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Stable Carbon and Oxygen Isotopic Compositions of Indian Carbonatites

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Abstract

Stable carbon and oxygen isotopic compositions of carbonatites are results of fractionation caused by various magmatic and post-magmatic processes during their generation and evolution. In the present work, we review available stable isotopic data from Indian carbonatites that span in age from Precambrian to Cretaceous. We explain the observed variations using various theoretical models and attempt to decipher the nature and temporal evolution of the mantle source(s) of these carbonatites. As observed elsewhere, $\delta^{18}O$ variations are larger compared to those of $\delta^{13}C$. However, the average and mode of $\delta^{13}C$ distributions in Indian carbonatites (~–4 ‰) are clearly higher than the global average. In general, $\delta^{13}C$ and $\delta^{18}O$ variations of Indian carbonatites can be grouped into (1) primary, unaltered carbonatites and (2) secondary, altered carbonatites. Primary variations are results of either batch crystallization under plutonic conditions, as observed in Hogenakal and northeastern Indian carbonatites, or fractional crystallization from CO_2+H_2O fluid-rich parent magmas, as observed in the rest. Secondary isotopic variations in all the carbonatites are apparently results of low temperature alteration by either meteoric water or CO_2-bearing aqueous fluids. Estimated $\delta^{18}O$ values of the mantle sources of Indian carbonatites (5.3–7.5‰) show the expected normal mantle signatures, but $\delta^{13}C$ values appear to be more variable (–6 to –3.1‰) than expected for a normal mantle. The younger carbonatites (<107 Ma) in particular appear to have been derived from ^{13}C enriched sources. Combined study of $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ data suggests that Indian carbonatites were derived from enriched mantle sources, and the enrichment probably took place some time in the Archean (~2.4 Ga). We suggest that the Indian sub-continental mantle, which was metasomatized by fluids from subducted oceanic crusts around that time, has remained a continuous source of carbonatites.

Introduction

CARBONATITES ARE derived from unique mantle melts that contain much higher amounts of elemental carbon (> 10%) compared to their source regions, where carbon is a trace element (< 500 ppm). Radiogenic isotopes, stable isotopes, noble gas isotopes, and phase equilibrium studies on various carbonatites clearly indicate that the mantle is the ultimate source of carbonatites. Being one of the largest extractors of carbon from the mantle, carbonatites hold keys to our understanding of the nature of mantle carbon and the long-term global carbon cycle. By definition, carbonatites are igneous rocks containing more than 50% carbonate minerals such as calcite, dolomite, ankerite, and siderite (Woolley and Kempe, 1989). Because of extremely low viscosity (e.g., Dobson et al., 1996) and short residence time in the crust (Pyle et al., 1991) carbonate magmas are likely to pass through the crust without significant contamination. In addition, very high contents of most of the incompatible trace elements, which are used as tracers in mantle studies, in these magmas tend to buffer any such contamination. These aspects clearly help carbonatites preserve mantle characteristics better than any other mantle-derived rock.

Carbonatites occur in both continental and oceanic settings, but are found mostly in the former, and hence provide useful information about the less-understood subcontinental mantle. Even though they are volumetrically minor, because of their widespread spatial and temporal distribution, they provide valuable information about the secular evolution of the subcontinental mantle on the whole-Earth scale. The observation that many carbonatites are associated with continental flood basalts (CFBs), the product of deep mantle plumes, has recently been considered seriously (e.g., Ray and Pande, 1999). Although we do not have a clear picture as to the cause for such associations, evidence is growing

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in favor of a plume origin for carbonatites (e.g., Bell and Tilton, 2002). The hypothesis of plume origin for carbonatites has gained favor mainly from observations that most carbonatites: (1) present within CFB provinces are temporally related to the flood basalts (Ray and Pande, 1999); (2) have isotopic ratios for Nd, Sr, and Pb similar to that of the Oceanic Island Basalts (e.g., Nelson et al., 1988); (3) show lower (un-degassed) mantle noble gas isotope signatures (Sasada et al., 1997; Tolstikhin et al., 2002); and (4) have a HIMU component, which is usually found in plume-derived melts (Bell and Tilton, 2002). However, opponents of the plume origin advocate a shallower mantle source because: (1) many carbonatites have a continental lithospheric component; (2) there has been repetition of carbonatite-alkaline magmatism in a given complex over time (Woolley, 1989); and (3) most importantly, generation of carbonatites requires melting of a carbonated mantle that would require a cooler than plume environment (Bailey and Woolley, 1995). Other important aspects of carbonatite magmatism that have not been fully understood include, nature and source of carbon (primordial versus recycled) and nature of origin of magma (primary melt versus magmatic differentiation).

Study of stable carbon and oxygen isotopic compositions has remained one of the valuable means for tracking carbonatite evolutionary pathways and deciphering the nature of inherited carbon. Most of the stable isotope work in these rocks has been confined to carbonate minerals for analytical convenience. For carbon isotopic compositions, these minerals obviously represent the whole rock; however, oxygen isotopic composition of the whole rock is dependent on the amount of silicate, phosphate, and oxide minerals apart from carbonates. Carbonatites occur as intrusive or extrusive rocks, and are formed by crystallization of carbonatite magmas. The C and O isotopic compositions of the primary magmas are modified during carbonatite formation, depending on the nature (batch vs. fractional) and temperature of crystallization. Being a major carrier of mantle fluids (CO_2 and H_2O), these magmas owe a fraction of the isotopic compositions of their end products to fluid activities (Ray and Ramesh, 1999a). In addition to primary (magmatic) processes, post-magmatic fluid-rock interactions also greatly modify the primary signatures. Therefore, to understand the mantle sources for carbonatites, it is imperative to model various primary and secondary processes, which shape the isotopic compositions.

Stable isotopic variations in carbonatites were first reviewed by Deines (1989). Since then an appreciable amount of isotopic data has been generated from many carbonatite complexes worldwide, and new models have been proposed to explain the observed variations (e.g., Santos and Clayton, 1995; Demény et al., 1998; Ray and Ramesh, 1999a, 2000). The fractionation behavior of C and O between various phases involved during the carbonatite generation and evolution and different crystallizing phases within the carbonatites is now better understood (e.g., Mattey et al., 1990; Scheele and Hoefs, 1992; Zheng, 1996, 1999; Haynes et al., 2003). We believe, at this juncture, that there is a need to assess our understanding of carbonatite evolution in terms of its stable isotopic composition. Toward this end, we evaluate the existing stable carbon and oxygen isotopic data on Indian carbonatites that range in age from Precambrian (~2400 Ma) to latest Cretaceous (~65 Ma), to decipher the processes involved in their formation and evolution, and characterize their mantle sources and evolution through time.

Geology and Geochemistry of Indian Carbonatites

Age of Indian carbonatites

Carbonatite in India was first discovered by Sukheswala and Udas (1963). Ever since, more than 20 major complexes have been identified (Krishnamurthy et al., 2000). However, many of them have not been well studied in terms of their geochemistry and geochronology. Based on their location in the subcontinent we have grouped them into southern Indian, northeastern Indian, and western Indian carbonatites. Figure 1 shows the locations of these carbonatites and their association with major fracture zones and CFB provinces (Deccan and Rajmahal-Sylhet). Based on the currently available chronological status (Table 1), these complexes can also be broadly divided into three similar groups. The southern Indian complexes are Precambrian (2400–700 Ma), the northeastern complexes were emplaced during the Early Cretaceous (107–105 Ma), and the western Indian complexes except for Newania were intruded during the Late Cretaceous (68–65 Ma). The Newania complex of Rajasthan (Fig. 1) shows repeated carbonatite activity with two identified pulses at 2270 Ma and 1550 Ma (Schleicher et al., 1997), and therefore is included with the group of Precambrian carbonatites. Table 1

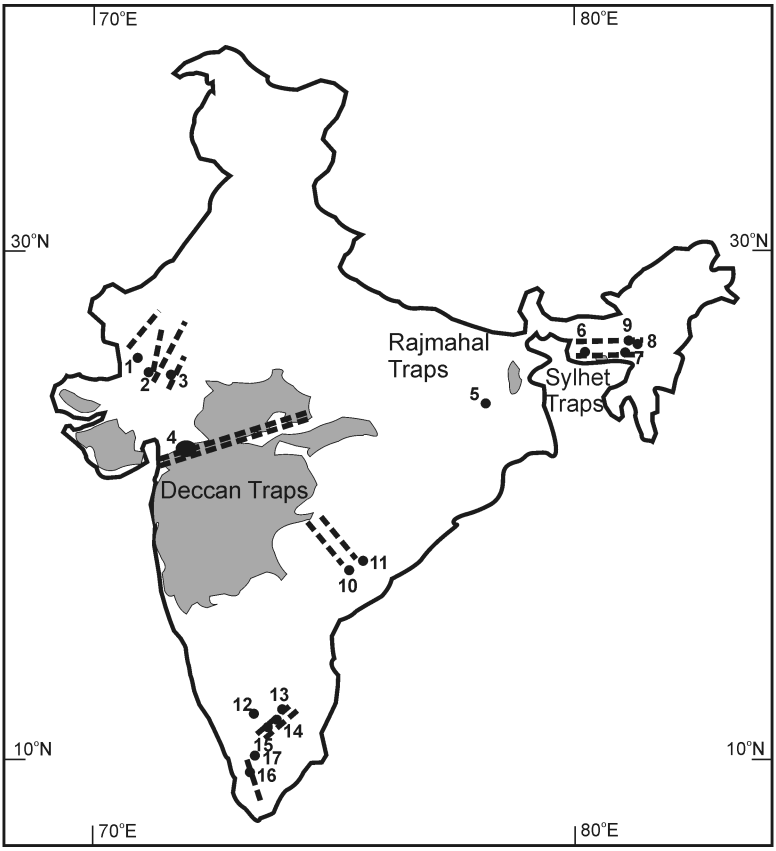

FIG. 1. Schematic map of India (modified from Krishnamurthy et al., 2000), showing continental flood basalt provinces (grey shading) and carbonatite complexes (numbered). Also shown are the fracture zones (dashed lines) in which the carbonatites occur. Complexes: 1 = Sarnu-Dandali; 2 = Mundwara; 3 = Newania; 4 = Chhota Udaipur (Amba Dongar-Siriwasan); 5 = Kutni-Beldih; 6 = Swangkre; 7 = Sung Valley; 8 = Jasra; 9 = Samchampi; 10 = Elchuru; 11 = Kunavaram; 12 = Hogenakal; 13 = Sevattur; 14 = Samalpatti; 15 = Pakkanadu-Malakkadu; 16 = Munnar; 17 = Khambamettu.

presents a compilation of available age data for Indian carbonatites showing the methods used, rocks/minerals dated, and appropriate references. It can be seen that the most reliable data (with least errors) are those dated by the ^{40}Ar-^{39}Ar method, using minerals from either carbonatites or coexisting alkaline silicate rocks. In the latter case, it is usually assumed that the alkaline silicate rocks are coeval/cogenetic with the carbonatites. As we shall see in our subsequent discussion, in most complexes such an assumption is valid.

Geology

The geology of these complexes has been discussed at length by Krishnamurthy (1988), Srivastava and Taylor (1996), and Viladkar (1998, 2001). Here we discuss only the relevant geological and geochemical findings and their bearing on the origin and evolution of these complexes. As regards to the general geology of various complexes studied in this work, we have compiled data from the literature. Table 2 gives a brief description of these complexes by listing the modes of intrusion, the host rocks into which they have been intruded, the type of carbonatite, the alkaline silicate rocks coexisting with the carbonatites, and the type of metasomatism (fenitization) caused by carbonatite activity in the region.

Southern Indian carbonatites. Southern Indian carbonatites studied here (Hogenakal, Sevattur, Samalpatti, Jogipatti, and Pakkandau) are concentrated in a narrow belt along a NNE-trending fault

TABLE 1. Summary of Available Age Data on Indian Carbonatites

Complex	Age (Ma) ± 2	Method	Reference	Remarks
Sarnu-Dandali	68.57 ± 0.08	^{40}Ar-^{39}Ar (biotite from pyroxenite)	Basu et al., 1993	
Mundwara	68.53 ± 0.16	^{40}Ar-^{39}Ar	Basu et al., 1993	
Newania	 (a) 2273 ± 13 (b) 1551 ± 46	Pb-Pb isochron (a) Dolomite carbonatite (b) Ankerite carbonatite	Schleicher et al., 1997	MSWD on these ages are 18 and 22, respectively.
Chhota Udaipur Complexes	65.0 ± 0.3	^{40}Ar-^{39}Ar (phlogopite from carbonatite and three WR alkaline rocks)	Ray and Pande, 1999	
Swangkre	107 ± 4	Fission track in apatites from carbonatite	Acharya et al., 1986	Quoted age:[1] 107 Ma
Sung Valley	(a) 107.2 ± 0.8 (b) 106 ± 11	(a) ^{40}Ar-^{39}Ar (phlogopite from carbonatite and a WR pyroxenite) (b) Rb-Sr isochron (carbonatite and pyroxenite WR and phlogopite from carbonatite)	(a) Ray et al., 1999 (b) Ray et al., 2000	Quoted age:[1] 107 Ma
Jasra	105.2 ± 0.5	U-Pb zircon/baddeleyite	Heaman et al., 2002	
Samchampi	~105	K-Ar of lamprophyres	Sarkar et al., 1996	
Hogenakal	2436 ± 154	Sm-Nd isochron WR (3 sovites + 2 pyroxenites)	Kumar et al., 1998	Quoted age:[1] 2410 Ma Average of all reliable dates
Sevattur	(a) 767 ± 8 (b) 801 ± 11 (c) 756 ± 11	(a) Rb-Sr isochron (syenites) (b) Pb-Pb isochron (ankerite carbonatite) (c) Rb-Sr isochron (syenite+pyroxenite)	(a) Kumar et al., 1998 (b) Schleicher et al., 1997 (c) Miyazaki et al., 2000	Quoted age:[1] 770 Ma Average of all reliable dates
Samalpatii	Equivalent of Jogipatti and Sevattur (?)	Age of Jogipatti 700 ± 30 Ma ; dated by K-Ar of phlogopite; Moralev et al., 1975		An age of 700 Ma has been assumed
Pakkanadu	(a) 771 ± 2 (b) 599 ± 30	K-Ar of phlogopites from carbonatite	Moralev et al., 1975	Not very reliable; an age of 700 Ma has been assumed

[1] Age used by the authors of the original contributions.

TABLE 2. Geology of Indian Carbonatite Complexes studied in this work[1]

Complex	Occurrence	Host/country rocks	Main carbonatite type	Association	Fenitization	References
Sarnu-Dandali	Dikes and veins (subvolcanic)	Malani rhyolites and Cretaceous sandstone	Calcite carbonatite	Pryroxenite, ijolite, syenite, and nephelinite	Sodic	Chandrasekaran et al., 1990; Basu et al., 1993
Mundwara	Dikes and veins (subvolcanic)	Erinpura Granite	Calcite carbonatite	Pyroxenite, melteigite, theralite, and syenite	Potassic	Le Bas & Srivastava, 1989; Basu et al., 1993
Newania	Pluton (plutonic)	Untala granite gneiss	Dolomite carbonatite and ankerite carbonatite	None	Sodic	Schleicher et al., 1997; Viladkar, 1998
Chhota Udaipur Complexes	Diatreme, flows, sills, dikes, and plugs (subvolcanic/volc.)	Deccan tholeiites and infratrappean sandstone and limestone.	Calcite carbonatite and ankerite carbonatite	Nephelinite and phonolite	Potassic and sodic	Viladkar, 1996; Ray et al., 2000
Swangkre	Dikes	Archean gneisses	Calcite carbonatite	Lamprophyre and ijolite	Not reported	Kumar et al., 1996
Sung Valley	Stock (plutonic-subvol.)	Shillong group metasediments	Calcite carbonatite, dolomite carbonatite, and phoscorite	Peridotite, pyroxenite, ijolite, syenite, melilite-bearing rocks	Sodic and potassic	Kumar et al., 1998; Veena et al., 1998; Ray et al., 1999
Sampchampi	Stock (plutonic-subvol.)	Archean gneisses	Calcite carbonatite	Pyroxenite, ijolite, nepheline syenite	Sodic and potassic	Kumar et al., 1998; Ray et al., 1999
Hogenakal	Lensoid bodies (plutonic)	Arhean charnokite gneisses	Calcite carbonatite	Pyroxenite and syenite	Not reported	Kumar et al., 1998; Pandit et al., 2002
Sevattur	Arcuate bodies (plutonic)	Granite gneisses	Calcite carbonatite	Pyroxenite and syenite	Sodic and potassic	Kumar et al., 1998; Miyazaki et al., 2000; Pandit et al., 2002
Samalpatti	Lenses and dikes (plutonic-subvol.)	Hornblende-epidote gneiss	Calcite carbonatite	Dunite, pyroxenite, and syenite	Sodic and potassic	Schleicher at al., 1998; Pandit et al., 2002
Pakkanadu	Fracture fills	Charnokite gneisses	Calcite carbonatite	Pyroxenite and syenite	Sodic	Pandit et al., 2002

[1] In the same sequence as in Figure 1.

system (Kumar et al., 1998). All occur within a few tens of km from each other. These carbonatites are plutonic and have pyroxenite and syenite as the chief alkaline silicate rock association. Calcite carbonatite is the main carbonatite type in all the complexes except Sevattur, where dolomite carbonatites dominate. Mineralogically, calcite and dolomite dominate the carbonate phases, whereas major accessories include apatite, pyroxene, phlogopite, and magnetite with traces of allanite, hornblende, and other exotic minerals found in carbonatites (e.g., Pandit et al., 2002). Carbonatites in most of the complexes carry xenoliths from the basement rocks, clearly pointing toward their magmatic nature (e.g., Pandit et al., 2002). Geochemical data suggest that a majority of these carbonatites are highly enriched in light rare earth elements (LREE) (e.g., Schleicher et al., 1998; Pandit et al., 2002) and bear no imprint of any metamorphic event subsequent to their crystallization (e.g., Kumar et al., 1998). Identical ages and overlapping initial radiogenic isotopic ratios of carbonatites and coexisting alkaline silicate rocks bear testimony to their cogenesis (e.g., Kumar et al., 1998; Schleicher et al., 1998). The majority of Sr and Nd initial isotopic ratio data for these carbonatites suggests their derivation from large ion lithophile element (LILE)–enriched mantle sources similar to enriched mantle-I (EM-I) (e.g., Schleicher et al., 1998; Pandit et al., 2002).

Kumar et al. (1998) envisaged a single enriched subcontinental mantle remaining a continued source for these carbonatite for ~1800 m.y. underneath the south Indian craton. On the contrary, the Pb isotopic ratios define an array, suggesting a possible mixing between a depleted mantle and a U-enriched component (crust/enriched source) involved in the generation of these carbonatites (Schleicher et al., 1998). Pandit et al. (2002) offered a different explanation for the origin of these complexes by suggesting a depleted mantle for the ~2.4 Ga old Hogenakal carbonatite and subsequent enrichment of its mantle source prior to the generation of other Neoproterozoic (~800 Ma old) carbonatites from the same source. Although enriched mantle sources have been invoked, none of the authors has explicitly suggested plume origin for these complexes. A recent noble gas isotope study (Basu and Murthy, 2003) found dominance of upper mantle volatiles, and thereby suggested little involvement of mantle plume(s) in the generation of southern Indian carbonatites.

Northeastern Indian carbonatites. Northeastern Indian carbonatites (Swangkre, Sung Valley, Jasra, and Samchampi; Fig. 1) intrude into Archean basement gneisses, schists, and metasediments of the Proterozoic Shillong Group. They occur in a horst-like feature called the Assam-Meghalay Plateau that is bound by two major fractures. These Early Cretaceous complexes are believed to be a part of the Rajmahal-Sylhet CFB province (Ray et al., 1999). Three of these complexes have been well dated (Table 1); the ages suggest synchroneity of these carbonatites (107–105 ± 2 Ma) with the flood basalts (116.0 ± 3.5 Ma; Ray et al., 2005) of the region. Although separated by considerable distances, these complexes show many petrological and geochemical similarities (Ray et al., 1999). Carbonatites in these complexes are mainly calcitic in nature, but dolomite carbonatites are not uncommon. Apart from calcite and dolomite, the carbonatites contain apatite, magnetite, olivine, phlogopite, and other typical minerals of carbonatites (Ray, 1997; Nag et al., 1999). Because of identical ages, overlapping $^{87}Sr/^{86}Sr$ initial ratios (Ray et al., 1999, 2000) and other petrological considerations (Nag et al., 1999), the coexisting carbonatites and alkaline silicate rocks in these complexes have been considered to be genetically related.

Based on $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, and $^{206}Pb/^{204}Pb$ isotopic ratios of these complexes, it has been suggested that their mantle sources show plume signatures and could be a mixture of EM-I and HIMU type mantle components (Veena et al., 1998; Ray et al., 2000; Veena, 2000). The latter feature is a general observation in young (< 200 Ma) carbonatites worldwide (Tilton and Bell, 1994). Based on geochronology and isotopic studies, various workers have suggested that probably the source of Rajmahal-Sylhet-Bengal CFB, the Kerguelen plume (e.g., Kent et al., 2002), was also responsible for the generation of these complexes (e.g., Ray et al., 2000). Noble gas and nitrogen isotopic compositions of Sung Valley apatites and carbonates bear signatures of lower mantle and recycled crust (Basu and Murty, 2003) that favors the plume hypothesis.

Western Indian carbonatites. Western Indian carbonatites are by far the most well studied carbonatites in India because of their spatial and temporal (for some) proximity to the Deccan CFB province (Fig. 1, Table 1). These represent wide-ranging carbonatite intrusions/extrusions associated with major pre-existing fracture zones. The oldest of these complexes, the Newania carbonatites, is a rare example in the world of primary dolomite carbonatite. The repeated carbonatite activity in Newania (Schleicher et al., 1997) is an indication of continuous supply of carbonate melt from a single mantle source, and therefore can be used as evidence against the plume origin of carbonatites. Another unique feature of Newania is that it is devoid of alkaline silicate rocks. Sr and Pb isotope studies, although inadequate, advocate an enriched mantle source for Newania (e.g., Deans and Powell, 1968; Schleicher et al., 1997). The other two complexes that occur in close proximity of Newania are 68.5 Ma in age (Fig 1., Table 1) and are dominated by alkaline silicate magmatism (pyroxenite, gabbro, syenite, etc.) with carbonatite representing a very minor fraction. These two volcanic centers are believed to be the earliest manifestations of the Deccan volcanism, and the $^{3}He/^{4}He$, $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios in these complexes clearly point to a lower mantle plume origin (Basu et al., 1993). Carbonate-silicate melt-immiscibility or fractional crystallization of a carbonate silicate melt is believed to have played a role in the generation of the coexisting alkaline silicate and carbonatites in these complexes (e.g., Shastry and Kumar, 1996; Ray, 1997).

Other important western Indian, Late Cretaceous carbonatites are exposed along the most conspicuous fracture zone, the Narmada-Son Fracture Zone, and form a major alkaline center around Chhota Udaipur (Fig. 1). Of the four alkaline and alkaline-carbonatite complexes of this center, Amba Dongar is the largest and the best studied in terms of geology, isotope geochemistry, and geochronology (Viladkar, 1996; Ray et al., 2000; Ray et al., 2003 and references therein). The importance of the carbonatites of the Chhota Udaipur subprovince lies in the following: (1) they represent a widespread carbonatite-alkaline activity covering an area of 1200 km^2; (2) Amba Dongar is one of the best examples of carbonatite ring dike complex (possibly a diatreme); (3) emplacement of these complexes took place at the Cretaceous/Tertiary boundary (65 Ma; Ray and Pande, 1999) toward the end of the Deccan CFB activity; (4) radiogenic isotopic ratios and trace elemental variations of carbonatites and alkaline silicate rocks suggest a genetic link between them, possibly by melt-immiscibility (Ray, 1998) and that an enriched mantle source (different from that of the Deccan tholeiites) was involved in their generation (Simonetti et al., 1995); (5) noble gas and nitrogen isotopic compositions of Amba Dongar carbonatites show signatures of lower mantle, thus confirming the involvement of a deep mantle plume in their generation (Basu and Murty, 2003); (6) the Amba Dongar complex contains one of the largest carbonatite-related fluorspar ore deposits of the world.

Overview of Available Stable Isotope Data

Sarkar et al. (1985) reported preliminary data of stable isotopic compositions of some Indian carbonatites, and they republished the same data again in 1992 (Sarkar and Bhattacharya, 1992). After a long gap, another small volume of new data appeared (Gwalani et al., 1993; Ray et al., 1994; Simonetti et al., 1995). Subsequently Srivastava and Taylor (1996) published a major volume of data from several Indian carbonatites. Since then numerous publications have appeared with high quality data from all major carbonatite complexes of India (e.g., Viladkar, 1998; Ray and Ramesh, 1999a; Ray et al., 1999; Viladkar and Schidlowski, 2000; Miyazaki et al., 2000). Carbon and oxygen isotopic compositions of carbonates from carbonatites in these works and in the present review are reported in standard delta notations as per mil deviations from a reference standard:

$$\delta^{13}C_{PDB} = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{PDB}} - 1\right] \times 10^{3}, \text{ and}$$

$$\delta^{18}O_{SMOW} = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{SMOW}} - 1\right] \times 10^{3}.$$

where PDB and SMOW are international standards, and stand for the Pee Dee belemnite and standard mean ocean water, respectively. Except for a few, all studies essentially report isotopic compositions of calcites from carbonatites, because the isotopic analyses have been performed using standard CO_2 extraction techniques by reacting samples with anhydrous phosphoric acid at 25°C for 1 to 24 hours (McCrea, 1950). Although some of the reported samples contain dolimite/ankerite/siderite, their extremely slow reaction guarantees little contribution to the CO_2 extracted from calcite, and thereby could not affect the isotopic compositions of calcite. The studies by Simonetti et al. (1995), Viladkar (1998), Ray and Ramesh (1999a), Ray et al. (1999), and Miyazaki et al. (2000) have used various CO_2 extraction techniques to analyze isotopic compositions of calcites and other coexisting carbonate

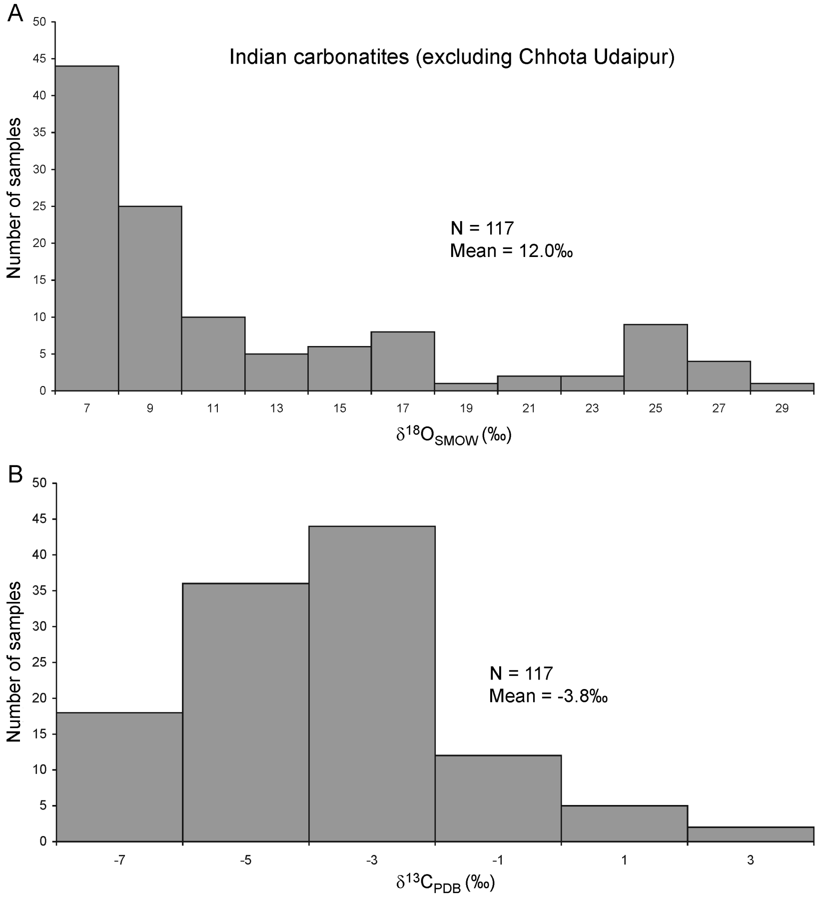

FIG. 2. Oxygen and carbon isotopic compositions of Indian carbonatites. A. $\delta^{18}O$ distribution. B. $\delta^{13}C$ distribution. Note that the plots exclude data from Chhota Udaipur complexes to avoid any undue bias. *Sources*: Sarkar et al. (1985); Gwalani et al. (1993); Simonetti et al. (1995); Srivastava and Taylor (1996); Kumar et al. (1998); Pandit et al. (1998, 2002); Schleicher et al. (1998); Viladkar (1998); Ray and Ramesh (1999a); Ray et al. (1999); Miyazaki et al. (2000); Viladkar and Schildlowski (2000).

minerals. The acid fractionation factor used for CO_2 extraction from calcite in all the studies is 1.01025 (Friedman and O'Neil, 1977); however, it is different for other carbonates and other temperatures of reaction. Also the $\delta^{18}O$ data for dolomites and ankerites from Viladkar (1998) and Viladkar and Schidlowski (2000) were not corrected for acid fractionation, which was performed by us using the acid fractionation factor of 1.01065 at 25°C reaction (Rosenbaum and Sheppard, 1986) before including them in this work. For better comparison, data from all sources are normalized to NBS-18 (IAEA carbonatite standard) isotopic compositions: $\delta^{18}O_{SMOW}$ = –23.0‰, and $\delta^{13}C_{PDB}$ = –5.06‰.

Figure 2 shows frequency distributions of $\delta^{18}O$ and $\delta^{13}C$ values in Indian carbonatites. To preclude any undue bias, the data from the carbonatites of the Chhota Udaipur subprovince have been excluded from this figure owing to their larger number. $\delta^{18}O$ values for Indian carbonatites cover a wide range (Fig. 2A) from about 6 to 30‰, with a mean of 12‰ and mode of 7.2‰. Fifty-nine percent of the data fall in the range of 6–10 ‰. The higher $\delta^{18}O$ values are usually from calcites from ferrocarbonatites or altered calcite carbonatites. Here we have not distinguished various forms of carbonatites such as plutonic, subvolcanic or volcanic. However, closer inspection of individual datasets reveals that some

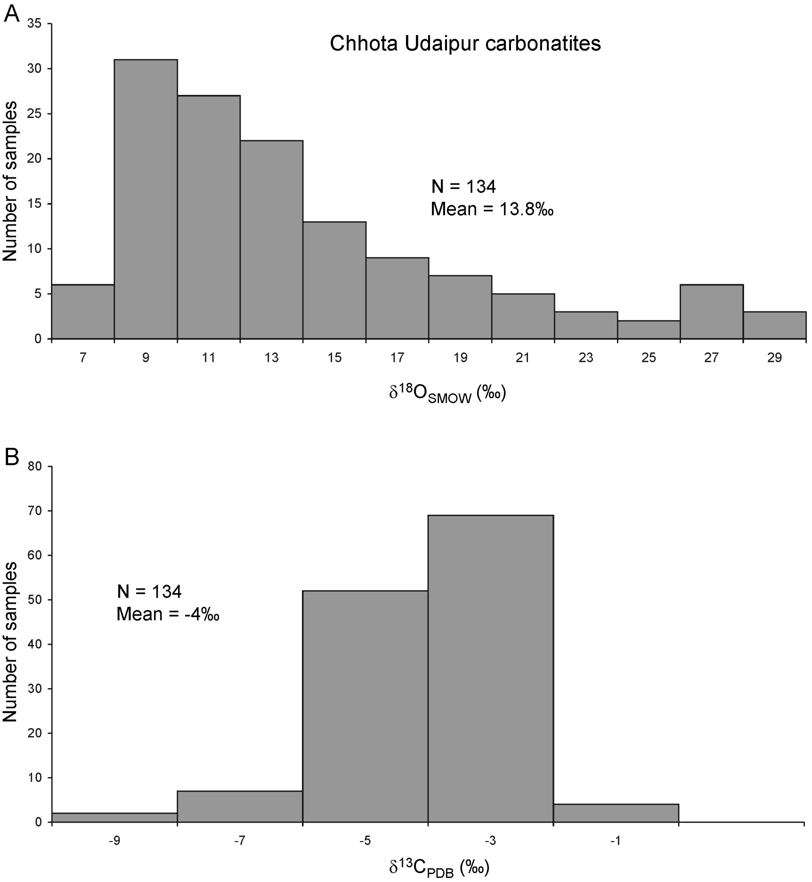

FIG. 3. Oxygen and carbon isotopic composition of carbonatites from Chhota Udaipur alkaline sub-province (Amba Dongar and Siriwasan). A. $\delta^{18}O$ distribution. B. $\delta^{13}C$ distribution. *Sources*: Gwalani et al. (1993); Simonetti et al. (1995); Srivastava and Taylor (1996); Ray and Ramesh (1999a); Viladkar and Schildlowski (2000).

of the plutonic complexes show much lesser spread in their $\delta^{18}O$ values (e.g., Hogenakal, Sung Valley). The $\delta^{13}C$ frequency distribution in these carbonatites (Fig. 2B) shows a narrower range (–8 to 4‰) with a mean and mode of –3.8 ± 2‰; 68% of the data fall in the range from –6 to –2‰. Similar to $\delta^{18}O$ variation, $\delta^{13}C$ of plutonic carbonatites has a much tighter spread compared to other types. Figure 3 illustrates the frequency distributions of $\delta^{18}O$ and $\delta^{13}C$ in carbonates from Chhota Udaipur carbonatites (Amba Dongar and Siriwasan). Although the range of variations for $\delta^{18}O$ is identical to that observed in rest of Indian complexes, the mode here is 9.6‰, and 74% of the data fall in a broader and higher range of 6–16‰ (Fig. 3A), which probably suggests that these carbonatites are more fractionated compared other Indian carbonatites. On the contrary, the $\delta^{13}C$ distribution is much narrower, with 90% of the data showing values in the range of –6 to –2 ‰ (Fig. 3B). The mean of carbon isotope distribution is –4 ± 1.3‰ and the mode, –3.3‰. Clearly, the observed carbon isotopic composition of Indian carbonatites shows a higher mean value (at around – 4 ‰) compared to that observed in carbonatites elsewhere (Deines, 1989).

In a very early study, Taylor et al. (1967) reported carbon and oxygen isotopic compositions of carbonatites elsewhere, and suggested a field in a $\delta^{18}O$ versus $\delta^{13}C$ plot for what they believed to represent primary/magmatic values. At that time it was probably not recognized that the unaltered magmatic isotopic compositions of carbonatites are highly sensitive to the crystallization process, and therefore in principle can show a much larger spread depending on the temperature, type of crystallization, and nature of fluids involved (Ray and Ramesh, 2000). However, inapt use of Taylor's field to distinguish primary from secondary isotopic compositions in carbonatites continues to the present. Recently based on their observations in Oldoinyo Lengai, Keller and Hoefs (1995), proposed a different field for "primary" isotope variations for carbonatites. But the consideration of most of the data available today from carbonatites worldwide clearly hints at a much wider field for the unaltered $\delta^{18}O$ and $\delta^{13}C$ values for igneous carbonatites that can be called "primary" (Ray and Ramesh, 1999a). This is based on the realization that unaltered $\delta^{18}O$ and $\delta^{13}C$ values of the carbonatite carbonates are correlated, and vary in tandem in response to primary crystallization processes (Pineau et al., 1973; Deines, 1989; Ray and Ramesh, 2000). We use this field (the polygon in Fig. 4A), but sparingly, to differentiate primary compositions from the secondary/altered values. Figure 4A shows some of the major, general evolutionary pathways for carbon and oxygen isotopic compositions of carbonatite carbonates. Generated within the mantle with isotopic compositions in equilibrium, uncontaminated carbonate magmas crystallize to produce either clusters or trends in the $\delta^{18}O$ versus $\delta^{13}C$ plot that can be called "primary variations" (Fig. 4A). Post-crystallization alteration can move these values in various directions, depending on the nature of alteration (Fig. 4A). Extensive discussions on such possible pathways are given in Deines (1989), Santos and Clayton (1995), Demény et al. (1998), and Ray and Ramesh (1999b).

The comparison of $\delta^{18}O$ and $\delta^{13}C$ data from Indian carbonatites with the above fields clearly reveals that each of these complexes has a composite evolutionary history (Figs. 4B and 4C). As can be seen, all Indian carbonatites have some isotopic compositions that fall in the mantle field; most lie in the field for primary carbonatites and the rest are probably altered carbonatites (Fig. 4B and 4C). The carbonatites that have preserved mantle isotopic signatures mostly belong to the Precambrian group except for a few samples from Late Cretaceous carbonatites. The fact that Indian carbonatites show mantle carbon and oxygen isotope compositions is an additional proof of their magmatic origin. As expected, data for some of the carbonatites plot as clusters, and others show trends within their primary variations (Fig. 4B and 4C). Although there are no major differences in the ranges of variations among the different types of carbonatites, dolomite carbonatites tend to have higher $\delta^{18}O$ values relative to calcite carbonatites for the same $\delta^{13}C$ values. Ferrocarbonatites on the other hand have higher $\delta^{18}O$ and $\delta^{13}C$ than dolomite carbonatites. Stable isotopic analyses of other carbonatite minerals (such as silicates, oxides, or phosphates) in Indian carbonatites are nonexistent. Figures 5A, 5B, and 5C show carbon and oxygen isotope fractionation between coexisting dolomite (or ankerite) and calcite from Indian carbonatites. Although the data are meager, it is quite clear that there are large variations in $\Delta_{\text{dolomite-calcite}}$ values (i.e., δ_{dolomite}-δ_{calcite}). It is apparent from Figure 5C that in most complexes, $\delta^{18}O$ of calcites from all types of carbonatites are much higher than those of coexisting dolomites. Using temperature-dependent fractionation factors of Sheppard and Schwarcz (1970) and Zheng (1999), we found that dolomite and calcite in these carbonatites, except for Sung Valley, are in isotopic disequilibrium. The data from Sung Valley suggest equilibrium temperatures in the range of 600–800°C.

Understanding the Variations

Primary variations

Magmatic processes. Stable isotopic variations in carbonatite minerals are a result of isotopic heterogeneity in the mantle source regions, fractionation processes that occur during the carbonatite generation and evolution (including retrograde isotopic exchange), and post-magmatic alteration processes (e.g., Deines, 1989; Ray and Ramesh, 1999a). Here we attempt to identify these fractionation processes and decipher the source characteristics of Indian carbonatites. The magmatic processes that are believed to cause $\delta^{13}C$ and $\delta^{18}O$ variations in carbonatites include extraction of carbonatite melts from the mantle, liquid immiscibility, crustal contamination, and fractional crystallization. Deines (1989) suggested that $\delta^{13}C$ and $\delta^{18}O$ variations in carbonatites could be related partly to the extraction of carbonate melt from a heterogeneous source region. Liquid immiscibility has been suggested as an important process in the formation of carbonatites (e.g., Kjarsgaard and Hamilton, 1989). Mattey et al. (1990) found from experimental studies that carbon isotopic fractionation between carbonate melt and silicate melt is very small (0.4‰) in the temperature and pressure ranges of 1200–1400°C and 5–30 kbar, which led them to suggest that

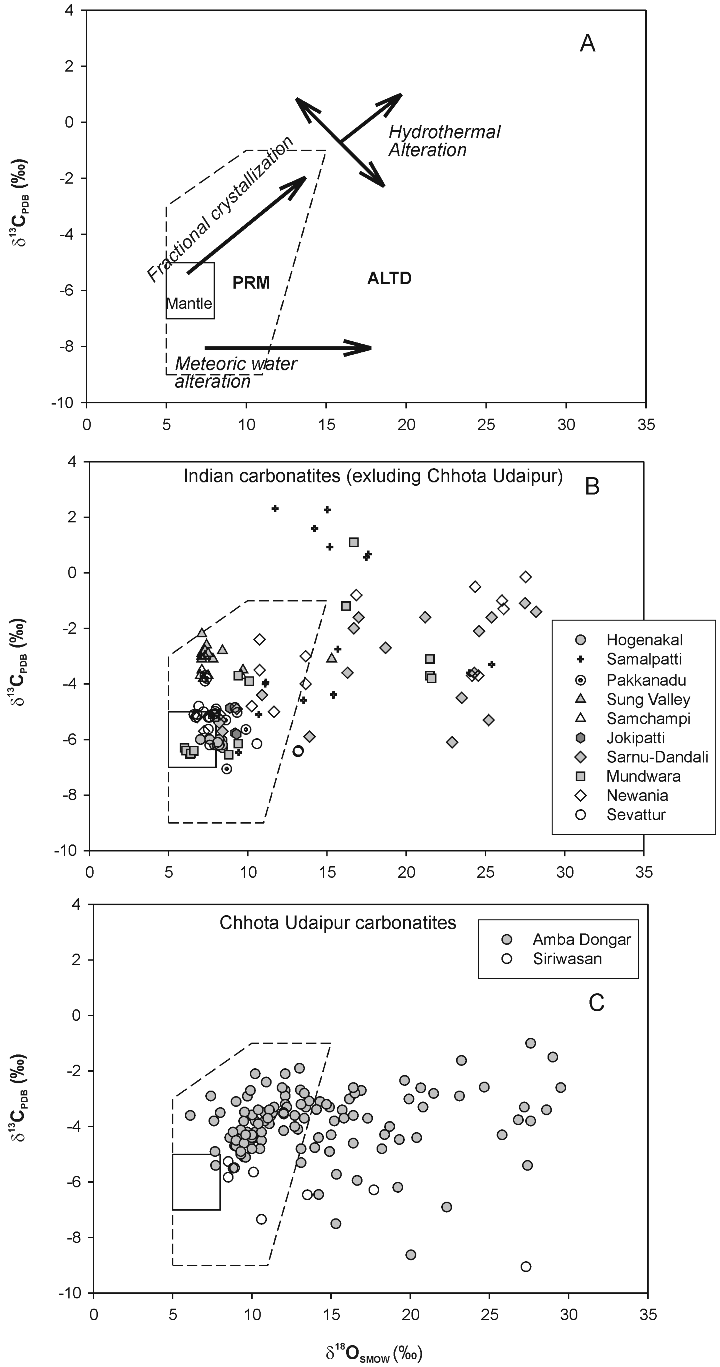

FIG. 4. A. Oxygen and carbon isotopic composition fields for primary (dashed areas) and altered carbonatites (outside dashed areas) as defined by Ray and Ramesh (1999). Arrows indicate possible pathways resulting from main processes involved in the isotopic evolution of carbonatites. Mantle envelope is defined based on data from Kyser (1990), Deines (1992), and Cartigny et al. (1998). Abbreviations: PRM = primary; ALTD = altered. B. δ^{13}C versus δ^{18}O composition of calcite carbonatites from various Indian carbonatites except for the complexes of Chhota Udaipur. C. The same variation in Chhota Udaipur complexes.

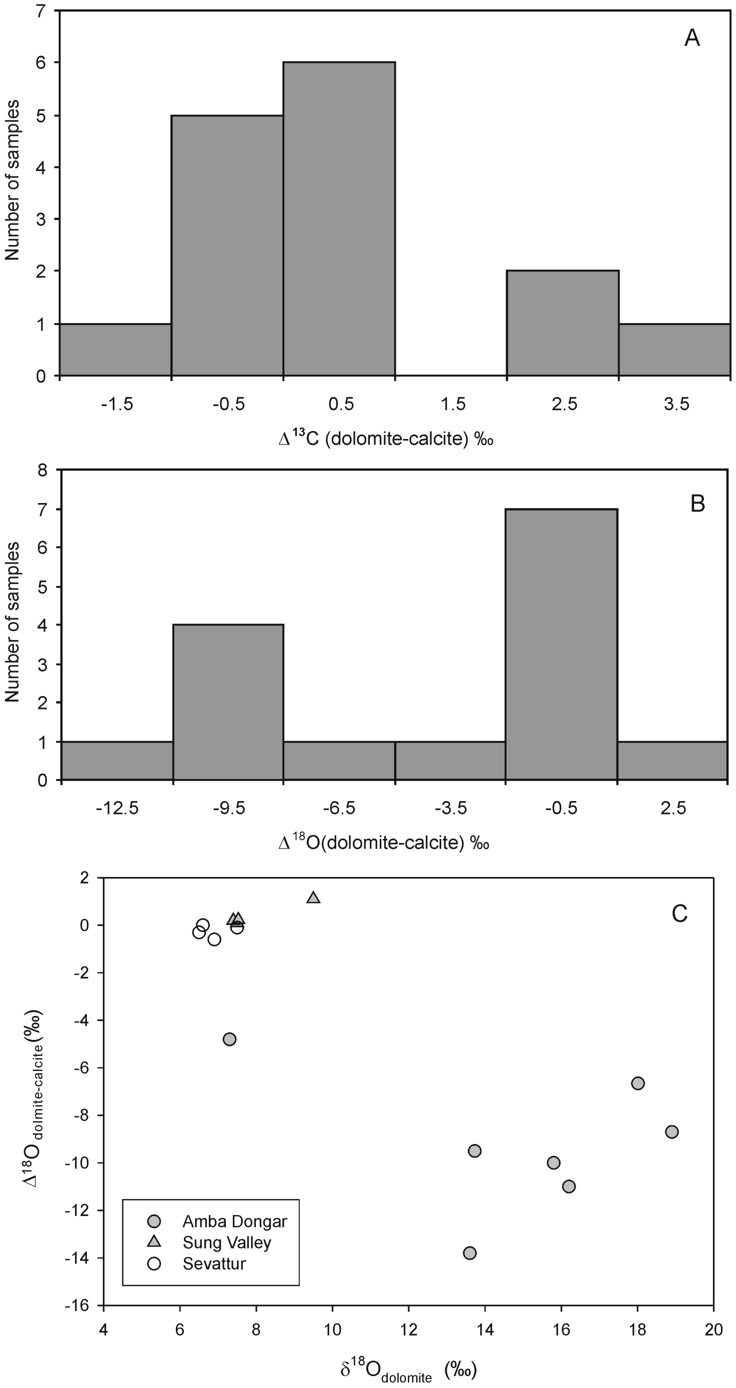

FIG. 5. A. Histogram for carbon isotope fractionation between coexisting dolomite/ankerite and calcite in carbonatites. B. Histogram for oxygen isotope fractionation between coexisting dolomite/ankerite and calcite. C. Oxygen isotope fractionation between coexisting dolomite and calcite from Amba Dongar, Sung Valley and Sevattur carbonatites. *Sources*: Simonetti et al. (1995); Ray and Ramesh (1999a); Miyazaki et al. (2000).

carbon isotopes do not fractionate during liquid immiscibility.

Contamination of carbonate magma by crustal rocks is another magmatic process that can affect their isotopic compositions. Carbon being a trace element in most crustal rocks, except for limestones, contamination by these rocks may not generate large variations in $\delta^{13}C$ compositions of carbonatites. $\delta^{18}O$ values of crustal rocks (excluding limestones) are not very different from those of carbonatites; hence, contamination effects may not be detected. Contamination due to limestones can generate isotopic compositions that are likely to fall between the mantle field and the sedimentary carbonate field in a $\delta^{13}C$ vs. $\delta^{18}O$ plot. In such a case, it is difficult to extract information about the source regions. Therefore, in such situations it is important to assess the extent of contamination using other isotope systematics (e.g., Sr). However, source studies of this work on Indian carbonatites have essentially ruled out crustal contamination, and in most instances, absence of older limestone formations in the vicinity of carbonatites makes our efforts easier.

From the data discussed above, it is clear that oxygen and carbon isotopic compositions of unaltered carbonatite carbonates either exhibit tight clusters or show correlated trends (Figs. 4B and 4C). This, we believe, is due to the type of crystallization process involved (batch vs. fractional). However, it is quite possible that both C and O isotopic ratios of the carbonates have evolved independently. To test such a hypothesis, we consider the primary variations separately for interpretation. The oxygen isotopic composition of a carbonatite melt derived from a mantle source depends on the source composition and temperature of melting. Calculations by Deines (1989) and Rosenbaum et al. (1994) based on the known oxygen isotope fractionation between mantle minerals and carbonates suggest that such a melt generated at about 1000°C by equilibrium melting would be ~2‰ enriched compared to that of its source. Assuming that the $\delta^{18}O$ of a peridotite mantle would lie in the range of 4–7‰, we should expect the carbonatite magma to have values between 6 and 9‰ (Deines, 1989; Rosenbaum et al., 1994). However, according to some recent studies, carbonatites can also be generated from eclogitic lithospheric mantle (e.g., Hammouda, 2003; Yaxley and Brey, 2004). If so, the $\delta^{18}O$ of such sources would be higher than a peridotitic mantle (e.g., 6–8‰; Kyser, 1990), and the $\delta^{18}O$ of carbonatite melts from these would be in the range of 8–10‰. Therefore, we expect the oxygen isotopic composition of uncontaminated and unfractionated carbonatite magma to fall between 6 and 10‰. Crystallization of carbonate minerals from this melt may not fractionate oxygen isotopes because of similar fractionating properties of the melt and the major minerals (i.e., carbonates); however, crystallization of accessory silicates, oxides, and phosphates are likely to change the oxygen isotopic composition of the melt (e.g., Deines, 1989; Haynes et al., 2003). Batch crystallization of the magma under plutonic conditions probably would not fractionate oxygen isotopes to a resolvable extent, but fractional crystallization is likely to enrich heavier oxygen isotopes in the melt (Deines, 1989). As clearly depicted by the positive correlation of La/Yb versus $\delta^{18}O$ (two important indices of fractional crystallization) in Amba Dongar carbonatites (Fig. 6A), most Indian carbonatites, with the exception of Hogenakal and northeastern complexes, show evidence of fractional crystallization.

Carbon isotopic fractionation. To test the hypothesis that the carbon isotopic composition evolves independent of oxygen isotopes, we used simple Rayleigh crystallization to model the $\delta^{13}C$ distribution of Chhota Udaipur carbonatites that show evidence for fractional crystallization. Using the method devised by Deines (1989) we assume that the observed frequency of a certain $\delta^{13}C$ value is proportional to the volume of carbonatite of that isotopic composition. Such an assumption for Chhota Udaipur would probably be justifiable because it is the most extensively sampled complex. In a single-component Rayleigh fractionation process, the $\delta^{13}C$ of the product (i.e., carbonatite) is a function of the initial isotopic composition of the source reservoir ($\delta^{13}C^{i}_{S}$), the fraction of remaining reservoir (f), and the temperature-dependent carbon isotopic fractionation factor between the product and the source ($\alpha^{13}C_{\text{product-source}}$). The relation is as follows:

$$\delta^{13}C_p = \alpha(\delta^{13}C^{i}_{s} + 1000)f^{(\alpha-1)} - 1000. \quad (1)$$

This relation is an equation of a straight line in the coordinates of $\log_{10}(1000 + \delta^{13}C_P)$ and $\log_{10}f$. We determined f from the cumulative frequency for a given isotopic composition and plotted the data in Figure 6B. Here, f is expressed in percentage (%) for convenience. The straight-line regression to the data has a good r^2 value of 0.97, and the relationship yields an acceptable α value of 0.9993. However, the estimated initial $\delta^{13}C$ for the source, –0.73‰, is

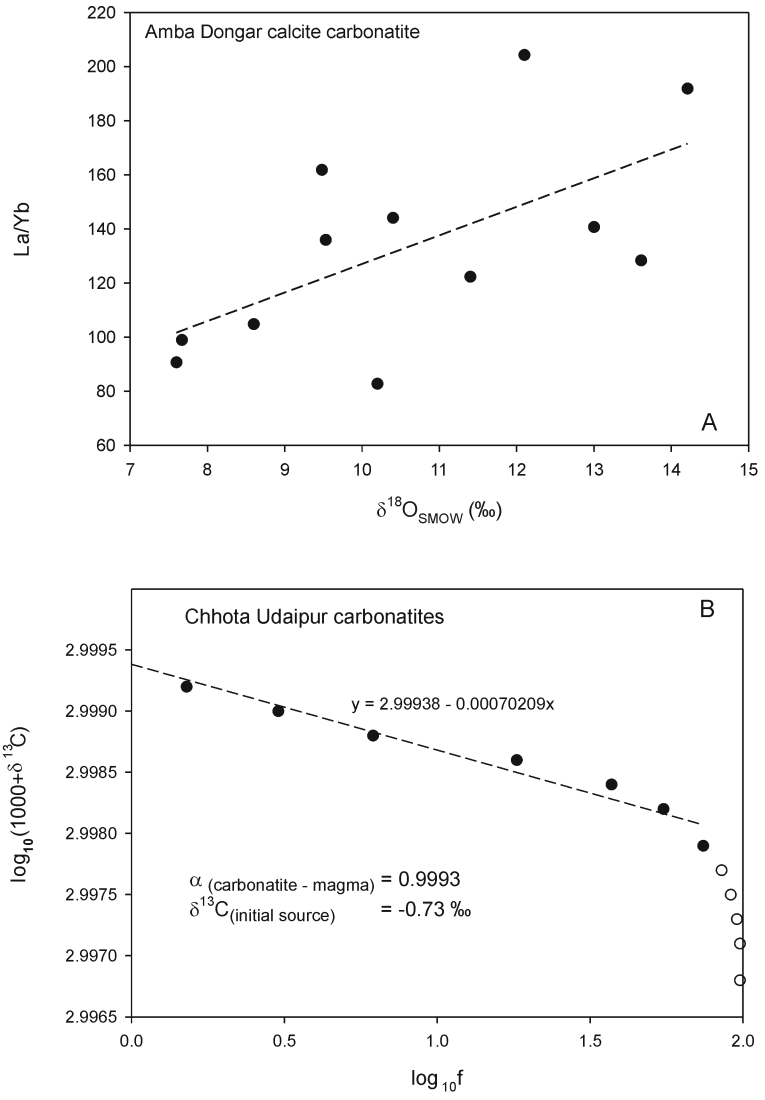

FIG. 6. A. Plot of La/Yb, an index of fractional crystallization, versus $\delta^{18}O$ of calcite carbonatites from Amba Dongar showing a positive correlation ($r^2 = 0.4$). B. Correlation between the amount of carbonate crystallized (in %) and carbon isotopic composition for the Amba Dongar and Siriwasan carbonatites. f = fraction of remaining reservoir. The line represents a linear regression for the observed data up to an f value of 85% (solid circles). Open circles representing data for f = 100–85% have been excluded from the regression for simplicity. See text for discussion.

too high and is inconceivable for any mantle-derived magma because the carbon isotopic composition of mantle sources is believed to lie within –6 and –4‰ versus PDB (e.g., Deines, 1992). This could mean that the carbon isotope fractionation may be a Rayleigh type, but it may not be the only melt-carbonate fractionation process that controls the isotopic composition of the final product. There could be other source components, such as CO_2 and H_2O (magmatic fluids), involved in the carbonatite formation. However, such fluids would likely cause fractionation in both C and O isotopes in the melt-fluid-carbonates system. Therefore, we need to consider processes that fractionate both carbon and oxygen isotopes simultaneously, and generate the observed primary trends in $\delta^{13}C$ vs. $\delta^{18}O$ plots.

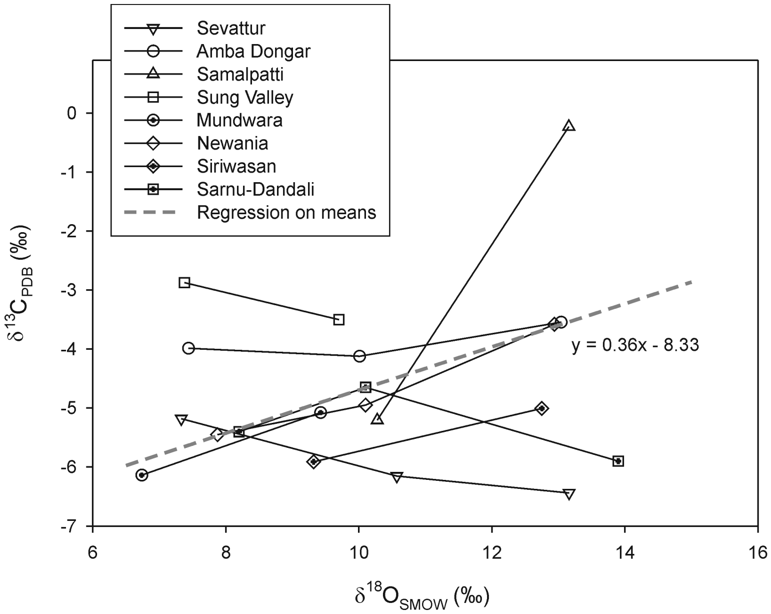

FIG. 7. Plot of $\delta^{13}C$ versus $\delta^{18}O$ values in the $\delta^{18}O$ range of 5.5–14.5‰. Solid lines join the means of $\delta^{13}C$ values in the $\delta^{18}O$ ranges of 5.5–8.5, 8.5–11.5, and 11.5–14.5. Linear regression for the means has a slope of 0.36 and $r^2 = 0.3$. Data from some carbonatites are excluded because of their limited variation.

To explain the covariation of carbon and oxygen isotope compositions in carbonatite carbonates, several models have been proposed (Pineau et al., 1973; Deines, 1989; Ray and Ramesh, 2000). Pineau et al. (1973) and Ray and Ramesh (2000) proposed that the expected correlations could be explained by Rayleigh isotopic fractionation during the fractional crystallization of fluid rich (CO_2- and H_2O rich) carbonatite magmas, whereas Deines (1989) envisaged a Rayleigh isotopic fractionation during simultaneous crystallization of carbonate and silicate phases to be the cause of such variations. We first attempt to analyze our data using the model of Deines. Similar to his observations on carbonatites from elsewhere, we also observe correlated variations of $\delta^{13}C$ and $\delta^{18}O$ in the $\delta^{18}O$ range of 5 to 15‰ (Fig. 4). Following his procedure, we assigned data from each locality that fall within $\delta^{18}O$ range of 5.5 to 14.5 into three groups: (1) 5.5–8.5‰; (2) 8.5–11.5‰; (3) 11.5–14.5‰. For each group, means of $\delta^{13}C$ and $\delta^{18}O$ values were computed and plotted in a $\delta^{13}C$ vs. $\delta^{18}O$ diagram (Fig. 7). The trends observed in Indian carbonatites are not systematic, as is also the case elsewhere (Deines, 1989). Only in the cases of Mundawara, Newania and Siriwasan, is there an apparent increase in $\delta^{13}C$ with the increase in $\delta^{18}O$. Surprisingly enough, the slope of the regression on the mean values (0.36) is close to a worldwide average and the model predicted slope of 0.4 (Deines, 1989). Such an observation could be used in support of the model of concurrent carbonate-silicate crystallization as the process responsible for the observed isotopic variation. However, we believe that the above observation is just a coincidence, and the model has limited validity because of the following: (1) it does not discriminate between melt immiscibility and fractional crystallization; (2) if liquid immiscibility occurs, then the molar ratio of carbon between carbonatite and silicate rock (taken as 1000) is unrealistic, inasmuch as the latter at most can contain carbonates up to 20% and the volume of carbonatites is much smaller (≤20%) than that of associated silicate rocks in a given complex; (3) the oxygen isotope fractionation factor (between silicate magma/rock and the primary magma) used to explain a slope of 0.4 is likely to generate lower $\delta^{18}O$ values for silicates compared to that of the primary magma, a feature not observed in general; and (4) the model assumes that the fraction of remaining carbon in the source is equal to the fraction of remaining oxygen, which may not always be true. In the complexes studied here, the slope of the correlations in each dataset varies from 0.1 to 0.7, which is very difficult to account for using the model of Deines (1989).

Multicomponent Rayleigh isotopic fractionation. Although the model proposed by Pineau et al. (1973) explains correlated variations in some complexes, it is an approximate model, and the validity of the main assumption that <30% of the oxygen in the system is present as silicates or water is difficult to justify (e.g., Deines, 1989). Therefore, a more appropriate model was developed by Ray and Ramesh (2000) to treat C and O isotopic fractionation during fractional crystallization (Rayleigh type) of a $CO_2 + H_2O$ fluid rich carbonate magma by modifying the model of Pineau et al. (1973). According to this model, the initial isotopic compositions of the magma, initial molar ratio of H_2O and CO_2, and the temperature of crystallization control the correlated variation of $\delta^{13}C$ and $\delta^{18}O$ of carbonatites. Most carbonatites worldwide that show the above correlation are calcite carbonatite. Because calcite is the major and in some occurences the only carbonate phase in calcite carbonatites, the isotopic composition of calcite and carbonatite may be considered equivalent. The C (and O) isotopic fractionation behaviors of a carbonate melt and calcite are probably very similar (Deines, 1989). Hence, it is reasonable to assume that the fractionation factors of C (and O) between calcite and carbonate melt have unit value, implying that the crystallization of calcite from a pure carbonate melt may not cause measurable isotopic variations. In contrast, if the calcite crystallizes in isotopic equilibrium with the associated magmatic fluids ($CO_2 + H_2O$), then significant fractionation can occur. Massive fenitization of country rocks in carbonatite complexes worldwide is indicative of the fact that carbonatites carry huge volumes of fluids. The present model assumes that calcite fractionally crystallizes from a fluid-rich carbonate magma, probably by the reaction: $Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+$. A similar reaction can also be written for dolomite crystallization in the case of primary dolomite carbonatites. The model is called Rayleigh isotopic fractionation from a multi-component source (RIFMS). Isotopically, CO_2 is the only source of carbon for calcite, while oxygen is contributed by both CO_2 and H_2O. Consequently, the carbon isotopic evolution will follow a single-component Rayleigh fractionation process, whereas that of oxygen, a two-component Rayleigh process. The details of the derivation of this model are given in Ray and Ramesh (2000). According to the model the carbon isotopic evolution of carbonatite is given by:

$$\delta^{13}C = \alpha^{c}(1000 + \delta^{13}C_{s}^{i})[f_{c}]^{(\alpha^{c} - 1)} - 1000 \quad (2)$$

where α^c is the fractionation factor of carbon between calcite and CO_2, f_c is the fraction of remaining carbon in the source, and $\delta^{13}C^{i}_{s}$ is the initial carbon isotopic composition of the source. The oxygen isotope evolution of the carbonatite is given by:

$$\delta^{18}O_{cal} = 10^{3}\left(\frac{\alpha^{o}_{c-1}}{a - b/f_{o}} - 1\right) + \left(\frac{\alpha^{o}_{c-1}}{a - b/f_{o}}\right)(\delta^{18}O_{s}) \quad (3)$$

where α^{o}_{c-1} is the fractionation factor of oxygen between calcite and the largest (and first) source component (CO_2 or H_2O), and f_o is the fraction of remaining oxygen in the reservoir. To determine the parameters a and b, we need the number of atoms contributed by various source components to the product, total number of atoms contributed, fractionation factors between various source components and the first/largest component, r (ratio of the initial number of moles of a component and the first component), and f_j (j^th critical value of f, when the j^th reservoir becomes exhausted). In the case of carbonate magmas, we believe CO_2 is the largest source component, hence, the values of critical f (i.e., f_{H_2O}), a, and b will be:

$$f_{H_2O} = 1 - \frac{3r_{H_2O-CO_2}}{2 + r_{H_2O-CO_2}} \quad (4)$$

$$a = \frac{1}{3}(2 + \alpha_{H_2O-CO_2}) \quad (5)$$

$$b = \frac{2}{3}(\alpha_{H_2O-CO_2} - 1)\left(\frac{1 - r_{H_2O-CO_2}}{2 + r_{H_2O-CO_2}}\right) \quad (6)$$

The $\delta^{18}O_s$ in Equation 3 is determined from the general equation of the RIFMS model:

$$(\delta^{18}O_s - \delta^{18}O_s^i) = \qquad (7)$$

$$10^3\left\{\left(\frac{\alpha^{o}_{c-1}}{a}\right)\ln\left(\frac{af_o - b}{a - b}\right) - \ln f_o\right\}$$

To plot $\delta^{13}C$ versus $\delta^{18}O$ of carbonatite at a given stage during the crystallization process, we need to correlate them through time, which is done by relating f_c and f_o:

$$f_c = \left(\frac{1 - r_{H_2O - CO_2}}{3}\right) + f_o\left(\frac{2 + r_{H_2O - CO_2}}{3}\right) \qquad (8)$$

The RIFMS model has four unknowns: (1) the temperature of crystallization that controls the fractionation factors α^c, $\alpha^{o}_{calcite-CO_2}$, and $\alpha^{o}_{H_2O-CO_2}$, (2) the initial molar ratio of H_2O and CO_2 in the source melt (i.e., $r_{H_2O-CO_2}$); (3) the initial carbon isotopic composition of the source (i.e., $\delta^{13}C^i_s$), and (4) the initial oxygen isotopic composition of the source (i.e., $\delta^{18}O^i_s$). In a forward model, three of these parameters can be assumed based on results from other tracer studies on carbonatites, and a successful model application to the observed data could reveal the fourth. The parameters that can be suitably assumed include, the temperature of crystallization, which is expected to be in the range ~800–550°C (e.g., Haynes et al., 2003), and the $\delta^{18}O^i_S$, which is believed to fall in the range of 6–10‰ (see the discussion above). Because carbonate minerals are not the only oxygen-bearing phases in the product, it is highly likely that other minerals (e.g., apatite, magnetite, phlogopite, monazite, pyroxene, olivine) would also account for additional oxygen isotopic fractionation in the source. Considering the observations made by various workers (e.g., Zheng, 1993, 1996, 1999; Haynes et al., 2003), we believe a ± 2‰ variation in the $\delta^{18}O^i_S$ during the model evolution can account for these variations. With the help of the above parameters, one can generate a series of RIFMS model curves for various initial $\delta^{13}C$ values to fit the observed data in a given complex and estimate the best initial $\delta^{13}C$ for the magma. Inasmuch as the $\delta^{13}C$ for a carbonate magma is believed to reflect that of its source region (Deines, 1989), the model can then provide estimates of the $\delta^{13}C$ of the mantle source regions of carbonatites.

Modeling results from Indian carbonatites. Among the southern Indian carbonatites those at Hogenakal show very limited variation in $\delta^{13}C$ and $\delta^{18}O$ compositions (Fig. 8A), with means at –6.0 ± 0.1 and 8.1 ± 0.4 (1σ)‰, respectively. Clearly, carbonatites in this complex have not formed as a result of fractional crystallization; rather a batch crystallization process appears to have been operative. This also attests to the fact that the Hogenakal complex is plutonic. Assuming little fractionation of isotopes of both C and O during crystallization, we infer that the mantle source of these carbonatites probably had $\delta^{13}C$ and $\delta^{18}O$ compositions of –6 and 6.1‰ (2‰ lower than the carbonate melt), respectively. Such a mantle falls well within a peridotitic mantle domain that has not undergone any form of metasomatism. Neoproterozoic carbonatites, on the other hand, show some kind of correlation in their isotope data that fall within the primary carbonatite field (Fig. 8A), suggesting fractional crystallization. Because these carbonatites are spatially and temporally close to each other, it is reasonable to assume that they have formed from a single parent magma. RIFMS model calculations at a temperature of crystallization of 800°C revealed that to explain the primary variations by fractional crystallization the magma requires an r-value (H_2O/CO_2 initial molar ratio) of 0.8, and initial $\delta^{13}C$ and $\delta^{18}O$ values of –5.0 and 8.5‰, respectively (Fig. 8A). Also the model requires a ± 2‰ change in the $\delta^{18}O$ of the parent magma, probably resulting from the crystallization of non-carbonates. The initial compositions of the magma suggest that the mantle source(s) of these carbonatites (Sevattur, Samalpatti, and Pakkanadu) probably had compositions ($\delta^{13}C$ = –5.0 and $\delta^{18}O$ = 6.5‰) different from that of Hogenakal. The fractionation factors used in the model calculations are taken from Friedman and O'Neil (1977), Richet et al. (1977) and Chacko et al. (1991).

The Precambrian Newania carbonatites of western India are dolomite carbonatites, and therefore, the RIFMS model equations need to be modified for dolomite crystallization. Dolomite crystallization in a RIFMS model can be represented by the reaction: $Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \rightarrow CaMg(CO_3)_2 + 4H^+$. Inasmuch as the ratio of oxygen atoms contributed by CO_2 and H_2O to dolomite remains identical to that during calcite precipitation, the model equations for isotopic evolution of the product essentially remain the same. In this case, we use fractionation

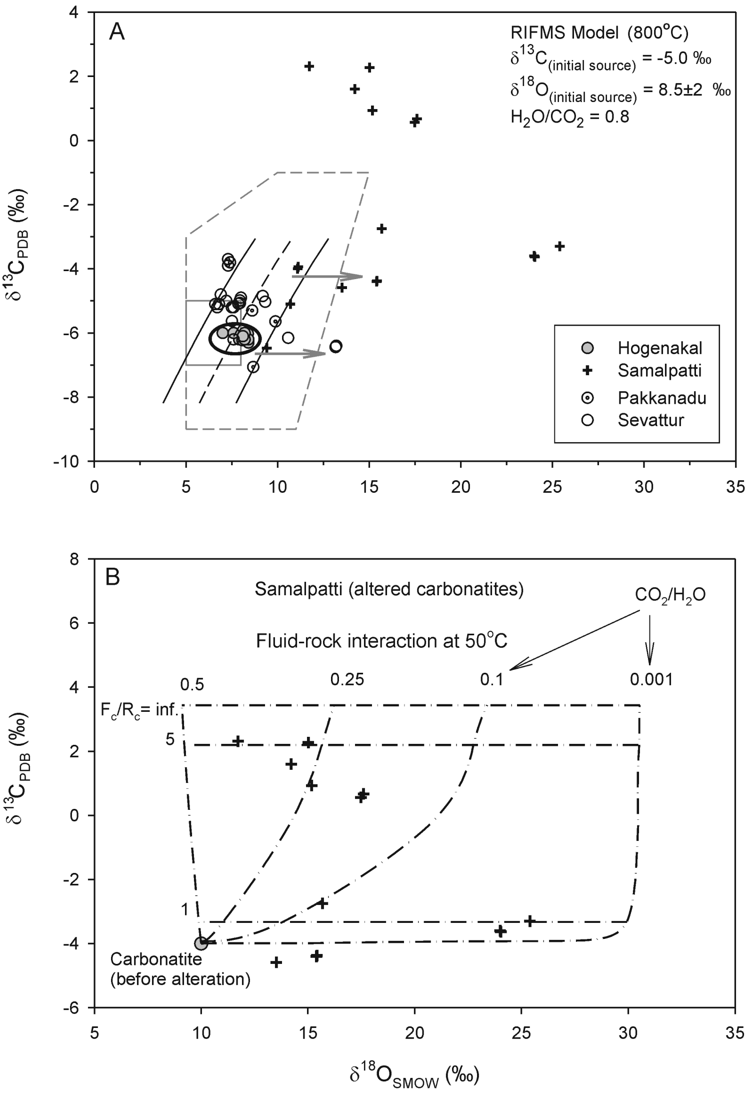

FIG. 8. Plot of $\delta^{13}C$ versus $\delta^{18}O$ of calcites from southern Indian carbonatites. The ellipse encloses data from the Hogenakal complex. The dashed line represents RIFMS model curve applied to the data for starting primary magma compositions of $\delta^{13}C = -5.0$ and $\delta^{18}O = 8.5$‰. The solid curves are model curves that represent ±2 ‰ variation in the $\delta^{18}O$ of the magma. Model calculations were performed at a temperature of crystallization of 800°C and $r_{H_2O-CO_2}$ value of 0.8. Primary carbonatite and mantle fields are as defined in Figure 4. Arrows show the direction of alteration of $\delta^{18}O$ by meteoric water. B. $\delta^{13}C$ versus $\delta^{18}O$ of altered carbonatites of Samalpatti compared with our fluid-rock interaction model curves at 50°C for various CO_2/H_2O and F_c/R_c ratios. The starting compositions for the rock: $\delta^{13}C = -4$ and $\delta^{18}O = 10$ ‰ (solid grey circle) and for the fluid: $\delta^{13}C = -4$ and $\delta^{18}O = 0$ ‰.

factors from Richet et al. (1977) and Zheng et al. (1999). Data from unaltered dolomites from Newania that appear to show a trend in the $\delta^{13}C$ versus $\delta^{18}O$ plot are best explained by RIFMS model curves at a crystallization temperature of 800°C, requiring an r-value of 0.9 and initial melt compositions of –5.0 and 9.0‰, respectively (Fig. 9A). Also, we require ±2‰ variation in the initial

$\delta^{18}O$ of the melt to explain all the data. The only difference we observe in the model here is that the slope of the curve is higher compared to that in the case of calcite crystallization, which is expected, because dolomites are known to enrich ^{18}O compared to calcites (Sheppard and Schwarcz, 1970; Zheng, 1999). The mantle source compositions of Newania carbonatites are inferred to be –5.0 and 7.0‰, respectively, which fall well within normal peridotitic mantle ranges. RIFMS model calculations for the Cretaceous calcite carbonatites of Rajasthan (Sarnu-Dandali and Mundwara) reveal that isotopic data from unaltered carbonatites from these complexes are best explained by fractional crystallization of a carbonate magma with an H_2O/CO_2 ratio of 0.8 and initial $\delta^{13}C$ and $\delta^{18}O$ of –5.0 and 8.5 ± 1.0‰, respectively at 800°C (Fig. 9B). The mantle source(s) of these much younger complexes ($\delta^{13}C = -5.0$ and $\delta^{18}O = 6.5$‰) appears to be similar to that of the Newania occurrence.

The data from Amba Dongar carbonatites include data from two groups/generations of carbonatites (I and II of Ray and Ramesh, 1999a). Group I rocks have been suggested to be older than group II rocks and in general show higher $\delta^{18}O$ (Ray and Ramesh, 1999a). Therefore, we chose to model these groups separately (Fig. 10A). Some of the data from Siriwasan that fall in the primary carbonatite polygon have been included with group I. Unlike other carbonatites examined earlier, the RIFMS model calculations suggest that the Chhota Udaipur carbonatites probably have been derived from ^{13}C enriched melts. The trends shown by group I are best explained by fractional crystallization of a carbonate magma having initial compositions of $\delta^{13}C = -4.0$ and $\delta^{18}O = 9.5 \pm 1$‰, whereas group II requires a parent magma with higher values: $\delta^{13}C = -3.2$ and $\delta^{18}O = 7.5 \pm 1$‰. Both crystallization processes probably occurred at the same temperature (800°C), and both melts had similar a H_2O/CO_2 molar ratio to start with (Fig. 10A). Clearly the mantle sources for these groups appear to be somewhat enriched (>1‰) compared with other western Indian carbonatites, even though their oxygen isotopic compositions (5.5–7.5‰) fall within the normal mantle range. Despite the fact that the RIFMS model explains the observed variations in Chhota Udaipur complexes, some data which fall within our primary carbonatite polygon remain unexplained. We suspect that these data represent samples that have undergone minor alteration, and need to be modeled along with the altered varieties.

Like the data from Hogenakal, the data from northeastern complexes are highly uniform (Fig. 11). The unaltered Sung Valley carbonatite carbonates tend to fall within a small range around the mean value of –2.9 ± 0.3 and 8.0 ± 0.4‰, whereas those from Samchampi and Swangkre lie around –3.6 ± 0.3 and 7.6 ± 0.2‰, respectively in a $\delta^{13}C$ versus $\delta^{18}O$ plot, probably suggesting that batch crystallization, not fractional crystallization, was responsible for the isotope evolution in these complexes. As mentioned previously, the dolomite-calcite equilibrium temperatures derived using carbon isotopic compositions are in the range of 600–800°C, which may be interpreted as the range of crystallization for the Sung Valley carbonatites. If we assume that all these carbonatites were derived from a single mantle source, then the isotopic compositions of their source would be –3.1 and 5.3‰ (average of all values), which is more enriched in ^{13}C than any other source region of Indian carbonatites.

Secondary variations

Carbonatites that in general do not fall within the primary carbonatite polygon as defined in Figure 4A, which have undergone secondary (post-magmatic) changes, are termed altered carbonatites. However, this definition by no means rules out the possibility that altered varieties could lie within the primary polygon. In such cases, petrography and use of other tracers (e.g., $\delta^{18}O$ vs. Sr; $^{87}Sr/^{86}Sr$) could prove highly beneficial. To explain these extreme variations of $\delta^{13}C$ and $\delta^{18}O$ in carbonatite carbonates, various models have been proposed (e.g., Deines, 1989; Santos and Clayton, 1995; Ray and Ramesh, 1999b). The enrichment only in the ^{18}O in carbonatites can be explained simply by interaction of carbonate minerals with pure meteoric water (e.g., Deines, 1989). The trend would be parallel (shown by horizontal arrows in Figs. 4A, 8A, 9B, and 11) to the $\delta^{18}O$ axis. However, other processes could also account for these extreme enrichments (see review by Deines, 1989). Here we deal with a simple closed system CO_2-bearing fluid-rock interaction model, as advocated by Ray and Ramesh (1999b), which could explain the observed extreme variations in both the isotopes in carbonate minerals of Indian carbonatites.

Fluid-rock interaction model. According to this model, in a closed-system condition the fluid-rock isotopic exchange of carbon and oxygen can be written as two simple mass balance equations:

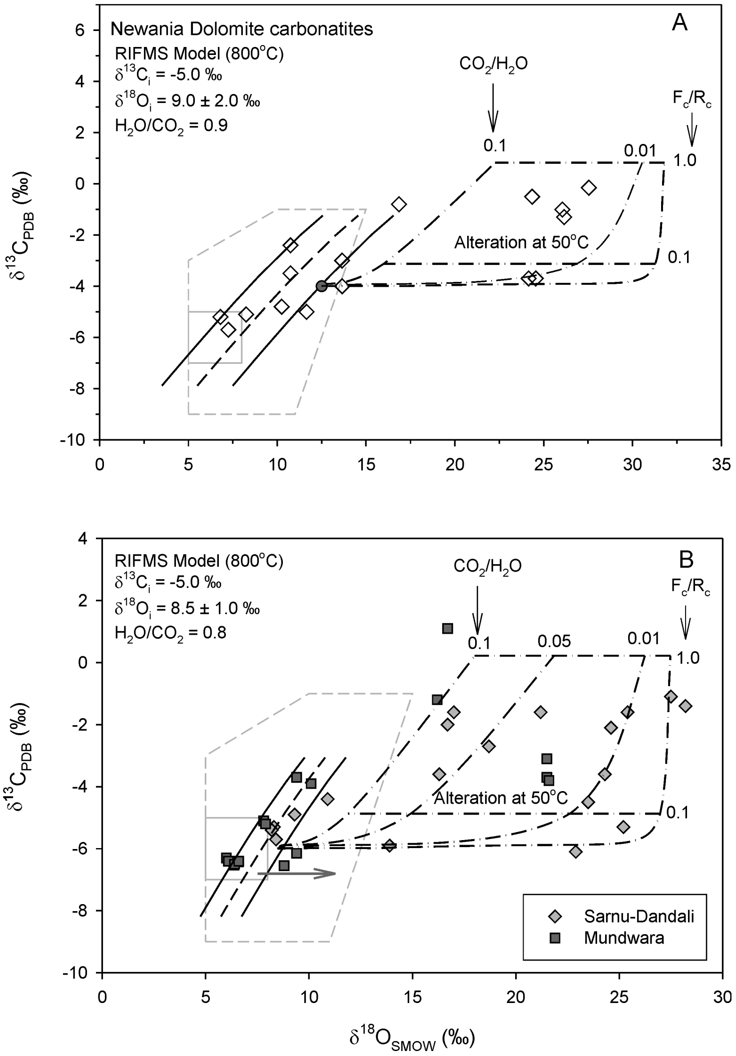

FIG. 9. A. Plot of $\delta^{13}C$ versus $\delta^{18}O$ of dolomites from the Newania carbonatite. The dashed line represents RIFMS model curve applied to the data for starting primary magma compositions of $\delta^{13}C = -5.0$ and $\delta^{18}O = 9.0$‰. The solid curves are model curves that represent ±2 ‰ variation in the $\delta^{18}O$ of the magma. Model calculations were performed for a temperature of crystallization of 800°C and $r_{H_2O-CO_2}$ value of 0.9. Also plotted are the fluid-rock interaction model curves (dash-dot-dash lines) for 50°C for the altered samples. The starting compositions for the rock: $\delta^{13}C = -4$ and $\delta^{18}O = 12.5$‰ (solid grey circle) and for the fluid: $\delta^{13}C = -4$ and $\delta^{18}O = 0$‰. B. RIFMS model curves plotted for calcites from Sarnu-Dandali and Mundwara carbonatites. Plot of $\delta^{13}C$ versus $\delta^{18}O$ of dolomites from Newania carbonatite. The model uses starting primary magma compositions of $\delta^{13}C = -5.0$ and $\delta^{18}O = 8.5 \pm 1$‰, and a $r_{H_2O-CO_2}$ value of 0.8. Fluid-rock interaction model curves are calculated for starting compositions of $\delta^{13}C = -6$ and $\delta^{18}O = 8.5$‰ for the rock and $\delta^{13}C = -1$ and $\delta^{18}O = -3$‰ for the fluid. The arrow shows the direction of alteration of $\delta^{18}O$ by pure meteoric water.

$$F_c\delta^{13}C^i_{fluid} + R_c\delta^{13}C^i_{rock} = F_c\delta^{13}C^f_{fluid} + R_c\delta^{13}C^f_{rock} \quad (9)$$

$$F_o\delta^{18}O^i_{fluid} + R_o\delta^{18}O^i_{rock} = F_o\delta^{18}O^f_{fluid} + R_o\delta^{18}O^f_{rock} \quad (10)$$

where F_c and F_o are amounts of carbon and oxygen, respectively, in the fluid expressed in moles. R_c and R_o are the same parameters for the rock. Superscripts i and f stand for initial and final, respectively. From two equations, final rock compositions can be obtained. The relations for the final rock compositions are:

$$\delta^{13}C^f_{rock} = \frac{(F_c/R_c)\left(\delta^{13}C^i_{fluid} + \Delta^c_{rock-fluid}\right) + \delta^{13}C^i_{rock}}{1 + (F_c/R_c)} \quad (11)$$

$$\delta^{13}O^f_{rock} = \frac{(F_c/R_c)\left(\delta^{13}O^i_{fluid} + \Delta^c_{rock-fluid}\right) + \delta^{13}O^i_{rock}}{1 + (F_c/R_c)} \quad (12)$$

where $\Delta^c_{rock\text{-}fluid}$ and $\Delta^o_{rock\text{-}fluid}$ stand for the isotopic fractionation of oxygen and carbon ($\Delta = 1000 \ln \alpha$), respectively, between rock and fluid. As the fluids are CO_2-bearing aqueous fluids, the oxygen fractionation between the rock (i.e., carbonate mineral) and the fluid will depend on the CO_2/H_2O ratio in the fluid. Defining x as the molar ratio of CO_2 to H_2O in the fluid, the relation for $\Delta^o_{rock\text{-}fluid}$ is:

$$\Delta^c_{rock-fluid} = 10^3 \ln\alpha^{18}O_{Cal-CO_2} + 10^3 \ln(1+2x) - 10^3 \ln\left(2x + \alpha^{18}O_{H_2O-CO_2}\right) \quad (13)$$

where $\alpha^{18}O_{Cal-CO_2}$ and $\alpha^{18}O_{H_2O-CO_2}$ are oxygen fractionation factors between calcite–CO_2 and H_2O–CO_2, respectively. This relation comes from the definition of $\alpha_{rock\text{-}fluid}$, where CO_2 contributes two oxygens and H_2O one. A covariance ($\delta^{13}C$-$\delta^{18}O$) plot requires values corresponding to same time of formation/interaction. Therefore, F_o/R_o and F_c/R_c are related by the equation:

$$F_o/R_o = \{(2x+1)/3x\}\{F_c/R_c\}. \quad (14)$$

Equation (14) is an important difference between the models of Santos and Clayton (1995) and Ray and Ramesh (1999b). Using the model equations (11) and (12), isotopic evolution curves can be generated considering appropriate initial compositions of the rock and the fluid at a given temperature by varying F_c/R_c (fluid-rock ratio) and CO_2/H_2O ratios and compared with a dataset. The fractionation factors of Richet et al. (1977) and Chacko et al. (1991) are used for model calculations.

Altered carbonatites from Indian complexes. Comparison of model curves with the extreme-uncorrelated variations of $\delta^{13}C$ and $\delta^{18}O$ in some carbonatites from Indian complexes clearly points out the fact that these have undergone extensive post-magmatic alteration. Model calculations reveal that the carbonatites of Samalpatti that show very high $\delta^{13}C$ and $\delta^{18}O$ appear to have been altered to various degrees (F_c/R_c = 1 to 5) by hydrothermal fluids (at 50°C) that contained various amounts of CO_2 (Fig. 8B). Similar considerations of carbonatites of Rajasthan (Figs. 9A and 9B) suggest that CO_2-bearing (CO_2/H_2O = 0.001 to 0.1) aqueous fluids were responsible for alteration of magmatic isotopic compositions in these complexes. Unlike Samalpatti rocks, carbonatites from Rajasthan appear to have undergone a lesser degree of alteration, as shown by the model-required lower fluid to rock ratios ($F_c/R_c \leq 1$; Fig. 9). Data from the altered carbonatites carbonates from Amba Dongar are best explained by their low-temperature interaction with CO_2-bearing fluids (Fig. 10B). Figures 10A and 10B show that values which fall within the primary carbonatite polygon, but remained unexplained by the RIFMS model, appear to represent altered samples and are easily explained by the fluid-rock interaction model. Except for Mundwara and Sarnu-Dandali carbonatites, model-predicted initial isotopic compositions ($\delta^{13}C$ and $\delta^{18}O$) of the fluid are –4 and 0‰, respectively. It should be noted that we are dealing with equations that have six unknowns and only two knowns. Therefore, predicted values are likely to change depending on other factors chosen for the model evolution. Nevertheless, it is quite clear that the isotopic data from altered carbonatite carbonates from all the Indian carbonatites bear signatures of low-temperature hydrothermal alteration. Moreover, calcites coexisting with dolomites are more prone to alteration than those that are not. Carbonatites from Siriwasan as a whole appear to be

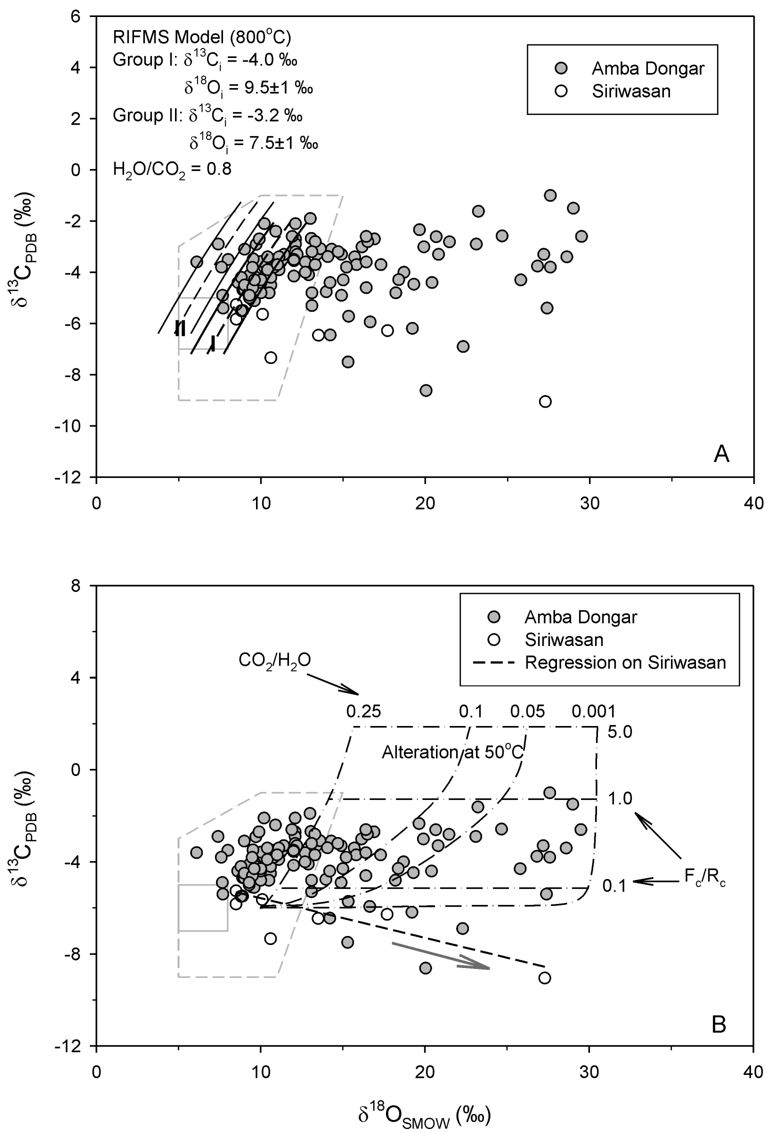

FIG. 10. A. Plot of $\delta^{13}C$ versus $\delta^{18}O$ of calcites from the Chhota Udaipur carbonatites compared with RIFMS model curves. Separate model curves have been generated to explain the isotopic evolution of group I and II calcite carbonatites of Amba Dongar. The solid model curves encompass the ±1‰ variation in the $\delta^{18}O$ of the primary magma. See text for discussion. B $\delta^{13}C$ versus $\delta^{18}O$ of altered carbonatites from Chhota Udaipur compared with fluid-rock interaction model curves. The starting compositions for the rock: $\delta^{13}C = -6$ and $\delta^{18}O = 10‰$ and for the fluid: $\delta^{13}C = -4$ and $\delta^{18}O = 0‰$. The dashed line (with the arrow) shows the evolution of Siriwasan carbonatites as a result of fluid mixing.

very different from the others (Fig. 10). They show a well-correlated trend starting from well within the primary carbonatite polygon ($\delta^{13}C = -5.3$; $\delta^{18}O = 8.5‰$) and ending outside at $\delta^{13}C = -9$ and $\delta^{18}O = 30‰$ (Fig. 10B). We propose that they represent a group of completely recrystallized carbonatites resulting from interaction/mixing of a hydrothermal fluid with the primary carbonatite/magma. In such a situation, other tracers would be necessary to fully understand the evolution of Siriwasan carbonatites.

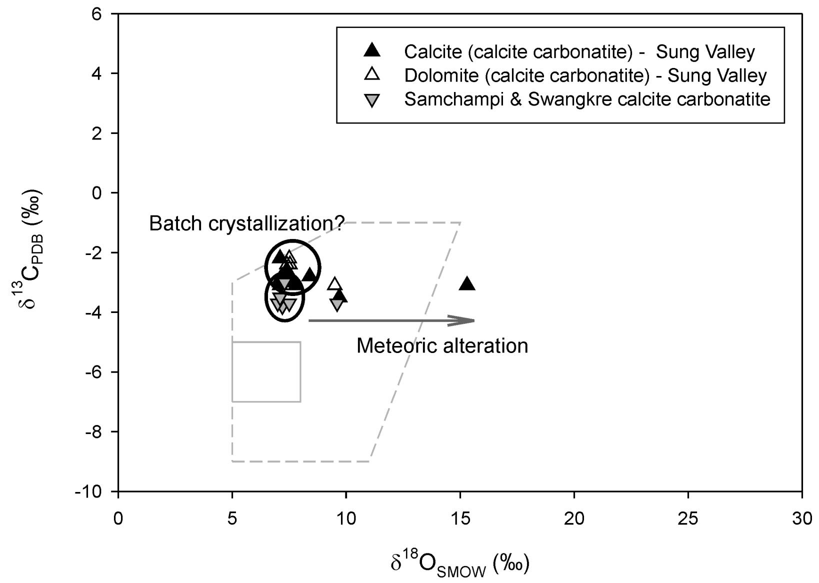

FIG. 11. Plot of $\delta^{13}C$ versus $\delta^{18}O$ of calcites and dolomites from northeastern carbonatites. The ellipses show the extent of variation in unaltered samples. The arrow shows the direction of alteration of $\delta^{18}O$ by meteoric water.

Discussion

From our modeling efforts, it is now clear that the primary stable isotopic variations in Indian carbonatites are a result of either batch crystallization (Hogenakal and northeastern Indian carbonatites) or fractional crystallization of mantle-derived carbonate magmas at temperatures in the range of 600–800°C. The mantle source compositions determined from the RIFMS model calculations for various complexes are presented in Table 3. These estimates indicate that the mantle sources for most of the complexes are similar to a normal carbonated peridotite as observed elsewhere. However, sources for Chhota Udaipur carbonatites and carbonatites from northeastern India exhibit significantly higher $\delta^{13}C$ values (>–4.0‰). Ray and Ramesh (1999) and Ray et al. (1999) attributed such enrichments of ^{13}C in the carbonatite sources to the incorporation of recycled crustal inorganic carbon. As discussed earlier, the generation of the carbonatites of the Chhota Udaipur subprovince and the Assam-Meghalaya Plateau of northeastern India is believed to be a result of plume activities that were responsible for the Deccan and the Rajmahal-Sylhet-Bengal CFB magmatism, respectively. In such a scenario, the enrichment of carbonatite sources could be visualized in terms of entrainment of metasomatized lithospheric mantle and/or incorporation of migrating ^{13}C-enriched fluids derived from subducted oceanic crust. In a non-plume model for the above CFBs, we should expect the Indian subcontinental lithosphere, the most suitable candidate as the source for these carbonatites, to be enriched in both isotopes. However, the lower values for $\delta^{18}O$ for these sources (Table 3) do not coincide with that of an eclogitic source (e.g., Kyser, 1990). We have also observed an interesting phenomenon in Amba Dongar, where two batches/generations of carbonatite appear to have come from two different protoliths, the later being more enriched in ^{13}C. This could mean that the source of Amba Dongar complex is heterogeneous; however, further evidence supporting this possibility is required.

With these new results, we now can make an effort to understand the temporal evolution of the Indian carbonatite source regions. Even though these carbonatites are widely distributed, and belong to various tectonic regimes, we suspect that in a general sense they represent the Indian subcontinental mantle through time. Like the $^{87}Sr/^{86}Sr$ of Canadian carbonatites with ages ranging from 2.7 to 0.12 Ga (Bell and Tilton, 2002), data from Indian carbonatites also show a major change in mantle

TABLE 3. Estimated Carbon and Oxygen Isotopic Compositions of Mantle Sources for Indian Carbonatites

Carbonatite complex	$\delta^{13}C_{PDB}$‰	$\delta^{18}O_{SMOW}$‰
Hogenakal	–6.0	6.1
Samalpatti, Sevattur, and Pakkanadu	–5.0	6.5
Newania	–5.0	7.0
Sarnu-Dandali and Mundawra	–5.0	6.5
Sung Valley, Samchampi, and Swangkre	–3.1	5.3
Amba Dongar		
Group I	–4.0	7.5
Group II	–3.2	5.5

differentiation, sometime around ~2.8 Ga (Fig. 12A). However, unlike Canadian counterparts, the $^{87}Sr/^{86}Sr$ of Indian carbonatites suggests the formation of a major enriched mantle reservoir during the late Archean. This event could be considered as the time of metasomatism of the Indian lithospheric mantle. This would mean that Indian carbonatites have been derived from a subcontinental lithospheric mantle, and not from plumes. The evolution of carbon isotopic composition of mantle sources does not support this. A plot of $\delta^{13}C$ versus age of Indian carbonatites (Fig. 12B) shows an enrichment of the subcontinental mantle (~1‰) sometime between 2.4 and 2.2 Ga. A possible repetition of carbonatite activity at Newania at ~1.5 Ga appears to have come from a geochemically similar (the same?) source as its precursor. Apparently the mantle sources of Indian carbonatites remain unchanged at least until ~700 Ma. No information exists regarding the nature of the carbonatite sources from 700 Ma until 107 Ma. At 107 Ma the mantle became significantly enriched in ^{13}C (by ~2%), as inferred from the northeastern Indian carbonatites. Similar enrichments occurred subsequently at ~65 Ma; however, the mantle sources of 68.5 Ma carbonatites of Rajasthan seem to have retained their $\delta^{13}C$ since ~1.5 Ga. The extreme enrichments in mantle below the Deccan and Rajmahal-Sylhet provinces could be attributed either to plume activities or to extraction of highly enriched material from the lithospheric mantle because of the associated massive flood basalt events.

Nonetheless, noble gas and nitrogen isotopic ratios in Amba Dongar and Sung Valley carbonatites not only favor a plume model but also support the idea of incorporation of recycled components in carbonatite sources (Basu and Murty, 2003). On the other hand, the carbon isotopic compositions of Sarnu-Dandali and Mundwara, which are believed to be of plume origin because of their high $^{3}He/^{4}He$ ratios (Basu et al., 1993), lack evidence of ^{13}C enrichment. But it is not necessary that the noble gas signature for a plume and carbon isotopic signature for the recycled carbon should complement each other. From the above discussion we are inclined to believe that subcontinental lithospheric mantle, which probably was metesomatized around 2.4 Ga, had remained a continued source for the Indian carbonatites. However, intermittent plume activities or massive melting events of nearby mantle to generate CFBs have produced massive carbonatites with enhanced fluid contribution from ancient subducted oceanic crust. The former explains the origin of all Precambrian carbonatites and the latter, all known Cretaceous carbonatites of India.

Summary and Conclusions

Our review of stable carbon and oxygen isotopic data from Indian carbonatites has revealed many interesting aspects of these rocks and the nature of Indian subcontinental mantle. Although the data exhibit wide variations, the majority of them fall within smaller ranges of values: $\delta^{18}O$ = 6–15‰; $\delta^{13}C$ = –6 to –2‰. The oxygen isotopic compositions of carbonatite carbonates are more variable compared to their carbon isotopic compositions, which are in agreement with the observation that the former are more prone to fractionation. The data from plutonic carbonatites show a narrower spread relative to subvolcanic carbonatites, indicating temperature and fluid control on crystallization and post-crystallization processes that in turn affected the isotopic compositions. The mean and the mode of the $\delta^{13}C$ distribution (~–4‰) in Indian carbonatites are clearly higher compared to that observed in carbonatites worldwide, which could mean that some if not all of these carbonatites contain ^{13}C enriched carbon from the mantle. The $\delta^{13}C$ and

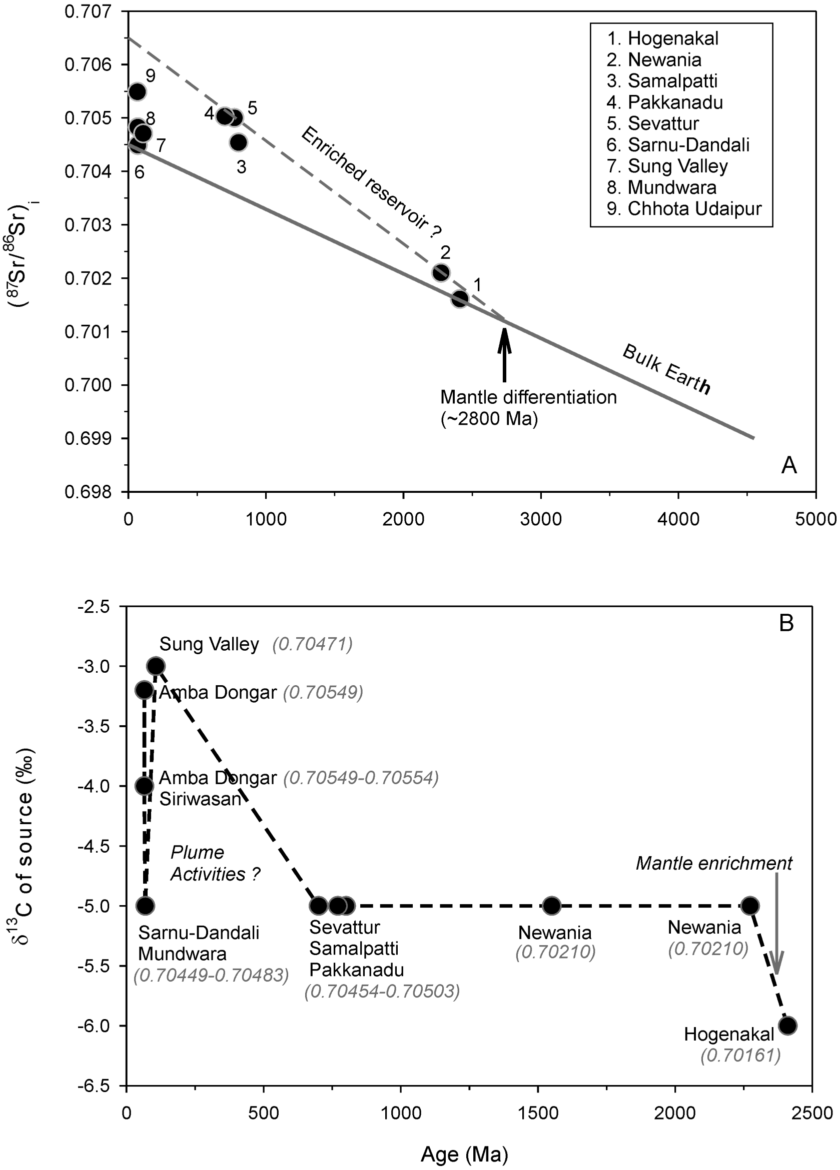

FIG. 12. A. Plot of minimum initial ^{87}Sr/^{86}Sr versus age for Indian carbonatites. The solid line represents the time evolution of ^{87}Sr/^{86}Sr of the bulk earth (Bell and Tilton, 2002). The ^{87}Sr/^{86}Sr evolution line (dashed) for Indian carbonatites intersects the bulk earth at ~2800 Ma, the time for possible crust formation in various parts of India. B. Plot of estimated δ^{13}C composition of the mantle sources versus age for Indian carbonatites. The minimum initial ^{87}Sr/^{86}Sr values for the carbonatites are given in the bracket next to their names.

δ^{18}O of the carbonates from Indian carbonatites suggest a composite evolutionary history. In general, these variations can be grouped into primary (unaltered) and secondary (altered). Primary δ^{13}C and δ^{18}O variations are typically correlated, are the results of primary magmatic processes, and therefore represent unaltered carbonatites. Secondary δ^{13}C and δ^{18}O variations may or may not be correlated, and have resulted from post-magmatic alteration.

The primary variations, which show clusters in a $\delta^{13}C$ versus $\delta^{18}O$ plot, are a result of batch crystallization, and are usually observed in plutonic carbonatites. Our RIFMS model (Ray and Ramesh, 2000) best explains the primary correlated variations, which are consequences of fractional crystallization of carbonate magmas. According to this model, magmatic fluids (CO_2+H_2O) carried by carbonate magmas are the major agents of fractionation during crystallization. Similarly, the secondary variations observed in carbonatites can be accounted for by means of low-temperature alteration using a simple fluid-rock interaction model (Ray and Ramesh, 1999a).

Our modeling results suggest that, except for Hogenakal and northeastern Indian carbonatites, all other Indian carbonatites owe their primary-correlated $\delta^{13}C$ and $\delta^{18}O$ variations to fractional crystallization (Rayleigh type) of carbonate magmas having H_2O/CO_2 ratios between 0.8 and 0.9, at a temperature of ~800°C. For the first time, we have successfully applied the RIFMS model to explain the $\delta^{13}C$ and $\delta^{18}O$ variations in dolomite carbonatites from Newania, and report that dolomite carbonatites fractionate both isotopes to a larger extent compared to calcite carbonatites at similar conditions during fractionation crystallization. Hogenakal and northeastern carbonatites appear to have formed by batch crystallization under plutonic conditions and show limited isotopic variation. The estimated oxygen isotopic compositions of the mantle sources for Indian carbonatites (5.3–7.5‰) fall well within normal mantle values, confirming their magmatic nature. Model calculations also suggest that there is at least a ±2‰ extra fractionation of ^{18}O needed to explain the observed primary variations. We believe that the crystallization of oxide, phosphate, and silicate minerals can easily account for this fractionation. The story of carbon isotopic composition is more complex and interesting. It appears that the $\delta^{13}C$ of Indian carbonatite sources varied with time from a more normal mantle to an enriched mantle value. We believe that such enrichment probably happened sometime around ~2.4 Ga, and was a result of metasomatism by fluids derived from recycled oceanic crust (that carried enriched carbon) of lithospheric mantle. This is because the Indian subcontinental lithospheric mantle has remained a continued source for carbonatites from ~2.4 Ga until 65 Ma.

The extreme isotopic variations observed in Indian carbonatites are typically from altered calcite carbonatites and calcites from ferrocarbonatites. Coexisting calcite and dolomite in most complexes are not in isotopic equilibrium where isotopic compositions of calcites are found to be altered. Oxygen and carbon isotope thermometry of calcite-dolomite equilibrium pairs in Sung Valley suggests a temperature of crystallization in the range 600–800°C. The extreme and uncorrelated variations of $\delta^{13}C$ and $\delta^{18}O$ in all the studied carbonatites are easily accounted for through alteration of magmatic carbonatites by CO_2-rich aqueous fluids of different compositions at low temperatures. The fluids responsible for alteration in most complexes appear to have been either pure meteoric water or hydrothermal fluids that derived their carbon isotopic composition from the carbonatites themselves.

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REFERENCES

Acharya, S. K., Mitra, N. D., and Nandy, D. R., 1986, Regional geology and tectonic setting of northeast India and adjoining region: Memoir of Geological Survey of India, v. 119, p. 6–12.

Bailey, D. K., and Woolley, A. R., 1995, Magnetic quiet periods and stable continental magmatism: Can there be a plume dimension?, *in* Anderson, D. L., Hart, S. R., and Hofmann, A. W., eds., Terra Nostra: Bonn, Germany, Alfred-Wegener-Stiftung, p. 15–19.

Basu, A. R., Renne, P. R., Das Gupta, D. K., Teichman, F., and Poreda, R. J., 1993, Early and late alkali igneous pulses and a high ^{3}He plume origin for the Deccan flood basalts: Science, v. 261, p. 902–906.

Basu, S., and Murty, S. V. S., 2003, Mantle gases in carbonatites: Geochimica Cosmochimica Acta, v. 67, A34.

Bell, K., and Tilton, G. R., 2002, Probing the mantle: The story from carbonatites: EOS (Transactions of the American Geophysical Union), v. 83, p. 273–277.

Cartigny, P., Harris, J. W., Phillips, D., Girad, M., and Javoy, M., 1998, Subduction-related diamonds?: The evidence for a mantle-derived origin from coupled $\delta^{13}C$–$\delta^{15}N$ determinations: Chemical Geology, v. 147, p. 147–159.

Chacko, T., Mayeda, T. K., Clayton, R. N., and Goldsmith, J. R., 1991, Oxygen and carbon isotope fractionation between CO_2 and calcite: Geochimica Cosmochimica Acta, v. 55, p. 2867–2882.

Chandrasekaran, V., Srivastava, R. K., and Chawada, M. P., 1990, Geochemistry of the alkali rocks of Sarnu-Dandali area, District Barmer, Rajasthan, India: Journal of the Geological Society of India, v. 36, p. 365–382.

Deans, T., and Powell, J. L., 1968, Trace elements and strontium isotopes in carbonatites, fluorites, and limestones from India and Pakistan: Nature, v. 218, p. 750–752.

Deines, P., 1989, Stable isotope variations in carbonatites, *in* Bell, K., ed., Carbonatites: Genesis and evolution: London, UK, Unwin Hyman, p. 301–359.

Deines, P., 1992, Mantle carbon: Concentration, mode of occurrence, isotopic composition, *in* Schidlowski, M. et al., eds., Early organic evolution: Implications for mineral and energy resources, Berlin, Germany, Springer-Verlag, p. 133–146.

Demény, A., Ahijado, A., Casillas, R., and Vennemann, T. W., 1998, Crustal contamination and fluid/rock interaction in the carbonatites of Fuerteventura (Canary Islands, Spain): A C, O, H isotope study: Lithos, v. 44, p. 101–115.

Dobson, D. P., Jones, A. P., Rabe, R., Sekine, T., Kurita, K., Taniguchi, T., Kondo, T., Kato, T., Shimomura, S., and Urakawa, S., 1996, In-situ measurement of viscosity and density of carbonate melts at high pressure: Earth and Planetary Science Letters, v. 143, p. 207–215.

Friedman, I., and O'Neil, J. L., 1977, Compilation of stable isotope fractionation factors of geochemical interest, *in* Data of Geochemistry, 6th ed., United States Geological Survey Special Paper, 440-KK, 49 p.

Gwalani, L. G., Rock, N. M. S., Chang, W. J., Fernandez, S., Allegre, C. J., and Prinzhofer, A., 1993, Alkaline rocks and carbonatites of Amba Dongar and adjacent areas, Deccan Igneous Province, Gujarat, India: 1. Geology, Petrography and Petrochemistry: Mineralogy and Petrology, v. 47, p. 219–253.

Hammouda, T., 2003, High-pressure melting of carbonated eclogite and experimental constraints on carbon recycling and storage in the mantle: Earth and Planetary Science Letters, v. 214, p. 357–368.

Haynes, E. A., Moecher, D. P., and Spicuzza, M. J., 2003, Oxygen isotope composition of carbonates, silicates, and oxides in selected carbonatites: Constraints on crystallization temperatures of carbonatite magmas: Chemical Geology, v. 193, p. 43–57.

Heaman, L. M., Srivastava, R. K., and Sinha, A. K., 2002, A precise U-Pb zircon/baddeleyite age for the Jasra igneous complex, Karbi-Anglong District, Assam, NE India: Current Science, v. 82, p. 744–748.

Keller, J., and Hoefs, J., 1995, Stable isotope characteristics of recent natrocarbonatite from Oldoinyo Lengai, *in* Bell, K., and Keller, J., eds., Carbonatite volcanism: Oldoinyo Lengai and the petrogenesis of natrocarbonatites: IAVCE I, Proceedings in Volcanology, v. 4, p. 113–123.

Kent, R. W., Pringle, M. S., Müller, R. D., Saunders, A. D., and Ghose, N. C., 2002, ^{40}Ar/^{39}Ar geochronology of the Rajmahal Basalts, and their relationship to the Kerguelen Plateau: Journal of Petrology, v. 43, p. 1141–1153.

Kjarsgaard, B., and Hamilton, D. L., 1989, The genesis of carbonatites by immiscibility, *in* Bell, K., ed., Carbonatites: Genesis and evolution, London, UK, Unwin Hyman, p. 388–404.

Krishnamurthy, P., 1988, Carbonatites of India. Exploration research of atomic minerals: Special Publication of Indian Atomic Minerals Division, v. 1, p. 81–115.

Krishnamurthy, P., Hoda, S. Q., Sinha, R. P., Banerjee, D. C., and Dwivedy, K. K., 2000, Economic aspects of carbonatites of India: Journal of Asian Earth Sciences, v. 18, p. 229–235.

Kumar, A., Charan, S. N., Gopalan, K., and Macdougall, J. D., 1998, A long-lived enriched mantle source for two Proterozoic carbonatite complexes from Tamil Nadu, southern India: Geochimica et Cosmochimica Acta, v. 62, p. 515–523.

Kumar, D., Mamallan, R., and Dwivedy, K. K., 1996, Carbonatite magmatism in northeast India: Journal of Southeast Asian Earth Sciences, v. 13, p. 145–158.

Kyser, T. K., 1990, Stable isotopes in the continental lithospheric mantle, *in* Menzies, M., ed., The continental lithosphere: Oxford, UK, Oxford University Press, p. 127–156.

Le Bas, M. J., and Srivastava, R. K., 1989, The mineralogy and geochemistry of the Mundwara carbonatite dykes, Sirohi district, Rajasthan, India: Neues Jahrbuch fur Mineralogie-Abhandlungen, v. 160, p. 207–227.

Mattey, D. P., Taylor, W. R., Green, D. H., and Pillinger, C. T., 1990, Carbon isotopic fractionation between CO_2 vapor, silicate and carbonate melts: An experimental study at 20 kbars: Contributions to Mineralogy and Petrology, v. 104, p. 492–505.

McCrea, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: Journal of Chemical Physics, v. 18, p. 849–857.

Miyazaki, T., Kagami, H., Shuto, K., Morikiyo, T., Ram Mohan, V., and Rajasekaran, K. C., 2000, Rb-Sr geochronology, Nd-Sr isotopes and whole rock geochemistry of Yelagiri and Sevattur syenites, Tamil Nadu, south India: Gondwana Research, v. 3, p. 39–53.

Moralev, V. M., Voronovski, S. N., and Borodin, L. S., 1975, New findings about the age of carbonatites and syenites from southern India: Journal of USSR Academy of Sciences, v. 222, p. 46–48.

Nag, S., Sengupta, S. K., Gaur, R. K., and Absar, A., 1999, Alkaline rocks of Samchampi-Samteran, district Karbi-Anglong, Assam, India: Proceedings of Indian Academy of Sciences (Earth and Planetary Sciences), v. 108, p. 33–48.

Nelson, D. R., Chivas, A. R., Chappel, B. W., and McCulloch, M. T., 1988, Geochemical and isotopic systematics in carbonatites and implications for the evolution of oceanic-island sources: Geochimica et Cosmochimica Acta, v. 52, p. 1–17.

Pandit, M. K., Sial, A. N., Sukumaran, G. B., Ramanathan, S., and Ferreira, V. P., 1998, Carbon and oxygen isotopic variation in Tamil Nadu carbonatites: Current Science, v. 74, p. 620–624.

Pandit, M. K., Sial, A. N., Sukumaran, G. B., Pimentel, M. M., Ramasamy, A. K., and Ferreira, V. P., 2002, Depleted and enriched mantle sources for Paleo- and Neoproterozoic carbonatites of southern India: Sr, Nd, C-O isotopic and geochemical constraints: Chemical Geology, v. 189, p. 69–89.

Pineau, F., Javoy, M., and Allégre, C. J., 1973, Etude systématique des isotopes de l'oxygéne, du carbone et du strontium dans les carbonatites: Geochimica et Cosmochimica Acta, v. 37, p. 2363–2377.

Pyle, D. M., Dawson, J. B., and Ivanovich, M., 1991, Short-lived decay series equilibria in the natrocarbonatite lavas of Oldoinyo Lengai, Tanzania: Constraints on the timing of magma genesis: Earth and Planetary Science Letters, v. 105, p. 378–396.

Ray, J. S., 1997, Stable and radioisotopic constraints on the evolution of Mesozoic carbonatite-alkaline complexes of India: Unpubl. Ph.D. thesis, M. S. University of Baroda, Vadodara, India, 186 p.

Ray, J. S., 1998, Trace element and isotope evolution during concurrent assimilation, fractional crystallization, and liquid immiscibility of a carbonated silicate magma: Geochimica et Cosmochimica Acta, v. 62, p. 3301–3306.

Ray, J. S., and Pande K., 1999, Carbonatite-alkaline magmatism associated with continental flood basalts at stratigraphic boundaries: Cause for mass extinctions: Geophysical Research Letters, v. 26, p. 1917–1920.

Ray, J. S., Pande, K., and Pattanayak, S. K., 2003, Evolution of Amba Dongar carbonatite complex: Constraints from ^{40}Ar-^{39}Ar chronologies of the Inner Basalt and an alkaline plug: International Geology Review, v. 45, p. 857–862.

Ray, J. S., Pattanayak, S. K., and Pande, K., 2005, Rapid emplacement of the Kerguelen plume-related Sylhet Traps, eastern India: Evidence from ^{40}Ar-^{39}Ar geochronology: Geophysical Research Letters, v. 32, p. L10303.

Ray, J. S., and Ramesh, R., 1999a, Evolution of carbonatite complexes of the Deccan flood basalt province: Stable carbon and oxygen isotopic constraints: Journal of Geophysical Research, v. 104, p. 29,471–29,483.

Ray, J. S., and Ramesh, R., 1999b, A fluid-rock interaction model for carbon and oxygen isotopic variations in altered carbonatites: Journal of the Geological Society of India, v. 54, p. 179–186.

Ray, J. S., and Ramesh, R., 2000, Rayleigh fractionation of stable isotopes from a multicomponent source: Geochimica et Cosmochimica Acta, v. 64, p. 299–306.

Ray, J. S., Ramesh, R., and Pande, K., 1999, Carbon isotopes in Kerguelen plume derived carbonatites: Evidence for recycled inorganic carbon: Earth and Planetary Science Letters, v. 170, p. 205–214.

Ray, J. S., Ramesh, R., Trivedi, J. R., and Patel, P. P., 1994, Stable isotopic studies on Amba Dongar carbonatites [abs.], *in* Symposium on mantle dynamics and its relation to Earth and volcanism, Calcutta India, p. 23–26.

Ray, J. S., Trivedi, J. R., and Dayal, A. M., 2000, Strontium isotope systematics of Amba Dongar and Sung Valley carbonatite-alkaline complexes, India: Evidence for liquid immiscibility, crustal contamination, and long-lived Rb/Sr enriched mantle sources: Journal of Asian Earth Sciences, v. 18, p. 585–594.

Richet, P., Bottinga, Y., and Javoy, M., 1977, A review of hydrogen, carbon, nitrogen, oxygen, sulfur, and chlorine stable isotope fractionation among gaseous molecules: Annual Review of Earth and Planetary Sciences, v. 5, p. 65–1101.

Rosenbaum, J., and Sheppard, S. M. F., 1986, An isotopic study of siderites, dolomites, and ankerites at high temperatures: Geochimica et Cosmochimica Acta, v. 50, p. 1147–1150.

Rosenbaum, J. M., Walker, D., and Kyser, T. K., 1994, Oxygen isotope fractionation in the mantle: Geochimica et Cosmochimica Acta, v. 58, p. 4767–4777.

Santos, R. V., and Clayton, R. N., 1995, Variations of oxygen and carbon isotopes in carbonatites: A study of Brazilian alkaline complexes: Geochimica et Cosmochimica Acta, v. 59, p. 1339–1352.

Sarkar, A., and Bhattacharya, S. K., 1992, Carbonatites from Rajasthan indicate mantle carbon- and oxygen-isotope composition: Current Science, v. 62, p. 368–370.

Sarkar, A., Bhattacharya, S. K., Srivastava, R. K., and Chandrasekaran, V., 1985, Stable isotope studies in Indian carbonatites, *in* Proceedings of the III National Symposium on Mass Spectrometry, Indian Society for Mass Spectrometry, E-10, p. 1–3.

Sarkar, A., Datta, A. K., Poddar, B. C., Bhattacharyya, B. K., Kollapuri, V. K., and Sanwal, R., 1996, Geochronological studies of Mesozoic igneous rocks from eastern India: Journal of South Asian Earth Sciences, v. 13, p. 77–81.

Sasada, T., Hiyagon, H., Bell. K., and Ebihara, M., 1997, Mantle-derived noble gases in carbonatites: Geochimica Cosmochimica Acta, v. 61, p. 4219–4228.

Scheele, N., and Hoefs, J., 1992, Carbon isotope fractionation between calcite, graphite, and CO_2: An experimental study: Contributions to Mineralogy and Petrology, v. 112, p. 35–45.

Schleicher, H., Kramm, U., Pernicka, E., Schidlowski, M., Schmidt, F., Subramaniam, V., Todt, W., and Viladkar, S. G., 1998, Enriched subcontinental upper mantle beneath southern India: Evidence from Pb, Nd, Sr, and C-O isotopic studies on Tamil Nadu carbonatites: Journal of Petrology, v. 39, p. 1765–1785.

Schleicher, H., Todt, W., Viladkar, S. G., and Schmidt, F., 1997, Pb/Pb age determinations on Newania and Sevattur carbonatites of India: Evidence for multi-stage histories: Chemical Geology, v. 140, p. 291–273.

Shastry, A., and Kumar, S., 1996, Trace and rare earth elements geochemistry of alkaline rocks of Sarnu-Dandali, Barmer, Rajasthan: Journal of the Geological Society of India, v. 48, p. 663–670.

Sheppard, S. M. F., and Schwarcz, H. P., 1970, Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite: Contributions to Mineralogy and Petrology, v. 26, p. 161–198.

Simonetti, A., Bell, K., and Viladkar, S. G., 1995, Isotopic data from the Amba Dongar carbonatite complex, west-central India: Evidence for an enriched mantle source: Chemical Geology, v. 122, p. 185–198.

Srivastava, R. K., and Taylor, L. A., 1996, Carbon- and oxygen-isotope variations in Indian carbonatites: International Geology Review, v. 38, p. 419–429.

Sukheswala, R. N., and Udas, G. R., 1963, Note on the carbonatite of Amba Dongar and its economic potentialities: Science and Culture, v. 29, p. 563–568.

Taylor, H. P., Frechen, J., and Degens, E. T., 1967, Oxygen and carbon isotope studies of carbonatites from the Laacher See district, West Germany and the Alnö district, Sweden: Geochimica et Cosmochimica Acta, v. 31, p. 407–430.

Tilton, G. R., and Bell, K., 1994, Sr-Nd-Pb isotope relationship in Late Archean carbonatites and alkaline complexes: Applications to the geochemical evolution of Archean mantle: Geochimica et Cosmochimica Acta, v. 58, p. 3145–3154.

Tolstikhin, I. N., Kamensky, I. L, Marty, B., Nivin, V. A., Vetrin, V. R., Balaganskaya, E. G., Ikorsky, S. V., Gannibal., M. A., Weiss, D., Verhulst, A., and Demaiffe, D., 2002, Rare gas isotopes and parent trace elements in ultrabasic-alkaline-carbonatite complexes, Kola Peninsula: Identification of lower mantle plume component: Geochimica et Cosmochimica Acta, v. 66, p. 881–901.

Veena, K., 2000, Radiogenic and stable isotopic systemtics of some Phanerozoic Indian carbonatites: Implications on mantle source characteristics: Unpubl. Ph.D. thesis, Osmania University, Hyderabad, India.

Veena, K., Pandey, B. K., Krishnamurthy, P., and Gupta, J. N., 1998, Pb, Sr and Nd isotopic systematics of the carbonatites of Sung Valley, Meghalaya, northeast India: Implications for contemporary plume-related mantle source characteristics: Journal of Petrology, v. 39, p. 1875–1884.

Viladkar, S. G., 1996, Geology of the carbonatite-alkalic diatreme of Amba Dongar, Gujarat: Ahmedabad, India, Gujarat Mineral Development Corporation, 74 p.

Viladkar, S. G., 1998, Carbonatite occurrences in Rajasthan, India: Petrology, v. 6, p. 272–283.

Viladkar, S. G., 2001, Carbonatite-alkaline complexes within Deccan basalt volcanic province, western India: Indian Journal of Geochemistry, v. 16, p. 25–42.

Viladkar, S. G., and Schildlowski, M., 2000, Carbon and oxygen isotope geochemistry of the Amba Dongar carbonatite complex, Gujarat, India: Gondwana Research, v. 3, p. 415–424.

Wooley, A. R., 1989, The spatial and temporal distribution of carbonatites, *in* Bell, K., eds., Carbonatites: Genesis and evolution, London, UK, Unwin Hyman, p. 15–37.

Wooley, A. R., and Kempe, D. R. C., 1989, Carbonatites: Nomenclature, average chemical compositions, and element distribution, *in* Bell, K., eds., Carbonatites: Genesis and evolution, London, UK, Unwin Hyman, p. 1–13.

Yaxley, G. M., and Brey, G. P., 2004, Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: Implications for petrogenesis of carbonatites: Contributions to Mineralogy and Petrology, v. 146, p. 606–619.

Zheng, Y.-F., 1993, Calculation of oxygen isotope fractionation in anhydrous silicate minerals: Geochimica et Cosmochimica Acta, v. 57, p. 1079–1091.

Zheng Y.-F., 1996, Oxygen isotope fractionations involving apatites: Application to paleotemperature determination: Chemical Geology, v. 127, p. 177–187.

Zheng Y.-F., 1999, Oxygen isotope fractionations in carbonate and sulfate minerals: Geochemical Journal, v. 33, p. 109–126.