Chapter Three

^{40}Ar-^{39}Ar geochronology and thermochronology: theoretical and experimental aspects

3.1 Fundamentals

The ^{40}Ar/^{39}Ar dating system is based on the decay scheme of the isotope ^{40}K. ^{40}K is one of the three naturally occurring isotopes of potassium (K). Potassium is produced during nucleosynthesis by the s-process. ^{40}K comprises of 0.01167 (±0.00004) atomic % of Potassium, with ^{39}K being the major isotope (93.2581 ± 0.0029 at.%) and ^{41}K making up the balance (6.7302 ± 0.0029 atomic %) (Garner et al 1975). ^{40}K, with 19 protons and 21 neutrons, decays spontaneously with a half life of 1250 Ma into ^{40}Ca and ^{40}Ar. It is the branch yielding radiogenic argon (^{40}Ar*) which is utilized for the K-Ar and ^{40}Ar/^{39}Ar dating methods. About 89.5% of ^{40}K atoms decay by electron (β-) emission into ^{40}Ca yielding 1.33MeV of energy. The remaining atoms (~10.5%) decay into ^{40}Ar dominantly by orbital electron capture releasing 1.51MeV of energy, but only a very small percentage of atoms (0.16%) decay directly to the ground state of stable ^{40}Ar, most of them (10.32%) decay into the excited state releasing an energy of 0.05 MeV, the excited state comes to the ground state by releasing further γ-rays of energy 1.46 MeV. The remaining small number of atoms (0.001%) decay by emission of a positron β^{+}.

K-Ar dating method has been applied to a variety of geological problems during the last 40-50 years, because potassium is widely distributed being an essential or minor element in many minerals and is the eighth most abundant element in the earth's crust. Potassium with atomic number 19 falls in the group 1a of alkali elements in the periodic table. It has an atomic radius of 2.03 Å and ionic radius of 1.33 Å. Ar is a noble gas and usually doesn't react or form bonds with other elements found in minerals. This makes the K-Ar dating viable unlike the K-Ca decay scheme, where Ca is very common in rocks and it becomes highly difficult to detect the radiogenic Ca. Ar has three naturally occurring isotopes ^{40}Ar, ^{38}Ar and ^{36}Ar and the atmospheric ratio of ^{40}Ar/^{36}Ar is used to correct for the initial ^{40}Ar present in the sample other than the radiogenic ^{40}Ar*. This ratio is recommended by Steiger and Jager (1977) for use in geochronology as 295.5 and is derived from the values of atomic abundances given by Neir (1950) as ^{40}Ar 99.600%, ^{38}Ar 0.0632 ± 0.0001% and ^{36}Ar 0 3364 ± 0.0006%. Any mineral containing K will accumulate the radiogenic ^{40}Ar* in course of time. In the laboratory the total ^{40}Ar is measured and accumulated ^{40}Ar* can be calculated after applying the correction for the atmospheric argon and for the other known sources of ^{40}Ar. The number of atoms of daughter produced (D), number of parent atoms remaining (N) and the decay constant (λ) will then provide the time elapsed (t) since the daughter started getting accumulating in the sample according to the following equation:

$$t = \frac{1}{\lambda} \ln(1 + \frac{D}{N}) \tag{3.1}$$

As decay constant λ is the total decay constant for ^{40}K yielding ^{40}Ca and ^{40}Ar, the above equation has to be modified for the fraction of decays yielding ^{40}Ar, which is the ratio of decay constants for electron capture (λ_e) and positron decay (λ_e') to the total decay constant. Hence taking only that fraction of total number of parent ^{40}K atoms which decay to ^{40}Ar, i.e. $[\{(\lambda_e+\lambda_e')/\lambda\}^{40}K]$, the above equation (3.1), for K-Ar dating, becomes:

$$t = \frac{1}{\lambda} \ln(1 + \frac{\lambda}{\lambda e + \lambda e'} \frac{^{40}Ar^*}{^{40}K}) \tag{3.2}$$

The time 't' then can be related to geologically meaningful event, e.g. for a volcanic rock, 't' would be the age of eruption because as soon as the lava erupts on the surface it cools and starts accumulating the ^{40}Ar*. But for a mineral of a plutonic rock this time 't' may not be the age of crystallization as a significant amount of time elapses before it cools to the temperature low enough to retain the ^{40}Ar* and 't' is said to be the 'cooling age' of that mineral.

3.1.1. Fundamental assumptions for K-Ar dating system

As with all other isotope dating methods, there are a number of assumptions that are made for K-Ar dating. These assumptions also apply to the ^{40}Ar-^{39}Ar method, though the latter provides greatly increased opportunities for testing these by performing step-heating experiments. The principal assumptions are given below.

1. The parent nuclide ^{40}K, decays at a rate independent of its physical state and is not affected by differences in pressure or temperature. This is a major assumption, common to all dating methods based on radioactivity. Available evidences suggest that it is well founded (Friedlander et al., 1981).
2. The ^{40}K/K ratio in nature is constant at any given time. As ^{40}K is rarely measured directly for dating purposes, this is an important underlying assumption. Isotopic measurements of K in terrestrial and extra-terrestrial samples indicate that the assumption is valid, at least to the extent that no authenticated differences greater than 1.3% have been reported in the ^{39}K/^{41}K ratio.
3. The radiogenic argon measured in the sample is produced by *in situ* decay of ^{40}K in the interval since the rock crystallized or re-crystallized. Violations of this are not uncommon but can be verified by the ^{40}Ar-^{39}Ar step-heating method.
4. Corrections can be made for non-radiogenic ^{40}Ar present in the rock being dated. For terrestrial rocks the general assumption is that all such argon is atmospheric in composition with ^{40}Ar/^{36}Ar being 295.5.
5. The sample must have remained a closed system since the event being dated. ^{40}Ar/^{39}Ar technique is robust enough to provide useful insight into the thermal histories if the samples do not satisfy this assumption.

3.1.2. The ^{40}Ar-^{39}Ar dating method

The K-Ar dating method requires two separate experiments for measuring parent ^{40}K and daughter ^{40}Ar as they are different elements. The ^{40}Ar-^{39}Ar method is modification of K-Ar technique which obviates this requirement of two separate measurements by converting the parent isotope to the same element as the daughter. The sample is irradiated by fast neutrons in a nuclear reactor to convert some of ^{39}K into ^{39}Ar. The fixed natural ratio ^{39}K/^{40}K provides an estimate for the parent ^{40}K by the measurement of ^{39}Ar. In order to know the conversion factor of ^{39}K to ^{39}Ar and to take care of other interfering nuclear reactions a sample of known K-Ar age and pure salts of K and Ca are irradiated along with the sample. The unknown age of the sample is then derived by comparison with the monitor sample.

The amount of $^{39}Ar_k$ i.e. number of atoms produced from ^{39}K, depends upon, duration of the irradiation, Δ, neutron flux of energy E, $\varphi(E)$, and neutron capture cross section at energy E for the reaction $^{39}K(n,p)^{39}Ar$, $\sigma(E)$ and the relation can be expressed as (Mitchell, 1968)

$$^{39}Ar_k = {}^{39}K\Delta\int \varphi(E)\sigma(E)dE \tag{3.3}$$

The rearranged K-Ar age equation

$$^{40}Ar^* = {}^{40}K\frac{\lambda_e + \lambda_e'}{\lambda}[(\exp\lambda t) - 1] \tag{3.4}$$

and the $^{39}Ar_k$ production equation give

$$\frac{^{40}Ar^*}{^{39}Ar_k} = \frac{^{40}K}{^{39}K}\frac{\lambda_e + \lambda_e'}{\lambda}\frac{1}{\Delta}\frac{[\exp\lambda t) - 1]}{\int \varphi(E)\sigma(E)dE} \tag{3.5}$$

This can further be simplified by introducing a dimensionless parameter J (Grasty and Mitchell, 1966) such that

$$J = \frac{^{39}K}{^{40}K}\frac{\lambda}{\lambda_e + \lambda_e'}\Delta\int \varphi(E)\sigma(E)dE \tag{3.6}$$

which simplifies the equation (3.5) as

$$\frac{^{40}Ar^*}{^{39}Ar_k} = \frac{(\exp\lambda t) - 1}{J} \tag{3.7}$$

which upon rearrangement gives the estimate of 't' as

$$t = \frac{1}{\lambda}\ln(1 + J\frac{^{40}Ar^*}{^{39}Ar_K}) \tag{3.8}$$

This equation shows that just by measuring the ratio $^{40}Ar^*/^{39}Ar_K$, the age 't' can be calculated, provided J is known, which can easily be calculated by irradiating a sample of known 't' as

$$J = \frac{(\exp\lambda t - 1)}{^{40}Ar^*/^{39}Ar_K} \tag{3.9}$$

This modification in the conventional K-Ar technique improved the precision of measurement, as ratios can be measured with more precision than the abundances. This requires a very small quantity of sample and it also solves the problem of sample inhomogeneity. As it is clear that the ^{40}Ar-^{39}Ar method relies upon a known age sample which is used to monitor the neutron fluence, this ***monitor sample*** is very critical. Usually the following criteria are followed for choosing a monitor sample. 1) It should have uniform $^{40}Ar^*$ to ^{40}K ratio distributed homogeneously in order to calculate the accurate and precise K-

Ar age of this sample. 2) It should be sufficiently coarse grained to minimize the health hazards due to the radioactivity after the irradiation. 3) It should be available in sufficient quantity. Several mineral standards of different ages are used by different laboratories as monitor samples McDougall and Harrison, 1999; Renne, 2000). The total fusion Ar-Ar ages are more precise and accurate than the K-Ar ages but they don't provide any additional information than the K-Ar ages. A major advancement was achieved when it was realized that after irradiation the sample need not be fused in a single step, instead it can be degassed incrementally in various steps and the gas released at each step can be analyzed for isotopic ratio for obtaining 't' and thus an age spectrum of many apparent ages can be obtained instead of a single total fusion age or K-Ar age.

This technique known as '***step heating***' or '***incremental heating***' technique (Merrihue and Turner, 1966) has additional advantage of providing the inner distribution of ^{40}Ar* relative to ^{39}K which in turn is related to ^{40}K. In principle radiogenic Ar and the parent ^{40}K or ^{39}Ar should be released in equal proportions in each step if the sample has not lost any radiogenic argon subsequent to its crystallization. These ratios or apparent ages when plotted against the cumulative % of ^{39}Ar released, would provide flat pattern in the age spectrum called as ***plateau age***. Any deviation from the plateau age shows the redistribution of ^{40}Ar* relative to ^{40}K. Since the diffusion of Ar is comparatively easier than the diffusion of K, any heating or metamorphism subsequent to crystallization will result in the loss of ^{40}Ar*, which then will get reflected in the age spectrum by lower ages in the corresponding temperature steps. The post-crystallization thermal disturbances experienced by the sample as revealed by the step heating experiment have been very useful in solving various geological problems and make this ^{40}Ar-^{39}Ar technique a more robust tool compared to the conventional K-Ar dating method.

3.2 ^{40}Ar/^{39}Ar thermochronology

The fact that the 't' obtained by the ^{40}Ar-^{39}Ar approach can be related to the thermal history experienced by the sample gave rise to a new field of ^{40}Ar-^{39}Ar thermochronology. The fundamental basis of the ^{40}Ar-^{39}Ar thermochronology is that the loss of radiogenic argon from the sample is a temperature dependent diffusion process.

3.2.1. Diffusion theory and diffusion equation

Random molecular motion tends to equilibrate the molecular/atomic concentration in a finite volume and this leads to the diffusion of Ar from areas of high concentration to areas of the low concentration in the sample. Fick's first law describes this molecular diffusion on basis of an analogy with the Fourier's law of heat conduction. This is represented as

$$\frac{n}{A_x} = F = -D\frac{\partial C}{\partial X} \tag{3.10}$$

where n is number of molecules, A_x is cross sectional area, F is flux across the unit area, D is the proportionality constant called diffusion constant, C is the concentration. The minus sign indicates that flow is from high concentration to low concentration. The change in concentration with time t in the three space coordinates can be derived and is represented as

$$\frac{\partial C}{\partial t} = D(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} + \frac{\partial^2 C}{\partial Z^2}) \tag{3.11}$$

This is referred to as Fick's second law. The solution of the above equation for different geometries and boundary conditions gives us the distribution of concentration at any time t within the solid of that geometry. These solutions then can be converted into the expressions for fractional loss after time t starting with a homogeneous distribution of concentration in the solid. For example the expression for a sphere of radius r would be

$$f = 1 - (6/\pi^2)\sum_{1}^{\infty}(1/n^2)\exp(-n^2\pi^2 Dt/r^2) \tag{3.12}$$

Where f is the fractional loss. Here D is taken as constant with time. These expressions for fractional loss for solids of different geometries are given in McDougall and Harrison (1999). This equation can be used to calculate theoretical age spectra for those solids who have experienced partial loss of radiogenic argon at some time t. However, it has been shown that the diffusion coefficient is dependent on temperature and follows the Arrhenius equation. Hence in the case of constant diffusion coefficient it is assumed that the temperature remains constant.

3.2.2. Arrhenius equation

The temperature dependence of diffusion coefficient is given as

$$D = D_0 \exp(-E/RT) \tag{3.13}$$

Where D_0 is the frequency factor ($D=D_0$ at $T=\infty$), E is the activation energy required to cross the threshold so that an atom can move in a crystalline lattice and the T is the absolute temperature. This equation will become an equation of straight line on taking the logarithm (to the base 10) of both sides as

$$\log D = \log D_0 - \frac{E}{2.303R}\frac{1}{T} \tag{3.14}$$

Arrhenius plot is obtained by plotting –logD versus 1/T. It will give a straight line with slope as E/2.303R and intercept on y as $-\log D_0$. This equation can be coupled with the solutions of diffusion equation that provide the concentration distribution at time t or the fractional loss *f*. Thus we can have a relationship between the diffusion coefficient D, temperature T and time t such as

$$\frac{E}{RT} = \ln(\frac{tD_0/r^2}{Dt/r^2}) \tag{3.15}$$

Here the dimension less parameter Dt/r^2 is given by the expression of fractional loss *f*. In this way we can assign a temperature T to the age t obtained for the system which undergone a fractional loss because of a square thermal pulse, i.e. temperature increased from T=0 to T. This forms the basis of thermochronology. Though this relationship is valid only for the diffusion coefficient D which doesn't change with time, i.e. temperature remains constant which is not very realistic scenario geologically, it can be extended to any realistic thermal history by just introducing time-dependent D, defined as

$$\zeta = \int_0^t \frac{D(t)}{r^2} dt \tag{3.16}$$

for (Dt/r^2) in equation (3.15) (Dodson, 1973; Lovera, et al., 1989) . This will introduce a time constant τ, according to the thermal history chosen, and the equation (3.15)will become as

$$\frac{E}{RT} = \ln(A\tau D_0/r^2) \tag{3.17}$$

Where A is a geometric constant (as the solution of diffusion equation (3.11) depends upon the geometry of grain) and τ is a function related to the form of integrated thermal history, e.g. if we assume the thermal history to be linear in 1/T (t=1/T), then time dependent diffusion coefficient can be written with a time constant τ such as $D=D_0\exp(-E/RT_0-t/\tau)$ or $D= D(0)\exp(-t/\tau)$, where D(0) is the initial diffusion coefficient. Here τ is defined as the time in which the diffusion coefficient D will become 1/e times the initial. T is some characteristic temperature of the system. This temperature T corresponding to age t indicates that at this temperature the retention of the daughter atoms became complete and the diffusive loss stopped. This is called the closure temperature.

3.2.3. Concept of closure temperature and equation

Minerals and rocks crystallize at high temperatures. At such high temperatures the radiogenic argon diffuses out of the system as soon as it forms from the decay of ^{40}K. The temperature at which the radiogenic argon starts to accumulate within the system and stops getting lost is called the closure temperature for argon. For volcanic rocks this temperature is achieved almost instantaneously as they cool very fast but for the minerals and rocks forming very deep inside the earth there is a significant time delay to reach the closure temperature. For such slowly cooling systems the age calculated gives the time at which the system attained its closure temperature This concept of closure temperature or blocking temperature was given by the Dodson (1973) and is represented diagrammatically below (Fig. 3.1). This diagram shows that in a slowly cooling mineral the daughter-to-parent ratio (D/P) is zero at very high temperature and passes through a partial accumulation zone (the curved portion in the lower diagram) and then increases constantly with time. The age calculated in lab (t_c) is the intercept of the constant growth line of D/P on the time axis and the corresponding temperature T_c is called the closure temperature for the daughter element.

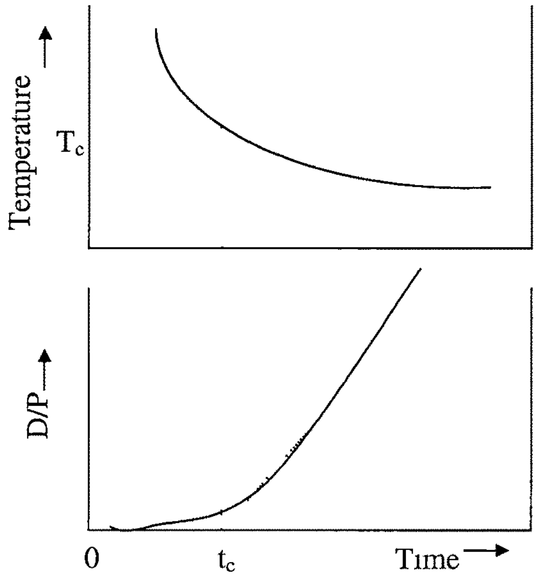

Fig. 3.1 Illustration of closure temperature concept. T_c is the closure temperature and t_c is the time. The diffusive loss of daughter (D) ceases when the system is cooled to T_c at time t_c, After that daughter to parent ratio (D/P) increases with the constant rate, corresponding to the decay constant.

Dodson (1973) has derived the expression for the closure temperature as

$$T_c = \frac{E/R}{\ln[\frac{ART_c^2 D_0 / r^2}{EdT/dt}]} \tag{3.18}$$

This expression requires an initial assumption of cooling history (dT/dt), however, it has been shown (Lovera et al., 1993) that the closure temperature is highly insensitive to the cooling history. This expression can be extended to the time dependent diffusion coefficient as well. This allows us to assign temperature to the age calculated for a mineral. If we analyze three different minerals from a same rock then we will have three time-temperature points for that rock and that provides us the cooling history of that rock as depicted in the following diagram (Fig. 3.2).

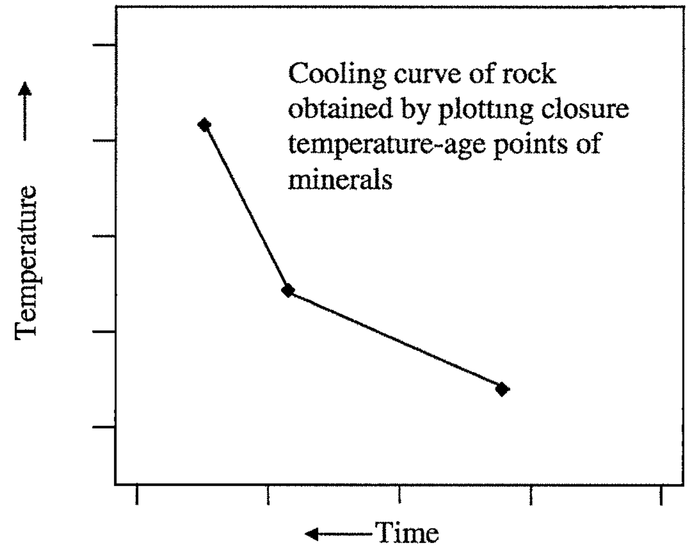

***Fig.3.2** Cooling history diagram as derived by plotting the age-closure temperature, pairs of different minerals. This is a traditional method of thermochronology.*

3.2.4. Assumptions

This approach of obtaining the cooling history requires the following assumptions.

1. The laboratory degassing follows the same volume diffusion process that governed the loss of radiogenic argon in nature.
2. Minerals are stable under vacuum heating.
3. Minerals have not experienced the subsequent loss of argon below the closure temperature.

4. Minerals were not recrystallized.

Age spectrum also provides us the information of the cooling history experienced by the sample. A theoretical age spectrum can be constructed using the diffusion properties of the sample obtained from the Arrhenius plot (as discussed in section 3.2.2), which will match the age spectrum obtained in the laboratory if the cooling history assumed to construct the theoretical spectrum is correct.

3.3 Multi Diffusion Domain (MDD) Model

It has been observed for many K-feldspars that the Arrhenius plots are not always straight lines as predicted by the above single site diffusion model. This has been explained by Lovera et al. (1989) by the multi diffusion domain (MDD) model. The MDD model, apart from the fundamental assumption that argon diffusion in the laboratory follows the same mechanism as in nature, is based on the following assumptions

1. The sample is composed of non-interacting, discrete diffusion domains of simple geometries.
2. The domain boundaries have zero argon concentration.
3. The parent ^{40}K is distributed homogeneously within each domain.
4. Cooling starts at very high temperatures and is very slow

The age spectra and Arrhenius plots for the MDD can be calculated by adding up the argon released from each separate domain. This extension has been done by Lovera et al. (1989) who presented a mathematical expression for calculating the age spectrum and the Arrhenius plot. The diffusion parameters and the distribution of domains of sample having multi diffusion domains are difficult to calculate from the Arrhenius plot alone, due to its non-linearity. The Arrhenius plot of such a sample would be nonlinear because of simultaneous release of argon from all the diffusion domains and to quantify the contribution from each of the domain a different way of plotting, independent of the heating schedule would be required (Lovera et al., 1991).

3.3.1 Log(r/r_0) plot

Lovera et al. (1991) proposed a new way of plot, known as log(r/r_o) plot. This plot is constructed by first estimating log (D/r_o^2), as the intercept of linear portion of the Arrhenius plot, on y-axis. Each successive D/r^2 is calculated according to eq. 3.12 taking the appropriate geometry of domains into consideration. Subtracting $\log(D/r^2)$ from the $\log(D/r_o^2)$ gives $2\log(r/r_o)$. It is then plotted after dividing by 2 with cumulative % of ^{39}Ar released. This provides an estimate of gas content of each separate domain size and is independent of laboratory heating schedule.

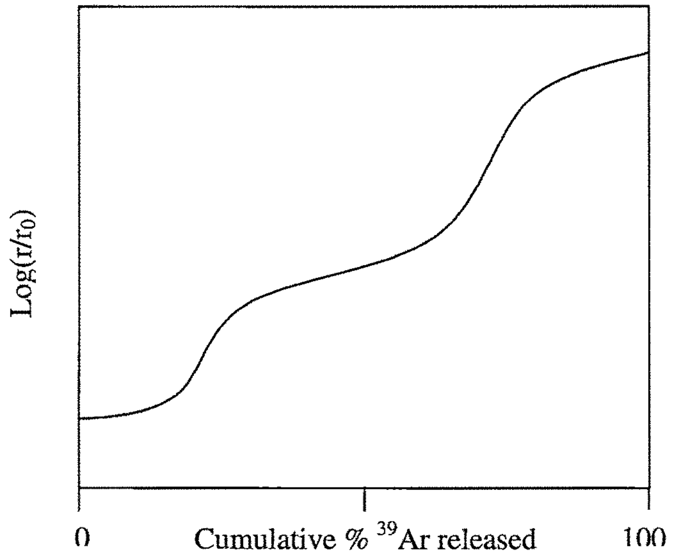

***Fig. 3.3** Log (r/r$_o$) plot. The local plateaus correspond to the sizes and the steep rises, from one plateau to another, correspond to the gas content of different diffusion domains.*

This plot (Fig. 3.3) shows the sizes in terms of the local plateaus and the gas contents of each domain is represented by the steep rises from one domain to another domain. Once the distribution of the domains is known from the above plot one can construct a theoretical age spectrum for different cooling histories to obtain the best fit with the age spectrum obtained in the laboratory and hence the corresponding cooling history can be ascertained. The MDD model thus provides the continuous cooling history from a single mineral instead of a temperature-time point.

The MDD model was developed for K-feldspars, however, it has been used for whole rocks in the present study. The rationale for using this model for whole rocks is that different minerals may be taken to represent the different diffusion domains which satisfy all the necessary criteria for using the MDD model. Most importantly, the rock must be devoid of any mineral such as biotite, which tends to break down under vacuum heating.

Recently (Lee, 1995), has proposed another process of argon loss which is called Multi Path (MP) model. MP model takes into account the defects and cracks in crystal that can lead to non-volume diffusion loss of argon. However, this model is not used here

3.4. Experimental Aspects

3.4.1. Sample Preparation

Whole rock sample were first examined under petrographic microscope and fresh sample chips were crushed and powdered in a stainless steel mortar and pestle to 100-150 μm size. From the homogenized powder a 600-700 mg aliquot was prepared. Mineral separation was done using the standard procedure of density and magnetic separations using heavy liquid and isodynamic Franz magnetic separator respectively. The final separation was done by hand picking coarse grains under a stereomicroscope. The whole rock and minerals then were cleaned and washed using 0.05N HCl in an ultrasonic bath to remove carbonate impurities. Samples were ultrasonicated with water several times to ensure removal of all HCl. The dried sample powder then was packed in aluminum foils along with the monitor sample and pure CaF_2 and K_2SO_4 salts and sealed in quartz vials. To monitor the neutron fluence variation in the reactor a 99.99% pure Ni wire was kept in each vial. The sealed vials were put in an aluminum reactor can and sent for the irradiation.

3.4.2. Irradiation of the sample

The samples were irradiated in the APSARA reactor of Bhabha Atomic Research Centre (BARC) Mumbai. This is a light water-moderated reactor of 1MW power. The total neutron flux is 10^{12} neutron/cm^2/sec out of which 50-60% is fast neutron flux. The irradiation is carried out in the D-4 position of the reactor, which is the core position and receives the maximum flux with the minimum variation. The irradiation was done for 100 hrs cumulative in two batches. The maximum and minimum durations of the irradiation in a step was 0.25 hrs and 6 hrs respectively. The maximum flux variation was determined by the ^{58}Co activity, produced from ^{58}Ni by the ^{58}Ni (n,p) ^{58}Co reaction. The maximum variation is found to be 5% horizontally and 6% vertically. The irradiated samples were cooled to bring the activity to a safe handling level. The samples were then packed in aluminum foils and stored in the sample tree of the extraction unit.

3.4.3. Interfering nuclear reactions

A sample consisting of a variety of elements gives rise to a wide range of nuclear reactions; however only those producing argon are of interest here. Isotopes of argon can be produced by interaction of neutrons with isotopes of calcium, potassium, argon, and chlorine (Merrihue and Turner, 1966; Mitchell, 1968; Brereton, 1970; Turner, 1971a). Out of these reactions many are of minor significance due to the small abundance of the target isotope in the sample or due to higher energy required for the reactions. The most important reactions for the ^{40}Ar/^{39}Ar dating are tabulated below (Table 3.1).

3.4.3.1 Reactions with calcium

Three argon isotopes ^{36}Ar, ^{37}Ar and ^{39}Ar are produced from reaction with calcium. Corrections are made for the ^{36}Ar and ^{39}Ar with the help of ^{37}Ar, which is neither present in atmospheric argon and nor produced in a significant amount during the irradiation, from ^{39}K. A pure calcium salt, CaF_2, is irradiated along with the sample and (^{36}Ar/^{37}Ar) and (^{39}Ar/^{37}Ar) ratios are measured in it, which then are used for obtaining the correction factors, after correcting for the atmospheric ^{36}Ar.

***Table 3.1** Important nuclear reactions producing argon isotopes by neutron bombardment [a,b] (from McDougall and Harrison, 1999).*

Argon Isotope Produced	**Target Element**	
	Calcium	**Potassium**
^{36}Ar	**^{40}Ca(n,nα)^{36}Ar (-7.04, 96.94)**	
^{37}Ar	**^{40}Ca(n,α)^{37}Ar (+ 1.75, 96.94)**	
^{39}Ar	**^{42}Ca(n,α)^{39}Ar (+0.34, 0.65)**	**^{39}K(n,p)^{39}Ar (+0.22, 93.26)**
^{40}Ar		**^{40}K(n,p)^{40}Ar (+2.29, 0.01167)**

[a] *Apart from these reactions, ^{36}Ar is also produced from ^{35}Cl, ^{37}Ar from ^{39}K and ^{36}Ar, ^{39}Ar from ^{38}Ar and ^{40}Ar from ^{43}Ca, ^{44}Ca and ^{41}K in insignificant amounts. ^{38}Ar is produced from ^{42}Ca, ^{39}K, ^{41}K, ^{40}Ar and ^{37}Cl, however usually not corrected for as it doesn't interfere the final results.*

[b] *In brackets are given the energy associated with the reaction (MeV) and the target isotope abundance (atom%)*

Thus while the correction factor $(^{39}Ar/^{37}Ar)_{Ca}$ is straight forward = $(^{39}Ar/^{37}Ar)_{m}$ in the CaF_2 (after correcting for the decay of ^{37}Ar and ^{39}Ar), where subscript 'm' stands for the measured, the correction factor for ^{36}Ar is obtained after correcting for the atmospheric ^{36}Ar with the help of ^{40}Ar as $(^{36}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}} = \{^{36}\mathrm{Ar}_m - ^{40}\mathrm{Ar}_m/295.5\}/^{37}\mathrm{Ar}$, since all the ^{40}Ar present in the CaF_2 is of atmospheric origin. Here the ^{37}Ar value used is the one after the decay correction {half life($t_{1/2}$) =35.1 days} during the irradiation and subsequent to it.

3.4.3.2. Reactions with potassium

The most important reaction for ^{40}Ar/^{39}Ar dating is with ^{39}K, $^{39}\mathrm{K}(n,p)^{39}\mathrm{Ar}$. Besides this, ^{40}Ar is also produced in significant amounts from ^{40}K according to the reaction $^{40}\mathrm{K}(n,p)^{40}\mathrm{Ar}$. The correction factor for $^{40}\mathrm{Ar}_K$ is derived by measuring argon ratios in the irradiated pure potassium salt, K_2SO_4 The ^{40}Ar measured in this salt then is corrected for the atmospheric ^{40}Ar and the correction factor is obtained as

$$(^{40}\mathrm{Ar}/^{39}\mathrm{Ar})_K = \{^{40}\mathrm{Ar}_m - ^{36}\mathrm{Ar}_m \mathrm{X}\ 295.5\}/^{39}\mathrm{Ar} \qquad (3.19)$$

Here it is assumed that all the ^{36}Ar measured in the potassium salt is of atmospheric origin.

3.4.4 Decay correction

^{37}Ar and ^{39}Ar produced in the reactor are radioactive. It is required to correct for their decay during and subsequent to irradiation of the sample until the time of analysis. As the half life of ^{39}Ar is 269 ± 3 yrs, no significant error is introduced during the time scale of irradiation to analysis(~1 year) if left uncorrected. However, the half life of ^{37}Ar is only 35.1 ± 0.1 days (Stoener et al., 1965) and the decay correction of ^{37}Ar is very important to arrive at the correct result. The relevant general equation for the decay factor after Brereton (1972) and Dalrymple et al. (1981) is

$$\text{Decay Factor} = \frac{\lambda t e^{\lambda t'}}{(1-e^{-\lambda t})} \qquad (3.20)$$

Where t is the duration of irradiation and t' is the time elapsed between the end of the irradiation and the analyses. The above equation is valid only when the irradiation is done continuously, though usually the irradiation is done in segments of various durations. In the latter case the equation used is given by Wijbrans (1985) as:

$$\text{Decay Factor} = \lambda\sum_{i=1}^{n} t_i \Big/ \sum_{i=1}^{n}\{(1-e^{-\lambda t_i})/e^{\lambda t_i}\} \qquad (3\ 21)$$

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

3.4.5 The Calculation of $^{40}Ar^*/^{39}Ar_K$

The final calculation of the age takes care of the above decay factors and reactor-produced argon isotopes. After the analysis of the sample, the total ^{40}Ar measured, $^{40}Ar_m$, would have all the components as

$$^{40}Ar_m = {}^{40}Ar^* + {}^{40}Ar_A + {}^{40}Ar_K \tag{3.22}$$

where superscript * indicates the radiogenic component and the subscripts 'A' and 'K' indicate atmospheric and potassium produced components of ^{40}Ar. Hence

$$^{40}Ar^* = {}^{40}Ar_m - {}^{40}Ar_A - {}^{40}Ar_K \tag{3.23}$$

And the total ^{36}Ar measured, $^{36}Ar_m$ will have components of atmospheric ^{36}Ar, $^{36}Ar_A$ and calcium produced ^{36}Ar, $^{36}Ar_{Ca}$ as

$$^{36}Ar_m = {}^{36}Ar_A + {}^{36}Ar_{Ca} \tag{3.24}$$

with the atmospheric ratio as $\{^{40}Ar/^{36}Ar\}_A = 295.5$

Then

$$^{40}Ar_A = 295.5\ [\,^{36}Ar_m - {}^{36}Ar_{Ca}] \tag{3.25}$$

substituting it in the eq.3.23 we get

$$^{40}Ar^* = {}^{40}Ar_m - 295.5\ {}^{36}Ar_m + 295.5\ {}^{36}Ar_{Ca} - {}^{40}Ar_K \tag{3.26}$$

The total ^{39}Ar measured, $^{39}Ar_m$, would have potassium produced ^{39}Ar, $^{39}Ar_K$, and Ca produced as $^{39}Ar_{Ca}$, i.e.

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

or

$$^{39}Ar_K = {}^{39}Ar_m - {}^{39}Ar_{Ca} \tag{3.27}$$

Dividing eq.(3.26) by eq. (3.27) and dividing both numerator and denominator on the right hand side by $^{39}Ar_m$ we get

$$\frac{^{40}Ar^*}{^{39}Ar_K} = \frac{(^{40}Ar/^{39}Ar)_m - 295.5(^{36}Ar/^{39}Ar)_m + 295.5(^{36}Ar_{Ca}/^{39}Ar_m) - (^{40}Ar_k/^{39}Ar_m)}{1-(^{39}Ar_{Ca}/^{39}Ar_m)} \tag{3.28}$$

As $$\frac{^{36}Ar_{Ca}}{^{39}Ar_m} = \frac{^{36}Ar_{Ca}}{^{37}Ar_{Ca}}\frac{^{37}Ar_m}{^{39}Ar_m} \tag{3.29}$$

$$= [\frac{^{36}Ar}{^{37}Ar}]_{Ca}[\frac{^{37}Ar}{^{39}Ar}]_{Ca} \tag{3.30}$$

because $^{37}Ar_{Ca} = {}^{37}Ar_{m}$, and as

$$\frac{^{39}Ar_{Ca}}{^{39}Ar_{m}} = [\frac{^{39}Ar}{^{37}Ar}]_{Ca}[\frac{^{37}Ar}{^{39}Ar}]_{m} \tag{3.31}$$

because $^{37}Ar_{Ca} = {}^{37}Ar_{m}$, and as

$$\frac{^{40}Ar_{K}}{^{39}Ar_{m}} = [\frac{^{40}Ar}{^{39}Ar}]_{K}\frac{^{39}Ar_{K}}{^{39}Ar_{m}} \tag{3.32}$$

$$= [\frac{^{40}Ar}{^{39}Ar}]_{K}[1 - \frac{^{39}Ar_{Ca}}{^{39}Ar_{m}}] \tag{3.33}$$

Substituting eq. (3.30), (3.31) and (3.33) in the eq. 3.28 one gets

$$\frac{^{40}Ar*}{^{39}Ar_{K}} = \frac{(^{40}Ar/^{39}Ar)_{m} - 295.5(^{36}Ar/^{39}Ar)_{m} + 295.5(^{36}Ar/^{37}Ar)_{Ca}(^{37}Ar/^{39}Ar)_{m}}{1-(^{39}Ar/^{37}Ar)_{Ca}(^{37}Ar/^{39}Ar)_{m}} - [\frac{^{40}Ar}{^{39}Ar}]_{K} \tag{3.34}$$

This equation is used to calculate the age at the each temperature step.

3.4.6. Argon extraction and purification

An argon extraction and purification system was developed indigenously (Venkatesan et al., 1986). Fig. 3.4 shows the schematic of this system. It is composed of a high vacuum line with two ion pumps, one diffusion pump, and one rotary pump, a furnace assembly in which a sample can be heated in a controlled manner, getter system for purification, isolation valves and charcoal trap cooled at liquid nitrogen temperature to move the gas from one section to another section. The furnace (Fig. 3.5) is a single vacuum chamber. It consists of a molybdenum crucible electrically heated by a concentric, tantalum mesh filament surrounded by tantalum radiation shields. The temperature of the crucible is controlled by a variac, which is calibrated with the help of an optical pyrometer. The temperatures are calibrated within ± 10°C. The outer SS jacket of furnace is connected to cold water supply. Samples are dropped into the crucible from a glass sample holder connected to the upper flange of the furnace.

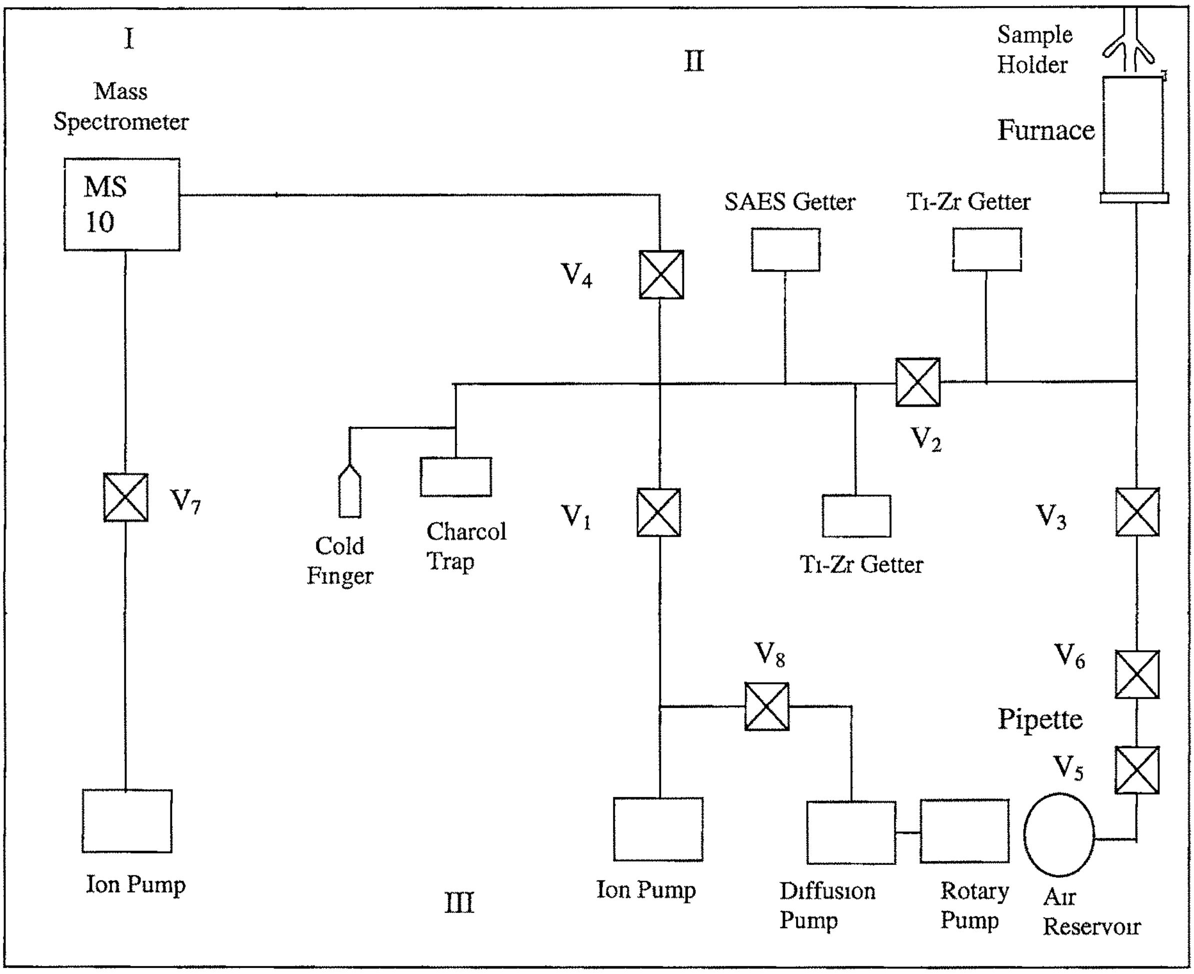

***Fig.3.4** Schematic diagram of the complete Argon Gas Extraction-Purification system. I: Mass Spectrometer, II: Extraction System and III: Pumping System.*

The gas purification system consists of four valves V_1 to V_4 and three getters, all interconnected and fitted into a single rectangular stainless steel block (Fig. 3.6). The gas is extracted from the sample by heating the sample for 55 min. at each temperature step. The released gas first comes into contact with Ti-Zr getter which is kept hot, most of the active gasses are either chemically combined or adsorbed by this getter. This cleaned gas then is allowed to react with another Ti-Zr getter and SAES getter by opening the valve V_2 (Fig. 3.4). The first Ti-Zr getter, in meantime is reduced to room temperature to adsorb the hydrogen.

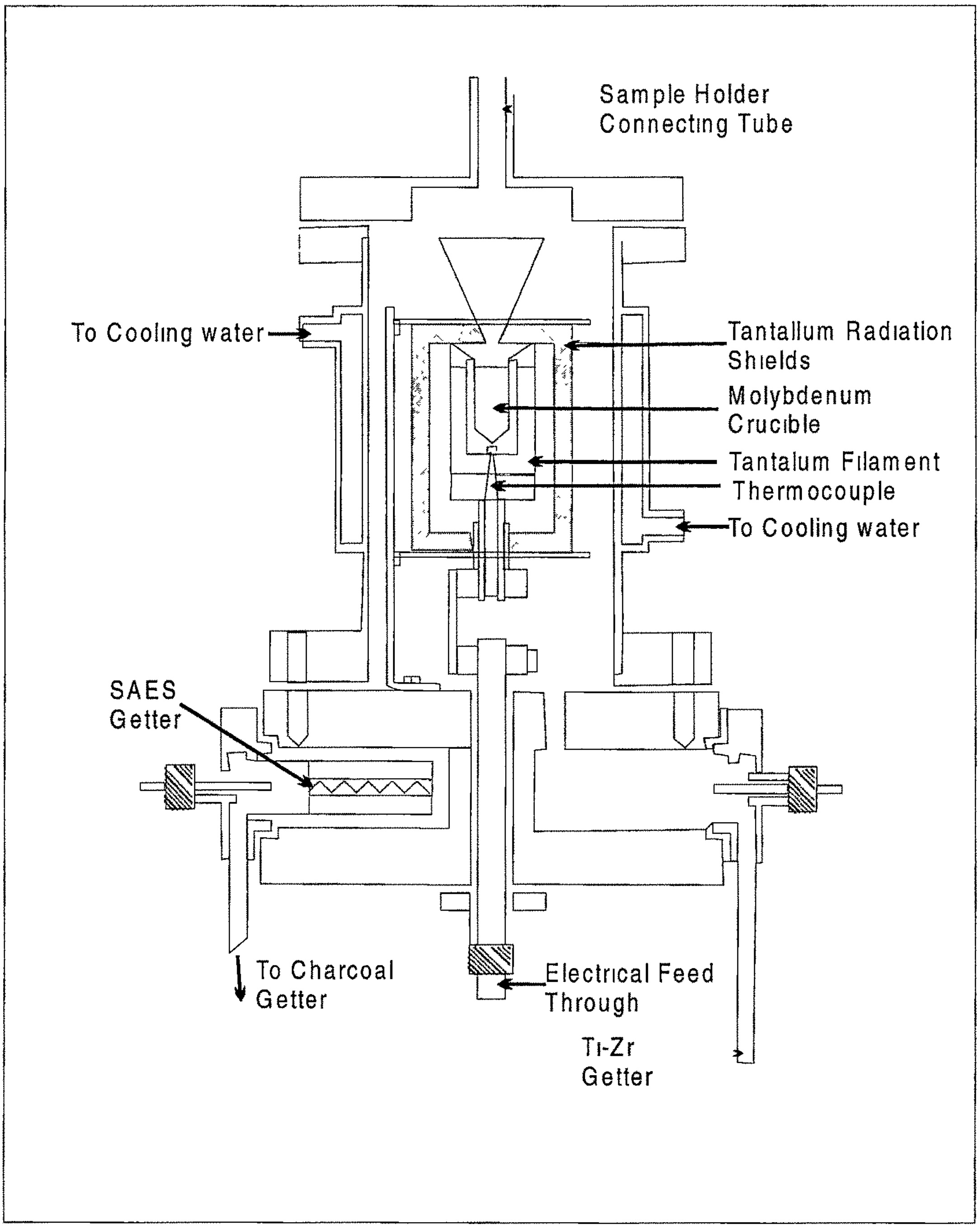

Fig.3.5 *A section through furnace and extraction unit.*

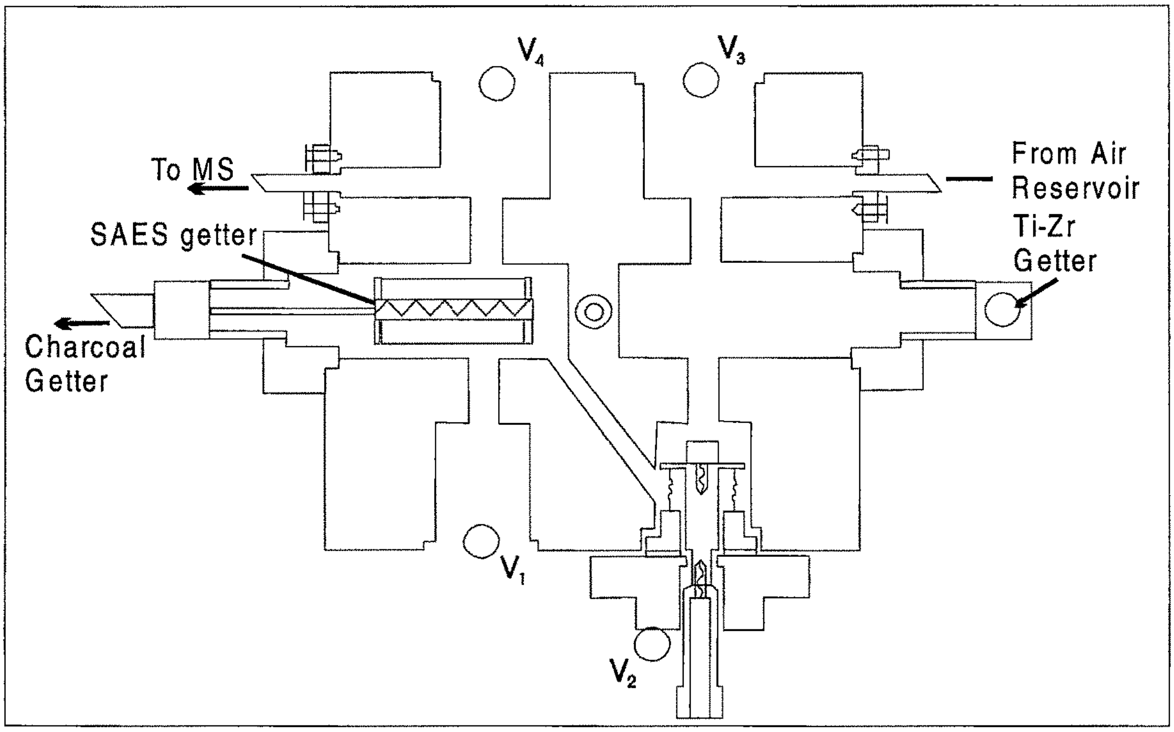

Fig.3.6 *Middle section of the S-S block showing assembly of the one of the valves*

The purified gas then is adsorbed on charcol which is kept at liquid nitrogen temperature. 15 min are given for this collection to ensure that almost all the purified gas is collected on the charcoal. It is then passed through cold finger kept at liquid nitrogen temperature to remove water vapour before admitting into the mass spectrometer, by opening V_4. After the gas gets equilibrated the V_4 is closed and the remaining unwanted gas is pumped by opening V_1 (Fig. 3.4). The gas is extracted and purified in this manner for usually 19-20 temperature steps starting at 400°C and going up to 1400°C at 50°C intervals.

3.4.7. Analysis, Data acquisition and Reduction

The purified gas is analyzed in AEI MS10 (180° deflection, 5cm radius) having 1.8 kilogauss permanent magnetic field and is operated in static mode. Ions of masses 40, 39, 38, 37 and 36 are collected by varying the accelerating voltage on a Faraday cup. The ion currents (pico amperes) are dropped across very high resistances of 10^{11} ohms to 10^{10} ohms according to the amount of gas.

The data acquisition of the resulting voltages is done sequentially through a computer. Peak heights and relative timings of peak measurements from the time of sample introduction (t_o) are fed to a curve-fit program to compute isotopic ratios and abundances corresponding to time zero (t_o). The ratios measured are corrected for system blanks for each temperature step. The system blanks are measured before and after the sample for 10 to 12 steps and the blanks are estimated for the other steps by interpolation. System blanks are measured following the same procedure as is used for the sample but without sample. The ^{40}Ar blank for the present work varied from 0.2 to 20 % of the sample gas for temperature steps up to about 1200°C and increases up to 30% and occasionally to 40% in the fusion step. Table 3.2 gives a typical blank variation in different steps for a sample.

***Table 3.2** Typical system blanks in percentage (Sample LK198)**

TEMP.(°C)	^{39}Ar	^{36}Ar	^{37}Ar	^{40}Ar
450	.00	.00	.00	1.38
500	.00	.00	.00	2.39
550	.00	.00	.00	2.33
600	.00	.00	.00	1.54
650	.00	.00	.00	3.16
700	.00	.00	.00	1.79
750	.00	.00	.00	1.97
800	.00	.00	.00	1.99
850	.00	.00	.00	1.81
900	.00	.00	.00	2.11
950	.00	.00	.00	1.82
1000	.00	8.11	.00	1.41
1050	.00	5.99	.00	1.05
1100	.00	4.11	.00	.70
1150	.00	9.21	.00	2.81
1200	.00	22.07	.00	9.35
1250	.00	20.05	.00	9.60
1300	.00	42.55	.00	27.64
1400	.00	34.04	.00	34.45
TOTAL	.00	7.26	.00	3.35

* The blanks are measured for each sample.

The blank corrected ratios are then corrected for mass discrimination (MD) based on analysis of atmospheric argon (Air Standard) introduced from a pipette system connected to the extraction line Each sample was preceded and followed by an Air Standard analyses and the average MD values were found for correcting the measured ratios. Mass spectrometer signal was calibrated with the known amount of ^{40}Ar* by repeated measurements of the monitor sample McClure Mountain Hornblende (MMHb-1). This helps in knowing the abundance of an isotope, and is called 'sensitivity for argon' and found to be varying from (0.1 to 0.8) $\times 10^{-7}$ ccSTP/mV.

Errors are calculated by quadratically propagating the errors in the measured ratios, blanks and interfering isotopes. Each box in the age spectra does not include error in J but the errors quoted on the plateau age and the integrated age includes error in J. All the errors quoted are 2σ. Plateau age is weighted mean of the apparent ages of at least four consecutive steps which are within 2σ and consist of minimum 50% of gas released. Weighted means are calculated using the method given by Bevington (1969) where $1/\sigma_i^2$ (σ_i is the standard deviation for the ith step) is taken as the weight. Isochron ages are calculated using the two-error regression method outlined by York (1969) of data points corresponding to plateau steps. The typical error on the age of the samples analyzed is less than 10%.