CHAPTER 3
METHOD

3-1. Sample Preparations

In order to obtain a radiometric age and to analyze a chemical composition from a submarine volcanic rock, it is important to use samples as fresh as possible. In this study, submarine rock samples dredged or collected are from outcrops appeared and displaced by the normal faults. In order to obtain fresh samples, faulted seamounts on the subducting oceanic plate are the most suitable, excluding samples from the Mizunagidori Seamount.

One of the major points during sample preparation was how to reduce the quantity of alteration parts in the material to be analyzed for whole rock basalts, groundmass and minerals. Crushed the small pieces of the samples are separated into the more fresh parts and the altered parts by handpicking. More fresh samples are washed with distilled water and the asetone in an ultrasonic generator for two days. These blocks are crushed into 90-100 or 10-30 mesh grains to use the Ar-Ar dating and into the rock powder for chemical analysis as the bulk rock, respectively. For dating, K-feldspar and groundmass are separated by a magnetic isodynamic separator.

Thin sections of each rocks (Appendix B) are prepared for microprobe analysis of rock-forming minerals or volcanic glasses in the sedimentary rocks.

3-2. Major and Trace Element Analyses of Bulk Rocks

X-ray fluorescence (XRF) analyses were carried out at Ocean Research Institute, University of Tokyo, and Faculty of Science, Tohoku University. Major and trace elements were analyzed on glass beads (0.5000 g sample to 5.0000 g solvent) and pressed powder pellets, respectively, using Rigaku3270 X-ray spectrometer in the Ocean Research Institute, University of Tokyo. On the other hand, for the samples of D181-R002, 10K#56-R001 and R002, XRF analyses were done by Rigaku RIX2000 in Fukushima University, and using the glass beads (1.8000 g sample to 3.6000 g solvent) prepared at Faculty of Science, Tohoku University.

Laser ablation microscope-inductively coupled plasma mass spectrometry (LAM-ICPMS) analyses of microscopic areas in thin sections for the sample of D181-R003 volcanic glasses was done by Perkin-Elme Sciex ELAN600 ICP with the laser microprobe system in Science and Engineering, University of Tsukuba. ICPMS for the bulk samples of 10K#56R-001 and R-002 was done by Nippon Jarrell-Ash ICAP Emission Spectrometer in Chemical Analysis Center, University of Tsukuba.

3-3. Electron Microprobe Analyses

Electron microprobe analyses (EPMA) of rock forming minerals and volcanic glasses were performed on a JEOL Ltd. JXA-733 at Ocean Research Institute, University of Tokyo, with 15-keV accelerating voltage and 1.2×10^{-8} A probe current. Beam sizes varied between 1-5 μ m without interference of neighboring phases..

3-4. Ar-Ar Dating

The Principle of Ar-Ar Method (K-Ar System)

Potassium, a parent element of K-Ar system, is one of the eight most abundant chemical elements in the Earth's crust, and is commonly included in many rock-forming minerals. The electron capture (EC) decay constant, which can therefore be taken to represent all of the routs from ^{40}K to ^{40}Ar, now has a recommended value of 0.581×10^{-10} yr^{-1}, equivalent to a half-life of 11.93 Byr (IUGS Subcommission on Geochronology; Steiger and Jager, 1977). Decay from ^{40}K to ^{40}Ca is emission of a β particle, and the β decay constant is now taken to be 4.962×10^{-10} yr^{-1}, equivalent to a half-life of 1.397 Byr. The sum of the decay constants for the two branches yields the total ^{40}K decay constant of 5.543×10^{-10} yr^{-1}, equivalent to a half-life of 1.25 Byr.

The fraction of ^{40}K atoms that decay into ^{40}Ar is given by the expression:

$$\frac{\lambda_{EC}}{\lambda_{total} + \lambda_{EC}}$$

Hence, substituting into the general decay equation, the growth of ^{40}Ar in a K-bearing rock or mineral can be written as:

$$^{40}Ar_{total} = {}^{40}Ar_0 + \frac{\lambda_{EC}}{\lambda_{total}} \cdot {}^{40}K\left(e^{\lambda_{total} \cdot t} - 1\right) \tag{3-1}$$

$$^{40}Ar^* = \frac{\lambda_{EC}}{\lambda_{total}} \cdot {}^{40}K\left(e^{\lambda_{total} \cdot t} - 1\right) \tag{3-2}$$

where ^{40}Ar* signifies radiogenic argon only. This is the situation which is normally

assumed in K-Ar dating.

The presence of any [36]Ar signal shows that common or non-radiogenic argon is present. In fact this is almost inevitable because of the great difficulty of removing all atmospheric argon from the system. If the sample was completely outgassed at the time of its formation, so that it contains no inherited non-radiogenic Ar, then the measured [36]Ar peak can be multiplied by 295.5 to correct the [40]Ar peak for atmospheric argon:

$$^{40}Ar^* = {}^{40}Ar_{total} - {}^{36}Ar \cdot 295.5 \qquad\qquad [3\text{-}3]$$

The age is calculated by re-arranging equation 3.2:

$$t = \frac{1}{\lambda_{total}} \cdot \ln\left[\frac{^{40}Ar^*}{^{40}K} \cdot \frac{\lambda_{total}}{\lambda_{EC}} + 1 \right] \qquad\qquad [3\text{-}4]$$

It is necessary to assume that the sample contained no 'excess' argon, because this might have a $^{40}Ar/^{36}Ar$ ratio different from atmospheric argon, leading to a mixture with indeterminate $^{40}Ar/^{36}Ar$ ratio, which could not be corrected for atmospheric contamination. In addition, K-Ar ages depend on closed-system behavior of the sample for K and Ar throughout its history.

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^{39}K may be converted to ^{39}Ar by irradiation with fast neutrons in a n,p (neutron capture, proton emission) reaction, permitting the K determination for a K-Ar age to be made as part of the argon isotope analysis:

$$^{39}_{19}K + n \rightarrow ^{39}_{18}Ar + p$$
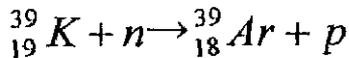
The production of ^{39}Ar from ^{39}K during the irradiation is expressed as:

$$^{39}Ar = ^{39}K \cdot \Delta t \int_{\min e}^{\max e} \phi_e \sigma_e de \qquad [3\text{-}5]$$

where Δt if the irradiation time, ϕ_e is the flux density of neutrons with energy e, and σ_e is the capture cross-section of ^{39}K for neutrons of energy e. The production must be integrated over the total range of neutron energies, which is a very difficult calculation in practice. Therefore, the normal procedure is to use a sample of known age as a flux monitor.

Taking the K-Ar decay equation [3-2], and dividing through on both sides by equation [3-5] yields:

$$\frac{^{40}Ar*}{^{39}Ar} = \underbrace{\frac{\lambda_{EC}}{\lambda_{total}} \frac{^{40}K}{^{39}K \cdot \Delta t \int_{\min e}^{\max e} \phi_e \sigma_e de} (e^{\lambda_{total}t} - 1)}_{\bigstar} \qquad [3\text{-}6]$$

However, terms showing the star are the same for sample and standard whose t is already

known. Therefore it is customary to refer to it as a single quantity whose reciprocal, J, can be evaluated as a constant (Mitchell, 1968).

$$J = \frac{e^{\lambda_{total} t} - 1}{\overline{\frac{^{40}Ar*}{^{39}Ar}}}$$

[3-7]

Rearranging equation [3-7] for samples of unknown age yields:

$$t = \frac{1}{\lambda} \cdot \ln\left[J\left(\frac{^{40}Ar*}{^{39}Ar}\right) + 1 \right]$$

[3-8]

In order to obtain an accurate value of J for each unknown samples, several standards need to be run, representing known spatial positions relative to the unknown samples within the reactor core (Mitchell, 1968). J values for each of the samples can be interpolated.

In this study age standards and unknown samples are simultaneously irradiated. Each J values of the unknown samples are applied for each medium value of some standard samples (Figure 3.1).

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Corrections

During the irradiation of ^{39}K, interfering Ar isotopes are generated by neutron reactions from calcium and other potassium isotopes. The principal interferences which must be a considered are:

^{40}K   n, p   → ^{40}Ar

^{40}Ca   n, nα   → ^{36}Ar

^{42}Ca   n, α   → ^{39}Ar
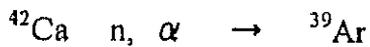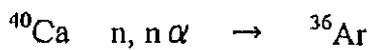
A simple atmospheric correction may be considered adequate:

$$\frac{^{40}Ar^*}{^{39}Ar} = \left(\frac{^{40}Ar}{^{39}Ar}\right)_{meas} - \left(\frac{^{36}Ar}{^{39}Ar}\right)_{meas} \cdot 295.5 \qquad [3.9]$$

The complete edition formula for corrections of the interfering isotope is:

$$\frac{^{40}Ar^*}{^{39}Ar} = \frac{\dfrac{^{40}Ar}{^{39}Ar} - 295.5 \cdot \dfrac{^{36}Ar}{^{39}Ar} + 295.5 \cdot \dfrac{^{37}Ar}{^{39}Ar} \cdot \left(\dfrac{^{36}Ar}{^{37}Ar}\right)_{Ca} - \left(\dfrac{^{40}Ar}{^{39}Ar}\right)_K}{1 - \dfrac{^{37}Ar}{^{39}Ar} \cdot \left(\dfrac{^{39}Ar}{^{37}Ar}\right)_{Ca}}$$

$$[3.10]$$

where ^{37}Ar/^{39}Ar is the interference monitor ratio measured for the unknown, which must be corrected for ^{37}Ar ($t_{1/2}$=35.4 days) decay from the time of irradiation till analysis, and

where $(^{36}Ar/^{37}Ar)_{Ca}$, $(^{39}Ar/^{37}Ar)_{Ca}$ and $(^{40}Ar/^{39}Ar)_K$ are production ratios of Ar isotopes from the subscribed elements. These production ratios are determined by irradiating pure salts of Ca and K respectively in the reacter of interest.

In this study CaF_2 and K_2SO_4 are used as irradiating salts. As during the irradiation, the samples were shielded by Cd foil in order to reduce thermal neutron-induced ^{40}Ar from ^{40}K (Saito, 1994), neutron-induced ^{40}Ar in this study can be omitted insignificant (Appendix D).

Step wise heating

The great advantage of the step wise heating technique over the conventional "total fusion" or K-Ar technique is that progressive outgassing allows the possibility that anormarous sub-systems within a sample may be identified, and, ideally, excluded from an analysis of the 'properly behaved' parts of the sample. In the case of partially disturbed systems, the domains of a sample which are most susceptible to diffusional Ar loss should be outgassed at relatively low temperature, whereas domains with tightly-bound Ar should release Ar at higher temperature.

In order to understand the histories or causes of disturbed samples, results of the step heating analysis are normally presented in one of two ways: as a isochron diagram (in this study, $^{39}Ar/^{40}Ar$-$^{36}Ar/^{40}Ar$ three isochron plot) or as an age spectrum. If the straight line array is obtained in the three isochron diagram it indicates a simple one stage closed-system history for the sample. The initial $^{40}Ar/^{36}Ar$ ratio which can identify in the three isochron plot may be meaningful in case of higher than the atmospheric ratio (called excess 40-argon).

Determination of a reliable eruption (or crystallization) age from the age spectrum depends on the identification of an 'plateau age'. A rigorous criterion for a plateau age is the identification of a series of adjacent steps which together comprise more than 50 % of the total argon release, each of which yields an age within 2 standard deviations of the mean (Dalrymple and Lanphere, 1974; Lee et al., 1991).

As the step wise heating method in this study, gases from the samples were extracted in 8 steps that is, at 600, 800, 900, 1000, 1100, 1200, 1300 and 1500 °C (Appendix D). Such technique is indispensable for age determinations of submarine rocks which may especially have partially disturbed systems such as 40-argon loss or excess 40-argon.