CHAPTER III

EXPERIMENTAL TECHNIQUES

This chapter describes the experimental techniques and methodology employed during the course of this work. The chapter is divided into three parts. In the first two parts K-Ar and ^{40}Ar-^{39}Ar dating techniques and their experimental details are discussed. The third part outlines briefly Rb-Sr dating method and the procedures for sample crushing, chemical processes for separation of Rb and Sr, mass spectrometric work for Rb and Sr isotopic analysis and XRF analysis. The XRF studies were carried out at Wadia Institute of Himalayan Geology (WIHG), Dehradun and the Rb and Sr isotopic studies were carried out at KDM Institute of Petroleum Exploration (KDMIPE), ONGC, Dehradun in addition to the analysis done at Physical Research Laboratory (PRL), Ahmedabad.

3.1. POTASSIUM-ARGON DATING

3.1.1. PRINCIPLE

Potassium in nature consists of three isotopes, viz. ^{39}K, ^{40}K and ^{41}K with abundances of 93.2581%, 0.01167% and 6.7302%, respectively. Of these ^{40}K is radioactive, decaying to ^{40}Ar (half life 1.25×10^9 years) by electron capture and to ^{40}Ca by β^{-1} decay (Fig. 3.1). The branch yielding radioactive argon ($^{40}Ar^*$) as daughter product provides the basis for the K-Ar dating technique through its accumulation over geological time.

In the simplest case of an igneous rock, the K-Ar method normally yields an age that is equal to the time that has elapsed since its eruption and cooling. The argon being an inert gas do not make any crystal lattice bonding and instead simply stay in the crystal lattices as neutral atoms. Any thermal shock at any time after its accumulation will cause diffusion of argon from the lattices. Thus, rocks that have experienced elevated

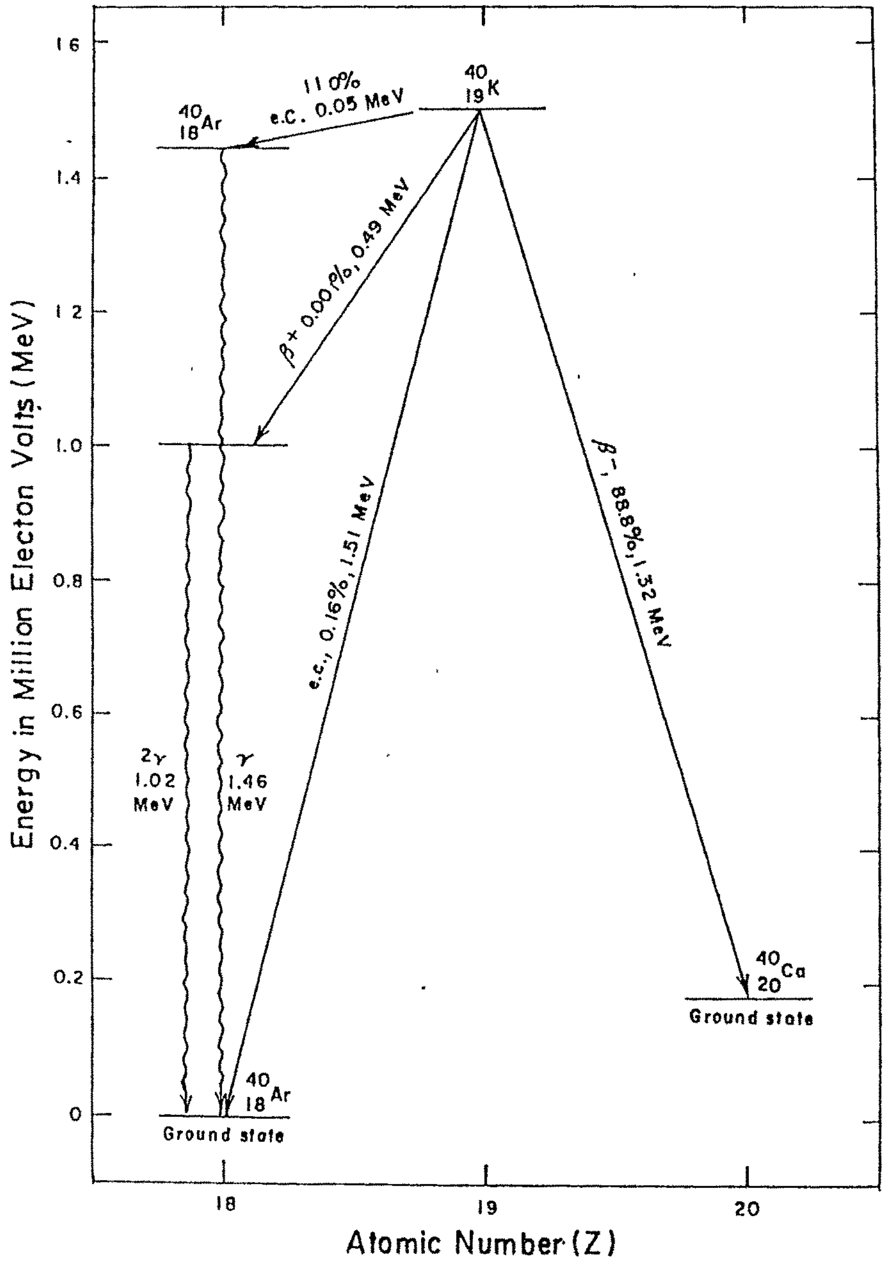

Fig. 3.1. Decay Scheme Diagram for the Branched Decay of $^{40}K_{19}$ to $^{40}Ar_{18}$ by Electron Capture and by Positron Emission and to $^{40}Ca_{20}$ by Emission of Negative Beta Particles.

temperature after crystallization may partially or completely lose accumulated radiogenic argon from their constituent minerals, depending upon the diffusion behavior, the temperature and the time involved. A K-Ar age, therefore, may register the time since crystallization and cooling below a critical temperature (which blocks argon diffusion), the time since cooling after a metamorphic event or an intermediate age that does not date a particular event, but simply reflects partial loss of radiogenic argon by diffusion during a metamorphic event.

As with all isotopic dating methods, there are number of assumptions that must be fulfilled for a K-Ar age to be related to any geological event. The most important assumptions are:

1. *The radiogenic argon measured in a sample is produced by in-situ decay of* ^{40}K *in the interval since the rock crystallized or is recrystallized.*
2. *Corrections can be made for non-radiogenic* ^{40}Ar *present in the rock being dated. For terrestrial rocks the assumption generally is made that all such argon is atmospheric in composition with* $(^{40}Ar/^{36}Ar)_{atm} = 295.5$.
3. *Potassium is homogeneously distributed in the sample.*
4. *The sample must have remained in a closed system since the event being dated. Thus, there should have been no loss or gain of potassium or* ^{40}Ar*, other than by radiogenic decay of* ^{40}K.

In the K-Ar dating method, the potassium and argon are measured on two separate portions of the sample. Potassium is measured as total potassium and the amount of total ^{40}K is calculated from the known present day isotopic composition of potassium (Steiger and Jager, 1977). The most commonly used techniques of potassium measurement are flame-photometry, atomic absorption spectro-photometry and isotope dilution mass spectrometry. Argon normally is determined by isotope dilution technique. Following purification of the argon, isotopic analysis is carried out by means of mass spectrometry, from which the content of ^{40}Ar can be calculated. Since, in the present work provision for isotope dilution is not available, sensitivity of the mass spectrometer for ^{40}Ar measurement is experimentally determined using a known age standard (e.g. MMhb-1 of 520.4 ± 1.7 Ma, Samson and Alexander, 1987).

3.1.2. AGE EQUATION

If $^{40}Ar^*$ is the radiogenic daughter accumulated by spontaneous decay of ^{40}K in a rock of age 't', then

$$^{40}Ar^* = (\lambda_e/\lambda) \times {}^{40}K\,(e^{\lambda t} - 1) \quad \text{----} \ (1)$$

$$\text{or } t = (1/\lambda) \times \ln\,[(\lambda.{}^{40}Ar^*/\lambda_e.{}^{40}K) + 1]$$

where,

λ_e = decay constant of electron capture (0.581×10^{-10}/a)

λ_β = decay constant of β^{-1} decay (4.962×10^{-10}/a)

$\lambda_e + {}_{\lambda\beta} = \lambda$ = Total decay constant (5.543×10^{-10}/a)

$^{40}K/K$ = 0.0001167 (Steiger and Jager, 1977)

3.2. ^{40}Ar-^{39}Ar DATING

3.2.1. PRINCIPLE

To overcome some of the shortcomings of the K-Ar method viz. potassium inhomogeneity in the sample, the loss of argon due to thermal event or the presence of excess argon etc., which bring uncertainty in the age interpretation, a new method i.e. ^{40}Ar-^{39}Ar method was developed (Merrihue and Turner, 1966) which is an analytical conversion of the conventional K-Ar method.

In the ^{40}Ar-^{39}Ar method, the sample to be dated is first irradiated in a nuclear reactor to transform a portion of the ^{39}K to ^{39}Ar by the fast neutron reaction i.e. $^{39}K(n,p)^{39}Ar$, which has a threshold neutron energy of 1.2 Mev. After irradiation, the sample is placed in an ultra-high vacuum system and the argon extracted from it by fusion is purified and analyzed isotopically in a mass spectrometer.

The amount of ^{39}Ar produced, due to irradiation with fast neutrons, is given by:

$$^{39}Ar_K = {}^{39}K\ \Delta t \int \phi(\varepsilon)\ \sigma(\varepsilon)\ d(\varepsilon) \quad \text{---- (2)}$$

where Δt is the irradiation time, $\phi(\varepsilon)$ is the neutron flux at energy ε and $\sigma(\varepsilon)$ is the neutron capture cross section at energy ε for $^{39}K(n,p)^{39}Ar$ reaction. The integration is for over all energies of the incident neutrons.

Combining eqn. (1) and (2) will give:

$$\frac{^{40}Ar^*}{^{39}Ar_K} = \frac{^{40}K\ (e^{\lambda t}-1)}{^{39}K\ \Delta t \int \phi(\varepsilon)\ \sigma(\varepsilon)\ d(\varepsilon)} \quad \text{---- (3)}$$

It is convenient to define a dimensionless irradiation parameter "J" as follows:

$$J = \frac{^{39}K \Delta t \int \phi(\varepsilon)\ \sigma(\varepsilon)\ d(\varepsilon)}{^{40}K} \quad \text{---- (4)}$$

substituting eqn. (4) in (3) gives:

$$\frac{^{40}Ar^*}{^{39}Ar_K} = \frac{e^{\lambda t}-1}{J}$$

which, upon rearrangement allows calculation of the age "t" of the sample as follows:

$$t = \frac{1}{\lambda} \ln\ (1 + J\ {}^{40}Ar^*/{}^{39}Ar_K) \quad \text{---- (5)}$$

where $^{40}Ar/^{39}Ar$ = the ratio of radiogenic ^{40}Ar to the potassium derived ^{39}Ar by neutron irradiation of the sample.

From eqn. (5) age of the sample can be calculated provided the irradiation parameter

"J" is known, which is dependent upon the duration of the irradiation, the neutron flux and the reaction cross section. Because of the difficulties encountered in accurately determining the relevant integrated fast neutron fluence that a sample has received, a monitor or standard sample, whose age is precisely known, is irradiated alongwith the unknown samples to monitor the fluence.

In the case of monitor sample, rearrangement of eqn. (5) will give:

$$J = \frac{(e^{\lambda t_m}-1)}{({}^{40}Ar^*/{}^{39}Ar_K)_m} \quad \text{----} (6)$$

Since age of the monitor sample (t_m) is known, so by simply measuring the $({}^{40}Ar^*/{}^{39}Ar_K)_m$ in the gas extracted from the monitor sample after irradiation, the parameter "J" can be determined.

This value of J is then used in eqn. (5), together with the $({}^{40}Ar^*/{}^{39}Ar_K)$ ratio measured on the unknown sample irradiated at the same time, to calculate its age "t".

When a rock is irradiated with fast neutrons, many reactions produce interfering argon isotopes. These sources of interference have been discussed in detail by Mitchell (1968), Brereton (1970), Dalrymple and Lanphere (1971), Turner(1971), Tetley et al. (1980) and Dalrymple et al. (1981). Out of the various possible reactions (Table 3.1), the following four reactions produce significant interferences:

$$^{40}Ca(n,n\alpha)^{36}Ar,\ ^{40}Ca(n,\alpha)^{37}Ar,\ ^{42}Ca(n,\alpha)^{39}Ar,\ ^{40}K(n,p)^{40}Ar$$

The measured concentrations of different argon isotopes represent the cumulative effect of various interferences as shown below:

$$^{36}Ar_m = {}^{36}Ar_{atm} + {}^{36}Ar_{Ca}$$

$$^{37}Ar_m = {}^{37}Ar_{Ca}$$

$$^{39}Ar_m = {}^{39}Ar_K + {}^{39}Ar_{Ca}$$

$$^{40}Ar_m = {}^{40}Ar_{atm} + {}^{40}Ar_K + {}^{40}Ar^*$$

where subscript **m** stands for measured, **Ca** for calcium derived, **K** for potassium derived, **atm** for trapped initial component and superscript * for radiogenic argon component.

Therefore, to determine $(^{40}Ar^*/^{39}Ar)_K$ ratio to be used in the age calculation, the $^{40}Ar/^{39}Ar$ ratio measured in the mass spectrometer needs to be corrected for atmospheric, calcium and potassium derived interfering isotopes.

Table 3.1.Interfering nuclear reactions caused by neutron irradiations of samples (Brereton, 1970)

Argon Isotope Produced	Calcium	Potassium	Argon	Chlorine
^{36}Ar	$^{40}Ca(n,n\alpha)$	-	-	-
^{37}Ar	$^{40}Ca(n,\alpha)$	$^{39}K(n,nd)$	$^{36}Ar(n,\alpha)$	-
^{38}Ar	$^{42}Ca(n,n\alpha)$	$^{39}K(n,d)$ $^{41}K(n,\alpha,\beta^-)$	$^{40}Ar(n,nd,\beta^-)$	$^{37}Cl(n,\gamma,\beta^-)$
^{39}Ar	$^{42}Ca(n,\alpha)$ $^{43}Ca(n,n\alpha)$	$^{39}K(n,p)^a$ $^{40}K(n,d)$	$^{38}Ar(n,\gamma)$ $^{40}Ar(n,d,\beta^-)$	-
^{40}Ar	$^{43}Ca(n,\alpha)$ $^{44}Ca(n,n\alpha)$	$^{40}K(n,p)$ $^{41}K(n,d)$	-	-

[a] This is the principal reaction on which the ^{40}Ar-^{39}Ar method is based.

Significant amount of ^{36}Ar and ^{39}Ar are produced from calcium during neutron irradiation, and unless proper corrections are made, erroneous ^{40}Ar-^{39}Ar ages will be obtained. The atmospheric ^{40}Ar is corrected by means of ^{36}Ar. Clearly, if the ^{36}Ar produced from ^{40}Ca during irradiation is not taken into account, there will be over correction for atmospheric ^{40}Ar, resulting in low apparent ages. ^{37}Ar is solely derived from ^{40}Ca and can be used to correct for both reactor induced ^{36}Ar and ^{39}Ar derived from calcium (Brereton, 1970). The correction factor, $(^{36}Ar/^{37}Ar)_{Ca}$ and $(^{39}Ar/^{37}Ar)_{Ca}$ are determined by measuring the relative production rates of these isotopes in pure calcium salt i.e. CaF_2 after neutron irradiation. Similarly, correction is also made for neutron induced ^{40}Ar produced from potassium. The correction factor $(^{40}Ar/^{39}Ar)_K$ is determined by measuring the relative production rates of these isotopes in the pure potassium salt i.e. K_2SO_4 after the irradiation. After incorporating these corrections the expression for $(^{40}Ar^*/^{39}Ar_K)$ becomes:

$$\frac{^{40}\mathrm{Ar}^*}{^{39}\mathrm{Ar}_K} = \frac{\left(\frac{^{40}\mathrm{Ar}}{^{39}\mathrm{Ar}}\right)_m - 295.5\left(\frac{^{36}\mathrm{Ar}}{^{39}\mathrm{Ar}}\right)_m - \left(\frac{^{36}\mathrm{Ar}}{37\mathrm{Ar}}\right)_{Ca} \times \left(\frac{^{37}\mathrm{Ar}}{^{39}\mathrm{Ar}}\right)_m}{1 - \left(\frac{^{39}\mathrm{Ar}}{^{37}\mathrm{Ar}}\right)_{Ca} \times \left(\frac{^{37}\mathrm{Ar}}{^{39}\mathrm{Ar}}\right)_m} - \left(\frac{^{40}\mathrm{Ar}}{^{39}\mathrm{Ar}}\right)_K$$

where $(^{40}Ar/^{39}Ar)_m$, $(^{36}Ar/^{39}Ar)_m$ and $(^{37}Ar/^{39}Ar)_m$ are the measured ratio of these isotopes and $(^{36}Ar/^{37}Ar)_{Ca}$, $(^{39}Ar/^{37}Ar)_{Ca}$ and $(^{40}Ar/^{39}Ar)_K$ are the neutron induced correction factors for calcium and potassium. The correction factors used to correct the effects of calcium and potassium interfering isotopes are given in Table 3.2.

The variation in Ca produced $(^{36}Ar/^{37}Ar)_{Ca}$ and $(^{39}Ar/^{37}Ar)_{Ca}$ ratios in the two irradiations is about 23% and 21%, respectively, while that in K produced $(^{40}Ar/^{39}Ar)_K$ the variation is quite large (about 41%). The larger variation in K produced $(^{40}Ar/^{39}Ar)_K$ ratio is probably due to large variations in the thermal neutron flux (Tetley et al., 1980).

Table 3.2. Results obtained on irradiated salts (these ratios are used to correct interfering isotopes; ^{37}Ar is corrected for decay).

Salt	$(^{40}\mathrm{Ar}/^{39}\mathrm{Ar})_K$ x 10^{-2}	$(^{39}\mathrm{Ar}/^{37}\mathrm{Ar})_{Ca}$ x 10^{-4}	$(^{36}\mathrm{Ar}/^{37}\mathrm{Ar})_{Ca}$ x 10^{-4}	Irradiation No.
K_2SO_4	7.5780	-	-	IRRN # 13
K_2SO_4	4.4807	-	-	IRRN # 16,17
CaF_2	-	9.058	1.488	IRRN # 13
CAF_2	-	7.115	1.150	IRRN # 16,17

3.2.2. DECAY FACTOR

As both ^{37}Ar and ^{39}Ar are radioactive, it is important to correct for their decay during and subsequent to irradiation. As the half life for ^{39}Ar is 269 ± 3 yrs (Stoenner et al., 1965) and the sample is analyzed within few weeks/months after the irradiation, the correction will always be negligible. In contrast, the half life of ^{37}Ar is only 35.1 days (Stoenner et al., 1965), significant decay will occur during irradiation, and in the interval between the end of the irradiation and analysis. Therefore, proper allowance for its decay must be made, more so because ^{37}Ar is used as the reference isotope to enable corrections to ^{36}Ar and ^{39}Ar produced from calcium during irradiation. Following Brereton (1970) and Dalrymple et al. (1981), the relevant general equation for the decay factor is:

$$\textbf{Decay Factor} = \lambda t\, e^{\lambda t'}/(1-e^{-\lambda t}) \quad \text{----}\ (7)$$

where t is the irradiation time and t' is the time elapsed between the end of the irradiation and analysis.

Further, because of operational requirements of the reactor, or for other reasons, irradiation may be done in a number of discrete intervals or segments. As given by Wijbrans (1985) and Pande et al. (1988), the generalized form of decay factor used for segmented irradiation is given by:

$$\textbf{Decay Factor} = \lambda \sum_{i=1}^{n} t_i / \sum_{i=1}^{n} \left[(1-e-\lambda^{t_i})/e^{\lambda t'_i}\right] \quad \text{-----} \ (8)$$

where t_i is the duration of irradiation of segment i. t_i' is the time elapsed between the end of the irradiation segment i and analysis of the sample, n is the total number of irradiation segments and λ is the decay constant for ^{37}Ar.

The most important advantage of ^{40}Ar-^{39}Ar method is the graphical depiction of the analytical data. The sample is normally heated in incremental temperature steps until fusion and at each temperature step isotopic ratio i.e ($^{40}Ar^{*}/^{39}Ar_K$) is measured, which should be identical if the sample has not been disturbed after formation. In this case both $^{40}Ar^{*}$ and $^{39}Ar_K$ belong to the same lattice sites occupied originally by ^{40}K. Hence the ratio of $^{40}Ar^{*}/^{39}Ar_K$ will remain constant. When these ratios (or apparent ages calculated using these ratios) are plotted against temperature (or more commonly cumulative % of ^{39}Ar) they define a spectrum of ages which are essentially parallel to the X axis. The age obtained from different temperature steps, which mutually agree (within experimental errors), is called as a plateau age and the diagram is known as the age spectrum diagram. However, if the sample has been affected by secondary thermal processes, then it would give a disturbed spectrum from which also useful information can be construed.

3.2.3. EXPERIMENTAL DETAILS

3.2.3.A. SAMPLE PREPARATION FOR IRRADIATION

Fresh whole rock samples, powdered to 20 to 80 mesh size by a stainless steel mortar and pestle, were used in all the studies. About 600-700 mg of homogenized powder of each sample was used for irradiation. The 520.4 ± 1.7 Ma old Minnesota Hornblende (MMhb-1) (Samson and Alexander, 1987) was used as a monitor.

The whole rock powder samples and monitor alongwith pure CaF_2 and K_2SO_4 were filled in cleaned quartz vials. Two type of vials were used for irradiation viz. 6-7 mm diam. vials for rock samples and 2-3 mm diam. vials for K_2SO_4, CaF_2 and monitor. To minimize the effects of the vertical flux gradient, all the vials were filled to the same height..

To determine the fluence received by each sample relative to that of the monitor pure Ni wire was included in each sample vial. These vials were sealed at atmospheric pressure and packed in an aluminium reactor can. The reactor can was sealed and irradiated for about 20 days in the **APSARA** reactor of Bhabha Atomic Reasearch Center (**BARC**), Bombay.

3.2.3.B. IRRADIATION OF SAMPLES

The samples were irradiated in two batches in **APSARA** reactor of **BARC**, Bombay. This is a light water moderated reactor with neutron flux of about 10^{12} neutron/cm^2/sec with the fast flux representing about 50-60% of the total. The samples were irradiated in D4 (core) position of the reactor which receives maximum flux with minimum variation. The irradiation was done for 73 and 75 hours at 1 MW power level in 12 and 15 discrete steps spreading over 20 and 25 days, respectively. The maximum and minimum duration of the irradiation in a step was of seven and one hour, respectively. The total flux received by the samples was about 2.6 x 10^{17} neutron/cm^2. The vertical variation in the fluence was not measured but the horizontal fluence variation as measured by ^{58}Co activity was found to be about 5.5 and 3.8%, respectively.

After irradiation, the samples were stored in a separate room for about a month to allow the high level, short lived radioisotopes to decay. Samples were then split into aliquots, weighed and wrapped in aluminium foils and loaded in the sample holder of the argon extraction system.

3.2.3.C. EXTRACTION AND PURIFICATION OF ARGON

A brief description of the technique employed in argon extraction and purification is given here. The approaches used in for both the conventional K-Ar and ^{40}Ar-^{39}Ar dating methods are similar. The major differences are that in K-Ar dating the sample is fused directly, while in ^{40}Ar-^{39}Ar dating the sample is heated in incremental steps until it is fused completely.

An argon extraction and purification system is illustrated schematically in Fig. 3.2. It consists essentially of a high vacuum line with appropriate pumping facilities, a furnace assembly in which a sample can be heated in a controlled manner to release argon, getter systems for purification of the released gases, isolation valves and activated charcoal trap cooled at -196°C for moving gas from one part of the line to another.

The furnace of the extraction unit is an all metal, compact and indigenously made resistance heater (Fig. 3.3). It consists of a molybdenum crucible with a plug forming its base into which a thermocouple is inserted. The crucible is electrically heated by a concentric tantalum filament which in turn is surrounded by tantalum heat shield in a stainless steel vacuum chamber. Power for the heater, derived from a variac controlled low voltage, high current transformer, is delivered by means of a copper feed-through. The temperature of the crucible is measured with a 95% Pt + 5% Rh - 80% Pt + 20% Rh thermocouple, which has been calibrated earlier by optical pyrometry. The temperatures are estimated to be accurate to ±50°C. The outer SS jacket of furnace is connected to chilled water supply for cooling purpose. Samples are dropped into the crucible from a glass sample holder connected to the top flange.

The gas purification system consists of five valves (V_1-V_4 and V_9) and five getters (Fig. 3.2). The valves V_1-V_4 are interconnected and fitted on a single rectangular stainless steel block. The middle section of this block is shown in Fig. 3.4.

The sample gas released from the crucible, first comes in contact with Ti-Zr getter connected between valve V_2 and V_3. The Ti-Zr getter is kept hot at around 800°C when most of the active gases will either chemically combine with or be absorbed by the getter. Further, on cooling to room temperature this getter will adsorb hydrogen present

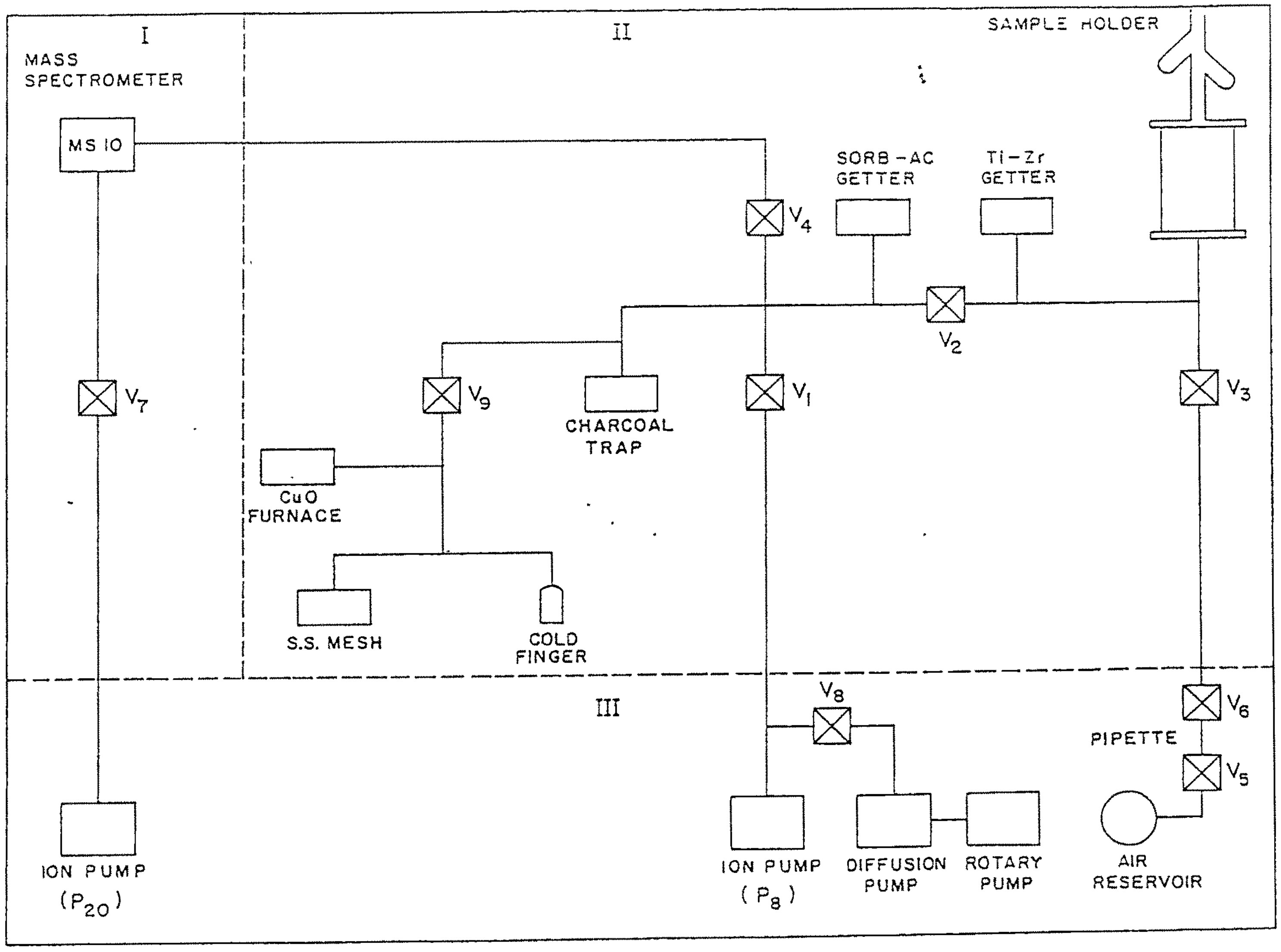

Fig. 3.2. Schematic of the Complete Mass Spectrometer, Gas Extraction - Purification System.

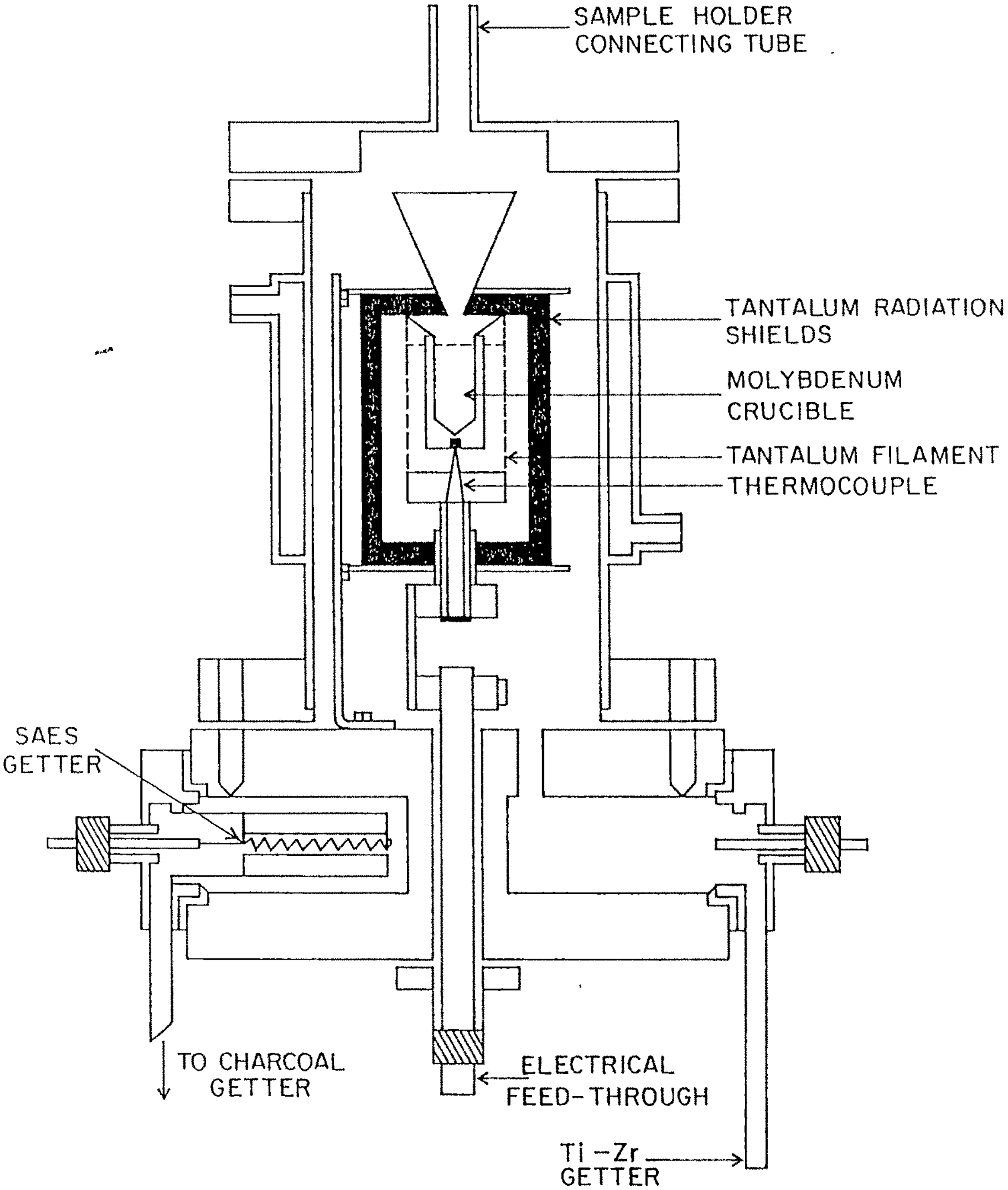

Fig. 3.3. Section through Gas Extraction Furnace and Purification Line.

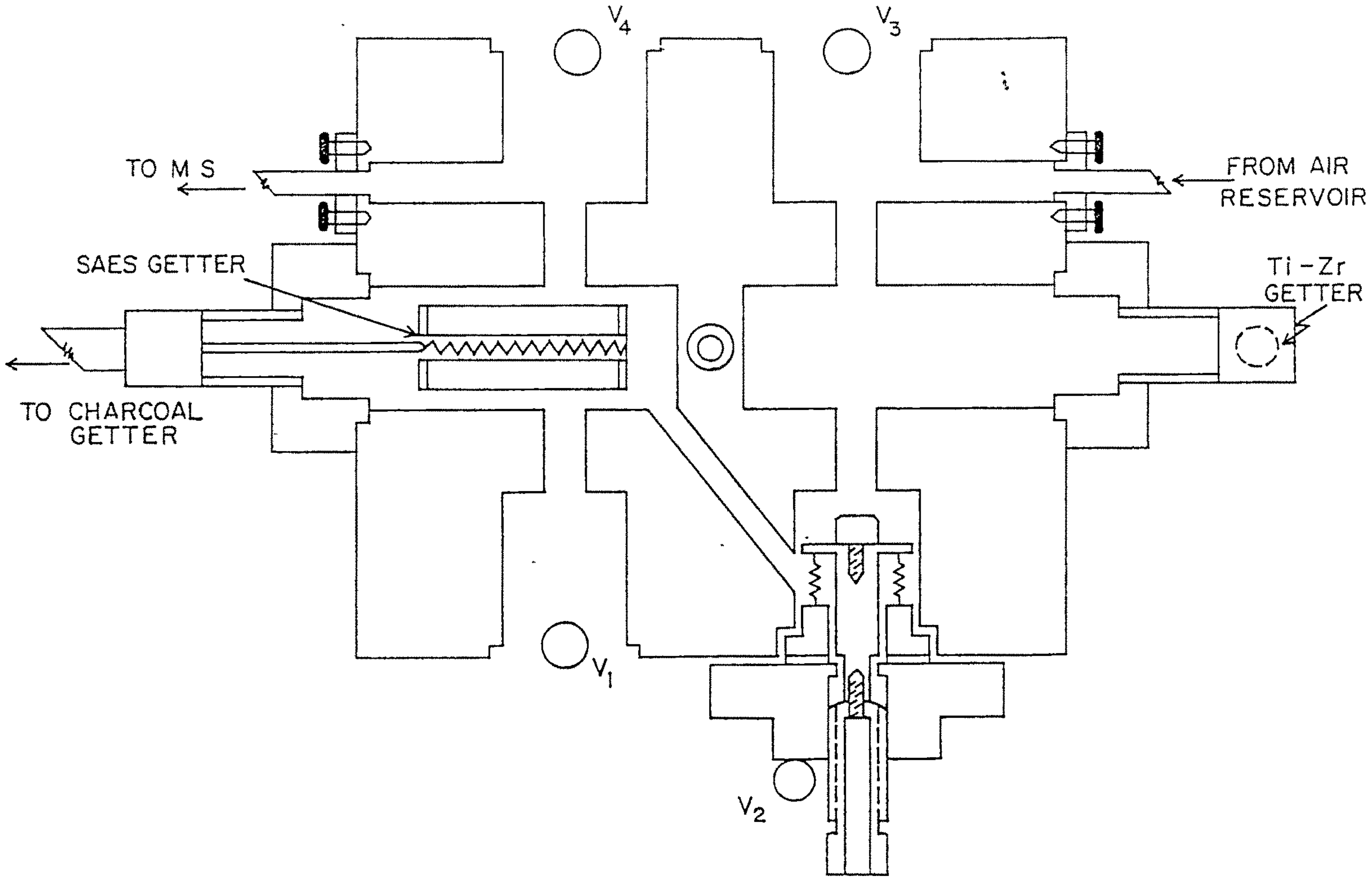

Fig. 3.4. Middle Section of the S-S Block with Only One Valve Assembly

in the sample gas. Thus, the cleaned gas, accumulated for about 50 minutes (typical duration of a temperature step) is allowed to react with SAES getter by opening valve V_2 for further purification. The water vapour is adsorbed on cold finger and the remaining gas is taken on stainless steel mesh kept at liquid nitrogen temperature.

The second round of cleaning is done by oxidation reactions in CuO furnace. The oxygen released from CuO furnace (kept at around 800°C) react with the hydrogen and hydrocarbons present in the sample gas and form water molecules and carbon dioxide, respectively, which are retained on the cold finger. The CuO furnace is isolated from charcoal finger by the valve V_9. The purified gas thus left with argon is adsorbed on the charcoal cooled at liquid nitrogen temperature. It is then admitted into the mass spectrometer after 10 minutes through valve V_4 for isotopic analysis. After the gas is equilibrated in the mass spectrometer, (say 2 minutes) V_4 is closed. The charcoal finger, cold finger and s.s. mesh are connected to ion pump (P_8) by opening valve V_9 and V_1 to pump out the remaining gas. The similar procedure is adopted for cleaning up and adsorption etc. in all the successive steps.

The procedure normally followed in a temperature step for the extraction and purification of argon can be described as follows:

00^{00} Cl V_3, V_2, F↑, Ti↑, Water on to cool furnace wall
00^{20} Ti↓
00^{45} SSM↓, Ch↓
00^{53} Cl V_1, Op V_2, LN_2 on CF, F↓
00^{55} LN_2 on SSM
01^{15} Cl V_9, LN_2 on Ch, SSM↑, CF↑, CuO↑
01^{23} Cl V_7, Op V_4, F (residual)
01^{25} Cl V_4, Cl V_2, Ti↑, Ch↑, F↑ (next step)
01^{30} CuO↓
01^{43} Op V_9, LN_2 on CF
01^{45} LN_2 on Ch
01^{55} Cl V_9, Ch↑, Cl V_7, MSBG, SSM↑ (heater), CF↑
02^{05} Check V_7 Cl, Op V_4, Let in gas into MS

02^{07} Cl V_4, Op V_1, V_9, Ch↑ (heater)

02^{32} Op V_7

The abbreviations used are:

Cl = Close, F = Furnace, Ti = Ti-Zr getter, SSM = Stain less Steel Mesh, Ch = Charcoal, LN_2 = Liquid Nitrogen, CF = Cold Finger, MSBG = Mass Spectrometer Back Ground, ↑ = Up, and ↓ = Down.

In the **K-Ar** studies, the samples were heated in a single temperature step to about 1500°C. At this temperature most of the rock-forming minerals melt away, while in the **^{40}Ar-^{39}Ar** studies, the samples were degassed in steps, normally sixteen, of successively higher temperature, starting from 400°C until fusion at about 1500°C. The K_2SO_4, CaF_2 and monitor sample (MMhb-1) were, however, degassed in single temperature (1500°C) step. The gas in each temperature step was purified following the procedure described earlier in this section and then admitted into the MS10S (180° deflection, 5 cm radius) mass spectrometer having permanent magnet of 1.8 kilo gauss. The mass spectrometer was operated in the static mode. By voltage scanning, the ions of masses 40, 39, 38, 37, and 36 were collected on a Faraday cup and the ion currents measured sequentially in picco amperes (pa) were recorded on a chart recorder Fig 3.5.

In case of **K-Ar** method, since there was no production of ^{39}Ar and ^{37}Ar, ion currents corresponding to ^{40}Ar, ^{38}Ar and ^{36}Ar were recorded. The peak heights and the corresponding time of peak measurements from the time 't_0' i.e. the time of admission of the gas into the mass spectrometer, measured manually, were used for the best fit (Bevington, 1969) to compute the required isotopic abundances and ratios.

The system blanks were measured at different temperatures before and after each sample. The blank measurement consisted of measuring the argon concentration by following the same procedure as for the sample but without having any sample in the crucible. Since the actual blank contribution during each heating step was not known, therefore, the blank correction at each temperature step was calculated using the graph made by plotting the measured blank against the temperature. The mean ^{40}Ar blank at 500°C was 4.4 x 10^{-9} cc STP, rising to 1.9 x 10^{-8} cc STP at 1500°C. Thus, the blank contribution to the sample gas were very small varying from 2-4% upto 1300°C

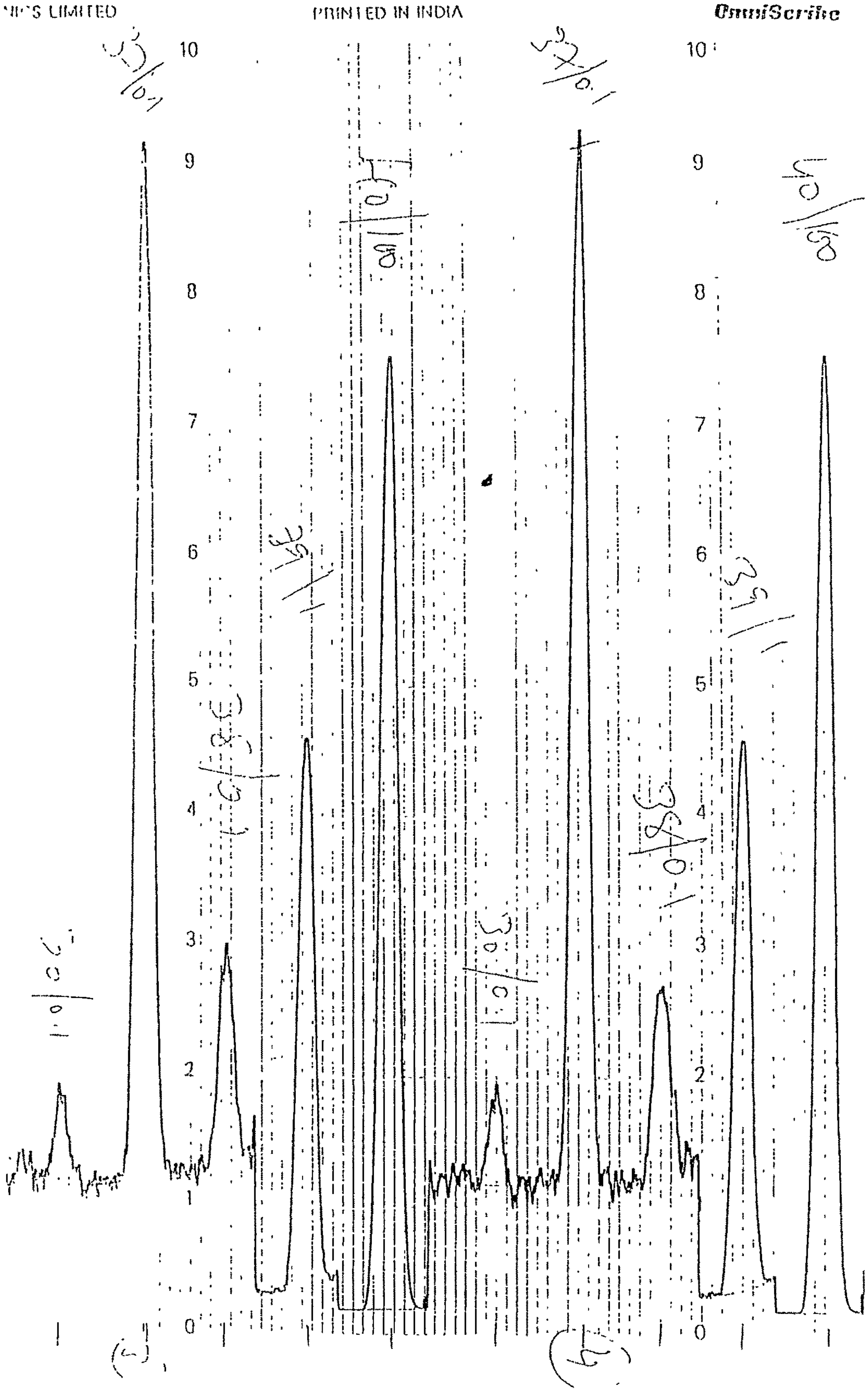

Fig. 3.5. Typical Argon Spectrum.

temperature but increased to about 10-20% in the fusion step. Typical blank contributions measured for the sample VA/181 at various temperature steps are given in Table 3.3.

Table 3.3. Percentage of system blanks calculated for different temperature steps in sample VA/181.

Temperature	Argon Isotopes			
°C	^{36}Ar	^{37}Ar	^{39}Ar	^{40}Ar
450	4.53	-	-	2.59
500	5.22	-	-	2.74
550	9.60	-	-	1.02
750	5.85	-	-	0.22
800	18.20	-	-	0.50
900	13.31	-	-	0.67
1000	4.02	-	-	0.36
1050	5.36	-	-	0.59
1150	10.17	-	-	1.08
1250	11.91	-	-	1.75
1350	26.40	-	-	3.81
1500	56.09	-	-	14.69

Mass discrimination (MD) corrections were done by analyzing atmospheric argon (AIR SPIKE) introduced from a pipette system. Each sample was followed and preceded by Air Spike analysis and an average of the pre and the post analysis was used for the MD correction. The measured atmospheric ^{40}Ar/^{36}Ar ratios fell randomly in the range of

308-312 and did not show any relation with the filament life. Mass spectrometer sensitivity was estimated from repeated measurement of the monitor sample (MMhb-1) and was typically in the range of 1.2-1.4 x 10^{-8} cc STP/pa. Errors were computed by quadratically propagating the errors in the measured ratios, blanks and interfering isotopes. An error of ±25% in the atmospheric argon blank was also applied. The error quoted on the apparent and integrated ages include the error in J but the error boxes in age spectra plots do not include the error in J. All the errors are quoted at 2σ level. Isochron ages have been computed using the two error regresssion method outlined by York (1969) of data points corresponding to the plateau steps. The plateau ages are weighted means of the apparent ages of steps forming the plateau. The total-gas or integrated ages have been computed by appropriate weighting of the apparent ages with $1/\sigma_i^2$. A plateau is considered defined if the ages recorded by 4 or more contiguous temperature steps, each representing >5% of the total ^{39}Ar evolved and together constituting >50% of the total ^{39}Ar evolved, are mutually concordant within 2σ uncertainty. If any of the steps in between do not agree with the other steps or the total ^{39}Ar constituting the plateau is less than 50%, we call it as a pseudo plateau.

3.3. RUBIDIUM-STRONTIUM DATING

3.3.1. PRINCIPLE

For Rb-Sr dating, the $^{87}Rb/^{86}Sr$ ratios measured for a set of whole rock or mineral separates are plotted against $^{87}Rb/^{86}Sr$ ratios which conform to a straight line on Sr-evolution diagram, provided all the samples had commenced with the same $^{87}Sr/^{86}Sr$ ratio and have remained in a chemically closed system since the time 't' of its formation (Nicolaysen, 1961; Lanphere et al., 1964). Such a straight line, called an isochron, is defined by the equation :

$$(^{87}Sr/^{86}Sr)_m = (^{87}Sr/^{86}Sr)_i + (^{87}Rb/^{86}Sr)\,(e^{\lambda t} - 1) \quad \text{----}\ (9)$$

where, λ is the decay constant of ^{87}Rb.

The slope of this isochron gives the time since the sample remained closed and the intercept on the ordinate directly gives the initial ^{87}Sr/^{86}Sr composition. In cases where there is independent geological and chemical evidence that the samples are cogenetic, t can be interpreted as the time elapsed since the whole rock samples last became closed to Rb and Sr. It can be seen from the eqn. (9) that the samples with poor radiogenic Sr enrichment closely determine the intercept while those with high radiogenic enrichment constrain the slope. Therefore, a good dispersion in the Rb/Sr ratios is desirable so as to have good control on the isochron.

Since the data points are subject to analytical errors, they do not strictly align on a straight line. This leads to the problem of determination of the slope and intercept for a given set of experimental points. The best fit line obtained by simple regression techniques, in which one of the co-ordinates is assumed to be free of errors, is not satisfactorily valid. Murthy and Compston (1965) and York (1966) developed a procedure in which allowance is made for errors in both the co-ordinates. The procedure assumes that the errors are uncorrelated and normally distributed. Individual weighting factors are assigned to each point. These are commonly the inverse square of experimental errors.

York (1966) gave somewhat simplified expressions for uncertainties in slope and intercept. However, he did not specify any criterion to test the goodness of fit of the straight line to the data. Mc Intyre et al. (1966) gave a slightly different weighting method and gave exact expressions for variances of slope and intercept and also specified that the goodness of fit can be judged by computing a quantity called **'mean square of weighted deviates (*MSWD*)'** given by:

$$\mathrm{MSWD} = (1/N\text{-}2)\left[\sum_{i=1}^{N} W_i\,(a + bx_i - Y_i)^2\right] \quad \text{----}\ (10)$$

Where W_i is a function of $W(X_i)$, $W(Y_i)$ and slope (b). The quantity under the bracket is distributed as χ^2 and has an expectation of N-2. MSWD should, therefore, be close to unity. If the MSWD significantly exceeds unity, it implies that either (a) the measurenments are less accurate than supposed in the calculation of weights or, (b) various assumptions underlying the expectation of a linear isochron plot have not been satisfied. In other words (a) some of the samples may have been in open system with respect to Rb and/or Sr, (b) the samples may not have commenced with the same initial $^{87}Sr/^{86}Sr$ ratio, and/or, (c) the samples may not be of the same age. In such cases, where MSWD greatly exceeds 1, the authors call the isochron an 'errorchron' and suggest various models for weighting the data in such a way as to make MSWD close to unity. Slope is recalculated with new weights. The underlying assumption is that the scatter of data in such cases is due to geological processes over and above the analytical errors. Brooks et al. (1968) recommended yet another weighting procedure. York (1969) gave a method for correlated errors. The relative merits of all these methods have been reviewed by Brooks et al. (1972). Williamson (1968), adopting a similar weighting technique as York (1966), showed that the least squares cubic is redundant and can be reduced to a linear equation. He also gave an exact expression for variance in the slope and intercept and also criteria for testing the goodness of fit by performing χ^2 test on the expression within the parenthesis in eqn. (10). However, York (1969) method has been followed for regression of the data presented in this study.

For the present study, only representative samples with good spread in Rb/Sr ratios were selected. The cut off value for MSWD has been fixed at 2. The uncertainty in the slope and intercept has been quoted at 2σ level. The ages have been calculated using the decay constant of ^{87}Rb as 1.42×10^{-11} yr^{-1} as recommended by IUGC Subcommission on Geochronology (Steiger and Jager, 1977). For petrogenesis purposes, $(^{87}Sr/^{86}Sr)_i$ ratios are calculated using $(^{87}Sr/^{86}Sr)_m$ and an appropriate age. The $(^{87}Sr/^{86}Sr)_i$, thus, calculated is the model value. The errors in the model $(^{87}Sr/^{86}Sr)_i$ ratios have been calculated by quadratically compounding the errors in $^{87}Rb/^{86}Sr$ ratios and $(^{87}Sr/^{86}Sr)_m$ using the following equation:

$$\sigma_{Ri}{}^2 = \sigma_{Rm}{}^2 + AR^2.\lambda^2.(e^{\lambda t})^2.\sigma_t{}^2 + (e^{\lambda t}-1)^2.\sigma AR^2 \quad \text{----} \ (11)$$

where,

$\sigma_{Ri} = \sigma(^{87}Sr/^{86}Sr)_i$, $\sigma_{Rm} = \sigma(^{87}Sr/^{86}Sr)_m$

$AR = (^{87}Rb/^{86}Sr)$ and $\sigma_{AR} = \sigma(^{87}Rb/^{86}Sr)$

Various processes involved in chemical and Rb-Sr isotopic studies are discussed below:

3.3.2. ROCK CRUSHING

Fresh samples each weighing about 10-15 kg were cleaned with brush and distilled water to remove surface contamination, if any. The samples were broken into small pieces using a hammer. Sample pieces containing mineral veins and inclusions were discarded and the residual pieces were then crushed to <3-5 mm size using a jaw crusher (Fritz pulverizer). The crushing surfaces of the pulverizer were cleaned before and after each sample with a high pressure air blast and preconditioned with a small amount of the sample being processed. Crushed samples were thoroughly mixed to ensure homogenization and then poured onto a clean paper for coning quartering. The opposite quarters were collected, which were further quartered to draw about 2-3 kg of the representative coarse fractions. About 1 kg of the coarse fraction was preserved in a polythene bag for further use, if required. The residual coarse fractions were further reduced to 1 mm size using again the jaw crusher and finally about 200-300 g of the representative sample was collected by coning quartering.

This sample fraction (<1 mm size) was powdered to <200 mesh size using a TEMA swing mill and stored in a pre-cleaned and conditioned polythene/plastic bottles. This fraction, which is a homogeneous representative of the whole rock sample, was used for Rb-Sr isotopic studies. Maximum care was taken to prevent any cross contamination.

3.3.3. Rb and Sr ISOTOPIC STUDIES

For dating as well as petrogenesis purpose only whole rock analysis was done. Rb and Sr isotopic studies were carried out at two places i.e. at Physical Research

Laboratory (PRL), Ahmedabad and Keshava Deva Malaviya Institute of Petroleum Exploration (KDMIPE), ONGC, Dehradun.

However, as majority of the samples were analyzed at KDMIPE, the details of various procedures followed at KDMIPE are discussed here. The precedures followed at PRL are given in Trivedi (1990). All chemical operations were carried in a clean HEFA filter laboratory. All labwares were either of teflon or quartz. The procedures for sample dissolution, spike addition and ion exchange chromatography, are given below:

About 150-200 mg of representative powder samples were weighed in a Mettler balance (AE 240) in a 25 ml teflon beaker and were moistened with a few drops of high purity double distilled water. Mixture of acids (4 ml HF + 2 ml HNO_3 + 2 ml $HClO_4$) were added in the samples and kept in pressure digestion bomb at 150°C for 16 hours. Samples were then evaporated to dryness at 90°C and one more acid treatment (HF + HNO_3) was given to ensure complete digestion. After evaporation of the acid mixtures, the residues were dissolved in about 5 cc of 6N HCl and dried before finally making the solutions in 3 cc of 2.5 N HCl.

3.3.3.A. ISOTOPE DILUTION

The ^{87}Rb and ^{84}Sr spikes of high purity were used for isotope dilution analysis. The isotopic abundances of the Rb and Sr spikes are given in Table 3.4. The spike concentrations were calibrated against standard solutions of normal Rb and Sr. Working (dilute) Rb and Sr spike solutions having concentrations of about 34 and 5 ppm, respectively, were prepared from mother (concentrate) spike solutions for day to day use. The exact spike concentrations were known only after applying dilution/correction factor. The spike solutions were added by weight before digestion of the samples to ensure complete mixing.

Table 3.4: Isotopic ratios of Rubidium and strontium spikes.

Strontium (^{84}Sr spike)	**(Natural ratios*)**
^{86}Sr/^{84}Sr = 0.057052	17.6728
^{87}Sr/^{84}Sr = 0.022779	
^{88}Sr/^{84}Sr = 0.181299	148.0137
Rubidium (^{87}Rb spike)	
^{85}Rb/^{87}Rb = 0.009107	2.5927

*As per Steiger and Jager (1977)

3.3.3.B. ION EXCHANGE CHROMATOGRAPHY

Ion exchange chromatography was used to separate Rb and Sr from the whole rocks. The ion exchange columns were made from quartz tube (I.D. 8 mm) and filled with Dowex 50 X 8% DVB (200-400 mesh) cation exchange resin to a height of 18 cm. 100 ml of 2.5 N HCl was used as eluent.

The sample solutions were centrifuged for 20 minutes in clean polypropyline centrifuge tubes and sucked in 5 ml weight burettes. The samples were then loaded onto the resin bed. The Rb and Sr fractions (28 to 36 and 54 to 72 ml fractions, respectively) were collected in separate beakers, evaporated to dryness and stored for mass spectrometric analysis. The columns were regenerated by passing 50 ml 6N HCl through column bed followed by 50 ml double distilled water and then 50 ml 2.5N HCl.

3.3.4. MASS SPECTROMETRY

At PRL, Ahmedabad, Rb and Sr isotopic studies were carried out on a 23 cm radius 60° sector magnetic field single focussing custom made mass spectrometer. The mass spectrometer is fitted with a thin lens ion source and a faradey cup for collection of ions. The filament holder with source slit is removable so that a new filament could be spot welded, degassed and loaded with sample. Tantalum filaments (0.030" x 0.001") of more than 99.99% purity were outgassed in a separate vacuum system at a temperature higher than that required for efficient ionization of Sr. Samples were taken in a precleaned disposable teflon pipette and evaporated directly on the centre of a predegassed filament. The mass spectrometer is pumped by two ion pumps, 30 l/sec pump for the analyzer tube and 80 l/sec pump for the source region. The source was initially pumped down to a pressure of 10^{-3} torr with a rotary and a sorption pump. It was than isolated from these pumps and gradually opened to the 80 l/sec ion pump. A working pressure of $\approx 10^{-7}$ torr in the source chamber was obtained within an hour after introducing a new sample. The ion acceleration potential used was 4500 V. Ion currents were measured on recently upgraded semi automated data collection system using an IBM PC/XT (Trivedi, 1990). This system controls the mass spectrometer in the peak switching mode, measures the ion currents digitally and computes isotopic ratios. Rb data were taken at 0.1-0.3 V signal level for ^{87}Rb whereas Sr data at 1-3 V level for ^{88}Sr. It was ensured that no residual Rb was left in the sample during Sr isotopic analysis.

At KDMIPE, Rb and Sr isotopic studies were carried out on VG 354 thermal ionization mass spectrometer (270 cm radius, 60° deflection and single focussing) (Fig. 3.6). The mass spectrometer is fitted with a faradey cup as well as a photo multiplier for collection of ions but the multiplier (Daly knob) was not used for Rb and Sr isotopic analysis. The sample turret has a housing of sixteen beads (filaments) which are degassed separately in a degassing unit before loading of the samples. The elements pumping the source housing of the mass spectrometer are the 110 l/sec ion pump, the source titanium sublimation pump and the source cold trap while the analyzer is pumped by means of a 30 l/sec ion pump and a titanium sublimation pump. Rough pumping of the mass spectrometer is done by means of an Edwards E2M5 two stage rotary pump through a zeolite trap and an additional liquid nitrogen cold trap. A working pressure of $\approx 10^{-7}$ torr in the source chamber is achieved within 2 hours after loading a new sample turret. The ion acceleration potential used was 8000 V with internal resistance of 10^{11} ohms. Rb and Sr isotopic measurements were done on an on line HP 9836 data acquisition system using General Peak Jumping (GPJ) software provided by V.G. Isotopes. Rb isotopic measurements were made in the range of 0.3-0.5 V corresponding to ^{87}Rb while those of Sr were made in the range of 0.5-2 V corresponding to ^{88}Sr. Mean of 45 and 150 cycles were taken for Rb and Sr analysis, respectively.

Based on replicate analyses of calibration mixtures and a few rock samples, the errors in the mass spectrometric determinations of ^{87}Rb and ^{86}Sr are estimated to be within ±0.5% leading to a random error of not more than ±1% for their ratios. ^{87}Rb and ^{86}Sr concentrations were calculated by isotope dilution technique. The ^{87}Sr/^{86}Sr ratios were corrected for mass fractionation assuming ^{86}Sr/^{88}Sr = 0.1194 in the sample. The analysis of the NBS 987 standard, made during the course of this study at KDMIPE, Dehradun, gave a mean value of 0.710219 ± 0.000058 as given in Table 3.5.

Table 3.5. ^{87}Sr/^{86}Sr values of NBS 987 standard measured during the course of this study

Sl. No.	Date	^{87}Sr/^{86}Sr
1	25.09.1992	0.710016 ± 0.000064
2	30.09.1992	0.710162 ± 0.000043
3	30.09.1992	0.710253 ± 0.000057
4	01.10.1992	0.710184 ± 0.000057
5	05.10.1992	0.710287 ± 0.000064
6	18.02.1993	0.710239 ± 0.000064
7	23.02.1994	0.710244 ± 0.000057

All measurements are normalised to (^{86}Sr/^{88}Sr) = 0.1194

Reference NBS 987 value is 0.710248 ± 0.000044

Errors quoted are at 2 σ level

Decay constant λ (^{87}Rb) = 1.42×10^{-11} yr^{-1}

3.3.5. X-RAY FLUORESCENCE STUDIES

Rb and Sr measurements for Tavidar volcanics and Mundwara igneous complex were carried out, on an energy dispersive XRF system (EDAX Philips Exam Six in combination with PV 9100), at Wadia Institute of Himalyan Geology, Dehradun, India.

Precision of these measurements as determined from replicate analysis of standards is 5%.