CHAPTER I

INTRODUCTION

Rocks derived from Earth's mantle and exposed on the crust allow us to learn about the mantle, its properties, physico-chemical processes occurring therein and its evolution th~~o~~rough time. Carbonatites are such mantle derived rocks. Though carbonatites represent <1% of all the magmatic rocks, they have attracted much attention because of their unusual physical and chemical properties. These are carbonate rich (>50 wt%) rocks characterized by high abundances of Sr, Ba, Zr, Nb, Th and rare-earth elements (Barker, 1996). These have been observed both in continental and oceanic plates, and occur in various types of tectonic settings. Continental carbonatites are commonly associated with alkaline (nephelinitic/kimberlitic) igneous provinces. Except the Na-rich carbonatites of Oldoinyo Lengai (an active carbonatite volcano, Tanzania), all the carbonatites of the world are Ca-rich carbonatites.

Being rich in carbonates, carbonatites are probably the best samples to study the mantle carbon inventory. Apart from this, the study of carbonatites and associated alkaline rocks can give important clues to many mantle and crustal processes such as melt extraction, recycling of crustal material, mantle metasomatism, mantle degassing, and silicate-carbonate liquid immiscibility. The present work focuses on six Mesozoic carbonatite-alkaline complexes of India. Specifically, the results obtained from stable and radioisotopic studies carried out in these complexes are presented and discussed with an aim to contribute to a better understanding of their mantle source regions and the evolution of the rocks present in these complexes through time.

1.1. CARBONATITES AND ALKALINE ROCKS

1.1.1. General Features

Carbonatites rarely occur in isolation and except a few cases, where these are associated with kimberlites (e.g., Saltpetre Kop and Premier Mine, South Africa), are almost always associated with silica-undersaturated nephelinitic rocks (LeBas, 1984). Carbonatite-alkaline complexes usually occur in continents and rarely in oceanic plates (e.g., Cape Verde and Canary Islands; LeBas, 1984) and have been observed in association with rift valleys, major faults, fold belts and plate margins (Woolley, 1989). Most of the carbonatite-alkaline complexes display oval or semicircular outline in a plan view, alkaline rocks constituting more than eighty percent of the total volume. Different lithological units in these complexes may be related either to their erosion level or their emplacement level within the crust (Santos and Clayton, 1995). Hence, carbonatite alkaline complexes may show characteristics of deep-seated plutons or subvolcanic intrusions or volcanic provinces. Fenitization of country rocks is a common feature around the carbonatites in all carbonatite complexes.

Carbonatites, by definition, are igneous rocks, which contain more than 50% by weight of carbonate minerals. If the carbonate is calcite, the rock is a calcite-carbonatite. Dolomite-carbonatite or beforsite is a carbonatite with dolomite as the major carbonate mineral. Ferrocarbonatite is essentially composed of iron-rich carbonate minerals (ankerite, siderite etc.). Natrocarbonatite, only found as an extrusive product, is composed of sodium-potassium, calcium carbonates. Carbonatites which have mixtures of different carbonate minerals are commonly named according to the established rules for quantitative composition of rocks at the 10-50-90% boundaries (Woolley and Kempe, 1989). In absence of modal analysis, chemical analysis can be used to name a carbonatite. If $[CaO] : [CaO + MgO + FeO + Fe_2O_3 + MnO]$ is greater than 0.8, then the rock is a calciocarbonatite; if it is less than 0.8 and $[MgO] > [FeO + Fe_2O_3 + MnO]$ it is a magnesiocarbonatite, but if $[MgO] < [FeO + Fe_2O_3 + MnO]$ it is a ferrocarbonatite (Woolley and Kempe, 1989).

The alkaline rocks of carbonatite complexes are generally olivine-poor nephelinites and phonolites or their plutonic equivalents. Sometimes these rocks can be very diverse in their composition in a given complex and may show effects of fenitization as a result of carbonatite emplacement.

1.1.2. Origin of Carbonatites

The origin of carbonatite-alkaline complexes is still a matter of debate. Several scenarios have been proposed to explain this. In general, these hypotheses attribute the formation of carbonatites to: (1) direct partial melting of mantle (Green and Wallace, 1988; Dalton and Wood, 1993; Sweeney, 1994); (2) fractional crystallization of carbonated silicate melts (Wyllie, 1987); or (3) carbonatite-silicate liquid immiscibility (LeBas, 1977; Kjarsgaard and Hamilton, 1989). Studies (field as well as experimental) have shown that none of the scenarios can uniquely explain the formation of carbonatites observed in nature. The hypothesis of direct melt, although explains many explaining usual properties of carbonatites, fails to explain the observed association of alkaline silicate rocks with the carbonatites. Liquid immiscibility may be the most important mechanism for the evolution of carbonatites and alkaline rocks but laboratory experiments to test this hypothesis although demonstrate ing that the carbonatite and silicate magmas are immiscible, do not necessarily prove that they are of a common parentage (Gittins, 1989).

1.1.3. Mantle Source Regions

The question regarding the nature of mantle source regions of carbonatites has been mainly addressed by the study of radiogenic isotope systematics (Rb-Sr, Sm-Nd and U-Th-Pb). As the carbonatites are highly enriched in Sr, Nd and Pb relative to the crust, the isotopic ratios involving these elements are relatively insensitive to the crustal contamination and hence the isotopic ratios must reflect those of the mantle source regions. Most isotopic studies of Sr, Nd and Pb in carbonatites younger than 200 Ma have shown that the data generally plot in the fields of ocean island basalts (OIB) in isotope correlation diagrams. (Fig.1.1 and Fig.1.2) (Bell et al., 1982; Bell and Blenkinsop, 1987; Nelson et al., 1988; Kwon et al., 1989; Tilton and Bell, 1994) and carbonatites older than 2.0 Ga show signatures of a much more depleted mantle (Barker, 1996) (Fig.1.2). In particular, Tilton and Bell (1994) showed that younger x3 carbonatites (< 200 Ma), in a plot of initial $^{87}Sr/^{86}Sr$ versus $^{206}Pb/^{204}Pb$ (Fig.1.3) fall in an array between EMI and HIMU mantle end-members reflecting the enriched nature of their source regions and older carbonatites (between 0.2 Ga and 2.0 Ga) show trends of increasing diversity and more highly radiogenic sources (Barker, 1996) (Fig.1.3). In an earlier study Bell and Blenkinsop (1987) had proposed lithospheric origin for the carbonatites and later Barreiro and Cooper (1987) proposed a metasomatized lithospheric mantle as the source region of carbonatites.

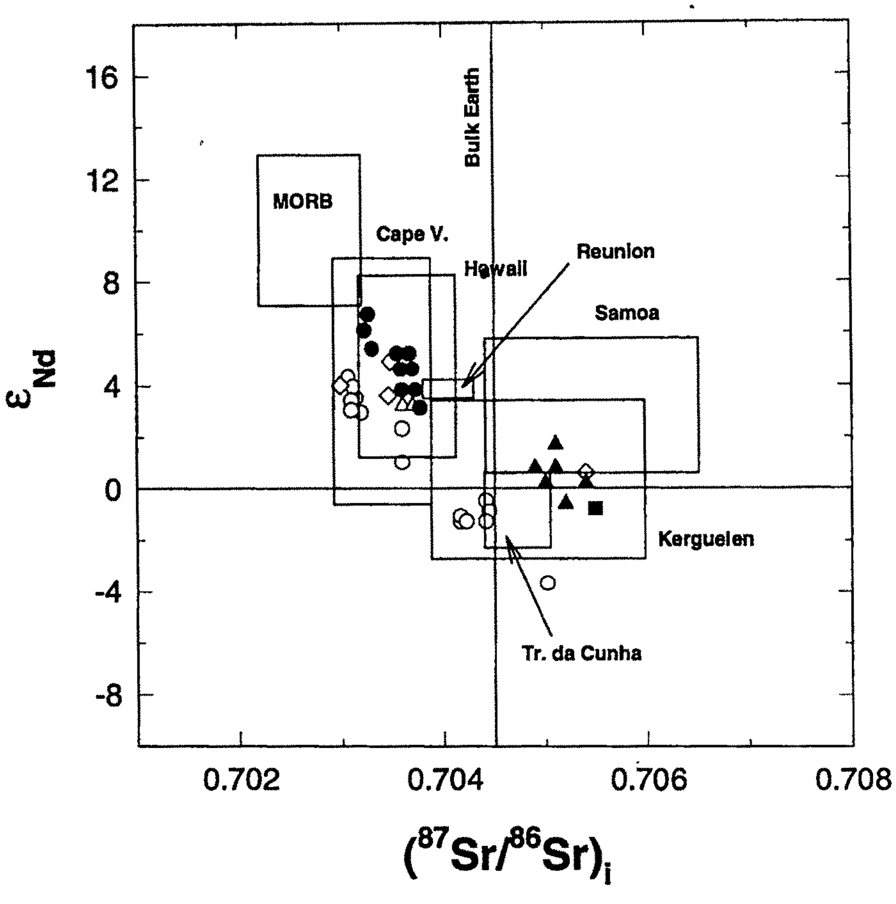

Fig. 1.1. *ε_{Nd} (T) versus initial $^{87}Sr/^{86}Sr$ for young (<200 Ma) carbonatites compared with the fields of MORB and OIBs. The ε_{Nd} (T) values were calculated using: $^{143}Nd/^{144}Nd = 0.512638$, and $^{147}Sm/^{144}Nd = 0.1967$. MORB and OIB data are from Rollinson, (1993) -a compilation. Carbonatite data are from Bell and Blenkinsop (1989) and Simonetti et al. (1995). Symbols: open circles = African carbonatites; open diamonds = Australian and New Zealandian carbonatites; open triangle = European carbonatites; filled square = Amba Dongar carbonatite, India; and filled triangle = South American carbonatites.*

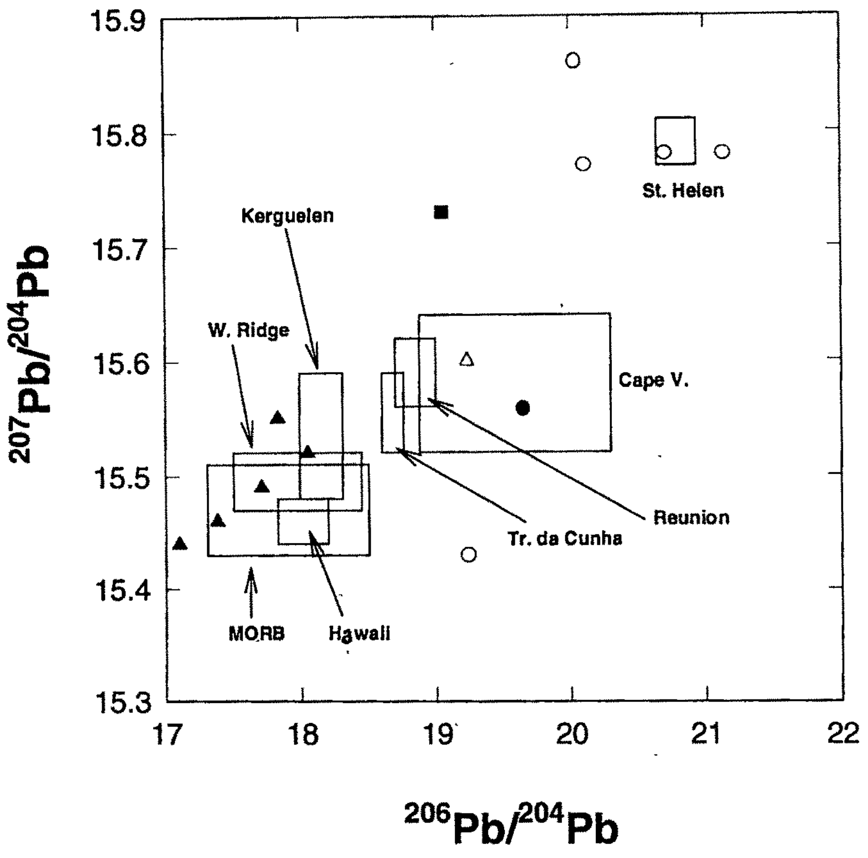

Fig. 1.2. $^{206}Pb/^{204}Pb$ - $^{207}Pb/^{204}Pb$ *correlation diagram for carbonatites with ages less than 200 Ma from different continents compared with fields of MORB and OIBs. Each datum point represents a single complex. Symbols are same as in Fig. 1.1. MORB and OIB data from Sun (1980); Richardson et al. (1982); and Rollinson (1993) -a compilation. Carbonatite data sources: Nelson et al. (1988); Toyoda et al. (1994); and Simonetti et al. (1995).*

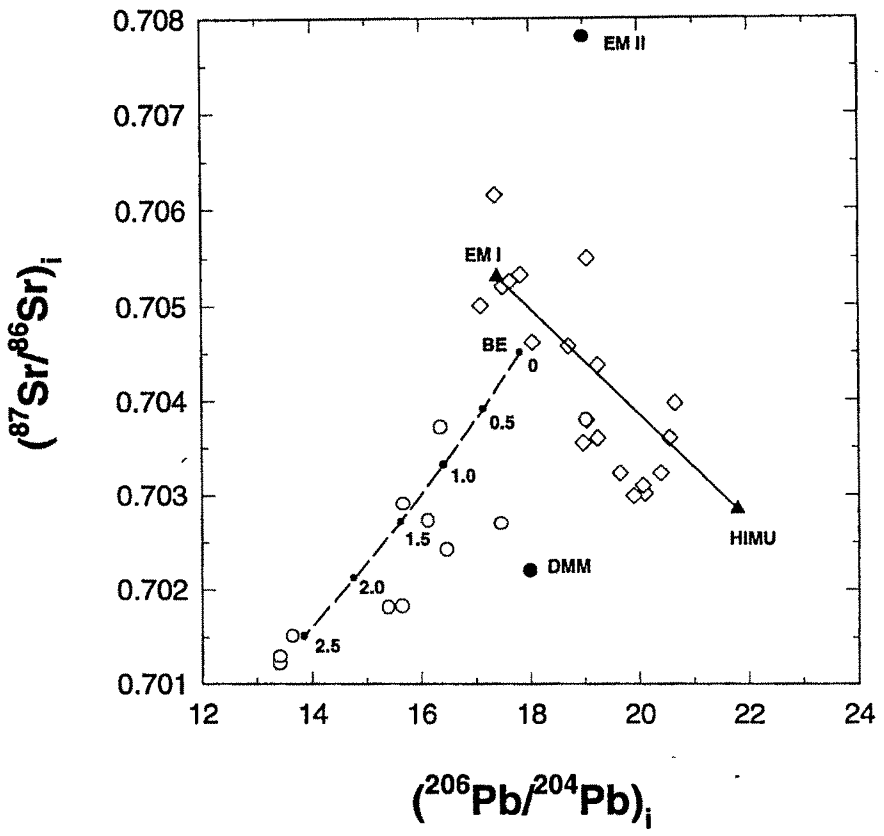

Fig. 1.3. *Initial $^{87}Sr/^{86}Sr$ versus initial $^{206}Pb/^{207}Pb$ for carbonatites plotted with different mantle-source end-members (EM I = Enriched Mantle I, EM II = Enriched Mantle II, HIMU = High μ mantle, and DMM = Depleted MORB Mantle) as defined by Hart et al. (1992). Symbols: open diamond = carbonatites with ages < 200 Ma; and open circle = carbonatites with ages between 200 Ma and 2.7 Ga. Solid curve is a hypothetical mixing curve between EM I and HIMU and dashed curve is the Bulk Earth (BE) evolution curve of Kwon et al. (1989) which is labeled with age in Ga. Data Source: Barker (1996).*

/4

However, increasing evidence from younger carbonatites, particularly from Pb isotope systematics, suggests an asthenospheric origin for these rocks (Nelson et al., 1988; Kwon et al., 1989). At this juncture, with the available data, it is difficult to decipher exactly whether carbonatites are lithospheric melts or asthenospheric melts.

Earlier it was believed that carbonatites remove the juvenile carbon that is locked inside the earth's mantle. However, more and more evidence has been accumulating that the crustal carbon is recycled into the mantle through subduction and this recycled carbon may feed the carbonatite magmas (Nelson et al., 1988; Hauri et al. 1993; Barker, 1996). The process by which mantle carbon gets incorporated into the carbonatite is not clearly understood. Stable carbon and oxygen isotopic compositions have been used to understand such processes and to characterize the source regions of carbonatite magma. The observed variation of $\delta^{13}C$ in carbonatites does not clearly indicate the involvement of recycled material in the formation of carbonatite magma (Barker, 1996). This is probably because the initial mantle isotopic signature gets modified during and after the emplacement of carbonatite magma by 'magmatic' and 'secondary alteration' processes. Barker (1996) suggests that the observed $\delta^{13}C$ variation is a result of a multi-step process involved (from subducted crust to solidified carbonatite) in the generation of carbonatite magma. However, most authors believe that with proper identification of the isotopic effects generated by different processes, one can find out the isotopic composition of the source region and the signatures (if any) of the recycled carbon.

1.2. INDIAN CARBONATITE-ALKALINE COMPLEXES

The carbonatite complexes of India have been reviewed by Sukheswala and Viladkar (1978) and Krishnamurthy (1988). These complexes (about 18 in number) occur in five distinct structural regimes (Fig. 1.4) associated with major rift systems and fold belts (Krishnamurthy, 1988). With the present chronological status, these complexes can be broadly grouped into two: (1) Precambrian carbonatites, all of which, except Newania, are present in the southern Indian Craton (Fig. 1.4); (2) Mesozoic carbonatites, which are present in the Deccan flood basalt province in the west and in the Assam-Meghalaya plateau in the east. Apart from the established carbonatite complexes (those shown in Fig. 1.4), there have been reports of small carbonatite occurrences (Ghosh Roy and Sengupta, 1993; Ramaswamy, 1996) from different parts of the country, but these have not yet been rigorously proved to be carbonatites.

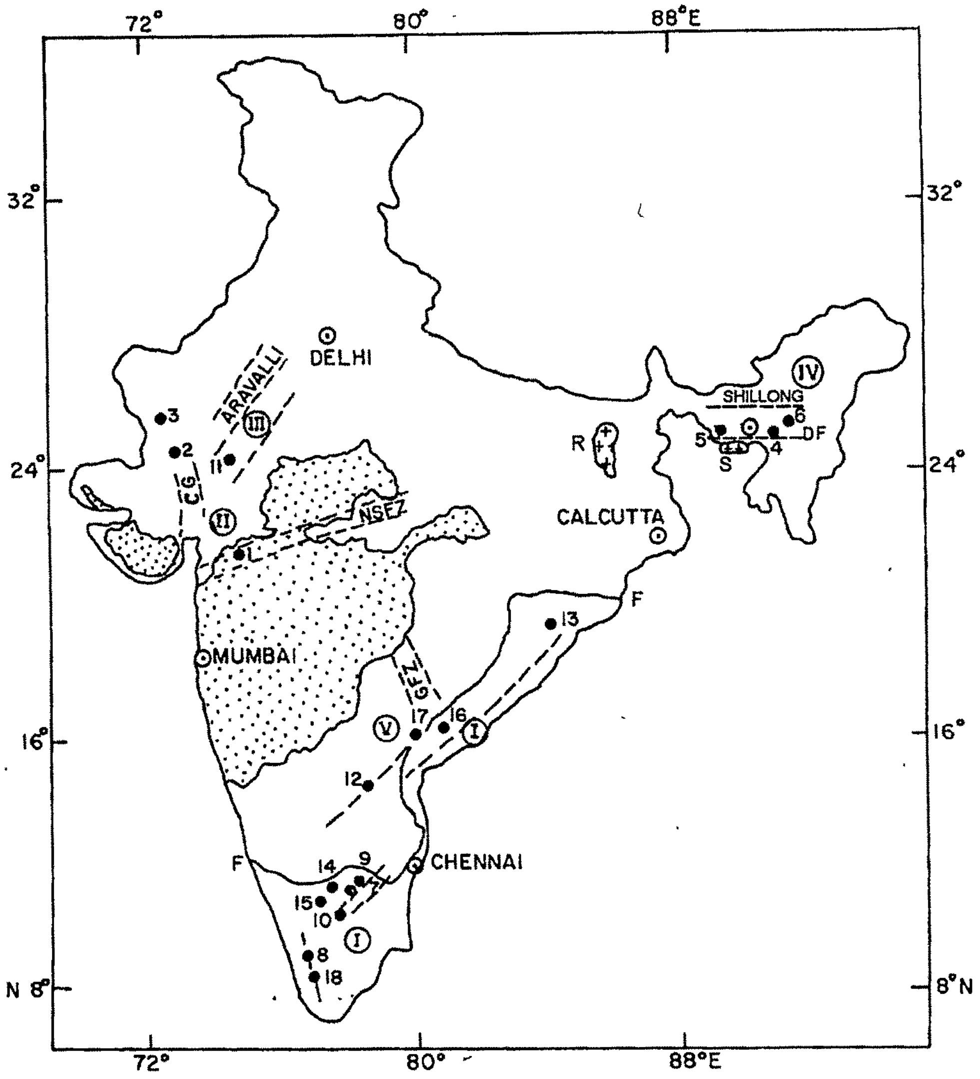

Fig. 1.4. Map of India showing the approximate locations of carbonatite-alkaline complexes (solid circles) and the extent of Deccan Traps (dotted region); Rajmahal (R) and Sylhet Traps (S) (area marked with crosses). The five structural regimes of Krishnamurthy (1988) are : (I) Eastern Ghat Belt; (II) Narmada-Son Fracture Zone (NSFZ) and Cambey Graben (CG); (III) Aravalli; (IV) Dauki Fault System (DF); and (V) Godavari Fracture Zone (GFZ). F-F : charnokite- non charnokite boundary. Carbonatite complexes are numbered in the sequence as they appear in Table 1.1. (Figure modified from Krishnamurthy, 1988).

Except Newania carbonatite of Rajasthan and Khambamettu carbonatite of Tamil Nadu, all other carbonatites of India are associated with alkaline silicate rocks. Chelima carbonatite of Andhra Pradesh is the only Indian carbonatite which is associated with Kimberlite (Sen and Rao, 1967). The nature of magmatism in Indian carbonatites varies from volcanic to plutonic. Most of the Mesozoic carbonatite alkaline complexes have volcanic to subvolcanic rock associations, whereas all the Precambrian complexes show plutonic rock associations. Calcite carbonatite is the major variety of carbonatite in all the Indian complexes except the Newania complex, where dolomite carbonatite is the major variety. Ferrocarbonatites and dolomite carbonatite are minor in many of these complexes. The nature of fenitization, like other carbonatite complexes of the world, varies from potassic to sodic depending on the depth of intrusion of these complexes. Table 1.1 gives a list of all the carbonatite complexes of India, their emplacement ages, types of carbonatite found in them, associated alkaline rocks and types of fenites observed along with the references from which these information have been taken.

Table 1.1. Indian Carbonatite Alkaline Complexes

Locality	Age (Ma)	Type of Carbonatite	Associated Alkaline Rocks	Type of fenite	References
Amba Dongar, Gujarat (1)	65[1]*	Calciocarbonatite and Ferrocarbonatite	Tinguaite, Nephelinite, and Phonolitic-Nephelinite	Sodic and Potassic	Viladkar, 1981; Srivastava, 1994
Mundwara, Rajasthan (2)	68.5[1]	Calcio-carbonatite	Pyroxenite, Alkaline Gabbro, and Syenite	Potassic	Subrahmanyam and Leelanandam, 1989, 1991; Basu et al., 1993
Sarnu-Dandali, Rajasthan (3)	68.5[1]	Calciocarbonatite and Ferrocarbonatite	Pyroxenite, Syenite, Ijolite, and Nephelinite	Sodic	Chandrasekaran et al., 1990; Basu et al., 1993

contd.

Sung Valley, Meghalaya (4)	107^{1*}	Calciocarbonatite and Magnesio-carbonatite	Alkali peridotite, Pyroxenite, Ijolite, and Uncompahgrite	Sodic and Potassic	Krishnamurthy, 1985
Swangkre, Meghalaya (5)	equivalent of Sung Valley	Calciocarbonatite	Ijolite and Lamprophyre	---	Nambiar and Golani, 1985
Samchampi, Assam (6)	,,	Calciocarbonatite, Magnesio-carbonatite	Pyroxenite, Melteigite, and Syenite	Potassic	Kumar et al., 1989
Samalpatti, Tamil Nadu (7)	700^3	Calciocarbonatite, Magnesio-carbonatite	Dunite, Pyroxenite, and Syenite	Sodic and Potassic	Moralev et al., 1975; Viladkar and Upendran, 1978
Munnar, Kerala (8)	740^2	Calciocarbonatite	Alkali granite and syenite	----	Santosh et al., 1987
Sevattur, Tamil Nadu (9)	770^2	Calciocarbonatite, Magnesio-carbonatite	Pyroxenite and Syenite	Soda-potassic	Kumar & Gopalan, 1991
Pakkanadu, Tamil Nadu (10)	771^3	Calcio-carbonatite	Dunite, Pyroxenite, and Syenite	Sodic	Moralev et al., 1975; Krishnamurthy, 1988
Newania, Rajasthan (11)	959^3	Magnesio-carbonatite and Ferrocarbonatite	None	Sodic	Deans and Powell, 1968
Chelima, Andhra Pradesh (12)	1340^2	Calcio-carbonatite	Kimberlite	----	Crawford, 1969; Sen and Rao, 1967
Borra, Andhra Pradesh (13)	1490^2	Calcio-carbonatite	Pyroxenite and Syenite	----	Raman and Viswanathan, 1977

contd.

Hogenakal, Tamil Nadu (14)	1990[2]	Calcio-carbonatite	Pyroxenite and Syenite	Sodic	Srinivasan, 1978; Natrajan et al., 1994
Kollegal, Karnataka (15)	----	Calcio-carbonatite	Pyroxenite and Syenite	----	Krishnamurthy, 1988
Kunavaram, Andhra Pradesh (16)	----	----	Syenite	----	Bose et al., 1976
Elchuru, Andra Pradesh (17)	----	----	Syenite	----	Bose et al., 1976
Khambamettu, Tamil Nadu (18)	----	Calcio-carbonatite	None	----	Balakrishanan et al., 1985

1= ^{40}Ar-^{39}Ar plateau ages; 2= Rb-Sr isochron ages; 3= K- Ar ages; and *= this work

Like many other carbonatites of the world, the origin of Indian carbonatites is also not clearly understood. In most complexes, fractional crystallization of a carbonated silicate magma or silicate-carbonate liquid immiscibility was believed to be responsible for the generation of carbonate magma (Krishnamurthy, 1988). In the case of Newania, absence of associated alkaline rocks led to the proposal of a dolomitic primary melt hypothesis for this complex (Krishnamurthy, 1988). Most of the carbonatites of Eastern Ghat mobile belt are suspected to have been affected by metamorphism, hence are not believed to bear the original magmatic signatures (Krishnamurthy, 1988).

Isotopic investigations on Indian carbonatite alkaline complexes are preliminary in nature and are available only for seven complexes; Amba Dongar (Simonetti et al., 1995), Sarnu-Dandali and Mundwara (Sarkar and Bhattacharya, 1992; Basu et al., 1993), Sung Valley (Krishna et al., 1991), Hogenakal (Natarajan et al., 1994), Sevettur (Kumar and Gopalan, 1991) and Newania (Deans and Powell, 1968). None of the above papers reports detailed study of stable carbon and oxygen isotopes in carbonatites and associated rocks. In the case of Sarnu-Dandali and Mundwara, the radioisotopic studies (Sr and He) are confined only to the alkaline rocks (Basu et al., 1993). Amba Dongar is the only complex whose Sr, Nd and Pb isotopes (only for carbonatites) have been studied in detail by Simonetti et al. (1995). Stable carbon and oxygen isotopic data from Sarnu-Dandali, Mundwara and Amba Dongar (Sarkar and Bhattacharya, 1992; Simonetti et al., 1995) essentially show magmatic nature of these carbonatites and the extreme variation of $\delta^{13}C$ and $\delta^{18}O$ observed in these complexes has been attributed to low temperature alteration processes. In a Sr-evolution diagram (Fig. 1.5; initial $^{87}Sr/^{86}Sr$ versus age plot), it can be seen that the initial $^{87}Sr/^{86}Sr$ in Indian carbonatites becomes increasingly radiogenic towards younger ages, an observation true for most carbonatites of the world in general (Nelson et al., 1988; Tilton and Bell, 1994; Barker, 1996). Two Precambrian carbonatites (Newania and Hogenakal) have lower initial $^{87}Sr/^{86}Sr$ than that of the bulk-earth, which probably suggests that these complexes were derived from depleted mantle sources. The Mesozoic carbonatites (Sung Valley, Sarnu-Dandali, Mundwara and Amba Dongar) have higher initial $^{87}Sr/^{86}Sr$ than that of the bulk earth indicating their derivation from enriched mantle sources. This observation is consistent with the hypothesis of plume origin of the complexes (Basu et al., 1993; Sen, 1995; Ghose et al., 1996), which will be discussed in detail in the next chapter. The initial $^{87}Sr/^{86}Sr$ of Sevattur complex has also been interpreted as a signature of an enriched mantle (Kumar and Gopalan, 1991). By studying Sr, Nd and Pb isotope systematics of Amba Dongar carbonatites Simonetti et al. (1995) suggested an LREE enriched mantle source for this complex (possibly an EMII type of mantle) and speculated that probably this complex was genetically related to the Reunion-Deccan plume, which was responsible for Deccan flood basalt eruption. In a preliminary study of Sr-Nd-Pb isotopes in Sung valley carbonatites, Krishna et al., (1991) found signatures of DUPAL anomaly in carbonatites, a property of present day Indian Ocean OIBs. This possibly indicates a OIB source derivation for this complex.

3 ?

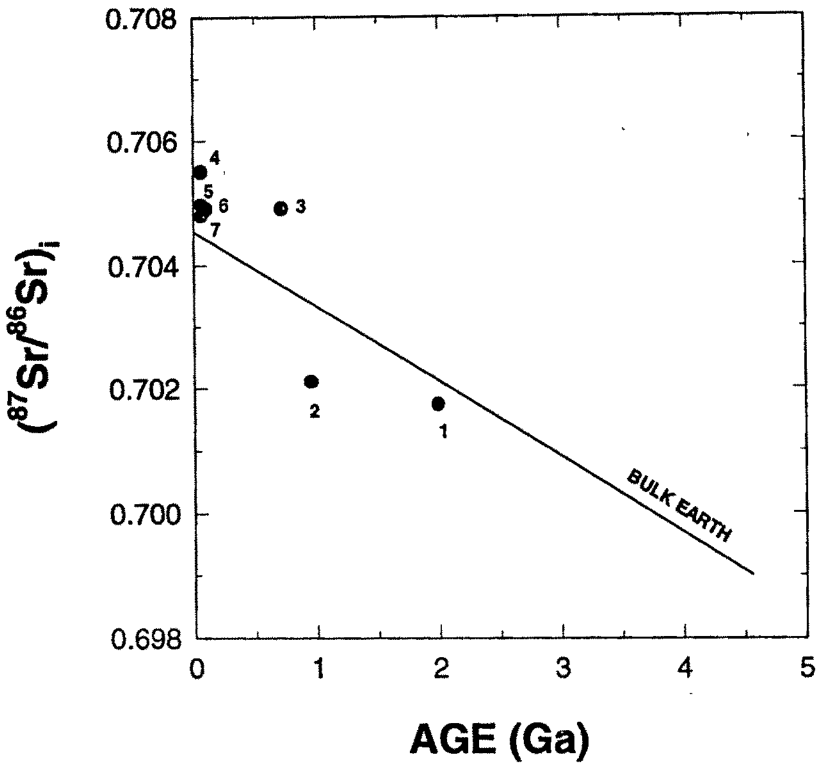

Fig. 1.5. Plot of minimum initial $^{87}Sr/^{86}Sr$ versus age for Indian carbonatites. 1 = Hogenakal, Natarajan et al. (1994); 2 = Newania, Deans and Powell (1968); 3 = Sevattur, Kumar and Gopalan (1991); 4 = Amba Dongar, Simonetti et al. (1995); 5 = Sarnu-Dandali and 6 = Mundwara, Basu et al. (1993); and 7 = Sung Valley, this study. Straight line is Bulk-Earth evolution line from Bell and Blenkinsop (1989).

1.3. PURPOSE OF THIS STUDY

In the geologic history of India, the Cretaceous period had remained eventful. In the Early Cretaceous India got separated from Australia and Antarctica with the initiation of Kerguelen hot spot, which generated Rajmahal Traps in eastern India. Towards the end of Cretaceous, Reunion hot spot got activated and generated the voluminous flood basalts of Deccan. Deccan and Rajmahal Traps are major constituents of two Large Igneous Provinces (LIP), which also include numerous minor acidic, alkaline and carbonatitic igneous complexes (Coffin and Eldholm, 1994). The Mesozoic carbonatite-alkaline complexes of India, which are present in these LIPs, are also hypothesized to have been generated by Kerguelen-Rajmahal and Reunion-Deccan plumes (Kent et al., 1992; Basu et al., 1993; Sen, 1995). This hypothesis of plume origin makes the study of the Mesozoic carbonatite complexes very important. I took up the study of six of these complexes (Amba Dongar, Mundwara and Sarnu-Dandali of Deccan Province and Sung Valley, Samchampi and Swangkre of Assam-Meghalaya Plateau).

In an attempt to characterize the source regions of the carbonatite alkaline complexes and to understand the origin and evolution of these, I used different tracers such as stable carbon and oxygen isotopes, strontium isotopes and trace elements. To find out the emplacement age of some of the complexes, I used ^{40}Ar-^{39}Ar method of dating. The main objectives of this work were to:

1. Establish the temporal relationship of these complexes with the plume originated Deccan and Rajmahal flood basalts.
2. Characterize the source regions on the basis of stable carbon and oxygen and strontium isotopes and confirm the hypothesized link between the Reunion and Kerguelen hotspots and the generation of these complexes.
3. Assess the role of different magmatic processes like partial melting, liquid immiscibility, crustal contamination and fractional crystallization in the generation of these complexes.
4. Distinguish primary (magmatic) and secondary stable carbon and oxygen isotopic variations in carbonatites by theoretically modelling them and apply these models to the observed data from Indian complexes in order to test the models and to understand the isotopic evolution of these complexes.

From the experimental point of view, analysis of C and O isotopes in the various carbonate constituents of carbonatites was difficult (as physical separation was almost impossible). In order to make this possible, I developed an appropriate experimental procedure by which CO_2 from different carbonate minerals could be chemically separated without significant mixing.

For this work, three major field trips to the study areas were undertaken and samples of carbonatites, alkaline rocks, metasomatic rocks and country rocks were collected, details of which are given in Chapter-III.

1.4. OUTLINE OF THE THESIS

This thesis is divided into five chapters. Chapter-I gives an introduction to carbonatites and a brief discussion about their origin and the nature of their mantle source regions, based on earlier studies. It also introduces the carbonatite-alkaline complexes of India. The objectives and the outline of the thesis are also given in this chapter. Chapter-II gives an overview of the geology of Mesozoic carbonatite-alkaline complexes of India on which the present work is based. It also briefly reviews the existing studies on these complexes. Chapter-III describes the experimental techniques used to study the isotopic ratios and trace elemental abundances in samples of carbonatites, alkaline rocks and other country rocks from the above mentioned complexes. These techniques include stable carbon and oxygen isotope analysis; strontium isotope ratio measurements by thermal ionization mass spectrometry (TIMS) ^{40}Ar-^{39}Ar dating technique; and trace elemental abundance measurements by instrumental neutron activation analysis (INAA). In this chapter the step-wise CO_2 extraction procedures developed for carbonate mixtures are also discussed. Following these procedures CO_2 from pure carbonate end-members was collected for C and O isotope ratio determinations. In Chapter-IV, I present and discuss the results of this work. Finally in Chapter-V, I summarize the ideas developed, from the present work, on the formation and evolution of carbonatites in general and the Mesozoic carbonatite-alkaline complexes of India in particular.