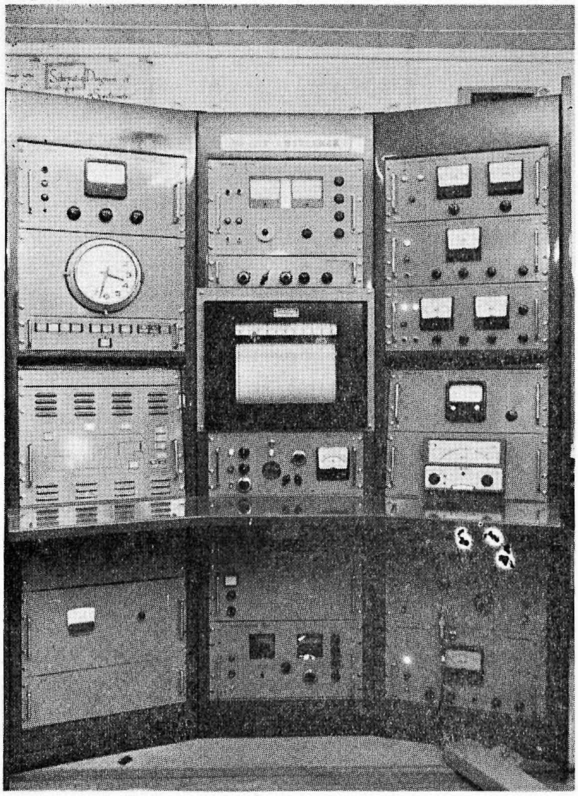


Fig. 12 Power source unit of Mitsubishi MS-315G mass spectrometer

mass spectrometer, a photograph of which is shown in Figure 12. The ion accelerating voltage is supplied by the Mitsubishi ND-1552 type high voltage supply, variable between 1 and 5 kv in 10-volt steps, and stabilized to 1×10^{-4}. The electrostatic scanning can be made by the scan controller connected to the high voltage supply. Two types of emission regulator have been used. One used in the earlier stage was of the all-transistor type, the emission current was variable between 0 and 500 μA, stabilized to 1×10^{-3}. This was later replaced by the electronic-tube-type regulator to have higher stability and more emission current. With this regulator the emission current is variable between 100 and 1500 μA, stabilized to 5×10^{-4}. The emission regulator also contains the divider circuit for the ionization voltage, which is used to supply appropriate potentials to the slit system of the ion source. The magnet current stabilizer consists of power supply, rectifier, D.C. amplifier, and magnet control. The magnet current is variable between 1 and 15 A, separated into 3 ranges: 1-5 A, 5-10 A, and 10-15 A, and stabilized to 1×10^{-4}. The current can be changed manually, or automatically increased or decreased. Automatic cyclic scanning can also be made. The scanning speed is changed by 4 ranges: 10, 20, 40, and 60 minutes to scan one current range.

III. 5. 2 Performance

Vacuum characteristics. As stated before the pressure in the mass spectrometer is measured with a Bayard-Alpert ionization gauge. The evacuation of the analyzer part of the spectrometer from atmospheric pressure is made in the following way. The system is evacuated by the mercury diffusion pump, the lower half of the trap is cooled with liquid nitrogen. The main magnet and the ion pump magnet are removed from the oven, the connector of the electrometer and drivers of the metal valves are removed, the oven shell is lowered, and then the bakeout is started. The temperature reaches about 200°C within one hour, 300°C in two hours. The pressure of the system gradually rises to 10^{-3} mmHg order, then decreases slowly. After the temperature has been maintained for 3 hours at about 300°C, the pressure normally is of the order of 10^{-4} mmHg. Longer bakeout and higher temperature greatly reduce the final pressure, although in most cases it is unnecessary. The heaters are turned off and the oven is allowed to cool. More liquid nitrogen is put on the trap. It takes about 2 hours to be cooled to room temperature, and the pressure decreases gradually to 10^{-7} mmHg during this period. Then metal valve MV1 is closed and the ion pump is turned on, and the system is evacuated with it. The trend of

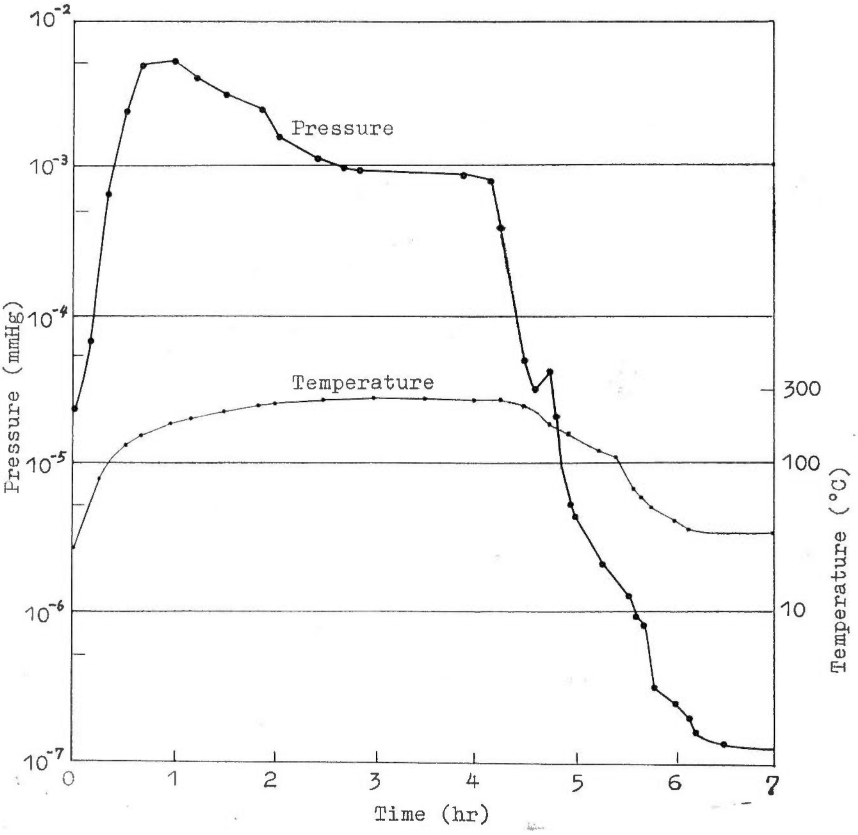


Fig. 13 Variation of pressure of mass spectrometer during bakeout

pressure decrease does not change, as the pumping speeds of the ion pump and the diffusion pump seem to be of the same order in this region of pressure. An example of the pressure variation during bakeout cycle is shown in Figure 13.

Except during the sample analysis the mass spectrometer is always evacuated only with the ion pump. The pressure in this case ranges $5 \times 10^{-8} - 2 \times 10^{-7}$ mmHg depending on the various conditions, such as previous sample pressure and room temperature. During sample analysis the greaseless valve before the pump is closed to interrupt the pumping. Most of the sample gas after use is evacuated with the ion pump of the inlet system, which has a higher pumping speed for rare gases. Using this pump, sample argon of 10^{-5} ml size is quickly evacuated without difficulty. Figure 14 shows the pumping of sample argon by the ion pump. Total amount of argon in the tube is about 10^{-5} ml and this is evacuated mostly within 5 minutes. In this case the total pressure in the spectrometer does not decrease parallel with argon amount in the lower pressure region due to the pressure of residual gases.

The vacuum characteristics of the sample inlet system are almost the same as those of the analyzer part of the spectrometer, because the vacuum systems are similar to each other. However, the sample inlet system is exposed to atmospheric pressure every time the sample tubes are replaced, and a slightly different procedure from that of the analyzer is adopted for normal operation, the details of which will be described later. The complete bakeout of the inlet system is made intermittently, and in this case the bakeout procedure is nearly the same as that for the analyzer. As shown in

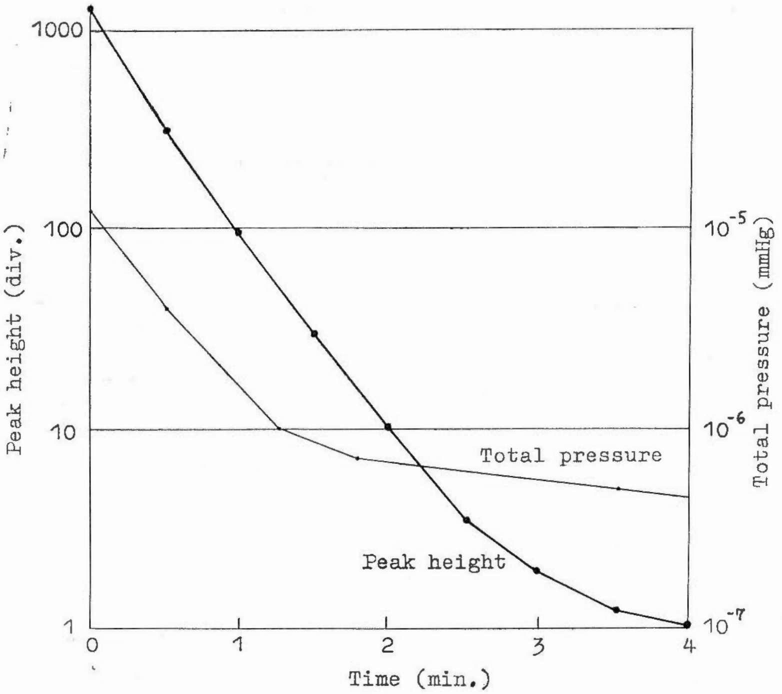


Fig. 14 Pumping characteristics of ion pump for argon sample

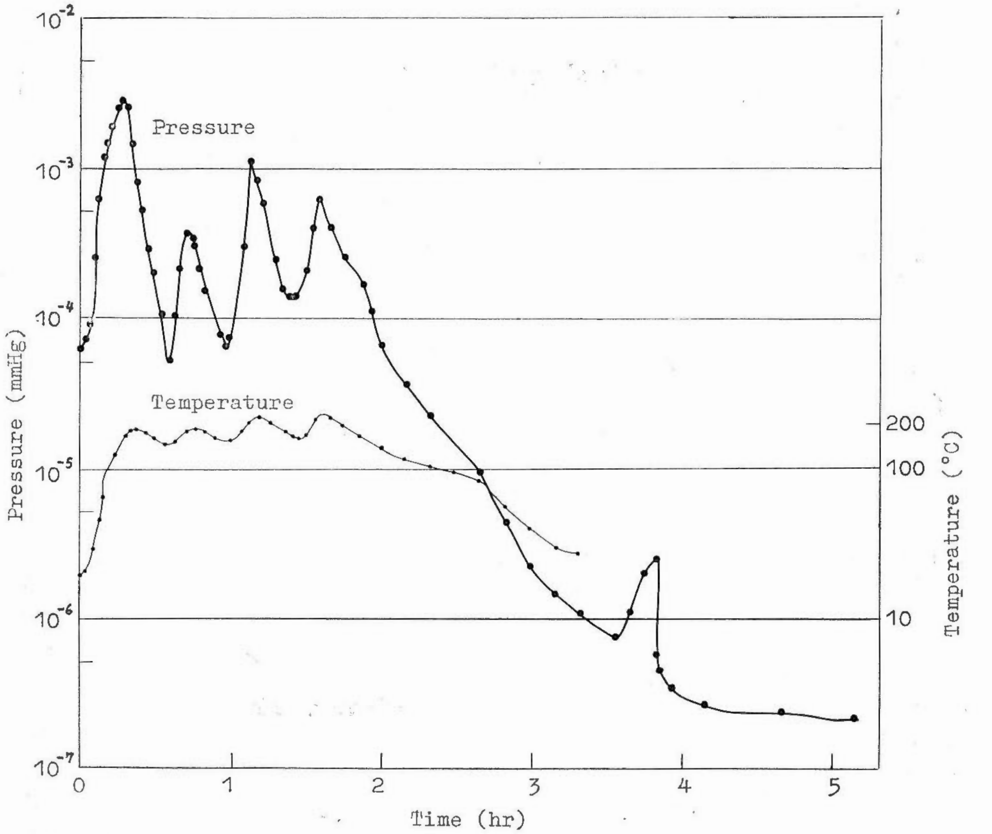


Fig. 15 Variation of pressure of inlet system during bakeout

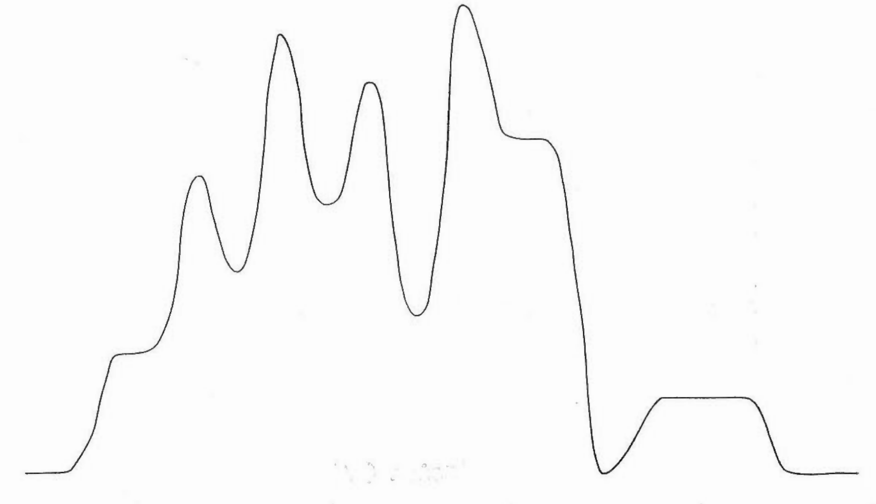


Fig. 16 Mass spectrum of double-charged Hg^{++}

Figure 15, the pressure of the system is reduced to 3 × 10^{-7} mmHg within 4 hours by 2 hours of bakeout at 150-200°C. Between sample analyses the pressure of the inlet system is always kept in the order of 10^{-7} mmHg using the ion pump only.

Ion current characteristics. The resolution of the mass spectrometer can be roughly estimated by the mass spectrum of double-charged Hg^{++} as shown in Figure 16. Peaks of masses 101 and 102 are nearly resolved, but peaks differing by 1/2 % are not resolved. From this the resolution is considered to be about 100, which is large enough for the analysis of argon isotopes.

The sensitivity is of critical importance for this mass spectrometer as an electron multiplier has not been used. Many factors, such as emission current, ion accelerating voltage, lens potentials and source magnet, control the sensitivity. Among these the emission current and the source magnet adjustment are the most important for the improvement of the sensitivity. Some performance data directly relating to the sensitivity are given in the following.

The relationship between the emission current and the peak height for Ar^{40} is shown in Figure 17. The peak height is not strictly proportional to the emission current, and there is a sign of saturation at a higher emission current. The emission current used in normal operation is 400 μA. The relationship between the ion accelerating voltage and the peak height for Ar^{40} is given in Figure 18. The peak height increases with the ion accelerating voltage. A similar relationship was shown by Higo et al. (1957) on the Hitachi RMU-5 mass spectrometer. It is generally said that a higher ion accelerating voltage is more efficient to gain sensitivity. However, the memory effect is increased with voltage, giving undesirable results on argon analysis. In normal operation the ion accelerating voltage is set at 1.8 kv.

Variation of the peak height for Ar^{40} with the electron accelerating voltage is shown in Figure 19. The relationship is of normal type; the peak height

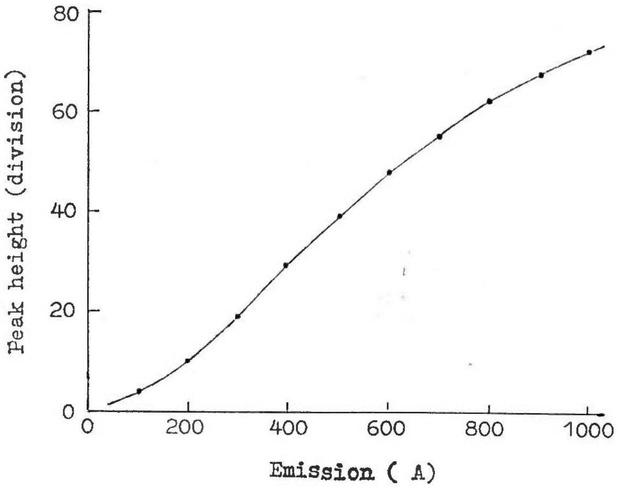


Fig. 17 Variation of peak height with emission current. Curve for Ar^{40}, ion accelerating voltage: 1.8 kv.

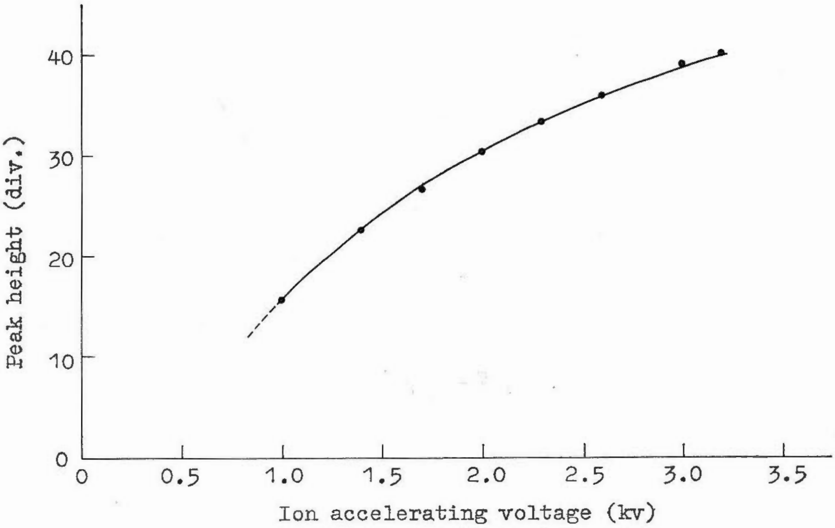


Fig. 18 Variation of peak height with ion accelerating voltage. Curve for Ar^{40}, emission current: 100μA, pressure: 6.8×10^{-6} mmHg.

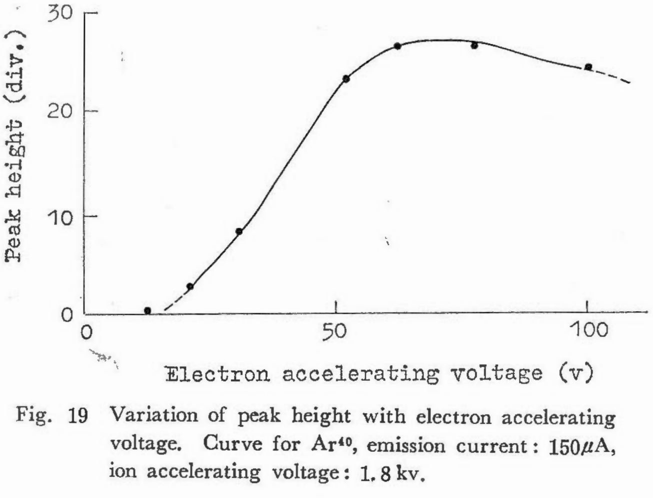


Fig. 19 Variation of peak height with electron accelerating voltage. Curve for Ar^{40}, emission current: 150μA, ion accelerating voltage: 1.8 kv.

reaches the maximum at about 70 v, then decreases slowly. The electron accelerating voltage in normal operation is 70 v. The potentials applied on the slit system of the ion source are also important for the sensitivity, and usually they are selected so as to give the highest ion current. As noted before the careful setting of the source magnet in the ion source region is very important as it makes the ion intensity higher by nearly 10 times.

The sensitivity of the spectrometer can be estimated by measuring a known amount of argon sample. This is usually done using the spike Ar^{38},

Table 3. Background peak heights under static operation

M/e	Peak height (mv, 10^{11} ohms) (1) Before closing	(2) 20 min. after closing	(3) 90 min. after closing
2	24	69	220
12	0.05	0.7	4.0
13		0.3	1.5
14	0.02	1.2	4.9
15	0.25	7.0	24
16	0.43	10	31
17	1.5	3.2	4.5
18	6.0	11	24
19		0.09	0.15
20			0.08
27			0.08
28	3.4	49	180
29		0.46	1.8
30		0.07	0.28
31			0.03
32	0.11	0.10	0.12
34			0.10
35	0.36	0.38	0.36
36		0.03	0.05
37	0.07	0.07	0.06
38		0.10	0.45
39		0.08	0.07
40		0.20	0.90
41		0.06	0.08
43		0.07	0.07
44	0.40	2.2	5.7
Pressure (mmHg)	2.6×10^{-7}	7.0×10^{-7}	1.8×10^{-6}

Under the normal operational conditions mentioned above and in static operation, the sensitivity for convenience is defined as the output voltage of the electrometer produced by the ion current relative to the partial pressure of argon in the analyzer tube. When the 10^{11}-ohm resistor is used, the sensitivity for Ar^{38} is about 2 v/10^{-5} mmHg. As the volume of the analyzer part is about 1 l, the sensitivity can also be expressed as about 1.5 v/10^{-5} ml Ar^{38}. This value is high enough for dating a Tertiary biotite, in which the radiogenic argon of 10^{-5}—10^{-6} ml/g is included. The noise level of the electrometer in the normal condition is about 0.1 mv, and 10^{-9} ml of argon is theoretically detectable.

Background characteristics. As the isotopic analysis of an argon sample with this instrument is always made by the static method of operation in which the analyzer tube is isolated from all pumping and then the sample is introduced, the background peak heights increase more or less during analysis and the background characteristics are of great importance for this spectrometer. Therefore, the background spectrum under static condition has been repeatedly examined during the study. An example of the variation of background peak heights under various conditions is given in Table 3, where the B-A gauge is turned on throughout the measurement with the emission current at 0.1 mA, and the 10^{11}-ohm resistor in use. The first column of Table 3 shows the background while the spectrometer is evacuated with the ion pump and the pressure is 2.6×10^{-7} mmHg. The main peaks are at masses, 2, 16, 18, 28,

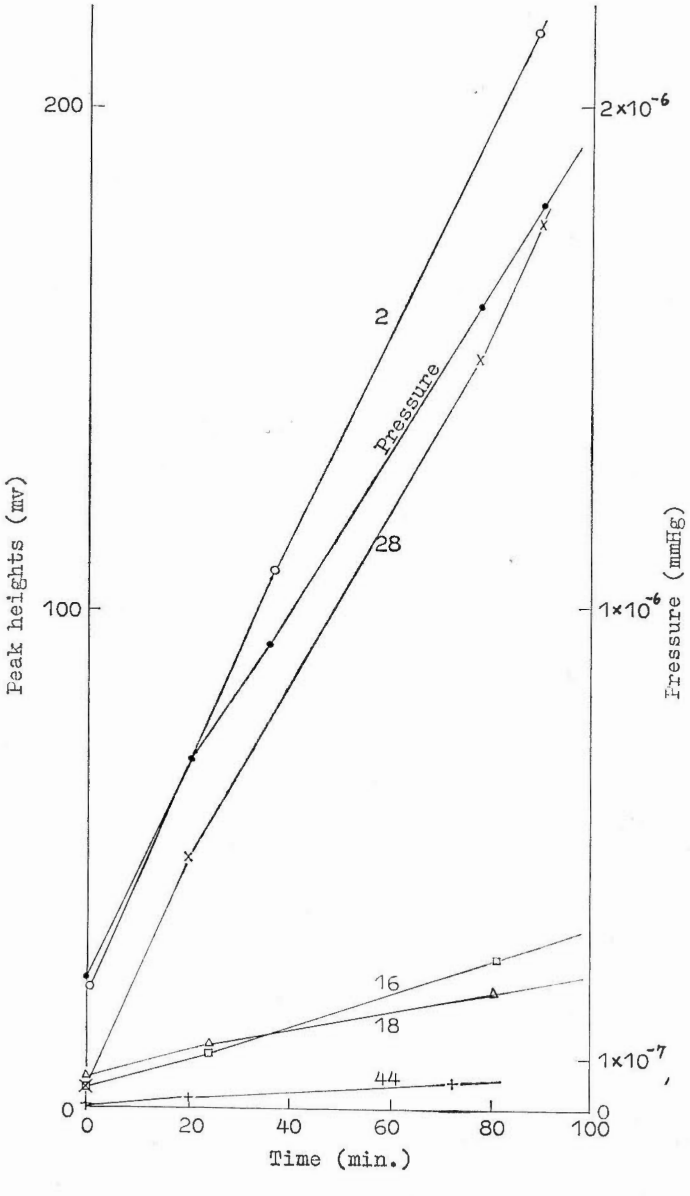


Fig. 20 Variation of background peak heights and pressure with time after isolating spectrometer from pump

and 44, probably corresponding respectively to hydrogen, methane, water vapor, carbon monoxide with trace of nitrogen, and carbon dioxide. Mass 2 peak is almost always the highest and the 28 peak is the second. Usually no peaks appear between masses 36 and 40, but masses 41 and 43 peaks sometimes appear. When the mass spectrometer is isolated from the ion pump by closing the greaseless valve, the pressure and most background peak heights increase with time. The variations of the main peak heights and pressure with time are shown in Figure 20. Each peak height increases at a nearly constant rate, and there is no sign of saturation during the period of 90 minutes in which the pressure increases from 2.6×10^{-7} to 1.8×10^{-6} mmHg.

The second and the third columns of Table 3 show the background peak heights 20 and 90 minutes after isolating the spectrometer tube from the ion pump. Most of the heights in the Table are calculated from the growth curve as shown in Figure 20, for it takes about 15 minutes to scan from mass 2 to 44 and all the heights can not be measured at one time. Besides the background peaks which are already present under pumping conditions, peaks at masses 13, 19, 20, 27, 29, 30, 34, 36-43 except mass 42 appear under static conditions. It is interesting to note that peak heights of masses 35-43 except 38 and 40 do not substantially change with time. The 38 and 40 peaks are probably argon isotopes introduced into the tube as sample, and the 40 peak of this size indicates that there is no large leak affecting the argon analysis. A rather high but constant peak at mass 35 and a small and constant one at 37 may be due to Cl^+ as the inside wall of the analyzer tube was coated using $SnCl_4$.

The behavior of mass 36 peak is of much importance as the atmospheric argon contamination is estimated by a rather small peak at mass 36. Although there is usually no peak at mass 36 when the spectrometer is evacuated with the pump, the peak sometimes appears and increases slowly when the tube is isolated from the pump as shown in Table 3. The background peak height of this amount, however, would not affect the measurement so long as the height does not change upon introduction of the gases containing no mass 36 component. Enhancement of the 36 peak is reported on some metal instruments when the sample contains much hydrogen. Although the experiment on this problem using hydrogen has not been made, the results of measurements on the standard samples and air argon show that the above-mentioned phenomenon does not occur on this mass spectrometer, hence it is considered that a small background peak at mass 36 is tolerable for the measurement of argon isotopes. In some cases the 36 peak does not appear even after closing the greaseless valve. It is not known whether this peak is due to hydrochloric acid or hydrocarbon.

The mass 28 peak is mostly CO and not N_2, because the 29/28 ratio is about 1 % and nearly the same as that of CO. Peaks at masses 12-16 are mainly CH_4 and its fragments; their relative heights roughly coinside with the pattern of CH_4. Most of the 14 peak is attributed to CH_2, a fragment of CH_4, and from this it is ascertained that the 28 peak is not N_2, which has a considerably high 14/28 ratio of about 8 %. Thus it is said that the main residual gases for this mass spectrometer are hydrogen, methane, water vapor, and carbon monoxide.

The behavior of the B-A type ionization gauge under static operation

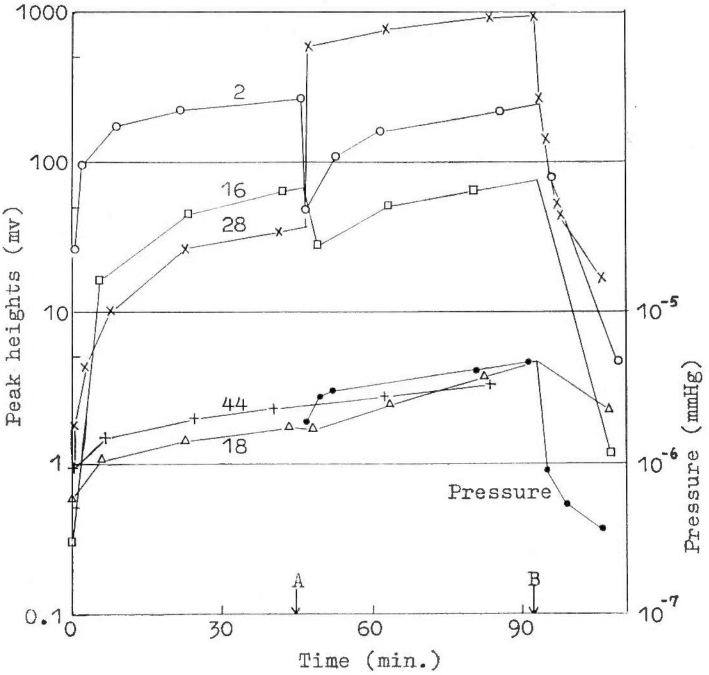


Fig. 21 Variation of background peak heights with time after isolating spectrometer from pump. The ionization gauge is turned on at time A, the greaseless valve is opened at time B.

is of some importance since the gauge is said to have a pumping action. Figure 21 is another variation diagram of the main background peaks after isolating the tube from the pump, where the gauge is turned off for the first 45 minutes, then it is turned on. The increase in the 28 peak under this condition seems to be slower than under the previous condition in which the gauge is on. Upon turning on the gauge the 2 and 16 peaks suddenly decrease, whereas the 28 peak suddenly increases, then the 2 and 16 peaks begin to increase after a minute or so. It is supposed, therefore, that the gauge has a large pumping ability for H_2 and CH_4, but in the on condition the gauge actually emits a relatively large amount of CO. The pumping action of the gauge for argon was examined using the sample argon. The decrease in Ar^{40} due to pumping is about 4 % for 5 minutes, and the rate of decrease does not substantially change even at a higher emission current of 1.0 mA, ten times as high as normally used. Although the pumping action of this gauge for argon is not so large as reported by Reynolds (1956) or Sugiura et al. (1964), it is better to turn off the gauge during the measurement of argon isotopes.

III. 5. 3 Isotopic analysis of argon sample

The isotopic analysis of the argon sample is carried out by the static method in which the analyzer is isolated from the pump before introduction of the sample.

After sample break seals are attached to the inlet system of the mass spectrometer as shown in Figure 11, the system is evacuated by the diffusion pump. The main trap is cooled with liquid nitrogen. The glass tubing is flamed with a torch for a few minutes, and MV4 valve is warmed with a blower for 20 minutes. During this procedure the pressure decreases slowly from 10^{-4} to 10^{-5} mmHg. After about one hour the pressure goes down to about 2×10^{-5} mmHg, then MV4 is closed and MV3 is opened, and the system is evacuated with the ion pump. Within the next two hours the pressure decreases to the order of 10^{-6} mmHg and now the sample analysis can be made. Usually, however, the system is continuously evacuated overnight to a pressure of $3\text{-}5 \times 10^{-6}$ mmHg, as a longer evacuation greatly reduces the pressure rise under static operation.

The background peak heights are first measured under the same conditions as for sample analysis; MV1 is always closed, the ionization gauge is turned off, two greaseless valves are closed, and MV2 is opened for a short period. In about 20 minutes the peaks between 35 and 41 are scanned 2 or 3 times using the highest measurable sensitivity range of the electrometer (10 mv full scale), and the change of peak heights, especially of the mass 36, is observed. Also the masses 2 and 28 peaks are checked. Usually the background peak heights at masses 38 and 40 are negligibly small as compared with the sample peak heights, and only the 36 background peak is of importance for the isotopic analysis of argon. Once the background is satisfactory, the greaseless valves are opened and gases accumulated in the spectrometer are evacuated. Within 10 minutes the pressure decreases to the normal

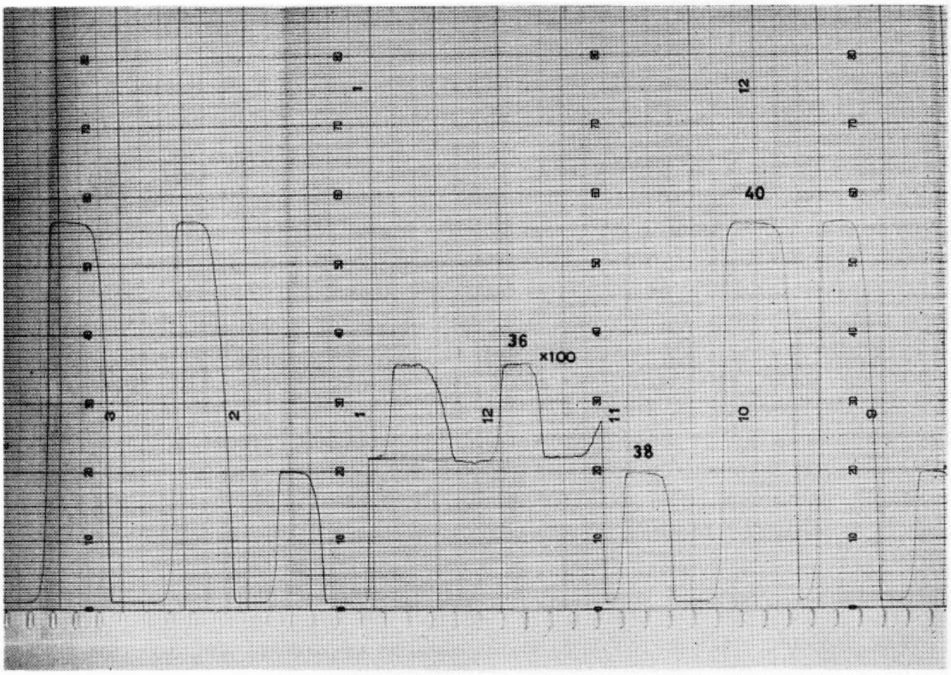


Fig. 22 Record of isotopic analysis of argon sample

state, and then the sample analysis is started. Greaseless valves are closed, the break seal of the sample tube is broken, and the MV2 is fully opened for about a minute in order to equilibrate the pressure between the inlet system and the analyzer part. Thus no fractionation in argon isotopes occurs. The peak heights reach the maximum within a minute, and scanning of 40, 38, and 36 peaks is started. At least 5 sets of these 3 peaks are scanned. The direction of scanning is reversed each time. The 10^{11}-ohm output resistor of the electrometer is used, and the scanning speed is very slow in the peak region so as to get a full peak height. The 36 peak is scanned usually with the highest measurable sensitivity: 10 mv full scale. The effect of a high 38 peak on the 36 peak is very slight in most cases. Figure 22 shows a record of the isotopic analysis of an argon sample.

The peak heights of argon isotopes normally decrease very slowly or do not change at all during the 20-30 minute period of measurement. In some instances where the argon sample is contaminated with relatively large quantities of gases such as nitrogen and carbon monoxide, the argon peak heights tend to increase at the beginning. This is probably because the relative sensitivity for argon is raised by the cleanup of the contaminant gases within the spectrometer tube. Besides the argon peak heights, masses 2, 28, and 35 peak heights are measured for the purpose of examining the contamination level. A big increase in these peaks from the background level would indicate that the sample argon is contaminated by other gases, and that the analysis is of poor character. Actually any change in the 35 peak height due to sample introduction has not occurred during the study.

After the analysis has been finished, the sample argon is first evacuated by the ion pump of the inlet system by opening MV2 and the greaseless valve of the inlet system. As has been noted before this ion pump has a higher pumping efficiency for argon and the small amount of argon sample used in the analysis is quickly pumped away from the spectrometer. After about 20 minutes the greaseless valve of the analyzer part is also opened to the other ion pump.

Although the normal operational vacuum is reached by continuous pumping for about 30 minutes after sample analysis the increase in the background 38 and 40 peaks measured by the static method is rather large under this condition. This is due to so-called "memory effect", and the ratio of the 40 to the 38 background peak is roughly the same as that of the previous sample. Therefore at least a few hours of pumping is needed to reduce this effect. The memory effect is clearly observed also by an increase in the 38 peak with time when the argon sample without the spike Ar^{38} is introduced into the spectrometer. The peak height of the mass 38, however, is always less than 1 % of the mass 40 peak so long as the amount of Ar^{40} is more than 10^{-6} ml, and so the memory effect on the isotopic analysis of argon in this study is thought to be negligible.

The measurement of the peak heights at masses 36, 38, and 40 is relatively easy as their change is very little, if any. The peak heights are tabulated, background corrections are applied, especially very carefully for the 36 peak, and 40/38 and 40/36 ratios and their averages are calculated. The standard deviation of the 40/38 measurement is usually about 1 %, whereas that of the 40/36 measurement ranges from 2 to 10 %.

The mass discrimination of this instrument has often been checked using the atmospheric argon. The determined Ar^{40}/Ar^{36} ratio always agreed with that obtained by Nier (1950) to within 2 %, though it was slightly lower than Nier's in some cases.

III. 6 Spike preparation

The enriched Ar^{38} for spike was purchased from Zurich University. The original concentration of Ar^{38} is 99.98 % according to the supplier's data. During the first half period of the study at the Geological Survey, the preparation of the spike Ar^{38} was made using the preparation system at Gakushuin University, which was constructed by Dr. H. Nagasawa. The system is similar to that described by Wasserburg and Hayden (1955), and its schematic diagram is shown in Figure 23.

Its main part consists of 60 capillary Y tubes of 2 mm internal diameter, connected to one another and to a mercury reservoir. Upon a branch of each Y tube is attached a break seal, of which the volume is previously measured with distilled water. Also a McLeod gauge, a reservoir of about 1 liter, and three mercury cut-off valves are attached to the system. In case of spike preparation, a spike tube containing an appropriate amount of Ar^{38} is attached to the system, and the system is evacuated. Once the vacuum is satisfactory, two mercury cut-off valves are closed to isolate the system from the evacuating line, and the spike Ar^{38} is released into the system. At this time the mercury level is just below the junctions of Y tubes. At least one hour is allowed to equilibrate Ar^{38} in the system, then the Y tubes are isolated by raising the mercury level to just above the junctions, and 60 break seals are sealed off with a torch.

The first set of spikes was calibrated by isotope dilution with a known amount of purified commercial argon, which was prepared also in the spike preparation system. The pressure of argon was measured with the McLeod gauge. The second set of spikes was also calibrated by the same method except that the standard argon was prepared in another system, in which

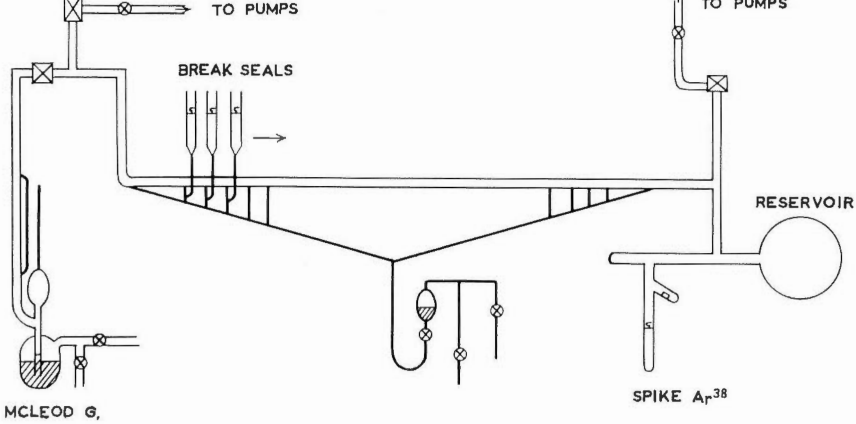


Fig. 23 Spike preparation system

Table 4. Calibration of spike Ar^{38}

Ar^{38} in ml STP/ml of break seal

(1)	(2)	(3)
7.27×10^{-6}	5.75×10^{-6}	2.818×16^{-6}
7.08×10	5.77×10	2.817×10
7.11×10	5.77×10	2.804×10
7.15×10^{-6}	5.76×10^{-6}	2.813×10^{-6}
Purified commercial argon	Purified commercial argon	Standard muscovite P–207

the argon pressure was measured on a mercury manometer, then reduced to the order of 10^{-1} mmHg by expanding into a 2-liter reservoir. The results of spike calibration are given in Table 4.

During the last half of the study the preparation of Ar^{38} spike was made with the system at the Geophysical Institute of Tokyo University, which was constructed by Dr. M. Ozima. The system is similar to the former one, except that the number of break seals attached is 20, and that the system can be baked at about 400°C. Calibration of spikes was made by fusing the standard mica P-207 with a break seal of the spike. The results are given also in Table 4. From these results the precision of spike calibration is considered to be about 1% or better.

The accuracy in the estimation of the spike Ar^{38} was checked also using P-207. Using 3 spikes in the second set (5.76×10^{-6} ml Ar^{38}/ml of break seal), the amount of radiogenic Ar^{40} in P-207 was found to be 2.809, 2.831, and 2.817×10^{-5} ml STP/g. The average value of 2.819×10^{-5} ml is close to the average of analyses from 10 laboratories: 2.835×10^{-5} ml/g (Lanphere and Dalrymple, 1965).

The isotopic composition of the spike argon was measured on a few of these spikes with the Mitsubishi instrument, the composition is Ar^{38}: 99.95_7, Ar^{40}: 0.03_8, Ar^{36}: 0.000_5.

IV. Calculations

The K-Ar age can be calculated by the equation

$$t = \frac{1}{\lambda_\beta + \lambda_e} \ln \left[1 + \frac{\lambda_\beta + \lambda_e}{\lambda_e} \cdot \frac{Ar^{40}}{K^{40}} \right] \qquad (1)$$

where
t = age
λ_β = decay constant of K^{40} for beta decay to Ca^{40}
λ_e = decay constant of K^{40} for electron capture to Ar^{40}
Ar^{40} = number of moles of radiogenic argon in the sample
K^{40} = number of moles of K^{40} in the sample

Throughout the present study the following constants are used, $\lambda_\beta = 4.72\times10^{-10}\,yr^{-1}$, $\lambda_e = 0.584\times10^{-10}\,yr^{-1}$ (Wetherill, 1957), $K^{40}/K = 1.19\times10^{-4}$ (Nier, 1950). The value for λ_β is an average of the recent determinations as mentioned by Long and Kulp (1962).

The volumes of radiogenic and atmospheric argon in the sample are related to argon isotopic ratios and the volume of spike argon by the equations

$$V_r = \frac{V_s}{1 + S^{36}_{38} + S^{40}_{38}} \left(A^{40}_{38} \left(1 + \frac{1 - S^{36}_{38} A^{38}_{36}}{A^{38}_{36}\, a^{36}_{38} - 1} \right) - \frac{1 - S^{36}_{38} A^{38}_{36}}{A^{38}_{36}\, a^{36}_{40} - a^{38}_{40}} - S^{40}_{38} \right) \tag{2}$$

$$V_a = V_s \frac{1 - S^{36}_{38} A^{38}_{36}}{A^{38}_{36} - a^{38}_{36}} \bullet \frac{1 + a^{38}_{36} + a^{40}_{36}}{1 + S^{36}_{38} + S^{40}_{38}} \tag{3}$$

where V_r = volume of radiogenic argon in the sample
V_a = volume of atmospheric argon in the sample
V_s = volume of argon in the spike
A^{40}_{38}, A^{38}_{36} = Ar^{40}/Ar^{38} and Ar^{38}/Ar^{36} ratio in the sample
S^{36}_{38}, S^{40}_{38} = Ar^{36}/Ar^{38} and Ar^{40}/Ar^{38} ratio in the spike
a^{36}_{38}, a^{36}_{40}, a^{38}_{40} = Ar^{36}/Ar^{38}, Ar^{36}/Ar^{40}, and Ar^{38}/Ar^{40} ratio in the atmospheric argon

The above equations are of generalized form, and may be simplified in actual calculation as the spike argon consists almost entirely of Ar^{38}. In practice, using the above-mentioned constants the equation (1) can be written in the following form (Miller and Brown, 1964)

$$t = 1885 \ln \left[1 + 16.04 \left(1 - \frac{a}{100} \right) G \right] \tag{4}$$

where t = age in million years
a = percentage of atmospheric argon in the sample
$G = \frac{\text{Total volume of argon (mm}^3)}{\text{Weight of sample (g)} \times K_2O\ (\%)}$

The fraction of atmospheric argon in the sample, i. e., $\frac{a}{100}$ in the above equation, is given by the next formula, which is derived from equations (2) and (3) by approximation

$$\text{Fraction of atmospheric argon} = \frac{a^{40}_{36} \left(1 - S^{36}_{38} A^{38}_{36} \right)}{A^{40}_{36} - S^{40}_{38} A^{38}_{36}}$$

The table showing the relationship between age and G as a function of percentage atmospheric argon has been made at the Department of Geodesy and Geophysics, Cambridge, and knowing the value of G and percentage atmospheric argon most ages can be directly read on the table without any complicated calculation.

Experimental errors in age determination are introduced by uncertainties in the measurements of both argon amount and K_2O content. The errors in the argon measurement arise from uncertainties in spike calibration and mass spectrometric analyses of Ar^{40}/Ar^{38} and Ar^{36}/Ar^{40}. Errors in the former two usually are small and estimated to be about 1 % or less, whereas the error in Ar^{36}/Ar^{40} measurement is larger, because the peak height at mass 36 is small. As has been noted before, the effect of this error in the determination of the radiogenic argon varies with the percentage of atmospheric argon.

This relationship is shown by the following equation (Lipson, 1958)

$$E = \frac{e \cdot f}{100 - f}$$

where e = the percentage error in Ar^{36}/Ar^{40}
f = percentage of atmospheric argon in the sample
E = the percentage error in radiogenic argon due to the error in Ar^{36}/Ar^{40}

Thus the error in radiogenic argon measurement increases with atmospheric argon percentage, and the effect of the error in Ar^{36}/Ar^{40} becomes great at higher percentage. The error in radiogenic argon determination with the Mitsubishi instrument is believed to be less than ±3 % in most cases, whereas the error with the Hitachi instrument is a little larger due to the relatively low 36 peak.

The error in K_2O determination is estimated to be about ±2 %. In this study the error in age is approximately the sum of the errors in argon and K_2O determinations.

V. Results

All the results obtained by the author at both the Department of Geodesy and Geophysics, Cambridge and the Geological Survey of Japan are summarized in Table 5, and sample localities are shown in Figure 24. As most results have already been published elsewhere, the complete descriptions of sample localities and rocks are not given in this study. The reference to each age result if any, and the laboratory where it was obtained are given in the table.

Table 5. Summary of K–Ar age determinations

Map No.	Sample	Rock type and mineral	K_2O (%)	Atmospheric contamination (%)	Laboratory	Age (m. y.)	Reference
	Hidaka metamorphic belt						
1	Hidaka 2, Nissho tunnel	G. B	8.24	49.7	G	16± 4	
2	Hidaka 1, Nissho tunnel	M. B	9.02	40.2	G	17± 2	
	Kitakami mountains						
3	Otomo	GD. B	6.00	11.0	C	107± 3	(1)
4	Takashizu	GD. B	7.53	4.8	C. T	114± 6	〃
5	Miyako	GD. B	7.33	12.3	C. T	123± 6	〃
6	Omoe	GD. B	6.63	6.0	C. T	122± 6	〃
7	Yamaya	GD. B	5.26	12.3	C	106± 6	〃
8	Origasa	GD. B	6.35	5.8	C	110± 5	〃
9	Nakamura	QD. B	5.98	28.2	C. T	129± 6	〃
				20.0	C. T	126± 6	〃
10	Hashino	QD. B	6.39	13.7	C. T	115± 6	〃
11	Semmaya	QD. B	5.82	5.7	C	119± 5	〃
	Abukuma plateau						
12	610729 S, Godo	GD. B	8.36	10.0	G	98± 6	
13	610722A19, Godo	S. B	6.71	12.1	G	90± 6	
14	F A 5, Hase	GN. B	8.58	7.9	G	102± 6	
	Nihonkoku gneiss						
15	T N61120106, Komata	GN. B	7.11	17.0	G	92± 6	(2)

	Tsukuba and Ashio mountain blocks							
16	Inada		G. B	7.22	35.5	G	60± 4	
17	Hirasawa		GN. B	6.60	52.5	G	56± 4	
18	Sori		GD. B	8.09	9.4	C	86± 4	(3)
19	GS 1, Sori		GD. B	8.32	13.5	G	85± 4	
	Hida metamorphic belt							
20	TN61101206, Amo		GN. B	5.28	9.4	G	175±11	(4)
21	TN65081201, Tsunokawa		GN. B	2.06	21.6	G	174± 9	〃
22	TN 63102808, Oki		GN. B	7.97	13.3	G	165±12	〃
					13.7	G	173±12	〃
23	TN 61091401, Amo		GD. B	2.40	17.2	G	167±12	(5)
24	TN 61091301, Shimonohara		QD. B	6.78	5.6	G	86± 6	(6)
	Ryoke metamorphic belt of central Japan							
25	KK66, Sonohara	Inagawa granire	G. B	5.44	6.8	C. T	72	(7)
26	KK56+70, Okunodaira–Hokizawa		G. B	6.31	17.9	C. T	70	〃
					22.4	C. T	70	〃
27	KK2, Fujisawa		G. B	6.44	7.4	C. T	63	〃
28	KK5, Unaido		GD. B	8.07	0.8	C. T	53	〃
29	KK69, Ichinose		QD. B	3.80	11.3	C	65± 3	〃
30	KK11, Araragi	Naegi granite	G. B	7.92	4.7	C. T	64	〃
31	S 1, Yaozu		G. B	6.45	18.1	C. T	68	〃
32	KK9, Inugaeri		G. B	7.48	9.5	C	68± 3	〃
	Granitic rocks of Chugoku district							
33	OT 1003, Shimogoya		G. B	7.36	36.1	G	36± 5	(8)
					42.0	G	33± 5	〃
					40.7	G	39± 5	〃
34	OT 1001, Sangenya		GD. B	6.57	8.8	G	49± 6	〃
					16.9	G	50± 6	〃
35	AN 116, Akawase		GD. B	5.12	28.6	G	64± 6	〃
36	AN 119, Ningyo–toge		G. B	6.88	16.3	C	57± 3	〃
37	KY 1001, Taroda–yashiki		G. B	5.48	17.1	G	57± 6	〃
					30.6	G	62± 6	〃
38	X 148, Mannari		G. B	5.45	22.4	G	86± 6	
39	Obatake		GD. B	8.95	14.1	C. T	82	(9)
				8.46	14.1	C. T	84	〃
	Maizuru structural belt							
40	Y63–6, Kayasaka–toge		AM. B	1.55	51.6	G	215±17	(10)
					41.4	G	216±17	〃
	Kurosegawa structural belt							
41	Mitaki–san		GD. T	1.98	35.5	G	163±13	
	North Kyushu							
42	Ud 10B, Yodokawa		GD. B	5.64	17.0	G	97± 6	(11)
43	It 1, Tsufunasaki		GD. B	6.27	10.3	G	90± 8	〃
					8.9	G	89± 7	〃
44	Nk 17 B, Noko Island		GD. B	5.48	17.4	G	97±10	〃
45	Ar 375, Katanawa–yama		A. B	8.42	14.3	G	83± 7	〃
46	Og 96 D, Kitabeta		GN. B	6.10	8.2	G	108± 9	(12)
					5.7	G	106±11	〃
47	Ainoshima		HF. T	2.52	27.5	G	81±11	

	Granitic rocks from Outer Zone of Southwest Japan						
48	S A 61122402, Nachi	GP. B	8.28	59.7	G	14± 2	
49	2105, Omogo	GD. B	3.12	76.8	G	14± 2	
50	2341, Takatsukiyama	GD. B	8.28	65.2	G	12± 2	
51	2501, Cape Ashizuri	GD. B+H	2.56	57.4	G	13± 2	
52	53030902, Kijo	GD. B	5.07	37.1	G	13± 2	
53	53031307, Osuzuyama	R. T	4.02	59.8	G	15± 2	
54	Okueyama	GD. B	7.95	20.7	C	21± 2	(13)
55	Ichibusayama	GD. B	6.72	35.8	C	14± 1	〃
56	Shibisan	GD. B	7.13	7.7	C	15± 4	〃
57	Koshikijima	GD. B	7.03	35.7	C	13± 4	〃
58	Takakumayama	GD. B	7.29	18.2	C	16± 1	〃
59	Kunimi mountains, K 16	GD. B	7.68	18.6	C	21± 1	〃
60	Kunimi mountains, K 34	GD. B	8.11	28.8	C	14± 1	〃
61	1003, Kosugidani	GD. B	8.57	29.4	G	14± 1	
62	1011, Kosugidani	GD. B	8.56	30.2	G	14± 1	
63	1101, Nagata	GD. B	8.28	75.2	G	13± 2	
	Ryukyu Islands						
64	TN 65021202, Kasari	GD. B	1.07	46.7	G	49± 6	(14)
65	TN 65021310, Yamma	QD. B	7.52	39.7	G	55± 4	〃
66	TN 65021401, Koniya	GD. B	2.90	20.6	G	54± 3	〃
67	TN 65021402, Koniya	GD. B	4.86	10.5	G	56± 3	〃

Rock types, G : granite, M : migmatite, GD : granodiorite, QD : quartzdiorite, S : schist, GP : granite porphyry, GN : gneiss, AM : amphibolite, A : adamellite, HF : hornfels, R : rhyolite.

Minerals, B : biotite, T : total rock, H : hornblende.

Laboratories, G : Geological Survey of Japan, C : Department of Geodesy and Geophysics, Cambridge, T : total volume method.

References, (1) Shibata and Miller, 1962 ; (2) Shibata and Nozawa, 1966 d ; (3) Shibata and Miller, 1963 ; (4) Shibata and Nozawa, 1966 a ; (5) Shibata and Nozawa, 1966 b ; (6) Shibata and Nozawa, 1966 c ; (7) Shibata et al., 1962 ; (8) Shibata and Yamada, 1965 ; (9) Miller and Shibata, 1961 ; (10) Shibata and Igi, 1966 ; (11) Shibata and Karakida, 1965 ; (12) Shibata and Yamamoto, 1965 ; (13) Miller et al., 1962 ; (14) Shibata and Nozawa, 1966 e.

Some results at Cambridge were obtained by the total volume method, and they are noted also in the table. All other results were obtained by the isotope dilution method with the spike Ar^{38}.

The age results are listed from the north to the southwest along the Japanese Islands, grouped according to their geographical and geological distributions.

Where no error is given for an age result, it is assumed to be less than ±5 %.

VI. Discussion of Results

VI. 1 Hidaka metamorphic belt

The Hidaka metamorphic belt lies along the central axis of the Hidaka mountains, central Hokkaido. It consists of metamorphic and migmatitic complexes, together with plutonic complexes consisting of a large quantity of basic rocks and smaller quantities of granitic and ultrabasic rocks. It is supposed that these rocks were formed over a considerably long period between

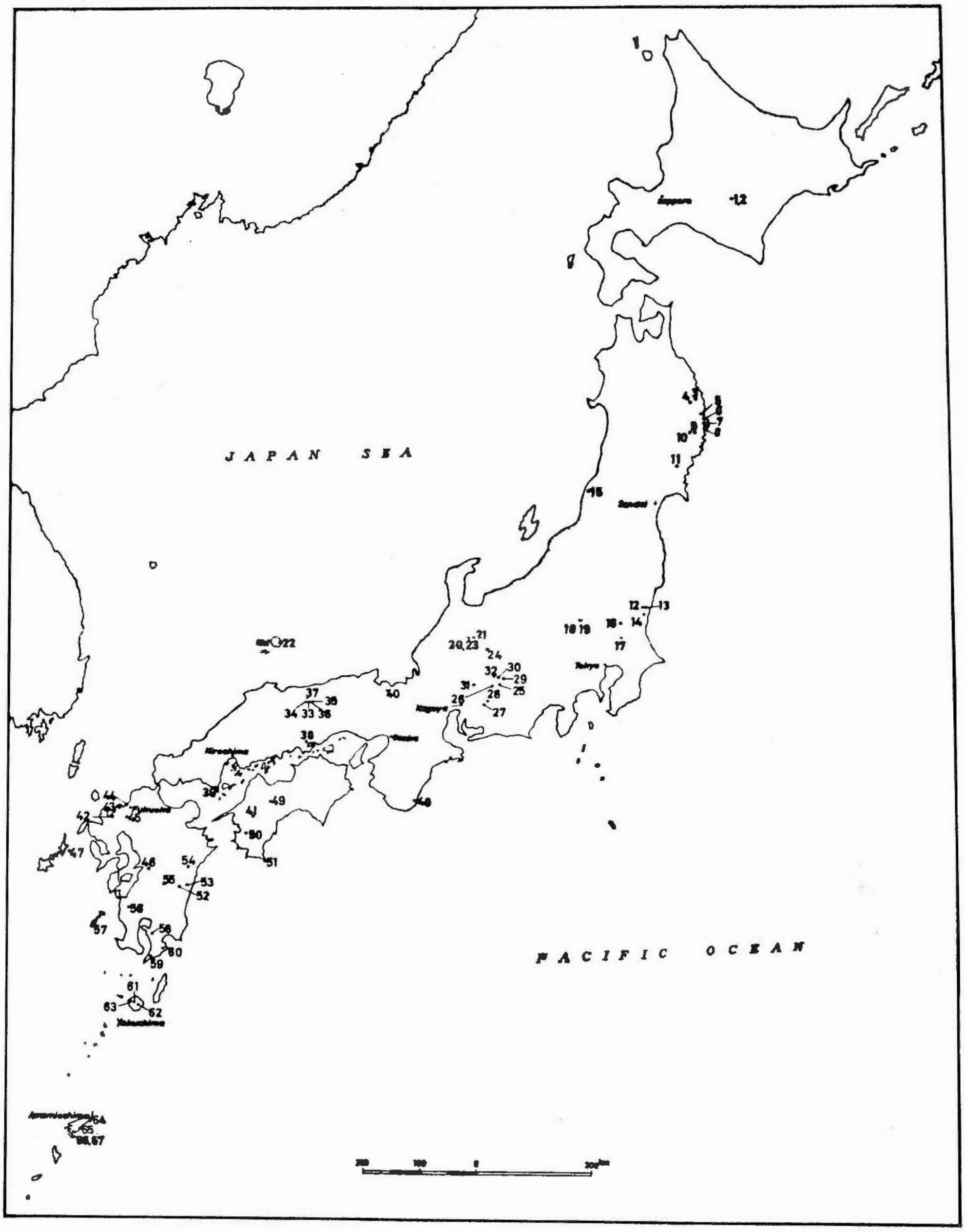


Fig. 24 Map of Japan showing sample localities.
Numbers 1 to 67 refer to Map Nos. in Table 5.

Cretaceous and Paleogene, and that a great upheaval during the middle Miocene brought gneiss and migmatitic rocks in the core of the Hidaka belt to the surface (Minato et al., 1965).

The K-Ar age determinations were carried out on two biotites separated from a granite and a migmatite from the Hidaka belt in the vicinity of the Nissho tunnel. The results of 16 m.y. for the granite and 17 m.y. for the migmatite are correlated to the late Miocene age according to the time-scale of Kulp (1961)*. In accordance with the above-mentioned view, this age could be interpreted as follows: although these rocks had been formed in much earlier time than the Miocene, they were held above some critical temperature for argon loss till the middle Miocene, when an intense upheaval and consequent final cooling caused the system to become closed to further argon loss. It is a little questionable, however, whether a considerably long period of more than 30 m.y. had elapsed between the metamorphic culmination and the unheaval in the Hidaka belt.

An alternative interpretation is that the migmatitic and granitic rocks were formed actually in the late Miocene, although there is no definite geological evidence of Miocene intrusion in the Hidaka belt. There exist in the Outer Zone of Southwest Japan many granitic rocks whose age of intrusion is believed to be late Miocene. It is therefore possible that the granitic rocks of the Hidaka belt may be correlated to those of the Outer Zone of Southwest Japan in respect to the character of the tectonic zone as well as the age of intrusion.

More data on isotopic ages are needed for the solution of this problem.**

VI. 2 Kitakami mountains

The granitic rocks are widely exposed in the Kitakami mountains of Northeast Japan. Except for a few bodies the granitic rocks are thought to be of the same age, and some of them are intruded into the Oshima group, Neocomian age, and overlain by the Miyako group, Aptian or Albian age.

The first isotopic age determination for this district was made by Imai et at. (1960) on a uraninite from an ore deposit which is related to the intrusion of the Miyako granite, giving an age of 94 ± 8 m.y. by U^{238}-Pb^{206} method and 109 ± 11 m.y. by U^{235}-Pb^{207} method. Recently Kawano and Ueda (1965a) made K-Ar age determinations on the granitic rocks of the Kitakami mountains, and their ages concentrate at about 120 m.y. except for that of the Hikami granite, which gave an age of 222 m.y. as the minimum.

The K-Ar age results obtained by Shibata and Miller (1962) on 9 biotites separated from the granitic rocks of this district are given in Table 5, and sample localities and ages also are shown in Figure 25. The ages range from 106 to 129 m.y. with an average of 117 m.y. A few ages considerably exceed the limit of experimental error (± 6 m.y.), and they might indicate the earlier or later phases of igneous activity. The Aptian-Albian boundary is placed at 120 m.y. (Kulp, 1961), therefore all the ages are consistent with the geological evidence.

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* This time-scale is exclusively used for correlation throughout the discussion.

** A recent K-Ar age determination on a granite near Esashi in northern Hokkaido, which is exposed on the northern extension of the Hidaka metamorphic belt, also gave an age of 17 m.y. (unpublished data by the author).

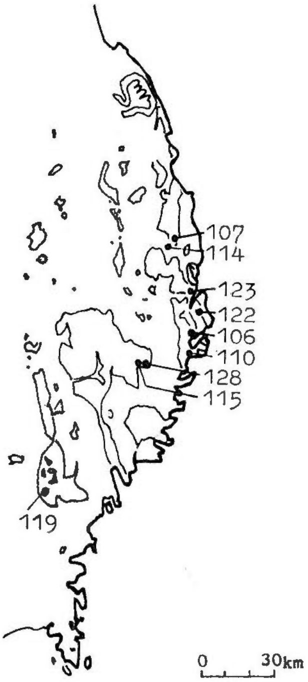

Fig. 25 K-Ar ages of granitic rocks from Kitakami mountains. Ages in m.y.

The Miyako granite is one of the important samples whose stratigraphical age limits are well defined, and its K-Ar age of 123 ± 6 m.y. is significant as a critical result in the early Cretaceous.

VI. 3 Abukuma plateau

The Hitachi area of the southern Abukuma plateau consists mainly of granitic rocks, Paleozoic formations and metamorphic rocks. According to Gorai (1958), the granitic rocks of the Abukuma plateau are divided into the older and younger intrusives, the former is considered to have been emplaced in the late Permian or the early Triassic, and the latter in the Cretaceous. In the Hitachi area the Irishiken granodiorite is widely exposed to the north of the metamorphic rocks, and it belongs to the older intrusives. Recent isotopic age determinations (Miller et al., 1961; Kawano and Ueda, 1965b) indicate that the K-Ar ages of most granitic rocks of the Abukuma plateau are 90-100 m.y., and that there is no difference in age between the older and the younger intrusives.

According to Kinoshita (1935) the metamorphic rocks of the Hitachi area are divided into 3 units in the descending order: the Ayukawa, the Akazawa, and the Oita series. The Ayukawa and Akazawa series are low-grade metamorphic rocks and correlated to the Gosaisho series, which is distributed widely in the southern Abukuma plateau, whereas the Oita series is of high-grade and correlated to the Takanuki series. The original rocks of these metamorphic rocks are thought to be lower Carboniferous, as some index fossils are found from the Ayukawa series. Kuroda and Kurahayashi (1952) considered that the crystalline schist of the Akazawa series was formed by a kind of dynamothermal metamorphism which was closely related to the intrusion of the Irishiken granodiorite.

The Oita series consists mainly of biotite gneiss and amphibole gneiss, which are correlated to the Nishidohira biotite gneiss and the Tamadare amphibole gneiss respectively, according to the study of Watanabe (1920), and is separated from other metamorphic rocks by serpentine. Therefore the Oita series is thought by some geologists to be different in type and origin from other metamorphic rocks of the Hitachi area (Kuroda and Kurahayashi, 1952; Gorai, 1958).

The age of metamorphism and granitic intrusion in the Abukuma metamorphic belt, in general, is only known to be later than Carboniferous and earlier than late Cretaceous from the stratigraphical data. Two widely different views have been postulated on this problem: one is for late Mesozoic metamorphism, and the other is for late Paleozoic to early Mesozoic metamorphism.

The K-Ar age determinations were made on biotites from the Irishiken granodiorite and the crystalline schist of the Akazawa series, both from Godo, Hitachi City, and from the Nishidohira biotite gneiss from Hase, Hitachi-ota City. The age of 98 m.y. for the Irishiken granodiorite, which agrees with the result of 90 m.y. obtained by Kawano and Ueda (1965b) within experimental error, appears to indicate late Cretaceous intrusion. Since the Irishiken granodiorite belongs to the older intrusives, most granitic rocks of the Abukuma plateau should be late Cretaceous or younger. There is a possibility that this age represents the recrystallization of the older granites caused by the intrusion of the younger granites. However, judging from rather limited age distribution for the Abukuma granitic rocks (Kawano and Ueda, 1965b), and from the preliminary results on U-Pb age (Omori and Hasegawa, 1957) and the Rb-Sr age (Aldrich et al., 1962), all of which show the Cretaceous age, it is more reasonable to consider that the intrusion of both older and younger granitic rocks in the Abukuma plateau took place in the late Cretaceous.

The K-Ar ages of the biotites from the Akazawa crystalline schist and the Nishidohira biotite gneiss are 90 m.y. and 102 m.y., respectively, and are similar to that of the Irishiken granodiorite, and also to that of the granitic rocks of the Abukuma plateau in general. Therefore it is suggested that the regional metamorphism in the Hitachi area took place also in the late Cretaceous in close connection with the granitic intrusion, although there still remains a possibility that the age represents the result of recrystallization by the intrusion of granitic rocks.

VI. 4 Nihonkoku gneiss

The Nihonkoku gneiss is a small mass of metamorphic rocks in the Asahi mountains in Northeast Japan. It is covered by the "green tuff" of Neogene age in some parts and is in contact with non-gneissose granitic rocks in some parts, and is isolated from other regional metamorphic areas (Chihara, 1963).

The Nihonkoku gneiss consists mainly of schist, granitic gneiss, and mylonite. The schist occurs as septa in gneiss and mylonite and is small in quantity. The granitic gneiss is often strongly mylonitic and is mainly biotite-granodioritic. The mylonite is developed in various types, mostly granitic in composition. The non-gneissose granitic rocks enclosing the Nihonkoku gneiss are intruded into the Paleozoic formation, probably Permian. However, the relationship between the granitic rocks and the gneiss is not clear.

The biotite separated from the granitic gneiss near Komata yielded an age of 92 m.y., which is correlated to late Cretaceous (Shibata and Nozawa, 1966d).

In the Asahi mountains Shimazu (1964) supposed a large tectonic line extending from the Nihonkoku gneiss to the southeast. The granitic rocks of this district are divided into two parts by this line, and the appearance and composition of the two are considerably different from each other. According to the K-Ar age determination of Kawano and Ueda (1966a), the ages of granitic rocks on the northeastern side of the line range from 55 to 61 m.y., whereas those on the southwestern side range from 85 to 89 m.y., supporting the existence of the above-mentioned tectonic line. The granite on which an age of 85 m.y. was obtained by Kawano and Ueda is petrographically grouped in the northeastern side, but it is included in the southwestern side according to the age result. Theretore the tectonic line might run more north than assumed in the southern district. The age of the Nihonkoku gneiss is proximate to those of granitic rocks of the southwestern side in the Asahi mountains, and it is reasonable to suggest that both rocks are closely connected with each other in the same plutonism, and are also contemporaneous with those of the Abukuma plateau.

VI. 5 Tsukuba and Ashio mountain blocks

The Tsukuba mountain block exists in the southern end of the Yamizo mountain range, which lies southwest of the Abukuma plateau. The rocks developed here are mainly biotite granite and metamorphic rocks. Okada et al. (1954) divided the granite of this area into three types: the Tsukuba-type, the Inada-type, and the Kamishiro-type, and they thought that the intrusion took place also in this order. The Tsukuba type is intruded into the upper Paleozoic sediments. Although there is no geological evidence on the age of intrusion except that it was post-Paleozoic, it has been supposed to be Mesozoic by some geologists. Recently Kawano and Ueda (1966a) obtained K-Ar ages of about 60 m.y. on 4 biotites from the granitic rocks of the Tsukuba area.

According to the investigation of Sugi (1930), the metamorphic rocks of the Tsukuba area are composed of various types of hornfels and injection-rocks. The hornfels is developed in the eastern part of the area, and is principally the product of thermal metamorphism. The injection-rocks are developed in the western part and are thought to have been formed by the reaction of the injected aplite from the biotite granite upon the metamorphosed sediments. These injection-rocks are grouped into four main-types: sillimanite-biotite-fels, biotite-fels with shimmer-aggregates, cordierite-biotite-fels, and biotite-fels. The metamorphic rocks are believed to have been derived from the sedimentary rocks of the Chichibu series, The K-Ar age determinations have been made on biotites from the biotite granite of the Inada type collected from Inada, and from the above-mentioned biotite-fels of the injection-rocks from Hirasawa. The age of 60 m.y. for the Inada granite indicates that the intrusion took place in the early Tertiary. The age of 56 m.y. for the injection-rocks is close to that of the biotite granite, and supports the above-mentioned concept.

The Ashio mountain block, situated to the northwest of Kanto Plain, consists of Paleozoic formations, granitic and rhyolitic rocks, and younger volcanic rocks.

The Sori granodiorite in the Ashio mountain block is an intrusive stock about 12 km long by 6 km wide, and is intruded into the Paleozoic formations, producing an extensive aureole of contact metamorphism (Kawata and Ozawa, 1955; Nozawa et al., 1958). It is overlain by Quaternary lavas at its northern margin. The rock is mostly homogeneous, showing the porphyritic appearance by large crystals of perthite, and is petrographically a coarse-grained biotite granodiorite.

The K-Ar age determination was first made by Shibata and Miller (1963) on the biotite granodiorite from a quarry about 1 km south of the Sori station, and an age of 86 m.y. was obtained. Kawano and Ueda (1966a) also obtained an age of 87 m.y. on the Sori granodiorite near the Sori station. Recently the Sori granodiorite was selected as one of the standard rocks of the Geological Survey of Japan for chemical analysis, and about 200 kg of the rock were collected from a quarry of the Kuwabara Stone Co. Ltd. about 1 km south of the Sori station. About 100 g of biotite were separated from this rock and have been used as a sub-standard sample for age determination. An age of 85 m.y. was obtained on this biotite. All these results indicate that the Sori granodiorite is late Cretaceous.

VI. 6 Hida metamorphic belt

The Hida metamorphic belt is one of the oldest metamorphic complexes in the Japanese Islands. It is the northernmost zone in the zonal arrangement of basement rocks in Southwest Japan. The rocks are composed of various types of gneiss, schist, and granitic rocks.

For these twenty years a controversy has been continued on the age problem of the Hida metamorphic rocks. Some geologists believe it to be Precambrian and some others insist on a Mesozoic age. Biotites from Hida metamorphic rocks gave the K-Ar ages of 170-190 m.y., indicating early Mesozoic (Kuno et al., 1960), whereas hornblendes gave two K-Ar ages; one is early Mesozoic similar to the biotite age, and the other is early Permian to early Carboniferous (Omoto, 1964).

The largest mass of the Hida metamorphic rocks is exposed in the Hida mountains. The Amo-Tsunokawa area lies near its southern periphery, along the Odori river, where the formation is composed mainly of biotite gneiss, biotite hornblende gneiss, and biotite-bearing quartzo-feldspathic gneiss. Two samples for the K-Ar age determination were taken from this formation (Shibata and Nozawa, 1966a).

A small mass of the metamorphic complex, called the Oki gneiss and composed of gneiss and granitic rocks, is exposed also in the Oki Islands, about

350 km west of the Hida mountains. The Oki gneiss is commonly believed to belong to the Hida metamorphic belt, because it is petrographically similar to the Hida metamorphic rocks, and is nearly on the probable extension of the Hida metamorphic belt. It is composed mainly of biotite gneiss, hornblende gneiss, crystalline limestone, diopside gneiss, and granitic rocks such as biotite granodiorite, muscovite granite and mylonite, including "augen gneiss". The granitic rocks are quite similar to some of the Funatsu granitic rocks in the Hida mountains. A sample was taken from the biotite gneiss formation in the Oki gneiss (Shibata and Nozawa, 1966a).

Accompanied by gneiss and schist many types of the granitic rocks are exposed in the Hida metamorphic belt. Most of the granitic rocks are grouped in two types: one is reddish pink-colored granodiorite and its allied rocks, called "Funatsu type", and the other is somewhat darker-colored quartzdiorite and its allied rocks, called "Shimonomoto type". These two are considered to belong to one plutonism and are together named "Funatsu granitic rocks". The Funatsu granitic rocks are intruded into the gneiss in the north and into the Paleozoic formation in the south, and are overlain by Jurassic conglomerate. The K-Ar age of about 180 m.y. was obtained on biotite of the Funatsu granitic rocks (Nagasawa et al., unpublished data). Therefore the age of emplacement of the Funatsu granitic rocks is probably early Mesozoic.

Besides, there are some other granitic masses of much smaller quantity which apparently belong to neither of two types of the Funatsu granitic rocks. They are exposed as small masses in the gneiss area but are not found in the Paleozoic area. Two typical examples of this kind are found near the Amo mine. One is called "Amo granite" and has a concordant shape to the surrounding gneiss. It is light-colored, coarse-grained, heterogeneous with abundant inclusions of gneiss. The other one has, in contrast to the Amo granite, a round outline discordant to the gneiss. It is medium- or fine-grained, light-colored, relatively homogeneous and nearly free from xenolithic inclusions of gneiss. So, it was once believed that the Amo granite might be synkinematic, and the other might be much younger and independent of the Hida metamorphism. A sample was taken from the latter (Shibata and Nozawa, 1966b).

Along the Japanese Alps in the Hida mountains, a vast volume of granitic rocks is exposed. They are mainly of granodiorite with subordinate volume of quartzdiorite and diorite. They are intruded into basement rocks, such as the Hida metamorphic rocks, the Funatsu granitic rocks, and Paleozoic formations. The Shimonohara quartzdiorite, whose K-Ar age determination was carried out by Shibata and Nozawa (1966c), is one of these granitic rocks and is a small stock of round shape about 500 m across. It is intruded into the phyllitic shale of Permian age with a sharp and steep contact plane. It is fine-grained, porphyritic, light-colored, non-gneissose, nearly homogeneous and poor in inclusions (Isomi and Nozawa, 1957).

The results of K-Ar age determinations on rocks from the Hida metamorphic belt are shown in Figure 26 as well as in Table 5. As for the metamorphic rocks the ages of 175 and 174 m.y. for the Amo-Tsunokawa area and an average age of 169 m.y. for the Oki area are all similar to each other and correlated to early Jurassic. The contemporaneity of the metamorphic rocks of the two areas further supports the general concept that the Oki gneiss belongs to the Hida metamorphic belt. These ages are also similar to the K-Ar ages on

Fig. 26 Distribution of metamorphic and granitic rocks in the Hida mountains and K-Ar ages. Ages in m.y.

biotite of the metamorphic rocks from other areas in the Hida metamorphic belt.

The biotite of the gneiss from Tsunokawa has a low K_2O content: 2.06 %. This is because some part of the biotite has been altered to chlorite, which is observed under the microscope. However, the age of this biotite is the same as that of biotite from Amo, whose K_2O is 5.28 %. This fact may show that in some cases the chloritization does not influence the K-Ar age determination.

As noted previously, much older K-Ar ages were found on the hornblende from the Hida metamorphic rocks. The hornblende is generally thought to be less susceptible to thermal events than biotite, and it seems to be certain that at least some of the Hida metamorphic rocks are much older than early Mesozoic, probably older than Permian.

Although the age problem of the Hida metamorphic belt is not yet settled, it should be noted that there was probably an event in early Mesozoic time, on regional scale throughout the Hida metamorphic belt including the Oki Islands, giving rise to the recrystallization of biotite.

As for the granitic rocks, an age of 167 m.y. on the biotite of the granodiorite from the Amo mine is correlated to middle Jurassic. This age is slightly younger than those of the metamorphic rocks and the Funatsu granitic rocks. This granodiorite, however, is supposed to belong to the same plutonism as the Funatsu granitic rocks, although their direct relation is not observed in the field.

An age of 86 m.y. for biotite of the Shimonohara quartzdiorite is correlated to late Cretaceous. According to unpublished data by Nagasawa et al., the K-Ar age of the granodiorite in the neighborhood of Unazuki, near the northern end of the Japan Alps region, is 88 m.y. on biotite and 69 m.y. on the whole rock excluding biotite. Thus both biotites gave the same age. These results are also not inconsistent with the geological evidence.

VI. 7 Ryoke belt of central Japan

The Inagawa granite is situated in the northwestern margin of the Ryoke metamorphic belt in central Japan. It is of batholithic type and distributed from the zone of banded gneiss into the low-grade metamorphic rocks, and its contact effect on the country rocks is slight. The rock consists mainly of coarse-grained hornblende-biotite granodiorite, and has gneissose structure in many localities.

The Naegi granite, on the other hand, is believed to be typical of shallow-emplaced granites and is developed to the northwest of the Ryoke belt. It has been called a "Cretaceous granite" and distinguished from those within the Ryoke metamorphic belt. The rock consists mainly of medium- to coarse-grained biotite granite, and pegmatite is included in some places. The U-Pb age of 60 m.y. (Kimura and Miyake, 1932) and the Th-Pb age of 50 m.y. (Kato, 1958) were obtained on the Naegi granite.

The relationship between the Inagawa and Naegi granites has been discussed in relation to the Nohi rhyolite. The Nohi rhyolite is a thick volcanic formation consisting mainly of lava tuff and welded rhyolitic tuff, and is distributed widely to the northwest of the Ryoke belt. The Nohi rhyolite was once considered to cover unconformably the Inagawa granite, while it is clearly intruded and contact-metamorphosed by the Naegi granite in many localities. Therefore a considerably long interval was supposed between the time of the emplacement of the Inagawa granite and that of the Naegi granite. However, the field evidence indicating that the Nohi rhyolite is intruded and metamorphosed by the Inagawa granite, was recently found (Yamada, 1966). So it is clear that the age of the main plutonism in the Ryoke belt of central Japan is younger than that of the extrusion of the Nohi rhyolite, and two types of granites are supposed to be closely connected with each other in the same plutonism.

The K-Ar age determinations were made on 5 biotite samples from the Inagawa granite and 3 biotite samples from the Naegi granite (Shibata et al., 1962). The results for the Inagawa granite range from 63 to 72 m.y. except for a result of 53 m.y., and those for the Naegi granite range from 64 to 68 m.y. These results indicate that the intrusions of the Inagawa and Naegi granites are contemporaneous and latest Cretaceous. The results also are consistent with the geological evidence found recently. Kawano and Ueda (1966b) recently obtained K-Ar ages of 60-73 m.y. on the granitic rocks of this district, which are in good agreement with the present results.

The K-Ar ages and Pb-α ages of 90-100 m.y. were reported for the Ryoke granites from Dando and Takato areas (Banno and Miller, 1965; Karakida et al., 1965). These granites occur in the high-grade zone of the Ryoke metamorphic belt, and are distinguished from the Inagawa and Naegi granites in age as well as in petrography. The biotites from the Ryoke metamorphic rocks from Dando and Takato areas, on the contrary, gave K-Ar ages of 63-69 m.y., which are younger than those of the associated Ryoke granites and similar to those of the Inagawa and Naegi granites.

VI. 8 Granitic rocks of the Chugoku district

In the Chugoku district granitic rocks of various types, commonly called the Cretaceous Chugoku batholith as a whole, are widely exposed. They are known to be intruded into the Permian-Carboniferous formations, the early Cretaceous Kwanmon group and its related volcanic rocks, and unconformably overlain by the Neogene rocks. The age of intrusion, therefore, is generally thought to be late Cretaceous or Paleogene.

The Cretaceous granitic rocks in the Chugoku district are divided into three groups: the San'in granitic complex, the central plutonic group, and the Hiroshima granitic complex (Yoshida, 1961; Kojima, 1964). The San'in and Hiroshima granitic complexes are distributed generally in the northern region and southern region respectively, of the Chugoku district. They are mostly biotite-granodioritic and form large continuous masses of batholith. The central plutonic group is distributed mainly in the central region of the Chugoku district, and characterized by groups of stocks, whose composition varies from diorite to granite.

The K-Ar age determinations were made on 5 samples from the San'in granitic complex (Shibata and Yamada, 1965), and on a sample from the central plutonic group.

According to Yamada (1961) and Murayama and Ozawa (1961), the granitic rocks in the vicinity of Ningyo-toge, which belong to the San'in granitic complex, are divided into three groups. The intrusive rocks of the 1st stage range from gabbro to granite-granophyre in composition and occur, in most parts, as small xenolithic bodies captured by the later intrusives. The intrusive rocks of the 2nd and the 3rd stages constitute the main part of the Chugoku batholith, and are composed of hornblende-biotite granodiorite, hornblende-biotite granite and biotite granite in the former and only leucoclatic biotite granite in the latter.

As to the stratigraphical age limit of these granitic rocks, the intrusives of the 1st stage are intruded into the Cretaceous volcanic rocks, while the 2nd stage intrusives are overlain by the lower Pliocene formation.

Age measurements were carried out on one biotite from the 1st stage intrusives (OT1003), three from the 2nd stage (OT1001, AN116, and AN119), and one from the 3rd stage (KY1001). The average age of 36 m.y. for the 1st stage intrusives is Oligocene, while ages of the 2nd stage are 50, 57, and 64 m.y. and the average age for the 3rd stage is 60 m.y., these are correlated to early Paleogene. These results are generally not inconsistent with geological evidence. Excluding the intrusives of the 1st stage, the granitic rocks of the area are thought to have been emplaced in nearly the same period in the early Paleogene.

Younger ages of 36-39 m.y. obtained for the intrusives of the 1st stage give a troublesome problem. Geologically this granite (OT1003) is thought to have been intruded and consolidated in the earliest stage among the granitic rocks here. Moreover, biotite of this granite is the freshest of the biotites used, as is supposed from its highest K_2O content. This probably excludes the possibility that argon diffusion took place most severely in this biotite. Recent determinations by Kawano and Ueda (1966b) on the granitic rocks from this district gave similar K-Ar ages to those obtained by the present study.

The central plutonic group of the Cretaceous granitic rocks is divided into two: the Ibaraichi and Kuchiwa plutonic groups on the basis of close connection to volcanic activities, and the ages of intrusion are supposed to be early and late Cretaceous, respectively (Yoshida, 1961). Another characteristic groups of granitic rocks, which are not defined in either of the above two groups, are exposed in limited areas within the distribution area of the central plutonic group, and are called the Mannari-type granitic rocks. These granitic rocks are distinguished by pink-colored hypidiomorphic potash feldspar, and at Mannari in Okayama; type locality, the rocks are called "Mannari stone" and quarried. Another distinguishing feature of these rocks is that they are always associated with the Paleozoic formations.

The K-Ar age determination was made on biotite separated from the Mannari-type granodiorite from Mannari. The age of 86 m.y. is correlated to late Cretaceous, and is generally consistent with the geological evidence, although the stratigraphical age limit of the Mannari granitic rocks is still uncertain. This age is very close to that of the Ryoke granitic rocks in the Yanai area, the details of which will be described in the following, and both of the rocks might have some connection with each other.

The Ryoke metamorphic belt in the Yanai area is composed of metamorphic rocks such as banded gneisses and biotite schists, and associated granitic rocks. Besides, the Cretaceous granitic rocks are developed in the northern part. The banded gneisses occupy the greater part of this area, and consist predominantly of siliceous banded gneiss, together with small quantities of micaceous banded gneiss and micaceous gneiss. The granitic rocks are divided into two: the older and younger complexes (Okamura, 1957). The older complexes are mostly concordant to the surrounding siliceous banded gneiss, and of migmatitic nature, whereas the younger ones are of intrusive type, having an intense thermal effect upon the surrounding rocks. The age of formation of these metamorphic and granitic rocks in this area is only known geologically to be between Permian and late Cretaceous.

The K-Ar age determination was made on biotite separated from the granodiorite of migmatitic nature, from Obatake, Yamaguchi Prefecture (Miller and Shibata, 1961). The rock belongs to the above-mentioned older complexes, and is called the "Obatake gneissose granodiorite" by Nureki (1961). The age of 83 m.y. is correlated to late Cretaceous. As to the ages of the Ryoke granites from other districts, the Inagawa and the Naegi granites of central Japan are 60-70 m.y. and younger than the present granodiorite, while the Ryoke granites of the Dando and Takato areas of central Japan and of the Abukuma plateau are 90-100 m.y. and slightly older. It seems that the ages of metamorphism as well as plutonism in the Ryoke belt vary with areas, and that the Ryoke belt has been formed in several stages of activity in late Cretaceous.

As previously noted the age of 83 m.y. for this granodiorite is very close to that of the Mannari granodiorite.

VI. 9 Maizuru structural belt

The Maizuru structural belt, which extends to WSW from Maizuru along the border line of the Chugoku and Tamba mountains, is characterized by the zonal arrangement of Paleozoic and Mesozoic formations and the so-called Yakuno intrusive rocks. Within the zone of the Yakuno intrusive rocks are exposed the high-grade metamorphic rocks (Kano et al., 1959; Igi et al., 1961), which have been called the Maizuru (Komori) metamorphic rocks. They are composed mainly of biotite gneiss, hornblende-biotite gneiss, amphibolite, and biotite schist.

From the stratigraphical relationship between the Permian and Triassic formations and the Yakuno intrusive rocks, the main part of the Maizuru belt is thought to have been formed by the tectonic movements in the Permian and Triassic periods. The Maizuru metamorphic rocks, on the other hand, are considered to have been formed before the Permian and unheaved to the surface in the Triassic. Igi (1959) considers that the Maizuru metamorphic rocks possibly have some relation to the Sangun metamorphic rocks, which are the low-grade metamorphic rocks composed of crystalline schist and dated geologically between Carboniferous and middle Triassic, and are distributed on the northwestern side of the Maizuru belt, nearly parallel to it. Another assumption is postulated by some geologists, that these rocks are the basement rocks of the Japanese Islands, probably of Precambrian age (Minato et al., 1965).

The K-Ar age determination was carried out on biotite separated from the biotite amphibolite in the Yakuno southern zone of the Maizuru area (Shibata and Igi, 1966). In this area the biotite amphibolite is most predominant, accompanied by small quantities of biotite gneiss, hornblende biotite gneiss, and fine-grained amphibolite. All the rocks are severely altered. Schistosity and gneissosity of the rocks are roughly parallel to the general trend of the Maizuru belt. The biotite amphibolite is gneissose, medium-grained, dark-colored rock. The biotite is considerably altered to chlorite.

The obtained age of 215 m.y. is correlated to late Triassic. The age is nearly equal to that of some of the Yakuno intrusive rocks, and also to the later period of the Sangun metamorphism, and supports the opinion that the Maizuru metamorphic rocks are contemporaneous to the Sangun metamorphic rocks. This result, however, does not necessarily exclude the opinion that the Maizuru metamorphic rocks were formed in much older time and the biotite was recrystallized by the event which occurred in the late Triassic.

Besides, it is to be noted that the potassium content of this biotite is extremely low due to the alteration to chlorite. As stated before the age is apparently not reduced by chloritization which followed the main metamorphism, and so the age for this biotite is also thought to be reliable.

The definite age of formation of the Maizuru metamorphic rocks, however, cannot be ascertained by the single result. More data on isotopic ages are needed to settle this problem.

VI. 10 Kurosegawa structural belt

The Outer Zone of Southwest Japan is divided into three belts: the Sambagawa, the Chichibu, and the Shimanto belts, by the Mikabu and Butsuzo tectonic lines. A characteristic tectonic zone runs parallel to the zonal arrangement of the Outer Zone in the middle part of the Chichibu belt, from the Kii Peninsula, through Shikoku, to Kyushu. This zone, called the Kurosegawa structural belt (Ichikawa et al., 1956), is characterized by the continuation of many lenticular bodies. Each of these lenticular bodies is generally composed of three rock groups: the Mitaki igneous rocks, the Terano metamorphic rocks, and the Okanaro group.

The Mitaki igneous rocks consist mainly of biotite-hornblende granodiorite, diorite and gabbro. The granodiorite is very heterogeneous and sheared, dark green-colored by chlorite. It is characteristic of these rocks that they have little contact metamorphic effect on the surrounding rocks, and bear some protoclastic features. These rocks are apparently in fault contact with the middle Permian group as well as the Okanaro group of Silurian-Devonian age. Therefore no direct evidence is known about their age.

The Terano metamorphic rocks are composed mainly of garnet-biotite-muscovite schist and amphibolite, and the lenticular meta-limestone is rarely included. These rocks are considered to have been formed before the Silurian and upheaved together with the Mitaki igneous rocks.

The Okanaro group is composed mainly of fine-grained rhyolite and its tuff, together with sandstone and shale, and the characteristic limestones are intercalated in some places. The limestones contain many species of fossil faunas which indicate middle to upper Silurian age.

The K-Ar age determination was made on the Mitaki igneous rocks from Mitaki-san by the total rock method. The result is 163 m.y., and is correlated to middle Jurassic. Since the biotite and hornblende are severely chloritized, most of potassium in the rock is included in perthite, which is known to lose more argon than biotite in many cases. Therefore, the age should be considered as the minimum.

VI. 11 North Kyushu

Granitic rocks are widely exposed in north Kyushu. They are divided into more than ten units according to geological relationship, petrographical features especially the character of zircons (Matsumoto, 1951; Karakida, 1952).

The Itoshima granodiorite is one of the earlier members among the successively-intruded granitic rocks of north Kyushu. It is intruded either concordantly or subconcordantly into the Sangun metamorphic rocks. The rock is moderately coarse-grained and schistose. The Kitazaki granodiorite is intruded into the Sangun metamorphic rocks in its northwestern part and into the folded strata of the lower Cretaceous Kwanmon group in its northeastern part, and is unconformably overlain by the coal-bearing sediments of Paleogene age.

The rock is moderately coarse-grained and schistose, and distinguished by purplish feldspar from other granitic rocks of this district.

The Sawara granite is intruded into the above two granodiorites and the metamorphic rocks, and is unconformably overlain by the coal-bearing sediments of Paleogene age. The rock is moderately coarse-grained, porphyritic and massive, and adamellite in composition.

The K-Ar age determinations were carried out on four biotites separated from the granitic rocks of north Kyushu; each from the Itoshima granodiorite and the Sawara granite, and two from the Kitazaki granodiorite (Shibata and Karakida, 1965). The obtained ages range from 83 to 97 m.y., correlated to late Cretaceous, and are generally consistent with the geological evidence. The age of 83 m.y. for the Sawara granite is slightly younger than those for the other two granodiorites. This fact also agrees with the evidence that the Sawara granite is intruded into these two granodiorites.

Recently, Karakida et al. (1905) obtained Pb-α ages of 110 m.y. on zircon from the Itoshima granodiorite, 115 m.y. on zircon from the Kitazaki granodiorite, and 90 m.y. on zircon and 90 and 94 m.y. on monazite from the Sawara granite. All these results are about 10 % higher than the present K-Ar ages of the corresponding granitic rocks. At present, it is uncertain that this is due to argon loss from biotites. Kawano and Ueda (1966b) obtained K-Ar ages of 76-97 m.y. on the granitic rocks of this district, which generally agree with the present results on the corresponding rocks.

The Higo metamorphic rocks, which crop out in relatively wide area to the south of Kumamoto, central Kyushu, are thought to be the western extension of the Ryoke metamorphic belt by some geologists, on the basis of the character of metamorphism. The rocks are composed of schists, gneisses, and migmatite, and the grade of metamorphism increases southwards, reaching the amphibolite facies at the highest (Yamamoto, 1962).

The K-Ar age determination was made on a biotite of the gneiss collected from Kitabeta. The rock belongs to the highest grade part of the Higo metamorphic rocks, and is biotite-plagioclase-garnet-quartz gneiss. The age of 107 m.y. is middle Cretaceous, and nearly the same as those of some Ryoke granitic rocks of central Japan and the Abukuma granites, but is slightly older than that of the Ryoke granite from the Yanai area. The result apparently supports the concept that the Higo metamorphic rocks are the probable extension of the Ryoke belt.

According to Saito and Nagasawa (unpublished data), the Higo plutonic rocks, which are distributed along the southern side of the Higo metamorphic rocks, gave an age of 108 m.y., which is very close to that of the Higo gneiss. Therefore there exists the possibility that the biotite age of the Higo gneiss indicates the time of recrystallization by the intrusion of the Higo plutonic rocks.

The Ainoshima island lies about 5 km off the east coast of the Nakadorishima island, one of the Goto Islands to the west of Kyushu. It is a tiny island of about 1 km across, and composed entirely of contact metamorphic rocks such as mica hornfels and andalusite-cordierite hornfels. It was once supposed that the hornfels was formed by the contact metamorphism of the Tertiary granite, which is exposed in the Goto Islands. However, this Tertiary granite had only a slight effect on the surrounding sediments, and metamorphic rocks of high-grade are not found in this area except in the Ainoshima island.

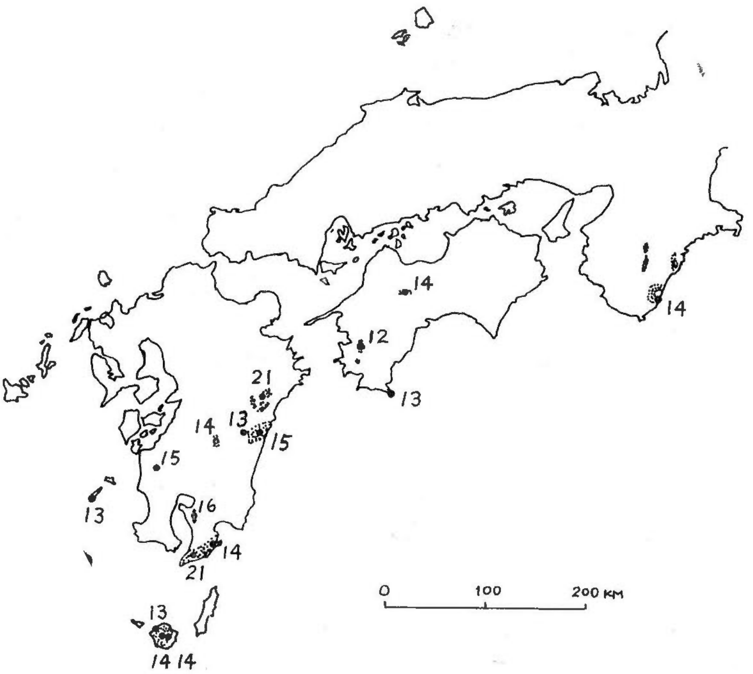

Fig. 27 Distribution of acidic rocks in Outer Zone of Southwest Japan and K-Ar ages. Ages in m.y.

Recently the metamorphic rocks of the Ainoshima island were supposed to have been formed by the regional metamorphism in close connection to the Sonogi metamorphic rocks, which are exposed mainly in Nishisonogi Peninsula of west Kyushu, and are composed of crystalline schists (Katada and Matsui, personal communication). Miller et al. (1963) obtained K-Ar ages of 70 and 83 m.y. on muscovites from the Sonogi metamorphic rocks.

The K-Ar age determination by the total rock method on the hornfels of the Ainoshima island gave an age of 81 m.y., which is correlated to late Cretaceous. This age is similar to those of the Sonogi metamorphic rocks, supporting the above-mentioned view.

VI. 12 Granitic rocks from the Outer Zone of Southwest Japan

In the Outer Zone of Southwest Japan the acidic rocks are sporadically distributed as small masses, from the Kii Peninsula through Shikoku and Kyushu, to Yakushima (Figure 27). Their rock types are mainly granite, granite porphyry, and rhyolite, and they resemble one another in petrographic character, chemical composition, inclusion, mineralization, and structural relationship to the surrounding rocks. Most of them are intruded into the Shimanto group, some are overlain by the upper Miocene formations. From these evidences the acidic rocks of the Outer Zone of Southwest Japan are generally thought to be of the similar age, probably Miocene.

The K-Ar age determinations were carried out on 14 samples of granitic rocks from Omogo, Takatsukiyama and Cape Ashizuri in Shikoku; Okueyama, Kijo, Ichibusayama, Shibasan, Takakumayama and Osumi Peninsula in Kyushu; islands of Koshikijima and Yakushima; and on each sample of the Kumano acidic rocks and the Osuzuyama rhyolite. Measurements were made on biotites separated from the rocks except the Osuzuyama rhyolite, for which the total rock method was applied. The results on most of the Kyushu granites have already been reported (Miller et al., 1962). All the results are listed in Table 5 and shown also in Figure 27.

Except for the Okueyama granite and one from Osumi (Kunimi mountains K16), all the ages for granitic and rhyolitic rocks fall in a narrow range of 14 ± 2 m.y., which is correlated to the latest Miocene, and further supports the similarity among these rocks. The K-Ar ages determined by Kawano and Ueda (1966b) on some of the acidic rocks from the Outer Zone of Southwest Japan agree with the present results within experimental error.

It is remarkable that the granitic rocks, exposed sporadically along the long distance of about 700 km, yield nearly identical ages.

The stratigraphical age limits of the rocks in relation to their isotopic ages are as follows. The Kumano acidic rocks (14 m.y.) in the Kii Peninsula are intruded into the Kumano group of middle Miocene. In Shikoku, the Omogo granite (14 m.y.) is intruded into the Ishizuchi group of middle Miocene. The Takatsukiyama granite (12 m.y.) is intruded into the Uwajima group, one of the Shimanto complex whose age is known to be between late Cretaceous and early Miocene. The Ashizuri granite (13 m.y.) is intruded into the Tosashimizu group of Oligocene to lower Miocene.

In Kyushu, the Osuzuyama rhyolite (15 m.y.) is extruded over the Iorigawa conglomerate of middle Miocene and unconformably overlain by the Miyazaki group of upper Miocene to lower Pliocene. This rock is another critical sample whose stratigraphical age is closely limited. The granitic rocks from Okueyama (21 m.y.), Kijo (13 m.y.), Ichibusayama (14 m.y.), Shibisan (15 m.y.), Koshikijima (13 m.y.), Takakumayama (16 m.y.), Osumi (Kunimi mountains K34, 14 m.y.), and Yakushima (14, 14, 13 m.y.) are all intruded into the Shimanto group mainly of upper Cretaceous to lower Miocene. Another granite from Osumi (K16, 21 m.y.) is intruded into the Eocene formation at Cape Sata.

As for the older age of 21 m.y. for two granites, the relationship between the Okueyama granite and other younger granitic rocks of about 14 m.y. is not clear, whereas in the Osumi Peninsula the 14 m.y. granite of the northern area was recently found to be intruded into the 21 m.y. granite of the southern area (Nozawa and Ota, 1967). Besides, occurrence of the granitic rocks whose ages are older than about 14 m.y. are supposed in the Kii Peninsula, where the middle Miocene Kumano group contains plenty of quartzose sandstone, of which the materials are angular and micaceous, and probably are derived from the neighboring granite. Thus all the geological evidence is in good agreement with the obtained ages.

The age of 14 m.y. for the acidic rocks of the Outer Zone of Southwest Japan may be interpreted in connection to the tectonic movement in this period throughout the Shimanto belt. It is supposed that the uplifting zones with N-S direction, which intersect the general trend of the Shimanto belt, were formed in the Kii Peninsula and Shikoku in the late Miocene period. In Kyushu also the similar type of tectonic zone is supposed (Nozawa, unpublished data). It is observed that the granitic and rhyolitic rocks are distributed in N-S direction in the axial parts of these uplifting zones. Therefore, the acidic rocks of the Outer Zone have probably been intruded or extruded during this period of uplift, thus giving the late Miocene age.

VI. 13 Ryukyu Islands

The Ryukyu Islands, which connect Kyushu with Formosa and constitute an island arc, are composed of a number of small islands. The Amami-oshima is one of the islands on the Ryukyu arc, about 300 km south of Kyushu. The island consists mainly of sandstone, shale, chert and schalstein with thin layers of limestone. Small masses of granitic rocks, named the Kasari, Yamma, and Koniya granites, are intruded into these sedimentary rocks.

The Kasari granite, exposed in elongated shape about 5 km long and 1 km wide in the northeastern part of the island, is biotite granodiorite in composition, medium-grained, light-colored, non-gneissose, mostly homogeneous and poor in inclusions except for a mylonitized part. It is intruded into the Ogachi shale formation. Recently a boulder containing ammonite of late Cretaceous age was found in the distribution area of this formation (Ishikawa and Yamaguchi, 1965), which strongly suggests that the Ogachi formation may be upper Cretaceous. The Yamma granite, exposed as a round mass about 3 km across in the southern part, is biotite quartzdiorite in composition, fine-grained, greyish dark-colored, non-gneissose and somewhat heterogeneous. It is intruded into the Ogachi formation. The Koniya granite, exposed also as a small round mass about 2 km across in the southern part, is biotite granodiorite in composition, fine-grained, greyish dark-colored, non-gneissose, somewhat heterogeneous but poor in inclusions. It is intruded into the Otana sandstone formation, whose age is not known yet.

The granitic rocks of Amami-oshima were formerly thought to be late Paleozoic or early Mesozoic (Hanzawa, 1935). Comparison of these granitic rocks with those of the Outer Zone of Southwest Japan has been tried by some geologists (Suzuki, 1937; Oba, 1959). Konishi (1965) proposes a geotectonic zoning on the Ryukyu Islands, in which the Kasari and Yamma granites are in the "Kunigami belt" and the Koniya and Tokunoshima granites are in the "Motobu belt", and suggests that most of these granites may be Miocene, but there is a possibility of some older granites in the Motobu belt.

The K-Ar ages determined on 4 biotites from the granitic rocks of Amami-oshima range from 49 to 56 m.y. and are correlated to Eocene (Shibata and Nozawa, 1966e). A slightly younger age of 49 m.y. for the Kasari granite is probably due to argon loss caused by severe chloritization, which is suggested by a very low K_2O content of the biotite. The detailed X-ray analysis indicates that the biotite samples from the Amami-oshima granites consist mainly of biotite and chlorite, with very small quantities of quartz and hornblende. The relative peak height of the 002 reflection of chlorite in the X-ray diffraction pattern decreases with increasing K_2O content, and the amount of chlorite in a biotite sample is roughly estimated from its K_2O content. It is to be noted, however, that the K-Ar ages for these biotites are similar to each other in spite of a wide variation in the K_2O content, and that the chloritization apparently has not affected the K-Ar age.

Thus it is probable that all the granitic rocks in Amami-oshima have been emplaced during the same period in the Eocene time, and are quite different in age from those of the Outer Zone of Southwest Japan, most of which gave a late Miocene age. Although these results are not inconsistent with the geological evidence, they are inconsistent with the opinion that the granitic rocks of Amami-oshima belong to those of the Outer Zone.

A K-Ar age of 61 m.y. was reported on the granitic rocks of Tokunoshima, about 40 km south of Amami-oshima (Kawano and Ueda, 1966b). The age is similar to that of the granitic rocks of Amami-oshima, and there may be some relation between these two rocks. Besides these results, the ages of granitic rocks from north and central Kyushu are 90-100 m.y., and the ages of 33 and 86 m.y. were reported on the quartz diorites from Formosa (Yen and Rosenblum, 1964). However, these ages are considerably different from the ages of granitic rocks from Amami-oshima and Tokunoshima. On the other hand there are some granitic rocks giving similar ages in the Inner Zone of Southwest Japan, e.g. in the Chugoku district and the Ryoke belt of central Japan.

The distributions of the Shimanto complex and the granitic rocks of the Outer Zone probably terminate in Yakushima. From the character of the granitic rocks as well as their K-Ar ages, it is suggested that the island of Amami-oshima is geologically not the extension of the Japanese mainland.

VII. General Discussion

VII. 1 Ages of granitic rocks

It is to be noted that the K-Ar ages of granitic rocks in Japan determined by the present study generally agree with the geological evidence, but that they disagree with the geological interpretations in some cases. Discussion on some of the latter cases is given in the following.

The ages of the older and the younger intrusives in some localities have been much discussed. In the Abukuma plateau the older intrusives are believed by some geologists to be intruded in the late Paleozoic or early Triassic, and the younger ones in the Cretaceous, although there is no definite geological evidence for the age of either of the intrusives. According to the K-Ar age determinations the ages of both intrusives are about 100 m.y. and no difference in age is observed. It might be interpreted that the biotite in the older intrusives had been recrystallized and lost all argon at the intrusion of the younger intrusives in the late Cretaceous, giving K-Ar ages of late Cretaceous. However, judging from the limited K-Ar age distribution for the Abukuma granitic rocks (Kawano and Ueda, 1966b), and from the late Cretaceous ages for these rocks obtained by the U-Pb method (Omori and Hasegawa, 1957) and the Rb-Sr method (Aldrich et al., 1962), it is more reasonable to suppose that there is little age difference between the older and the younger intrusives and that both were emplaced in the late Cretaceous.

Another example concerning this problem is on the age of granitic rocks in the Ryoke belt of central Japan. Among many granitic masses in this district, the Inagawa and the Naegi granites are two distinct types; the former is of batholithic type and the latter shallow-emplaced type. It was once supposed that the Inagawa granite is older than the Naegi granite, and that the age difference between the two is rather great. The present K-Ar age determinations gave similar ages for both the granites, apparently contradicting the above interpretation. However, recent finding of field evidence showing a close relation between the Inagawa and the Naegi granites solved this problem.

A Miocene age of the granite from the Hidaka mountains in central Hokkaido gives an important suggestion on the geotectonic movement of the Hikada belt. It is thought by some geologists that the metamorphic and plutonic complexes were formed by the end of Paleogene and upheaved to the surface in the late Miocene. According to this view the Miocene age of the granite could be interpreted as due to the complete loss of radiogenic argon which was produced during the period between formation and upheaval of the rock. However, it may be more natural to consider that the granite was intruded and consolidated in the period of the great upheaval which took place in the late Miocene. The Hidaka belt is generally correlated to the Shimanto belt of Southwest Japan, where many masses of granitic rocks were intruded in the late Miocene. This evidence further supports the Miocene intrusion of granites in the Hidaka belt.

The age of the granitic rocks in Amami-oshima has been much discussed in connection with the granitic rocks of the Outer Zone of Southwest Japan, which are proved to be mostly late Miocene. The K-Ar age determinations gave the Eocene age for the granitic rocks of Amami-oshima. The results are not inconsistent with the field evidence, and are very different from ages of the granitic rocks of Outer Zone. Therefore it is suggested that the Amami-oshima is geologically not the simple extension of the Japanese mainland.

One of the important facts found by this study concerns the ages of the granitic rocks from the Outer Zone of Southwest Japan. Except for two cases, 14 samples of granitic and rhyolitic rocks gave the limited K-Ar age of 14 ± 2 m.y. These rocks are exposed sporadically in the Shimanto belt of Southwest Japan, along the very long distance of about 700 km from the Kii Peninsula to Yakushima, and it is very significant that they have nearly the same age. It is thought that these rocks were intruded during the period of tectonic movement which took place in the late Miocene and produced uplifting zones. The limited K-Ar ages indicate that the major igneous activity took place in a short period in the late Miocene. More precise age measurements on these rocks will probably give some information on the duration of the igneous activity in the Shimanto belt.

Another important fact to be noted is the characteristic age distribution of granitic rocks in Japan. The K-Ar ages obtained for the granitic rocks are roughly grouped into three: older, middle, and younger ages. The older ages are about 170 m.y., and granitic rocks of these ages are found mainly in the Hida belt of central Japan. As noted previously the Hida belt can be extended to the Oki islands, where the older ages are expected for the granitic rocks. Thus the granitic rocks of older ages are distributed in rather limited areas in the inner zone of Southwest Japan. The Mitaki granite from the Kurosegawa belt in the Outer Zone of Southwest Japan gave an older age of 163 m.y. The actual age of emplacement of this granite must be older than that, because the age was obtained by the total rock method and some argon was probably lost from perthite in the rock. The Kurosegawa belt is quite a different complex in the Outer Zone and the K-Ar age of the Mitaki granite should be discussed

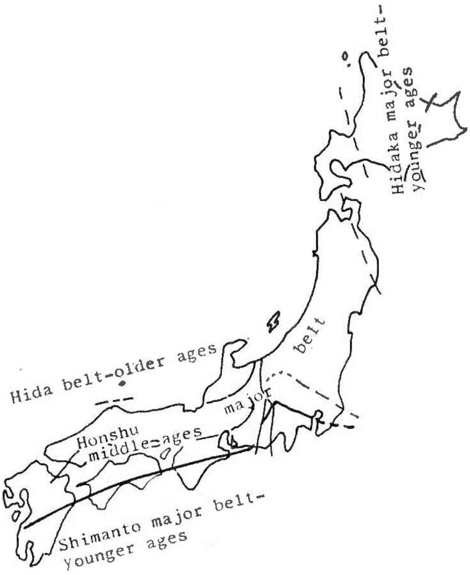

Fig. 28 Correlation between age distribution and tectonic provinces (after Minato et al., 1965) in Japan.

separately. Also, the Hikami granite in Northeast Japan gave a K-Ar age of 222 m.y. (Kawano and Ueda, 1966a), and is a small granitic mass whose geological position is not yet ascertained.

The younger ages range from 12 to 21 m.y., but they concentrate mostly at about 14 m.y. The granitic rocks exposed in the Shimanto belt of the Outer Zone and in the Hidaka belt of central Hokkaido have these younger ages. The Hidaka belt has generally been correlated to the Shimanto belt, and the similar ages obtained for the granitic rocks of both belts further support this view.

The middle ages range mostly from 60 to 120 m.y. Most of the granitic rocks in Japan have these ages, and are distributed in the median zone of the Japanese Islands. The age distribution of these rocks within the zone is rather complicated, and it is difficult to group them clearly from the present results. In Northeast Japan, the granitic rocks in the Kitakami mountains have ages of 110-120 m.y., and those of the Abukuma plateau have ages of about 100 m.y. In the Tsukuba area the granite has an age of 60 m.y. In central Japan the Ryoke granites have ages of 60-70 m.y. It may be said that in Southwest Japan the granitic rocks of the inner or northern zone are younger than those of the outer or southern zone. Namely, the San'in granites give ages of 50-60 m.y., whereas the Sanyo granites give ages of 83 and 86 m.y. The granitic rocks of north Kyushu have ages of 90-100 m.y.

The age distribution above-mentioned roughly corresponds to the zonal arrangement of the tectonic provinces of the Japanese Islands (Figure 28). The granitic rocks of older ages are exposed in the Hida belt of the Honshu major belt (Minato et al., 1965), those of middle ages are in the median and outer zones of Honshu major belt, and those of younger ages are in the Shimanto and Hidaka belts. Although there exist a few exceptions which disturb the zonal arrangement, it seems that they do not have a serious effect on the idea of the zonal arrangement of K-Ar ages. It is supposed that each group of granitic rocks was intruded during the period of tectonic movement by which the major structure of the tectonic belt was formed.

It is also to be noted that these groups of granitic rocks become successively younger towards the Pacific Ocean, and this may have an important bearing on the tectonic development of the Japanese Islands.

VII. 2 Ages of metamorphic rocks

The age of regional metamorphism in Japan is controversial, because it is not closely defined by geological evidence. Usually two opinions are expressed on the age of each metamorphism; one emphasizes the younger age for the metamorphism and the other the older age. The K-Ar ages on metamorphic rocks obtained in this study are, as expected, generally close to the younger age. Minerals in a rock tend to lose radiogenic argon by even a mild thermal event and so their K-Ar ages are likely to become younger than those of the original crystallization. When rocks were subjected to repeated metamorphism, their K-Ar ages will probably indicate the time of the latest metamorphism. For example, the age of the Hida metamorphic rocks is supposed to be Mesozoic by some geologists but to be Precambrian by others. The K-Ar ages on biotites of the Hida metamorphic rocks are found to be Jurassic. However, some K-Ar ages on hornblendes of the Hida metamorphic rocks are found to be Paleozoic and so the rocks are supposed to have been formed before Jurassic.

Another example is K-Ar ages of the Ryoke metamorphic rocks. Geologically, two ages are postulated on these rocks; late Paleozoic to early Mesozoic and late Mesozoic. The K-Ar ages are found to be the younger. Moreover, the local variation of K-Ar ages of granitic and metamorphic rocks in the Ryoke belt is conspicuous. They are 60-70 m.y. in central Japan, about 85 m.y. in the Chugoku district, and about 100 m.y. in north Kyushu and in the Abukuma plateau.

A K-Ar age for the Maizuru metamorphic rocks is very significant in relation to the age of the Sangun metamorphic rocks. Both rocks are thought by some geologists to have some relation to each other, and the age of 215 m.y. is consistent with the geologically suggested age for the Sangun metamorphic rocks, although the Maizuru metamorphic rocks are expected to be Precambrian by others.

The hornfels in the Ainoshima island may have an important bearing on the regional metamorphism in this district. This rock is supposed to be related to the Sonogi metamorphic rocks as one of the paired metamorphic belts. A K-Ar age of 82 m.y. for this hornfels is similar to those for the Sonogi metamorphic rocks, and supports the above view.

An important fact on the K-Ar ages of metamorphic rocks obtained by this study is that the ages are similar to those of the associated granitic rocks in most of the major metamorphic belts of Japan. A Miocene age of a migmatite from the Hidaka mountains in central Hokkaido is similar to that of the associated granite. In the Abukuma plateau the ages of the Akazawa schist and the Nishidohira gneiss are close to that of the Irishiken granodiorite

In the Tsukuba area the injection-rocks have a similar age to that of the Inada granite. A K-Ar age of the Nihonkoku gneiss is nearly the same as those of the associated granitic rocks. The ages of the Hida metamorphic rocks are similar to those of the Funatsu granitic rocks. A migmatite from the Ryoke belt in the Yanai district gives a late Cretaceous age which is close to that of the Sanyo granites. In Kyushu the Higo gneiss, which is thought to be the western extension of the Ryoke belt, has also the same age as that of the associated granite.

These results may indicate that the metamorphic rocks were formed in close connection with the intrusion of the associated granitic rocks. An alternative interpretation is that the metamorphic rocks had lost all radiogenic argon at the intrusion of granitic rocks and so they show a similar age to that of the associated granitic rocks. If this be true, an extensive are study may give the older K-Ar ages on the metamorphic rocks in a rather distant area from the granitic rocks, due to the partial loss of radiogenic argon from rocks. Although there are no age data at present to solve this problem, it is reasonable to consider that a regional metamorphism, or at least a large-scale thermal event by which the radiogenic argon was completely lost from minerals, took place in nearly the same period as the intrusion of the associated granitic rocks.

Anyhow, the complicated history of metamorphic rocks in Japan is difficult to solve by K-Ar age determinations only. The Rb-Sr method of age determination is believed to be a useful means to solve this problem.

VII. 3 Critical samples

It is necessary for the construction of the geological time scale to have reliable age determinations on minerals or rocks whose stratigraphical positions are well defined. Lavas and tuffs intercalated with fossiliferous strata are excellent materials for this purpose so long as they are not altered. Besides, in some cases intrusive rocks containing mica are important, although they are usually not so well defined stratigraphically as are volcanic rocks. Two samples are thought to be critical in this study.

The Miyako granite in the Kitakami mountains is known to be intruded into the Oshima group of Neocomian age, and overlain by the Miyako group of Aptian or Albian age. A biotite of the Miyako granite gave a K-Ar age of 123 ± 6 m.y. According to the time scale of Kulp (1961), the Aptian-Albian boundary in the lower Cretaceous is defined as 120 m.y. Therefore the obtained age is consistent with the time scale.

Another example of a critical sample is the Osuzuyama rhyolite, which is extruded over the Iorigawa conglomerate of middle Miocene and is unconformably overlain by the Miyazaki group of upper Miocene to lower Pliocene. The Miocene-Pliocene boundary is placed at 13 ± 1 m.y., and the age of 15 m.y. for the Osuzuyama rhyolite also supports this boundary age.

Many more isotopic ages for critical samples are needed to construct a more refined time scale especially adapted for the geological history of the Japanese Islands.

VII. 4 Chloritization and K-Ar ages

Biotite is most commonly used in the K-Ar age determination, for it is

Table 6. K-Ar ages on altered biotites

Sample	Locality	Rock type	K_2O (%)	Age (m.y.)
	Amami-oshima granites			
TN 65021202	Kasari	GD	1.07	49± 6
TN 65021310	Yamma	QD	7.52	55± 4
TN 65021401	Koniya	GD	2.90	54± 3
TN 65021402	Koniya	GD	4.86	56± 3
	Hida metamorphic rocks			
TN 61101206	Amo	GN	5.28	175±11
TN 65081201	Tsunokawa	GN	2.06	174± 9
	Maizuru metamorphic rocks			
Y 63-6	Kayasaka-toge	AM	1.55	215±17 216±17

GD : granodiorite, QD : quartzdiorite,
GN : gneiss, AM : amphibolite.

one of the common rock forming minerals and its argon retentivity is high. However, biotite is liable to alter to chlorite in many instances, and it is an important problem whether a reliable K-Ar age can be obtained on a chloritized sample. Usually a severely altered sample is not used for the determination, hence there are few works on this problem. Evernden et al. (1964) measured K-Ar ages on many biotites in basalts and tuffs of Tertiary age and obtained reliable ages on severely chloritized samples. During the course of this study several samples of altered biotites have been dated and apparently concordant results were obtained. Detailed discussion on these results is given in the following, and the related data are shown in Table 6.

Four biotites from the Amami-oshima granites give nearly the same K-Ar age in spite of a wide variation in K_2O content of the biotites. The K_2O content of a fresh biotite is normally over 7 %, and low K_2O values are probably due to potassium loss by chloritization. Especially, the K_2O content of the biotite from the Kasari granite is as low as 1.07 %; about 1/7 of that of the Yamma granite. Its K-Ar age, however, is only 10 % lower than others. The Amami-oshima granites are petrographically similar to one another, and particularly the Kasari granite is in the same tectonic zone as the Yamma granite. Therefore it may be said that the chloritization of biotites apparently had little effect on the K-Ar ages.

The K-Ar ages of biotites from the Hida metamorphic rocks are known to be 170-190 m.y. Two values on these rocks obtained by this study are 174 and 175 m.y. and are consistent with the previous results. The biotite of the gneiss from Tsunokawa is considerably altered to chlorite, and its K_2O content is 2.06 %, but its K-Ar age is equal to the general age for biotites of the Hida metamorphic rocks. This also indicates that the chloritization does not affect the K-Ar age.

The biotite separated from the Maizuru metamorphic rocks is severely chloritized and its K_2O is 1.55 %. As noted before, the Maizuru metamorphic rocks are related to the Sangun metamorphic rocks by some geologists, and so the K-Ar age of 215 m.y. for this biotite is thought to be consistent with the geological consideration. Therefore this result again indicates that the K-Ar age has not been affected by the chloritization of biotite.

The results above mentioned all show that the biotite samples which are considerably altered to chlorite give concordant K-Ar ages. A possible explanation for this fact is that the altered part of a biotite has lost both argon and potassium completely, whereas the unaltered part of the biotite has not lost any of argon or potassium or has lost both at the same rate.

The biotite samples used here are thought to have been altered to chlorite not by weathering in the recent time, but by the retrogressive metamorphism such as hydrothermal alteration which followed the main plutonism or metamorphism, although it is not ascertained by geological evidence. In the latter case the K-Ar ages on the chloritized samples should be nearly equal to the age of the main plutonism or metamorphism and they are reliable. Where the chloritization is due to weathering in the recent time, argon is likely to be lost from the mineral more easily than potassium and so a younger age than expected may be obtained.

It is known that biotite is altered to clay minerals such as vermiculite and montmorillonite in a certain stage of weathering. So the detailed X-ray analysis was made on biotites from the Amami-oshima granites and the Maizuru metamorphic rocks in order to examine the existence of clay minerals. The X-ray diffraction patterns of the untreated samples apparently indicate that each sample consists mainly of biotite and chlorite, with very small quantities of quartz and hornblende. Three of these samples: the most severely altered two and the freshest one, were boiled in 1 N ammonium nitrate for 10 minutes

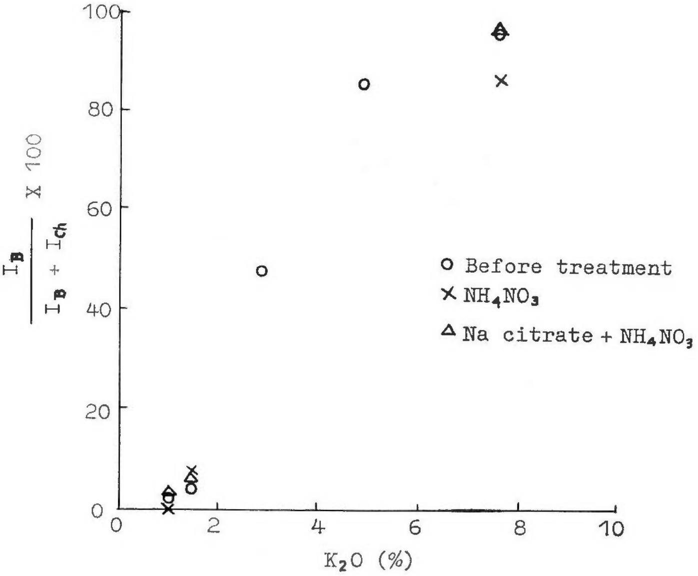

Fig. 29 Relationship between relative peak height of X-ray diffraction and K_2O content for biotites.

I_B : peak height of 001 reflection for biotite.
I_{ch} : peak height of 002 reflection for chorite.

and then analyzed to detect vermiculite. Aluminum vermiculite was looked for after the above samples were boiled in 1 N sodium citrate for 1 hour and then in 1 N ammonium nitrate for 10 minutes. All the samples were treated with ethylene glycol and analyzed to detect montmorillonite. All these treatments did not change the X-ray diffraction patterns of the samples. It is certain therefore that the samples contain neither vermiculite nor montmorillonite, and that they consist mainly of biotite and chlorite. The relationship between the K_2O content of a sample and the relative peak height of the 001 reflection of biotite is shown in Figure 29. It is clear that the relative peak height of biotite increases with its K_2O content.

From the results of the X-ray analysis the chlorite in the samples used here is not supposed to be the product of recent weathering, but supposed to be the product of the hydrothermal alteration which followed the main thermal event. Therefore the K-Ar ages on these samples probably have not been reduced by the chloritization, or even if reduced the time interval between the thermal event and the hydrothermal alteration would have been too short to be detected by the age determination. Thus the K-Ar ages determined here on the altered biotites are thought to be reliable.

VIII. Conclusions

(1) The experiments indicate that radiogenic argon is completely extracted from a mineral by fusion without flux using a radio-frequency heater, and properly purified from other gases by hot titanium sponge and CuO furnace.

The all-glass Reynolds-type mass spectrometer gives satisfactory performance data on the argon isotopic analysis. The getter ion pumps greatly facilitate the vacuum maintenance of the spectrometer. Using the isotope dilution technique radiogenic argon of less than 10^{-6} ml STP can be determined with the precision and accuracy of about $\pm 3\%$. The error for potassium analyses is estimated to be within $\pm 2\%$ for both flame photometry and tetraphenylboron method.

(2) The K-Ar ages of granitic rocks of Japan indicate a zonal arrangement corresponding to the geotectonic provinces of Japanese Islands, and are generally divided into three groups: older, middle, and younger ages, becoming successively younger from the continental side to the Pacific side.

The granitic rocks of older ages, around 170 m.y., are distributed in the innermost zone of the geotectonic provinces, the Hida belt; those of middle ages, which have a rather wide range of 60-120 m.y., are in the median and outer zones of the Honshu major belt (Minato et al., 1965); and those of younger ages, 10-20 m.y., are in the outermost zone, the Shimanto and probably the Hidaka belts.

A few cases of irregularity in the age distribution, for instance the older age of the Mitaki granite or the Hikami granite, probably have little effect on the idea of the zonal arrangement of K-Ar ages.

It is thought that these groups of granitic rocks were intruded during the periods of tectonic movements by which major structures of the corresponding geotectonic provinces were formed.

(3) The K-Ar ages of the metamorphic rocks are similar to those of the

associated granitic rocks in most of the major metamorphic belts of Japan, namely, the Hidaka, Abukuma, Hida, and Ryoke belts. This may indicate that the metamorphic rocks are closely related to the associated granitic rocks in the formation of the metamorphic belts, and that both were formed nearly in the same period.

However, an alternative interpretation that the K-Ar ages of the metamorphic rocks indicate the ages of recrystallization of biotites by the intrusion of the granitic rocks, or that they only represent the ages of the last metamorphism, should not be neglected. Rb-Sr age determinations on these metamorphic rocks will probably give some important information on the actual ages of metamorphism.

(4) Altered biotites from the Amami-oshima granites and from the Hida and the Maizuru metamorphic rocks gave apparently concordant K-Ar ages. The results of X-ray analysis indicate that these samples consist mainly of biotite and chlorite, and that they do not contain clay minerals such as vermiculite and montmorillonite. It is supposed that these biotite samples were altered to chlorite not by recent weathering, but by the hydrothermal alteration which followed the main plutonism or metamorphism, thus their K-Ar ages are thought to be reliable.

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本邦産花崗岩・変成岩のK–Ar年代測定

柴田　賢

要旨

K–Ar 法により本邦産花崗岩・変成岩約70個の地質年代を測定した。前半では測定技術の詳細を記述し，後半では得られた結果について地質学的考察を行なつた。

(1) 測定に用いた試料は大部分が岩石から分離した黒雲母で，その純度はほぼ90％以上である。鉱物中のアルゴンの抽出，精製は石英―パイレックス製の高真空装置内で行なつた。鉱物を高周波電気炉で加熱溶融させ，加熱中に一定量の Ar^{38} をスパイクとして加え，発生したガスはチタンスポンジと CuO 炉を用いて精製し，最後にアルゴンを取りだした。質量分析計を用いてこのアルゴンの同位体比測定を行ない，放射性壊変により生じた Ar^{40} の量を求めた。

微量アルゴン測定用として製作された三菱 Reynolds 型質量分析計に関する種々の特性をくわしく検討した。装置全体の焼出しと金属コックの使用により，10^{-8}mmHg 以下の高真空と低バックグランドを容易に得ることができた。またイオンポンプを排気系に採用することにより高真空の維持がきわめて容易となり，とくにアルゴンをおもな測定対象とする装置においてもイオンポンプの有効性が確認された。同位体比測定はすべて静作動で行ない，二次電子増倍管を使用しないで 10^{-9}ml 以下のアルゴンの検出が可能であり，10^{-6}ml のアルゴンの同位体比を ±3％ の精度で測定できることがわかつた。

鉱物中のカリウムの定量は主として炎光光度法によつて行なつたが，一部試料についてテトラフェニルボロン法による定量を試み，ほぼ満足すべき結果を得た。カリウムの測定誤差は ±2％ 以内と推定される。

(2) 花崗岩の K–Ar 年代は次のとおりである。日高山地：16×10^6年，北上山地：$102\sim129\times10^6$年，阿武隈山地：98×10^6年，筑波地区：60×10^6年，足尾山地：86×10^6年，飛騨山地：167，86×10^6年，中部地方領家帯：$63\sim72\times10^6$年，山陰地方：$36\sim64\times10^6$年，山陽地方：86×10^6年，四国黒瀬川帯：163×10^6年，北九州：$83\sim97\times10^6$年，外帯酸性岩類：$12\sim21\times10^6$年，奄美大島：$49\sim56\times10^6$年，これらの年代は大体において地質学事実と矛盾しない。

わが国の花崗岩の K–Ar 年代はほぼ日本列島の地質構造に対応した帯状分布を示し，大陸側から太平洋側に向かつてしだいに若くなる3帯に分けられる。これらの花崗岩をかりに古期，中期，新期とすれば，古期花崗岩は約 170×10^6年の年代をもち，本州区飛騨帯に分布し，中期花崗岩は $60\sim120\times10^6$年と広い年代範囲をもつもので，飛騨帯を除く本州区全域にわたつて分布し，新期花崗岩は $12\sim21\times10^6$年の年代をもち，四万十区および日高区に分布する。この新期花崗岩は外帯酸性岩類と呼ばれるもので，ほとんどが $14\pm2\times10^6$年なるかぎられた範囲の年代をもつことがいちじるしい特徴である。しかし奄美大島の花崗岩は始新世の年代を示し，外帯酸性岩類とは異なる系列のものであることがわかつた。上記帯状分布は小規模にやぶられるが，そのために基本的構造がかわることはないと考えられる。これらの花崗岩の貫入は，構造帯の地殻変動と密接な関係をもつて行なわれたものと推定される。

(3) 変成岩の K–Ar 年代は次のとおりである。日高山地：17×10^6年，日立地区：90，102×10^6年，日本国片麻岩：92×10^6年，筑波地区：56×10^6年，飛騨山地：174，175×10^6年，隠岐片麻岩

：169×10^6年，舞鶴変成岩：215×10^6年，肥後片麻岩：107×10^6年，相島：81×10^6年。

変成岩のK–Ar年代に関して注目すべきことは，わが国の主要な変成帯，すなわち日高帯，阿武隈帯，飛驒帯，領家帯において変成岩のK–Ar年代が，変成岩に随伴する花崗岩のK–Ar年代にほぼ等しいという事実である。このことは変成岩の生成が花崗岩の貫入と密接な関係をもつていることを示すものと解釈される。しかし古い時代に生成した変成岩が，花崗岩の貫入により再結晶してアルゴンを失つたために両者がほぼ同じ年代を示すにいたつたという解釈に対しても考慮が必要である。

(4) 奄美大島花崗岩，飛驒および舞鶴変成岩から分離した，いちじるしく変質した黒雲母について求めたK–Ar年代は，地質学的事実，あるいわ既存の結果と矛盾しない。X線回折による検討の結果，これらの試料は緑泥石と黒雲母のみからなることがわかつた。黒雲母の変質は最近の風化によるものではなくて，火成・変成作用直後の後退的変質作用の時期に起こつたものと推定され，したがつて求められたK–Ar年代は信頼のおけるものと考えられる。

地質調査所報告は１報文について報告１冊を原則とし，その分類の便宜のために，次のようにアルファベットによる略号をつける。

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  - b．岩石・鉱物
  - c．古生物
  - d．火山・温泉
  - e．地球物理
  - f．地球化学
- B．応用地質に関するもの
  - a．鉱　床
  - b．石　炭
  - c．石油・天然ガス
  - d．地下水
  - e．農林地質・土木地質
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No. 222
HOSHINO, K.: Fracture system of Oshima Island, Kyūshū: A study of jointing in brittle sedimentary rocks, 1967 (in English)

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SHIBATA, K.

K-Ar Age Determinations on Granitic and Metamorphic Rocks in Japan

Ken SHIBATA

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The experimental methods of K-Ar age determination are described in full detail. Various performance data are obtained on the Reynolds-type mass spectrometer. The K-Ar age determinations were made on some sixty samples of granitic and metamorphic rocks from various regions of Japan. The K-Ar ages of granitic rocks indicate a zonal arrangement corresponding to the geotectonic provinces of Japanese Islands, and are divided into three groups. The K-Ar ages of metamorphic rocks are similar to those of the associated granitic rocks in most of major metamorphic belts of Japan.

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