CHAPTER III

EXPERIMENTAL TECHNIQUES

This chapter describes the experimental techniques used in the present work to study the isotopic and trace elemental characteristics of different samples from the Mesozoic carbonatite complexes of India. The chapter is divided into six sections. The first section (3.1) describes the samples collected for this work. The technique of stable carbon and oxygen isotope analysis in carbonatites and other carbonate bearing rocks are described in the section 3.2 with a detailed discussion on the CO_2 extraction procedure, developed during this work, to analyze oxygen and carbon isotopic compositions in individual carbonate phases present in natural multicarbonate mixtures. The section 3.3 describes the ^{40}Ar-^{39}Ar dating technique and details of the experimental procedures followed in our laboratory. Brief descriptions of Sr isotope analysis by thermal ionization mass-spectrometry, trace elemental analysis by instrumental neutron activation analysis, mineral identification by X-ray diffractometry, and Rb and Sr concentration measurements by atomic absorption spectrophotometry are given in sections 3.4, 3.5, 3.6 and 3.7, respectively.

3.1. SAMPLES FOR THIS WORK

Three field trips were undertaken, two to Amba Dongar (November, 1993 and June, 1995) and one to Sung Valley (December, 1994), to collect samples for this work. Samples of various carbonatites, alkaline rocks, metasomatic rocks and country rocks were collected. The main criteria for selection of samples were freshness in hand specimen and the collection of samples which fairly represented a particular exposure. Samples of carbonatites and metasomatic rocks from Mundwara and Sarnu-Dandali complexes were kindly provided by late Dr. R. K. Srivastava of M. S. University, Udaipur; samples of Samchampi complex were given by Mr. S. K. Sengupta of Geological Survey of India, Guwahati. Five carbonatite samples from Sung Valley complex and a carbonatite sample of Swangkre complex were given by Dr. P. Krishnamurthy of Atomic Mineral Division, Hyderabad.

Petrographic studies (thin section and X-ray diffractometry) were carried out to identify different minerals and to classify the rock types. Carbonatite samples, by definition, had more than 50% modal carbonate and they displayed magmatic features. Metasomatic rocks contained <10% carbonate. Alkaline rocks of Amba Dongar and Sung Valley were sampled particularly for dating and Sr-isotopic studies. Amba Dongar alkaline rocks had ~ 7% carbonate (mostly calcite) in them. Country rocks and hydrothermal calcite veins, which were associated with the fluorite deposits of Amba Dongar complex were also sampled. Table 3.1 gives a brief description of samples used in different studies.

Table 3.1. Description of the samples analysed in the present work

Sample	Description
Amba Dongar	
AD-1	Medium grained calcite carbonatite. Collected from a small dyke which intrudes into coarse grained calcite carbonatites. (90 % carbonate).
AD-2	Medium grained calcite carbonatite. Apart from carbonates (~80%), the rock has secondary minerals like fluorite, micro crystalline silica and hematite.
AD-3	Fine grained calcite carbonatite. It contains secondary veinlets of Fe-rich carbonates and shows replacement texture. (~70% carbonate).
AD-4	Limestone (Bagh beds). A micrite, has no fossils. A lot of microcrystalline silica is present. Collected from a road side exposure near Moti Chikli.
AD-6	Sandstone (Bagh beds). Quartz is the dominant mineral.
AD-8	Medium grained calcite carbonatite collected from the fluorite mine from a dyke that intrudes into coarse grained calcite carbonatite. (90 % carbonate).
AD-9/2	Medium grained calcite carbonatite. (92% carbonate).
AD-10/1	Very coarse grained monomineralic calcite carbonatite collected from the fluorite mine. A deeper level carbonatite.
AD-10/2	Very coarse grained monomineralic calcite carbonatite like AD-10/1.
AD-12	Very fine grained ferrocarbonatite collected from the southern-most ferrocarbonatite plug. Ankerite is the major carbonate, calcite to ankerite ratio is 24:76. Shows signs of hydrothermal alteration. (52 % carbonate).
AD-13/1	Fine grained calcite carbonatite collected from a vein in the southern part of the eastern limb of the ring dyke. (75 % carbonate).
AD-13/2	Medium grained calcite carbonatite collected close to AD-13/1. (85 % carbonate.

AD-14	Nephelinite from the base of main dome. It has phenocrysts of nepheline, aegirine augite and melanite garnet. Groundmass contains calcite and analcite. Collected from an exposure at the base of rig dyke (Western margin).
AD-16	Nephelinite. Groundmass does not contain calcite. Collected from a site close to AD-14.
AD-17	Nephelinite for Khadla village. Groundmass contains calcite.
AD-18	Nephelinitic tuff. Groundmass contains carbonates (Khadla).
AD-19	Dark brown coloured ferrocarbonatite, contains a lot of iron oxide. Calcite to ankerite ratio is 60:40. Collected from a small exposure within the calcite carbonatite main dyke.
AD-20	Jasper rich vein. (~7 % carbonate).
AD-21	Banded (gray and red) calcite carbonatite. (88 % carbonate).
AD-24	Fluoritized carbonatite. (2 % carbonate).
AD-25	Fine grained ferrocarbonatite. Calcite : Ankerite = 8:92.
AD-26	K-feldspar rich rock (fenite). (2 % carbonate).
AD-27	Medium grained calcite carbonatite. From a small dyke that intrudes into coarse grained calcite carbonatite. (90 % carbonate).
AD-28	Sodic fenite. (4 % carbonate).
AD-29	Brownish yellow coloured, fine grained calcite carbonatite vein. The vein intrudes into the coarse grained calcite carbonatites. (65 % carbonate).
AD-30	Highly altered calcite carbonatite vein. (51% carbonate).
AD-31	Coarse grained calcite carbonatite. (85 % carbonate).
AD-32	Coarse grained monomineralic calcite carbonatite.
AD-33	Fine grained ferrocarbonatite from the main ferrocarbonatite plug. Ankerites in these have been altered to calcite and iron oxides. Calcite to ankerite ratio = 40:60.
AD-34	Ferrocarbonatite, collected from the same exposure as AD-33. Ankerite is the only carbonate present in this.
AD-35	Highly altered ferrocarbonatite, calcite:ankerite = 20:80.
AD-38	Monomineralic coarse grained calcite carbonatite.
AD-39	Fine grained calcite carbonatite from a vein that cuts across course grained calcite carbonatite.
AD-40	Medium grained calcite carbonatite. (95 % carbonate).
AD-41	Fine grained, brownish yellow, calcite carbonatite vein. (75 % carbonate).
AD-42	Medium grained calcite carbonatite, shows recrystallization of calcites. (79 % carbonate).
AD-43	Highly altered calcite carbonatite vein from east part of the ring dyke. (66 % carbonate).

AD-44/1	Highly altered, fluoritized, red coloured calcite carbonatite. (55 % carbonate).
AD-45	Calcite bearing tinguaite. Minerals present are; nepheline, aegirine augite, melanite and calcite. (7 % carbonate).
AD-46	Phlogopite bearing calcite carbonatite from a vein that intrudes into sodic fenites and alkaline rocks. Such veins are numerous inside the mine.
AD-47	Calcite bearing tinguaite. Minerals present; nepheline, aegirine-augite, K-feldspar and magnetite. Calcite constitutes 8 % of the total rock. Collected from an exposure close to the fluorite mine.
AD-49	Medium grained calcite carbonatite. A common carbonatite on the western benches of the mine. (~ 80 % carbonate).
AD-50	Silicified carbonatite. Contains very little carbonate. At places original carbonatite texture is preserved.
AD-51	Calcite carbonatite from a vein. (93 % carbonate).
AD-52	Phlogopite bearing calcite carbonatite vein that intrudes into an alkaline rock. (91 % carbonate).
AD-54	Coarse grained calcite carbonatite. (95 % carbonate).
AD-55	Fine grained, highly altered ferrocarbonatite. (calcite:ankerite = 15:85).
AD-58	Calcite vein associated with fluorite deposits.
AD-59/1	Micritic limestone similar to AD-4.
AD-61	A calcareous sand stone. (25 % carbonate).
AD-62	Fine grained, fossiliferous limestone. (80 % carbonate).
AD-64	Calcite carbonatite (90 % carbonate).
AD-65	Phonolite
AD-66	Nephelinite
AD-67	Nephelinitic tuff
AD-69	Phonolite
AD-70	Calcite bearing nephelinite (6 % carbonate).
AD-71	Calcite bearing tinguaite (7 % carbonate).
NS-20/2	Very coarse grained monomineralic calcite carbonatite.
NS-20/O/2	Very coarse grained monomineralic calcite carbonatite.
NS-20/O/3	Very coarse grained monomineralic calcite carbonatite.
NS-20/O/4	Coarse grained calcite carbonatite. (85 % carbonate).
NS-20/6	Coarse grained calcite carbonatite. (93 % carbonate).
NS-20/8	Coarse grained calcite carbonatite. (88 % carbonate).
NS-20/9	Coarse grained calcite carbonatite. (87 % carbonate).
NS-20/10	Coarse grained calcite carbonatite. (92 % carbonate).
NS-20/11	Phlogopite bearing medium grained calcite carbonatite. From a vein that intrudes into coarse grained calcite carbonatite. (87 % carbonate).

NS-20/13	Coarse grained calcite carbonatite. (85 % carbonate).
Mundwara	
M-1	Coarse grained calcite carbonatite (93 % carbonate).
M-2	Na-amphibole bearing calcite carbonate (83 % carbonate).
M-3	Yellowish brown fine grained calcite carbonatite. Shows signs of alteration.
M-15	Coarse grained calcite carbonatite. (88 % carbonate).
M-39	Medium grained calcite carbonatite. (87 % carbonate).
M-40	Highly altered calcite carbonatite. (76 % carbonate).
M-121	Highly altered calcite carbonatite. (62 % carbonate).
Sarnu-Dandali	
C-94	Fine grained calcite carbonatite. (77 % carbonate).
C-119	Coarse grained calcite carbonatite. (86 % carbonate).
C-142	Fine grained calcite carbonatite. (73 % carbonate).
C-143	Coarse grained calcite carbonatite. (90 % carbonate).
C-149	Brownish red, fine grained ferrocarbonatite. (58 % carbonate).
C-177	Brownish red, fine grained ferrocarbonatite. (69 % carbonate).
C-245	Coarse grained calcite carbonatite.
C-290	Medium grained calcite carbonatite.
C-291	Calcite carbonatite, shows signs of recrystallization.
A-18	Carbonate bearing K-feldspar rich rock. (8 % carbonate).
A-161	Fine grained ferrocarbonatite.
A-800	Carbonate bearing potash fenite (~10 % carbonate).
A-805	Ferrocarbonatite
A-807	Ferrocarbonatite
A-808	Ferrocarbonatite
A-841	Highly altered calcite carbonatite.
Sung Valley	
SV-1	Medium grained dolomite bearing calcite carbonatite, contains olivine and phlogopite apart from other characteristic minerals. (calcite:dolomite = 83:17).
SV-2	Dolomite carbonatite. Collected from a vein that intrudes coarse grained pyroxenite.
SV-3	Very coarse grained pyroxenite. Apart from pyroxene (mainly augite), it contains phlogopite.
SV-4	Very coarse grained pyroxenite.
SV-5	Phlogopite bearing calcite carbonatite.
SV-6	Apatite rich calcite carbonatite.
SV-7	Phlogopite bearing calcite carbonatite.
SV-10	Apatite rich calcite carbonatite.

SV-11	Calcite carbonatite. Olivine and Phlogopite bearing.
SV-12	Phlogopite bearing calcite carbonatite.
SV-13	Dolomite bearing calcite carbonatite. (calcite:dolomite = 92:08).
SV-15	Magnetite rich calcite carbonatite.
SV-18	Dolomite bearing calcite carbonatite. (calcite:dolomite = 80:20).
SV-19	Olivine-rich, dolomite bearing calcite carbonatite. (calcite:dolomite = 87:17).
SV-20	Dolomite bearing calcite carbonatite. (calcite:dolomite = 88:12).
PKS-145	Coarse grained magnetite-rich calcite carbonatite. (88 % carbonate).
PKS-164	Calcite Carbonatite (85 % carbonate).
PKS-270	Olivine bearing calcite carbonatite. (82 % carbonate).
PKS-241	Dolomite bearing calcite carbonatite. (88% carbonate).
PKS-279	Calcite carbonatite, contains olivine and amphiboles. (87 % carbonate).
Samchampi	
71	Calcite carbonatite.
C1/93	Coarse grained calcite carbonatite.
165	Calcite carbonatite.
177	Dolomite bearing calcite carbonatite (calcite:dolomite = 89:11).
179	Dolomite bearing calcite carbonatite (calcite:dolomite = 90:10).
Swangkre	
WKS-1	Medium grained calcite carbonatite.

Note: Like most of the carbonatites of the world, the carbonatite samples described above contain accessory minerals like magnetite, apatite, phlogopite, barite, pyrochlore, fluorite, monazite etc. (determined from thin section study). Carbonate percentage and the type of carbonate mineral(s) present in a sample were determined respectively from, the CO_2 yield during the acid reaction performed for stable isotope analysis and X-ray diffractometry. The samples of fenites, fluoritized carbonatites, silicified carbonatites and some highly altered rocks (as described in the above table), which contain < 50 % carbonate, have been termed as metasomatic rocks in this work.

3.2. STABLE ISOTOPIC STUDIES

3.2.1. Principle

Most naturally occurring elements consist of more than one stable isotope. In elements of lower atomic masses, it is possible for the isotope to get fractionated through physico-chemical processes as a result of the mass difference between the isotopes. The stable isotopes of light elements H, C, N, O and S have been used extensively as important tracers for many geological processes. The extent of fractionation of the isotopes of these elements helps us in finding the temperature of a process, source of an element, extent of alteration and nature of diffusion processes. In the case of igneous rocks, study of isotopes of carbon (^{12}C and ^{13}C) and oxygen (^{16}O and ^{18}O) tells about the nature of the source regions of these rocks and the isotopic effects generated during magmatic and post-magmatic-alteration processes.

I measured carbon and oxygen isotopic compositions of the carbonates present in carbonatites and alkaline rocks. The stable isotopic ratios are generally measured relative to a standard or reference and are expressed as a δ value in per mill (‰) units. For carbon and oxygen, the δ values respectively are :

$\delta^{13}C = [(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{V\text{-}PDB}] / [(^{13}C/^{12}C)_{V\text{-}PDB}] \times 10^3$

and

$\delta^{18}O = [(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{V\text{-}SMOW}] / [(^{18}O/^{16}O)_{V\text{-}SMOW}] \times 10^3$

where V-PDB (Vienna Pee Dee Belemnite) is the standard used for carbon isotopic ratio and V-SMOW (Vienna Standard Mean Ocean Water) is the standard for oxygen isotopic ratio (Gonfiantini, 1981).

3.2.2 Experimental Details

3.2.2a. Sample Preparation

Fresh samples were powdered using a stainless steel mortar and pestle. Homogenized powders of grain size < 200 mesh (75μm) were taken. Sample powders were then dried at 110°C for 10-12 hours in an oven to remove moisture from them. Then 10 - 20 mg of each sample powder was taken for isotopic analysis.

3.2.2b. Extraction of CO_2 from carbonates of carbonatites and other rocks.

Carbonatite carbonates are either pure calcites or mixtures of calcites and dolomites/ankerites. For measurements of carbon and oxygen isotopic ratios mass-spectrometrically we need to extract CO_2 from them. For pure calcite bearing samples the standard CO_2 extraction procedure, suggested by McCrea (1950), was followed. ~10 mg of each sample was taken in glass bottles with side-arms which contained ~2 ml of 100% orthophosphoric acid (H_3PO_4) in the side arms. These bottles were evacuated and kept in a 25°C constant temperature water bath for 6 hours to allow them to attain the temperature of 25°C. Then the bottles were tilted inside water to react the sample with H_3PO_4. The reaction was allowed to continue for 24 hours at 25°C and the liberated CO_2 was cleaned of water vapour and collected in glass bottles after measuring the pressure with a pre-calibrated Hg-manometer. The yield of CO_2 was 100% for pure calcite samples. The gas was then allowed into a mass-spectrometer after another round of cleaning for carbon and oxygen isotopic ratio measurements.

For carbonatites which have different proportions of calcites, dolomites and ankerite, the above procedure is likely to generate CO_2 which will have contamination from different carbonates. Hence, to get CO_2 from pure physically inseparable end-members during the acid reaction, a selective step-wise CO_2 extraction (chemical separation) procedure was developed which is discussed in detail in the following paragraphs.

Chemical separation techniques, to separate coexisting carbonate minerals for accurate determination of the oxygen and carbon isotope compositions, have been based on differential reaction rates of various carbonate minerals with phosphoric acid under variable temperatures. Fig.3.1 shows the reaction rates of pure carbonate minerals with phosphoric acid at 25°C and 50°C. Most of the earlier studies tried to separate calcite-CO_2 from dolomite-CO_2 (Epstein et al., 1964; Walters et al., 1972; Wada and Suzuki, 1983) and some studies separated CO_2 from mixtures of calcite and other carbonate minerals such as siderite, ankerite and magnesite (Fritz et al. 1971; Rosenbaum and Sheppard, 1986; Al-aasm et al., 1990). However, so far extraction protocols have not been proposed for multiple-carbonate samples. An attempt was made to develop an extraction procedure for calcite and dolomite/ankerite mixed samples with the following specific aims to:

- reduce the grain size effect on the reaction rates
- reduce the reaction time to a reasonable interval
- avoid using multiple temperature steps as proposed by many earlier workers
- efficiently separate pure end-members without any significant mixing
- propose the exact procedure(s) to be followed for samples having varying proportions of calcite and dolomites

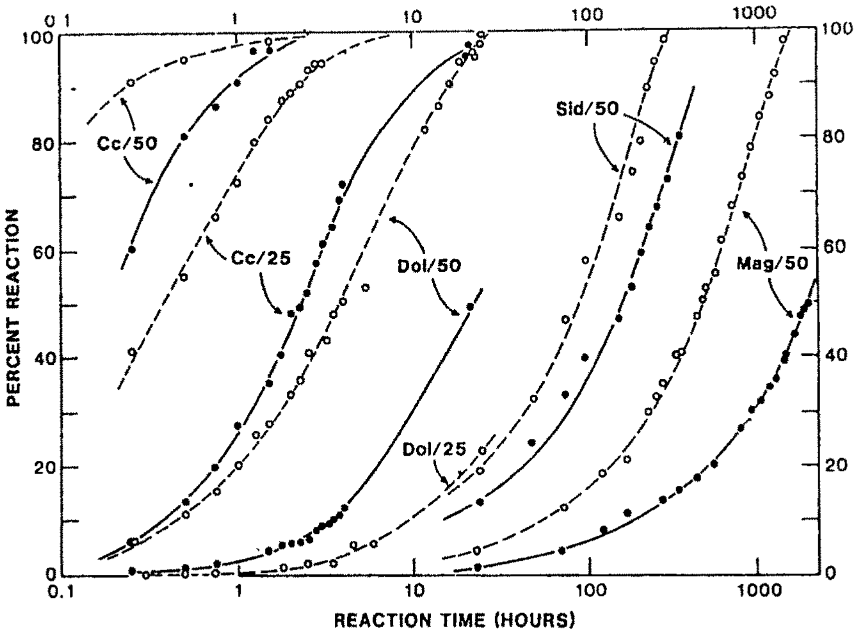

Fig.3.1. Reaction rates of pure carbonate minerals (expressed in cumulative percent of theoretical yield) with phosphoric acid vs. reaction time (in hours) at 25°C and 50°C, respectively. The open circles denote the < 200 mesh grain size fraction and the filled circles represent the 100-140 mesh size fraction (from Al-aasm et al., 1990)

For this experiment, pure calcite and dolomite (verified by X-ray diffractometry) standards were selected, powdered and sieved to <325 and >400 mesh size (between 37 to 45 μm size) and then dried in oven at 110°C. Such uniform fine grained powders were used to enhance the reaction rate as well as to reduce the grain size effect on the reaction. When these pure calcite and dolomites were reacted with H_3PO_4 at 25°C, it was found that for calcite 100% CO_2 comes out after 10 hours reaction time and for dolomite 100% CO_2 comes out after 120 hours of reaction. However, ~ 50 to 55% of the total gas from calcite (also dolomite), collected before the completion of the reaction, was found to give $\delta^{13}C$ and $\delta^{18}O$ values of pure calcite (dolomite) (within experimental uncertainty), i.e. 50 to 55% of the total gas amount appears to be good enough to measure the isotopic compositions of calcite or dolomite. This confirms the observations made by Epstein et al. (1964), Al-aasm et al. (1990) and Knudsen and Buchardt (1991). Our results are presented in tables 3.2 and 3.3. It was found that for pure dolomites 72 hours of reaction time is sufficient to give the true representative CO_2 of the whole sample and for pure calcite 15 min. reaction time is sufficient. Pure calcite and pure dolomite isotopic compositions (averages of eight measurements each) were found to be:

Calcite: $\delta^{13}C_{V\text{-}PDB} = -2.8 \pm 0.1$ ‰
$\delta^{18}O_{V\text{-}PDB} = -10.9 \pm 0.2$ ‰
Dolomite: $\delta^{13}C_{V\text{-}PDB} = +0.6 \pm 0.1$ ‰
$\delta^{18}O_{V\text{-}PDB} = -9.1 \pm 0.2$ ‰

$\delta^{13}C$ and $\delta^{18}O$ of dolomite are 3.4 ‰ and 1.8 ‰ higher than those of calcite, respectively.

Table 3.2. Yield and isotopic composition of calcite-CO_2 from various mixtures

Sample	Calcite:Dolomite	% Yield of Calcite-CO_2	Reaction Time (min.)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
MX-15	22:78	54	5	-2.6	-10.8
MX-18	32:68	49	15	-2.7	-10.8
MX-22	36:64	67	15	-2.7	-10.7
MX-26	21:79	73	15	-2.7	-11.1
MX-19	80:20	78	30	-2.8	-10.8

MX-28	62:38	78	30	-2.8	-10.8
MX-34	100:00	63	30	-2.9	-10.8
MX-30	91:09	77	60	-2.8	-10.8
MX-1	80:20	84	120	-2.8	-11.0
MEAN				-2.8±0.1	-10.8±0.1
Pure calcite (av of 8)	100:00	100	600	-2.8 ± 0.1	-10.9 ± 0.2

Table 3.3. Yield and Isotopic composition of dolomite-CO_2 from various mixtures

Sample	Calcite:Dolomite	% Yield of Dolomite-CO_2	Reaction Time (hours)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
MX-5	20:80	57	78	0.7	-9.1
MX-9	19:81	56	72	0.7	-9.2
MX-11	21:79	55	72	0.6	-9.0
MX-17	20:80	56	72	0.6	-9.0
MX-19	80:20	59	72	0.5	-9.2
MX-20	64:36	56	72	0.6	-9.1
MX-25	32:68	57	72	0.6	-9.0
MX-26	21:79	55	72	0.7	-9.1
MX-27	43:57	58	72	0.6	-9.2
MX-30	91:09	70	120	0.6	-9.1
MX-32	10:90	64	120	0.6	-9.3
MX-33	11:89	64	120	0.6	-9.1
MEAN				0.6±0.1	-9.1±0.1
Pure dolomite (av of 8)	0:100	100	120	0.6 ± 0.1	-9.1 ± 0.2

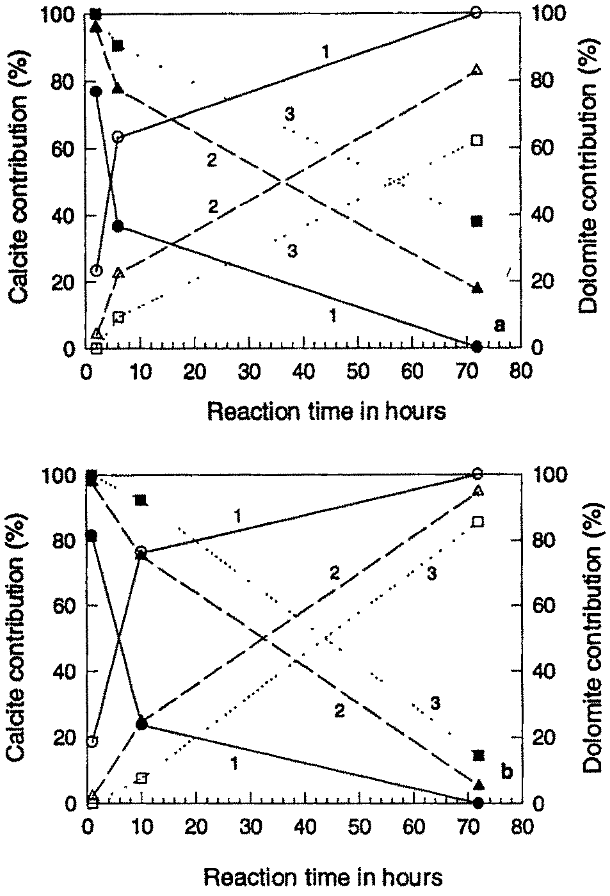

Fig. 3.2. *Calcite and dolomite contributions to CO_2 extracted at different steps versus reaction time for three different mixtures (1 for calcite:dolomite = 20:80; 2 for calcite:dolomite = 60:40; 3 for calcite:dolomite = 80:20). (a) plots the results from procedure-I and (b) from procedure-II (see section 3.2.2b). Filled symbols (represent calcite contributions and corresponding dolomite contributions are represented by open symbols. The contributions of the calcite and dolomite were calculated knowing the $\delta^{13}C$ of the end-members and the $\delta^{13}C$ of the extracted gas. $\delta^{13}C$ was preferred to $\delta^{18}O$ because the analytical uncertainty of the former is less.*

Different weight proportions of these calcite and dolomite powders were physically mixed to prepare samples having wide ranges of calcite:dolomite ratios. Then the samples were taken in side-arm reaction vessels (35 cc) with the side arms filled with ~2 ml of 100% H_3PO_4 acid. After evacuation samples were reacted at 25°C. CO_2 was extracted following stepwise extraction procedures advocated by earlier workers (Walters et al., 1972; Al-aasm et al., 1990). Many different combinations of intermediate extraction were also tried out. Results of two such procedures are shown in Fig.3.2 for three different mixtures (calcite:dolomite in Mix-1 = 20:80, in Mix-2 = 40:60 and in Mix-3 = 80:20). In procedure-1, first 2 hours reaction time was given for calcite CO_2 to evolve which was then extracted out of the bottle, then after 6 hours the CO_2 was extracted and rejected as it contained mixed CO_2 and then after 72 hours the CO_2 was collected for dolomite-CO_2 . In this procedure each time an aliquot of CO_2 was taken out in a particular volume (46.7 cc) in the extraction line. In procedure-2, only 1 hour was given for calcite-CO_2 while dolomite-CO_2 was collected from the reaction of the sample from 10 hours to 72 hours time with an in between (1 to 10h) CO_2-rejection. In this procedure, except for the calcite fraction (i.e. 1 hour extraction), each time all CO_2 was extracted out of the bottle. Then the gases collected at different steps were measured for $\delta^{13}C$ and $\delta^{18}O$ compositions. In Fig.3.2, dolomite-CO_2 and calcite-CO_2 contributions are plotted (calculated from $\delta^{13}C$ of CO_2 collected in different steps) against the reaction time. It was observed that in all mixtures except the mixtures having calcite > 80% (curve-3, Fig.3.2), the CO_2 extracted in the first step (which was expected to contain only calcite-CO_2) had contributions from dolomite (curves-1 and 2, Fig.3.2). Similarly in the last step, the CO_2 extracted (which was expected to contain only dolomite-CO_2) had contributions from calcite except for mixtures having >80% dolomite. It was also observed that the extent of contamination of calcite-CO_2 by dolomite-CO_2 in mixtures increased with the increase in the dolomite content in the sample and vice-versa. High CO_2 pressure inside the reaction bottles found to reduce the reaction rate resulting in low yield of dolomite-CO_2.

Different other combinations of reaction durations were tried out but all failed to give pure end-member values following a single extraction procedure for various mixtures. Finally, I came out with two different procedures for two different kinds of mixtures using which it was possible to get the isotopic compositions of the pure end-members. The proposed two procedures for calcite enriched mixtures (calcite >50%) and dolomite enriched mixtures (dolomite >50%) are given below:

For mixtures having Calcite >50% (25°C):

1. CO_2 to be collected after first 30 minutes of reaction: Calcite-CO_2.
2. 30 min. to 1 hour of reaction: Mixed CO_2, to be pumped.
3. 1 hour to 4 hours of reaction: Mixed CO_2, to be pumped.
4. 4 hours to 10 hours of reaction: Mixed CO_2, to be pumped.
5. 10 hours to 72 hours of reaction: To be collected for Dolomite-CO_2.

For mixtures having Dolomite >50% (25°C):

1. CO_2 to be collected after 15 minutes of reaction: Calcite-CO_2.
2. 15 min. to 10 hours of reaction: Mixed-CO_2, to be pumped.
3. 10 hours to 72 hours of reaction: To be collected for Dolomite-CO_2.

In between pumping steps are required to reduce the overlying CO_2 pressure on the reactants to make the reaction faster (law of mass action) and also to reduce the chance of intermixing of dolomite-CO_2 with calcite-CO_2. In the case of calcite enriched mixtures, three intermediate steps of pumping are required to remove mixed CO_2 and to reduce the overlying CO_2 pressure, while in dolomite enriched mixtures we need only one such intermediate pumping. These procedures were found to work satisfactorily for various mixtures except for the mixtures having <10% calcite (or dolomite) (Table 3.4). From such mixtures it was extremely difficult to take out the pure CO_2 of the minor carbonate. Hence such mixtures may be treated as pure carbonates of the major carbonate mineral. In such a case isotopic compositions of the major carbonate would be affected only if the isotopic compositions of the minor mineral are very different from those of the major. Table 3.4 gives the results of $\delta^{13}C$ and $\delta^{18}O$ measurements of calcite and dolomite fractions from different mixtures from which CO_2 was extracted following the above described selective extraction procedures. In Fig.3.3, cumulative yields are plotted against the reaction time. For calcite dominant mixtures almost 100% total yield could be achieved in 72 hours (Fig.3.3a), whereas for dolomite dominant samples the cumulative yield was around ~85% after 72 hours (Fig.3.3b). Though all CO_2 from dolomite did not evolve in 72 hours of reaction in the case of dolomite dominant mixtures, the CO_2 from the last extraction (~55% of the total expected CO_2 from dolomite fraction) when analyzed for $\delta^{13}C$ and $\delta^{18}O$, gave the pure dolomite values.

Table 3.4. $\delta^{13}C$ and $\delta^{18}O$ of calcite and dolomite of various carbonate mixtures.

I. Results of mixtures having calcite >50% by weight

Calcite:Dolomite	30 min. CO_2		72 hours CO_2	
	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}PDB}$ (‰)	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}PDB}$ (‰)
91:09	-2.8	-10.7	0.4	-9.4
80:20	-2.8	-10.8	0.6	-9.2
74:26	-2.8	-10.8	0.6	-9.2
66:34	-2.8	-11.0	--	--
64:36	--	--	0.6	-9.1
62:38	-2.8	-10.8	--	--

II. Results of mixtures having dolomite >50% by weight

Calcite:Dolomite	15 min. CO_2		72 hours CO_2	
	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}PDB}$ (‰)	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}PDB}$ (‰)
09:91	-2.1	-10.2	0.6	-9.3
10:90	-2.1	-10.5	0.6	-9.1
18:82	-2.4	-10.6	--	--
20:80	--	--	0.6	-9.1
21:79	-2.7	-11.1	0.7	-9.1
22:78	-2.6	-11.0	0.7	-9.1
32:68	-2.7	-10.6	0.6	-9.1
36:64	-2.7	-10.7	--	--
43:57	-2.7	-10.6	0.6	-9.2

Note: Reproducibility of $\delta^{13}C$ and $\delta^{18}O$ measurements is 0.1 ‰ for standards (see section 3.2.2c). End-members compositions are calcite: $\delta^{13}C$ = -2.8 ± 0.1 ‰ & $\delta^{18}O$ = -10.9 ± 0.2 ‰, dolomite: $\delta^{13}C$ = 0.6 ± 0.1 ‰ & $\delta^{18}O$ = -9.1 ± 0.2 ‰ (average of eight measurements). All the above $\delta^{18}O$ values for dolomite-CO_2 are uncorrected for the difference in acid fractionation between dolomite and calcite.

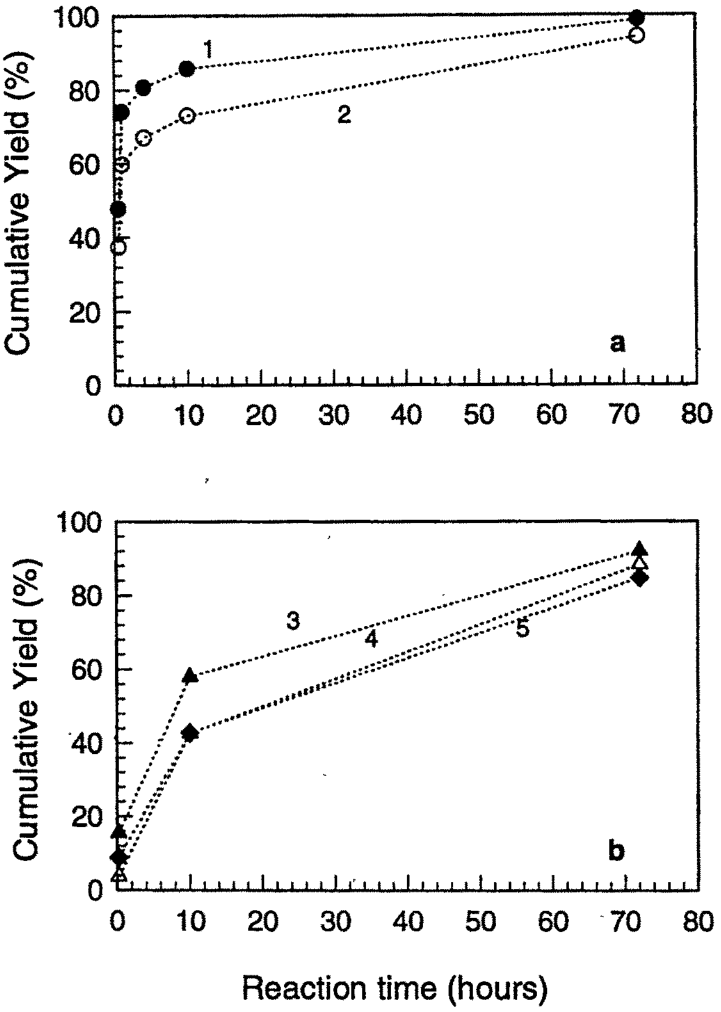

Fig.3.3. *Plot of cumulative CO_2 yield vs. reaction time for different carbonate mixtures when, (a) calcite is > 50 % and (b) dolomite is > 50 %, in the mixture. CO_2 was extracted following the selective extraction procedures (see section 3.2.2b). Calcite: Dolomite in 1 = 80:20; 2 = 62:38; 3 = 43:57; 4 = 32:68; and 5 = 20:80. (From sample weight, weight proportions of calcite and dolomite, manometric pressure of CO_2 collected, the yield was calculated as observed number of micromoles/ expected number of micromoles of CO_2).*

Following the selective CO_2 extraction procedures, CO_2 from calcites, dolomite/ankerites of dolomite bearing calcite-carbonatites, dolomite carbonatite and ferrocarbonatites were extracted for isotopic measurements. This is because the time taken to evolve CO_2 from ankerite is similar to that from dolomite (Rosenbaum and Sheppard, 1986).

3.2.2c. Mass Spectrometry

$\delta^{13}C$ and $\delta^{18}O$ of CO_2 were measured using a triple collector VG Micromass 903 mass-spectrometer with respect to a pre-calibrated internal laboratory standard CO_2 (Foram-Standard CO_2) and then converted to V-PDB and V-SMOW respectively. The acid fractionation factors used for $\delta^{18}O$ measurements of calcite, dolomite and ankerite were 1.01025 (Friedman and O'Neil, 1977), 1.01186 and 1.01177 (Rosenbaum and Sheppard, 1986), respectively. The whole process of data collection and reduction was automated. For this SIRA software (VG Isotech) was used.

(i) Calibration of laboratory standard CO_2

The Foram- CO_2 laboratory standard (Lab Std) was calibrated against V-PDB using an international standard NBS-19 (Toilet Seat limestone). For NBS-19, IAEA recommended values ($\delta^{13}C_{\text{V-PDB}} = -1.95$ and $\delta^{18}O_{\text{V-PDB}} = -2.2$) were used. The calibration procedure involved the following steps.

1. $\delta^{45\ \text{NBS-19}}{}_{\text{V-PDB}}$ and $\delta^{46\ \text{NBS-19}}{}_{\text{V-PDB}}$ were calculated from the recommended $\delta^{13}C$ and $\delta^{18}O$ values using Craig equations, (Craig, 1957) modified for a triple collector machine (Gonfiantini, 1981).
2. Ten samples of NBS-19 were analyzed following McCrea (1950)'s CO_2 extraction procedure and mean values of $\delta^{45\ \text{NBS-19}}{}_{\text{Lab Std}}$ and $\delta^{46\ \text{NBS-19}}{}_{\text{Lab Std}}$ were taken.
3. $\delta^{45\ \text{Lab Std}}{}_{\text{NBS-19}}$ and $\delta^{46\ \text{Lab Std}}{}_{\text{NBS-19}}$ were calculated using the equation: $\delta^{\text{Lab Std}}{}_{\text{NBS-19}} = (-\delta^{\text{NBS-19}}{}_{\text{Lab Std}})/(1+10^{-3}\ \delta^{\text{NBS-19}}{}_{\text{Lab Std}})$
4. The $\delta^{45\ \text{Lab Std}}{}_{\text{V-PDB}}$ and $\delta^{46\ \text{Lab Std}}{}_{\text{V-PDB}}$ values which were required (called offsets) for calibration were found out using the relations:

$$\delta^{45\ \text{Lab Std}}{}_{\text{V-PDB}} = \delta^{45\ \text{Lab Std}}{}_{\text{NBS-19}} + \delta^{45\ \text{NBS-19}}{}_{\text{V-PDB}} + 10^{-3}\ \delta^{45\ \text{Lab Std}}{}_{\text{NBS-19}}\ \ \delta^{45\ \text{NBS-19}}{}_{\text{V-PDB}}$$

$$\delta^{46\ \text{Lab Std}}{}_{\text{V-PDB}} = \delta^{46\ \text{Lab Std}}{}_{\text{NBS-19}} + \delta^{46\ \text{NBS-19}}{}_{\text{V-PDB}} + 10^{-3}\ \delta^{46\ \text{Lab Std}}{}_{\text{NBS-19}}\ \ \delta^{46\ \text{NBS-19}}{}_{\text{V-PDB}}$$

(ii) Precision and Reproducibility

The mass spectrometric precision (1σ) for a single sample (12 sets of ratios) was better than ±0.01 ‰ for $\delta^{13}C$ and ±0.02 ‰ for $\delta^{18}O$. When the same gas was run several times the reproducibility of the measurements remained the same as the precision of individual runs given above.

An international carbonatite standard NBS-18 was run at regular intervals of time (Table 3.5), whose long term average matches well with the IAEA (1995) values within 1σ level of error. For inter-laboratory comparison an internal standard (MAKMARB; a homogenized powder of pure marble) was sent to Godwin Laboratory (Cambridge), whose $\delta^{13}C$ and $\delta^{18}O$ values agree well with our long term averages within the 1σ level of error (see Table 3.6).

Table 3.5. International carbonatite standard (NBS-18)

Date	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}PDB}$ (‰)
6.8.93	-5.11	-23.08
16.8.93	-5.13	-23.15
8.4.94	-4.92	-22.98
15.4.94	-4.96	-22.85
14.6.94	-5.12	-22.99
25.5.95	-5.05	-22.97
27.12.96	-5.06	-22.88
30.1.96	-5.04	-22.83
8.3.96	-5.11	-23.02
22.8.96	-5.13	-23.09
28.8.96	-5.02	-23.05
18.8.96	-5.04	-23.09
Mean	-5.058 ± 0.068 (1σ)	-22.998 ± 0.102 (1σ)
IAEA Recommended Values (1995)	-5.029 ± 0.049 (1σ)	-23.035 ± 0.172 (1σ)

Table 3.6. MAKMARB (Makrana Marble - an internal calcite standard)

Date	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}PDB}$ (‰)
30.6.93	3.72	-10.83
19.7.94	3.69	-10.79
9.9.94	3.86	-10.54
7.10.94	3.86	-10.67
14.4.95	3.77	-10.69
25.5.95	3.88	-10.71
3.8.95	3.76	-10.70
2.9.95	3.86	-10.33

4.9.95	3.74	-10.59
18.9.95	3.77	-10.74
27.12.95	3.78	-10.90
1.1.96	3.90	-10.63
Mean	3.81 ± 0.08 (1σ)	-10.69 ± 0.12 (1σ)
Cambridge Values (1983)	3.81 ± 0.03 (1σ)	-10.63 ± 0.05 (1σ)

3.2.2d. Inter-laboratory Comparisons

To check our measurements for systematic errors, inter-laboratory comparison was done by comparing our results on one of our internal carbonate standards (MAKMARB) with the results obtained by Godwin Laboratory (Cambridge). As already discussed, Table 3.6 gives this comparison and it can be seen that the results agree among themselves within the experimental uncertainties (1σ). In addition to this, I also measured some carbonatite samples (Qaqarssuk carbonatites) provided by Dr. Christian Knudsen of the Geological Survey of Greenland, Denmark on our request. These samples include pure calcite bearing calciocarbonatites, carbonatites containing different proportions of calcite and dolomite and beforsites (pure dolomite bearing carbonatites). For pure calcite samples the CO_2 extraction procedures followed in both the laboratories were similar (25°C reaction and total CO_2 extraction after 24 hours but the H_3PO_4 used by them was 98 %), whereas for samples having calcite and dolomite mixtures the extraction procedures were slightly different. In their case (Knudsen and Buchardt, 1991), calcite-CO_2 was extracted after 2 hours and dolomite-CO_2 was extracted from the acid reaction between 4 to 18 hours of time with an in-between pumping (2 to 4 hours). I extended the reaction for the rejection interval from 2 hours to 4 hours (2 to 6 hours) and dolomite-CO_2 was collected from the reaction interval 6 hours to 24 hours. For pure dolomite bearing samples, again, similar procedures were followed (24 hours reaction and complete extraction). The comparison of results is given in Table 3.7. It was found that in the case of pure calcites (320536,7), there is a systematic difference between $\delta^{13}C$ (also $\delta^{18}O$) values measured by Knudsen and Buchardt (1991) and results of this work (Table 3.7 and Fig.3.4a). My $\delta^{13}C$ values are ~0.31 ‰ more negative. This is also seen in the calcite-CO_2 of the calcite-dolomite mixtures. Similarly my $\delta^{18}O$ values for pure calcites are more positive by ~0.35 ‰. The other samples show an enrichment of 0.3 to 0.7 ‰ in calcite-CO_2. Likewise, for pure dolomite (320488) my $\delta^{13}C$ value is 0.51 ‰ more negative and $\delta^{18}O$ value is 1.37 ‰ more negative, whereas the dolomite-CO_2 from mixtures show difference ranging between +0.33 to -0.42 ‰ in $\delta^{13}C$ and +1.62 to -0.62 ‰ in $\delta^{18}O$. I have already eliminated systematic errors by the analyses of international carbonatite standard (NBS-18) and inter-laboratory comparison of internal standard (MAKMARB) of our laboratory measurements. Such an exercise was probably not done by Knudsen and Buchardt (1991). Hence, the observed systematic difference in the δ values of Greenland samples measured by us and them could be due to the inter-laboratory differences in the analytical conditions (choice of mass spectrometric reference material; instrumental drift effects; percentage of H_3PO_4 in the acid used etc.). $\delta^{13}C$ and $\delta^{18}O$ values of dolomites from mixed carbonates and dolomite carbonatites showed random differences (Table 3.7 and Fig.3.4b) which could be attributed to the differences in the extraction procedures. As I have increased the pumping interval for the mixed-CO_2, it is possible that my dolomite-CO_2 is less contaminated with calcite-CO_2.

Table 3.7. Inter-laboratory comparison for Qaqarssuk carbonatite samples*

Sample	Mineral	Modal % carbonate	Knudsen & Buchardt (1991)		This Study	
			$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
252540	calcite	47	-1.04	16.39	-1.37	16.72
	dolomite	53	-2.73	10.58	-2.40	12.20
320411	calcite	30	-3.27	7.32	-3.58	8.02
	dolomite	70	-3.21	7.50	-3.47	6.96
320430	calcite	59	-3.9	7.93	-4.28	8.42
	dolomite	41	-3.35	8.84	-3.77	8.22
320488	dolomite	100	-2.74	10.39	-3.25	9.02
320536	calcite	100	-4.60	7.50	-4.87	7.76
320537	calcite	100	-4.68	7.11	-5.03	7.56
320522	ankerite	100	-2.52	9.93	-2.83	10.52

* dolomite $\delta^{18}O$ values were corrected in both cases using acid fractionation factor of 1.01109 (Knudsen and Buchardt, 1991).

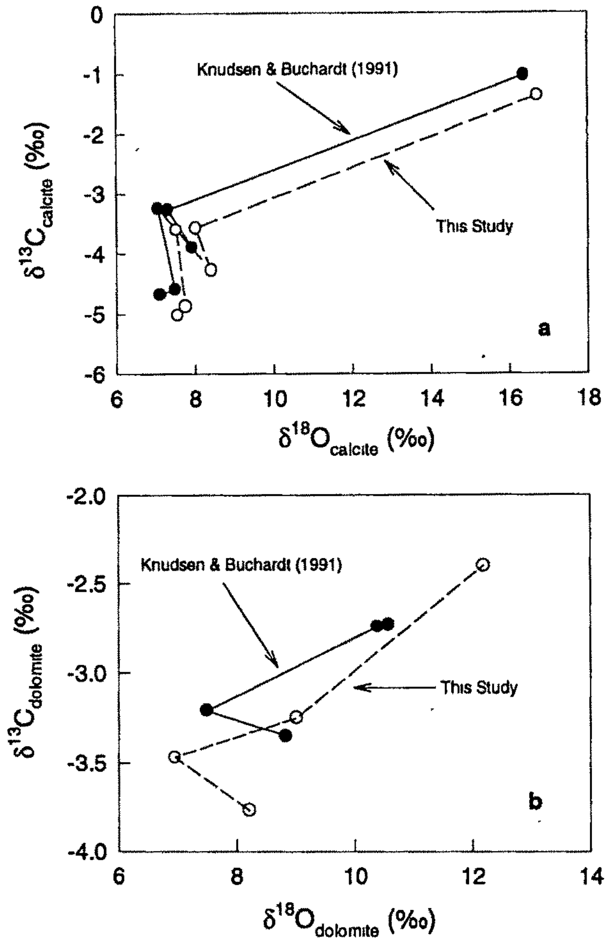

***Fig. 3.4.** Plots of $\delta^{13}C$ and $\delta^{18}O$ of calcites (a) and dolomites (b) from Qaqarssuk carbonatite samples. Filled circles are results from Knudsen and Buchardt (1991) and open circles represent values from this study on the same samples. Solid lines join values of Knudsen and Buchardt (1991) and dashed line join values of the present study.*

3.3 ^{40}Ar-^{39}Ar METHOD OF DATING

3.3.1a Principle

Potassium (Z=19), an alkali metal, has three naturally occurring isotopes ^{39}K, ^{40}K and ^{41}K. Out of these ^{40}K is radioactive, 11.2 % of which decays to stable ^{40}Ar by electron capture (decay constant = 0.581×10^{-10} y^{-1}) and 88.8 % decays to ^{40}Ca by beta decay (decay constant = 4.962×10^{-10} y^{-1}). The growth of radiogenic ^{40}Ar in a K-bearing system closed with respect to K and Ar during its life time is used to determine the age of the system by the K-Ar method of dating. The details of this dating technique have been provided by McDougall (1966), Damon (1970) and Hunziker (1979). As discussed by these authors this method has major limitations such as (i) difficulty in knowing the loss or excess of Ar in the sample, which can lead to uncertainty in the age of the sample; (ii) sample heterogeneity can cause erroneous K and Ar estimations as these analyses are done in two different aliquots of a sample; (iii) quantity of sample required is large, hence, small samples cannot be dated using this method. The ^{40}Ar-^{39}Ar method of dating is a variant of K-Ar method, which overcomes these limitations.

The basis of ^{40}Ar-^{39}Ar method of dating is the formation of ^{39}Ar by irradiation of the samples with fast neutrons (threshold energy = 1.2 MeV) following the reaction $^{39}K_{19}(n,p)^{39}Ar_{18}$. This reaction permits the K determination for a K-Ar age as a part of the argon isotope analysis in a single aliquot of the sample. The ^{39}Ar thus produced is radioactive, however, because of its large half life (269±3 years), it can be treated as a stable isotope during the short time involved in the analysis. After irradiation, the sample is either fused or incrementally heated until fusion and argon released during this process is measured for isotopic ratios mass-spectrometrically.

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

$$^{39}Ar_K = {}^{39}K\, \Delta T \int \Phi(\varepsilon)\, \sigma(\varepsilon)\, d\varepsilon \qquad (1)$$

where ^{39}K is the number of atoms of this isotope in the irradiated sample, ΔT is the length of irradiation, $\Phi(\varepsilon)$ is the neutron flux density at energy ε and $\sigma(\varepsilon)$ is the neutron capture cross section at energy ε for the $^{39}K_{19}(n,p)^{39}Ar_{18}$ reaction. The integration is over all energies of the incident neutrons. The equation for the number of radiogenic ^{40}Ar atoms in the sample is

$$^{40}Ar^* = (\lambda_e/\lambda)\, {}^{40}K\, (e^{\lambda t}-1) \qquad (2)$$

where λ_e is the decay constant for electron capture and λ is the total decay constant of ^{40}K ($= \lambda_e + \lambda_\beta$; where λ_β is the decay constant for the β^- decay of ^{40}K to ^{40}Ca). Hence combining (1) and (2) we get an expression for $^{40}Ar^*/^{39}Ar_K$ which is

$$^{40}Ar^*/^{39}Ar_K = (\lambda_e/\lambda)\, [{}^{40}K\, (e^{\lambda t}-1)] \,/\, [{}^{39}K\, \Delta T \int \Phi(\varepsilon)\, \sigma(\varepsilon)\, d\varepsilon] \qquad (3)$$

To simplify, it is conventional to define the quantity

$$J = (\lambda/\lambda_e)\ {}^{39}K/{}^{40}K\ \Delta T \int \Phi(\varepsilon)\ \sigma(\varepsilon)\ d\varepsilon \quad (4)$$

then rewrite equation (3) as

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

which gives the age equation upon rearrangement:

$$t = (1/\lambda)\ \ln\ [(\ ^{40}Ar^*/^{39}Ar_K)\ J + 1] \quad (6)$$

The equation (6) can give us the age of the sample provided the quantity J is known. J depends on neutron flux density and capture cross section that are difficult to determine. However, J can be determined by irradiating a sample of known age (called a monitor) together with samples whose ages are unknown. After measuring $^{40}Ar^*/^{39}Ar$ of the monitor, the equation (5) is used to find J :

$$J = (e^{\lambda t_m} - 1)\ /(^{40}Ar\ ^*/^{39}Ar)_m \quad (7)$$

where subscript m denotes monitor; t_m is the age of the monitor.

This value of J is then used in equation (6), together with the $^{40}Ar^*/^{39}Ar_K$ of the samples irradiated at the same time, to calculate the ages of these samples. The dates obtained by complete fusion are called as "total argon release dates" which have similar limitations as K-Ar dating method but avoid problems arising from sample heterogeneity.

3.3.1b. Correction for Interfering Isotopes

If the only contaminant present in the irradiated sample were atmospheric argon, then $^{40}Ar^*/^{39}Ar_K$ could be calculated from measured $^{40}Ar/^{39}Ar$ and $^{36}Ar/^{39}Ar$ ratios using

$$^{40}Ar^*/^{39}Ar_K = (^{40}Ar/^{39}Ar)_{meas} - (^{40}Ar/^{36}Ar)_{atm}(^{36}Ar/^{39}Ar)_{meas} \quad (8)$$

where "meas" is used for measured and "atm" is used for atmospheric. $(^{40}Ar/^{36}Ar)_{atm}$ is normally taken as 295.5. However, when a rock is irradiated, many undesirable neutron reactions with different elements produce interfering argon isotopes. These reactions 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).

The most important interfering reactions are those involving Ca and K: $^{40}Ca(n,n\alpha)^{36}Ar$, $^{42}Ca(n,\alpha)^{39}Ar$, and $^{40}K(n,p)^{40}Ar$. Therefore, to determine the actual $^{40}Ar^*/^{39}Ar_K$ ratio of the sample, the $^{40}Ar/^{39}Ar$ ratio measured needs to be corrected for atmospheric, calcium and potassium derived interfering isotopes. Another isotope of Ar, ^{37}Ar, which is primarily derived from ^{40}Ca by the reaction $^{40}Ca(n,\alpha)^{37}Ar$, is used in correction of both reactor induced ^{36}Ar and ^{39}Ar (Brereton, 1970). The correction factors $(^{36}Ar/^{37}Ar)_{Ca}$ and $(^{39}Ar/^{37}Ar)_{Ca}$ are determined by measuring the relative production rates of these isotopes in a pure calcium salt (CaF_2) irradiated along with the samples. The correction factor $(^{40}Ar/^{39}Ar)_K$ is determined by measuring the relative production rates of these isotopes in an irradiated pure potassium salt (K_2SO_4). Incorporating these corrections the expression for $(^{40}Ar^*/^{39}Ar)_K$ becomes

$$^{40}Ar^*/^{39}Ar_K=\{(^{40}Ar/^{39}Ar)_{meas}-295.5[(^{36}Ar/^{39}Ar)_{meas}-(^{36}Ar/^{37}Ar)_{Ca}(^{37}Ar/^{39}Ar)_{meas}]\}/\{1-(^{39}Ar/^{37}Ar)_{Ca}(^{37}Ar/^{39}Ar)_{meas}\} - \{(^{40}Ar/^{39}Ar)_K\} \qquad (9)$$

where $(^{40}Ar/^{39}Ar)_{meas}$, $(^{36}Ar/^{39}Ar)_{meas}$ and $(^{37}Ar/^{39}Ar)_{meas}$ are measured ratios and $(^{36}Ar/^{37}Ar)_{Ca}$, $(^{39}Ar/^{37}Ar)_{Ca}$ and $(^{40}Ar/^{39}Ar)_K$ are the correction factors determined for a given reactor.

3.3.1c. Decay correction

^{37}Ar and ^{39}Ar produced by irradiation are radioactive, so it is important to correct for their decays in the total time involved in analysis. Fortunately, the larger half life of ^{39}Ar (269±3 years) enables us to neglect the correction involved for its decay. However, ^{37}Ar has a half life of only 35.1 days, therefore, significant decay of it will occur during the time involved in the whole process of analysis. Therefore, proper corrections must be made for this. The general equation for the decay factor given by Brereton (1970) and Dalrymple et al. (1981) is :

$$\text{Decay factor} = \lambda t\, e^{\lambda t'}/(1-e^{-\lambda t}) \qquad (10)$$

where t is the irradiation time, t' is the time elapsed since the end of the irradiation and analysis and λ is the decay constant for ^{37}Ar. If the irradiation was done in a number of discrete intervals or segments then the decay factor is calculated using the following equation (Wijbrans, 1985 and Pande et al., 1988).

$$\text{Decay factor} = \lambda \sum_1^n t_i \Big/ \sum_1^n [(1-e^{-\lambda t_i})/e^{-\lambda t'_i}] \qquad (11)$$

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.

3.3.1d. The Incremental Heating Technique

A series of dates (apparent ages) can be obtained for a single sample by releasing argon from it in steps at increasing temperatures. If the sample has remained undisturbed (i.e. closed with respect to argon and potassium) since its formation then the apparent ages calculated at each step should be constant. However, if radiogenic argon was lost from some crystallographic sites after its initial cooling, then the ^{40}Ar/^{39}Ar ratios of the gas released at different steps may vary so also may the apparent ages. Customarily, the apparent ages calculated for different steps are plotted against cumulative ^{39}Ar percentage, which is called an age spectrum. In the case/ when apparent ages of different steps (more than four) are constant (within experimental errors), an age called plateau age for the sample is calculated taking the weighted mean of all plateau step ages. Samples affected by metamorphism or other secondary processes show disturbed age spectra and in such cases no plateau age can be calculated. However, a disturbed spectrum may give much many other useful information, which 's are discussed in detail by McDougall and Harrison (1988).

The ^{40}Ar-^{39}Ar method of dating requires a correction for the presence of trapped ^{40}Ar (as discussed in the section 3.3.1b). This component is normally taken to be atmospheric so that ^{40}Ar/^{36}Ar = 295.5. However, this assumption may not be valid always because there are possibilities when ^{40}Ar/^{36}Ar of non-radiogenic component is inherited (incorporation of a non-atmospheric component during crystallization). To evaluate such possibilities argon isotope correlation diagrams (^{40}Ar/^{36}Ar vs. ^{39}Ar/^{36}Ar and ^{36}Ar/^{40}Ar vs. ^{39}Ar/^{40}Ar) are useful. In a ^{40}Ar/^{36}Ar vs. ^{39}Ar/^{36}Ar plot (popularly known as isochron diagram) the plateau steps are plotted and fitted with straight lines, whose intercepts give the non-radiogenic (or trapped) ^{40}Ar/^{36}Ar. The ^{36}Ar/^{40}Ar vs. ^{39}Ar/^{40}Ar plot (known as inverse isochron diagram) also helps in a similar manner.

3.3.2. Experimental Details

3.3.2a. Sample Preparation for Irradiation

Whole rock samples of alkaline silicates and phlogopite mineral separates from carbonatites were analyzed. For whole rocks, fresh samples were powdered in a stainless steel mortar and pestle to 100-150 µm size. About 600-700 mg aliquot of homogenized powders were used. For mineral separates (phlogopite), minerals were hand picked from whole rock powders and about 100-200 mg of pure mineral separates were taken for analysis. Whole rock powders and mineral separates were ultrasonicated with 0.05N HCl (to remove unwanted carbonates) and water several times and dried before being packed for irradiation. The 520.4±1.7 Ma old Minnesota Hornblende (MMhb-1) (Samson and Alexander, 1987) was used as a monitor.

The samples and monitor along with pure CaF_2 and K_2SO_4 were packed in aluminum foils and filled in flat-bottomed quartz vials. Two type of vials were used, one 6-7 mm diameter for rock/mineral samples and the other 2-3 mm diameter type for CaF_2, K_2SO_4 and monitor. To minimize the effect of vertical neutron flux gradient, all the samples were filled to the same height. To monitor the fluence variation, high purity Ni wire, of the same height as the sample, was placed in each vial. These vials were then sealed and packed in an aluminum reactor can. The reactor can was then sealed and sent for irradiation.

3.3.2b. Irradiation of samples

The samples were irradiated in two batches in APSARA reactor of BARC, Mubmai. APSARA is a light-water moderated reactor with total neutron flux of about 10^{12} n cm^{-2} s^{-2} with the fast neutron 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 98 and 100 hours at 1 MW power level in 19 and 22 discrete steps spreading over 19 to 22 days, respectively for two batches. The maximum and minimum duration of the irradiation in a step was 7 and 0.05 hour, respectively. The maximum neutron fluence variation as determined by ^{58}Co activity, which was generated by the same neutron reaction that produces ^{39}K, ^{58}Ni(n,p)^{58}Co, was found to be 6.0 and 5.0%, respectively in vertical and horizontal directions. The irradiated samples were allowed to cool for a few weeks to reduce the activity of the samples for safe handling. Samples were then wrapped in aluminum foils and stored in the sample holder of the extraction system.

3.3.2c. Argon Extraction and Purification

Argon extraction and purification was carried in an compact UHV furnace and purification system indigenously developed (Venkatesan et al., 1986). Fig.3.5 shows the schematic of the complete system. It essentially consists 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 gas, isolation valves and activated charcoal trap cooled at -196°C for moving gas from one part of the system to another.

The furnace consists of a molybdenum crucible electrically heated by a concentric, tantalum mesh filaments surrounded by tantalum radiation shields in a stainless steel vacuum chamber. 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 with a ± 10°C precision. 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 four valves (V_1 to V_4) and three getters, all interconnected and fitted into a single rectangular stainless steel block. The sample gas released from the crucible, first comes in contact with Ti-Zr getter connected between valves V_2 and V_3. The Ti-Zr is kept hot at around 800°C when most of the active gases will either chemically combine with or get absorbed by the getter. Further, on cooling to room temperature this getter absorbs the hydrogen present in the sample gas. Then this cleaned gas, accumulated for about 50 minutes (typical duration given for a temperature step) is allowed to react with another Ti-Zr getter and with SAES getter by opening valve V_2 for further purification. The purified gas is then adsorbed on the charcoal cooled at liquid nitrogen temperature. It is then admitted into the mass-spectrometer, after removing water vapour by passing the gas through the cold finger kept at liquid nitrogen temperature, by opening V_4. After the gas is equilibrated in the mass-spectrometer, V_4 is closed and remaining gas along with other unwanted gases adsorbed to different units are pumped by opening V_1.

In step-wise extraction (incremental heating) procedure, the samples were degassed in steps, normally nineteen steps of successively higher temperature, starting from 450°C until fusion at about 1400°C with an interval of 50°C. The K_2SO_4, CaF_2 and the monitor sample were, however, degassed in a single (1400°C) temperature step. The gas in each step was purified following the procedure described earlier and then admitted into an AEI MS10 (180° deflection, 5 cm radius) mass-spectrometer having a permanent magnet of 1.8 kilogauss. 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. The acquisition of ion currents (measured sequentially in pico amperes) was done by a computer. Peak heights and relative timing of peak measurement from the time of sample introduction (T_o), which were acquired by a "peakjump" routine, were fed to a curve-fit routine (Bevington, 1969) to compute required isotopic ratios and abundance corresponding to zero time.

Each sample was preceded and followed by several steps of system blank measurements. System-blank estimation consists of measuring the argon concentration for a particular temperature step by following the same procedure as for samples but without any sample in the crucible. 10 to 12 steps of blank measurement were normally done and blank contribution for all temperature steps were calculated by interpolation. The ^{40}Ar blank contributions to the sample gas, in the present work, varied from 0.5 to 10% of the sample-gas for temperature steps up to about 1200°C and increases up to 20% and occasionally to 30% in the fusion step. Table 3.8 gives a typical blank variation in different temperature steps for a sample.

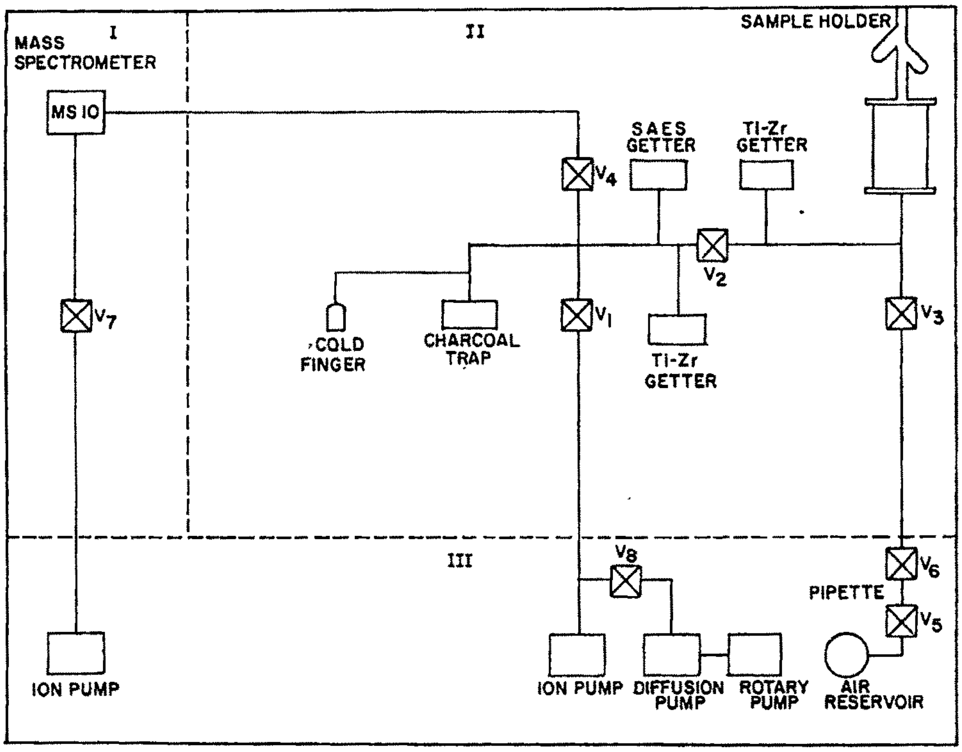

Fig. 3.5. *Schematic of the complete Argon Gas Extraction - Purification system. I = Mass Spectrometer, II = Extraction System and III = Pumping System.*

Table 3.8. Typical percentage of system blanks for sample AD-16

Temperature	^{40}Ar (%)
450	2.3
500	7.8
550	5.8
650	3.3
700	2.7
750	4.3
800	4.8
850	6.3
900	4.5
950	4.3
1000	2.5
1050	0.67
1100	1.02
1150	4.99
1200	16.56
1250	24.98
1300	26.6
1400	22.4

Mass discrimination (MD) corrections were determined based on analysis of atmospheric argon (AIR SPIKE) introduced from a pipette system connected to the extraction line. Each sample was preceded and followed by an AIR SPIKE analyses and average MD values were found out for corrections in sample ratios. Mass-spectrometer sensitivity was estimated from repeated measurements of the monitor sample (MMhb-1) and was found to be typically in the range of 0.94 - 2.58 x 10^{-7} cc STP/mv. Errors were computed by quadratically propagating the errors in the measured ratios, blanks and interfering isotopes. The error quoted on the apparent and integrated ages include the error in J but the error boxes in age spectra do not include the error in J. All the errors are quoted at 2σ level. The plateau ages are weighted means of the apparent ages of steps forming the plateaus. A plateau is defined when four of more temperature steps, representing more than 60% of the total ^{39}Ar of the sample, give constant apparent ages (within 2σ levels of error). Weighted means of apparent ages are calculated using the method of Bevington (1969) where $1/\sigma^2_i$(σ_i is the standard deviation for step i) is taken as the weight. Isochron ages have been computed using the two error regression method outlined by York (1969) of data points corresponding to the plateau steps.

3.4. STRONTIUM ISOTOPIC STUDIES

3.4.1. Principle

Rubidium (Z=37) is an alkali metal. It has two naturally occurring isotopes ^{85}Rb and ^{87}Rb of which ^{87}Rb is radioactive. ^{87}Rb decays to stable ^{87}Sr by β^- decay (decay constant = 1.42×10^{-11} y^{-1}). Strontium is an alkaline earth element and normally replaces calcium in crystal lattices. Strontium has four naturally occurring isotopes (^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr) all of which are stable. The decay scheme of ^{87}Rb to ^{87}Sr is generally used to date rocks which have remained closed to Rb and Sr since their formation. Because of the difference in the geochemical properties of Rb and Sr the Rb/Sr ratio acquires widely different values in rocks and minerals and hence, ^{87}Sr/^{86}Sr ratios also vary widely. The Sr isotopic evolution of a system gets affected by complex geological processes; however, evidence for these phenomena is normally preserved in the "initial ^{87}Sr/^{86}Sr ratio" of the system. It is this property of Rb-Sr isotope systematics which is used to understand the petrogenetic aspects of the igneous rocks.

3.4.2. Sample Preparation

Fresh samples (each about 4 or 5 kg) were cleaned and broken into small pieces using a hammer. Then these were 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 and preconditioned with a small amount of the sample to be processed. Crushed sample pieces were mixed thoroughly to ensure homogenization. Then about 300 gm coarse fraction of the each sample was selected by coning and quartering for powdering. This sample fraction was then powdered to <200 mesh size (i.e. <0.074 mm) using a TEMA swing mill and stored in a pre-cleaned and pre-conditioned polythene bottles. This fraction, which is a homogeneous representative of the whole rock sample, was used for Sr-isotopic measurements. Phlogopites were hand picked from whole rock powders for Sr-isotopic measurements. Most of the measurements were carried at our laboratory and part of the measurements were carried out at National Geophysical Research Institute, Hyderabad.

Sr-isotopic analyses were carried out for whole rock samples of alkaline silicate rocks, carbonatites, sandstones, limestones and mineral separates of phlogopite. For dissolution of silicates, about 100-150 mg of representative powder sample was taken in a 25 ml teflon beaker. Mixture of acids (6 ml HF + 2 ml HNO_3) was added in the samples and kept at 150°C in closed cap condition for 6 to 8 hours and then evaporated to dryness at ~100°C. Then a few drops of HNO_3 and 2 ml of 2.5N HCl were added to ensure complete digestion. If samples were not completely dissolved another cycle of acid treatment was given. The final solution was taken up in 2.5N HCl. Carbonatites being mixtures of carbonates, oxides and silicates needed a different dissolution procedure for complete dissolution. First a HNO_3 + HCl treatment was given to carbonatites and then to dissolve the silicates and oxide minerals HNO_3 + HF treatment was given. HF amount was decided by the amount of silicates/oxides present in a particular sample. Care was taken to avoid calcium/strontium fluoride precipitation (this was done by HNO_3 + HCl treatments). Again the final solution upon complete dissolution was taken in 2.5N HCl. The solutions were spiked with ^{87}Rb and ^{84}Sr enriched solutions for Rb and Sr concentration measurements.

3.4.3. Isotope Dilution

To measure the Rb and Sr concentrations in the sample, isotope dilution technique was followed (Long, 1966). For this, high purity ^{87}Rb and ^{84}Sr spikes were used. The isotopic ratios of the spikes are given in Table 3.9. Concentrations of the spikes were calibrated against standard solutions of normal Rb and Sr (NBS984 and NBS987). Dilute Rb and Sr solutions (concentrations about 17.59 ppm and 1.59 ppm respectively) were prepared from concentrated spike solutions for our experimental purpose. The spikes were periodically checked for concentrations to guard against evaporation losses. The spike solutions were added to sample solutions and mixed thoroughly by means of several cycles of evaporation and HCl addition.

Table 3.9. Isotopic ratios of spikes

^{87}Rb SPIKE

$^{85}Rb/^{87}Rb = 0.008$

^{84}Sr SPIKE

$^{88}Sr/^{84}Sr = 0.0009$

$^{86}Sr/^{84}Sr = 0.0011$

$^{87}Sr/^{84}Sr = 0.0002$

3.4.4. Ion Exchange Chromatography

Ion exchange chromatography was employed to separate pure Rb and Sr fractions from the sample solutions. The ion exchange columns were made from quartz tubes (I.D. = 0.8 cm) and filled with Dowex 50W X8 (200 to 400 mesh size) cation exchange resin to a height of 19 cm. Elution was done using 2.5N HCl. The columns were frequently calibrated to ensure optimum collection of Rb and Sr fractions. Sample solutions were centrifuged for about five minutes in clean 3 ml quartz centrifuge tubes and then loaded gently onto the resin bed using pipettes. The Rb and Sr fractions were collected in separate teflon beakers, evaporated to dryness. The columns were cleaned between samples with at least 200 ml of 6N HCl and 10 ml of distilled water and conditioned with 25 ml of 2.5 N HCl.

3.4.5. Mass Spectrometry

At our laboratory, Rb and Sr isotopic measurements were carried out on a 23 cm radius, 60° sector magnetic field and single focusing mass-spectrometer fabricated in-house (Trivedi et al., 1982). The mass-spectrometer is fitted with a thin lens ion source and a Faraday cup for collection of ions. The filament holder with first source slit is removable so that a new filament could be fitted with a new sample. For our study Tantalum filaments (0.030" x 0.001") of more than 99.9% purity were used. Filaments were spot welded on the sample holders and degassed in a separate vacuum system at a temperature (>1800°C) higher than the Sr ionization temperature. Dried sample was added with a drop or two of high purity phosphoric acid and loaded onto a precleaned filament using a disposable quartz pipette and evaporated. Then the filament was loaded in the source. A working pressure of $\sim 10^{-7}$ torr in the source chamber was obtained in an hour after loading a new sample. The ion acceleration potential used was usually 4500V. The filament was heated with a highly stable DC current supply. Ion currents were measured on a semi automated data acquisition system using an IBM PC. This system controls the mass-spectrometer in the peak switching mode, measures the ion currents digitally and computes the isotopic ratios. It was ensured that no cross contamination of Rb occurs in Sr separates. At National Geophysical Research Institute (NGRI), Hyderabad, Sr isotopic measurements were carried out on a VG 354 thermal ionization mass-spectrometer.

Errors in the mass spectrometric determinations of ^{87}Rb and ^{86}Sr, at our laboratory, 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/^{88}Sr ratios were corrected for mass fractionation (linear) assuming ^{86}Sr/^{87}Sr = 0.1194. The long term average of ^{87}Sr/^{86}Sr for NBS987, measured in our laboratory, is 0.71025±0.00007 (at 2σ). Typical 2σ errors in ^{87}Sr/^{86}Sr measurements of my samples were 0.0002 (for those measured at our laboratory) and 0.00004 (for those measured at NGRI).

3.5 TRACE ELEMENTAL STUDIES

Trace and rare earth elemental analyses were done by instrumental neutron-activation analysis (INAA). The samples were crushed, dried at 110°C and packed in small aluminum foils and sealed in a quartz vial. This quartz vial was then put in a container suitable for irradiation at the CIRUS reactor of the Bhabha Atomic Research Center, Bombay. The neutron flux in this reactor is $\sim 10^{13}$n cm^{-2}s^{-2}. The samples were irradiated for 15 days together with USGS basalt standard BCR-1. After the irradiation, the gamma-ray spectra of the samples were obtained using a coaxial germanium detector (148-cm^3, high purity Ge-detector having a resolution of 2.2 keV for 1333 keV gamma rays of ^{60}Co). Counting of samples and the standard was done and concentration of several trace elements including nine rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu) were measured following the standard procedures as outlined by Laul (1979).

Concentration of these elements in BCR-1 were taken from Laul (1979). Typical errors of counting (1σ) are as follows:

Elements	1σ Error (%) in BCR-1	1σ Error (%) in samples
(i) La, Ce, Sm, Eu and Tb	0.6	0.5 - 1.5
(ii) Nd, Yb, Lu, Hf and Ba	1.2	1.0 - 4.0
(iii) Gd	3.0	4.0 - 6.0
(iv) Zr and Cr	5.0	7.0 - 17.0

3.6 X-RAY DIFFRACTOMETRY

X-ray diffractometry (XRD) was done on carbonatite samples at our laboratory to find out the type of carbonates present in them. For this purpose a Philips PW1730, manually operated, X-ray diffractometer was used. CuK_α X-ray was used for my samples. A semi-quantitative calculation was performed using the peak areas of different carbonates (calcite, dolomite and ankerite) to find out their modal ratios (Cal:Dol, Cal:Ank) in the samples. This information was required for the stable isotopic measurements already discussed in Section 3.2.2.

3.7. ATOMIC ABSORPTION SPECTROPHOTOMETRY

Sr and Rb concentration in some samples were also measured by Atomic Absorption Spectrophotometry (AAS). ~0.5 g dry powder of the sample was dissolved in acid following the procedure described in section 3.4.2 and made to 25 ml in 1N HCl. Rb concentration was directly measured in this solution, whereas Sr concentration was measured after 1000 times dilution. The measurements were done in a Perkin Elmer

AAS (model 305A), following the procedures described by Sarin et al. (1979). The precision of measurements was ≤ 4 % (2σ) for both Rb and Sr. To check the accuracy of the measurements an alkaline rock sample (AD-47) was used, whose Rb and Sr concentrations (Rb=95 ppm & Sr=93 ppm) were pre-determined by isotope dilution technique and it was found that the concentrations measured by AAS (Rb=98 ppm & Sr=94 ppm) are indistinguishable from those measured by isotope dilution within 2σ level of error.