

**Table 3.** Excited singlet-state  $pK_a$  ( $pK_a^*$ ) values by different methods

$pK_a^*$	From rate constants	Fluo. titration†	Forster cycle†		
			Abs.	Flu.	Ave.
	1.54	19	4.9	-1.75	1.65

†From ref. 5.

acid-base pair in the two electronic states and cancel each other.

1. Weller, A., *Prog. React. Kinet.*, 1961, 1, 187.
2. Schulmann, S. G. and Capamacchia, A. C., *J. Phys. Chem.*, 1975, 79(14), 1337.
3. Weller, A., *Z. Physik. Chim.*, 1955, 3, 238.
4. Weller, A., *Z. Physik. Chim.*, 1958, 17, 224.
5. Swaminathan, M. and Dogra, S. K., *J. Chem. Soc. Perkin Trans. II*, 1984, 947.
6. Iotgeonson, M. J. and Hartter, D. R., *J. Am. Chem. Soc.*, 1963, 85, 878.
7. Swaminathan, M. and Dogra, S. K., *Indian J. Chem.*, 1983, A22, 853.
8. Haris, C. M. and Sellinger, B. K., *J. Phys. Chem.*, 1980, 84(11), 1366.
9. Haris, C. M. and Sellinger, B. K., *J. Phys. Chem.*, 1980, 84(8), 891.
10. Weller, A., *Z. Electrochem.*, 1952, 56, 662; 1954, 58, 849.
11. Vander Donckt, E., *Prog. React. Kinet.*, 1970, 5, 273.
12. Forster, Th., *Z. Electrochem.*, 1950, 54, 531.

**ACKNOWLEDGEMENTS.** I thank Prof. S. K. Dogra, Department of Chemistry, Indian Institute of Technology, Kanpur, for providing the research facilities and Dr A. K. Mishra for help in the measurement of lifetimes of the excited species

14 February 1991; revised accepted 3 October 1991

## Carbonatites from Rajasthan indicate mantle carbon- and oxygen-isotope composition

A. Sarkar\* and S. K. Bhattacharya

Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India

\*Present address: Department of Geology, Presidency College, Calcutta 700 073, India

The stable-isotope ratio of carbon ( $\delta^{13}\text{C}$ ) in carbonatites is believed to represent the composition of juvenile carbon in the earth's mantle. We have carried out the first analysis of oxygen and carbon isotopes in a suite of Indian carbonatites from Mundwara and Barmer alkaline complexes of Rajasthan. The data show a Raleigh fractionation trend of an original carbonatite magma at 700°C, followed by reequilibration of ferrocarnatites and alteration of alvikites at low temperature. Only the unfractionated sovites represent juvenile (mantle) carbon- and oxygen-isotope values. We

suggest that mantle carbon ( $\delta^{13}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) below the Indian crust have values of -6.4‰ (PDB) and +6.1‰ (SMOW) respectively and are similar to values obtained elsewhere.

KIMBERLITES and diamonds, being mantle-derived, have also been considered in studies of the composition of juvenile carbon in the mantle<sup>1,2</sup>. But, compared to the  $\delta^{13}\text{C}$  in diamonds and kimberlites (and also the  $\text{CO}_2$  trapped in MORB glasses), carbonatite  $\delta^{13}\text{C}$  shows a large scatter (as high as 10‰)<sup>3</sup>. This might be due to the inhomogeneous composition of mantle carbon source or might represent an unusual fractionation process while the carbonatite magma was being emplaced<sup>2,4</sup>. Though occurrences of a number of carbonatite bodies have been reported in India<sup>5,6</sup>, so far no attempt has been made to derive their isotopic compositions. We report here the first measurements of oxygen- ( $\delta^{18}\text{O}$ ) and carbon-isotope compositions of a series of carbonatites from Barmer and Mundwara alkaline complexes of Rajasthan and try to add some new input to the carbonatite problem.

Samples of carbonatites (veins, bands and dykes) were collected from Mundwara alkaline complex, Sirohi<sup>5</sup> (lat. 24° 49' 48" N, long. 72° 32' 19" E) and Sarnu-Dandali complex (lat. 25° 46' 22" N, long. 71° 43' 17" E) of Barmer district. These are post-Cretaceous intrusives and are probably related to an ill-defined post-Deccan alkaline province. The carbonatites are classified into sovite (containing pure calcite), alvikite and ferrocarnatite (containing iron calcite and siderite respectively). Both alvikites and ferrocarnatites can be further classified into various early and late phases (R. K. Srivastava, personal communication). All the samples were powdered and dried at 150°C under vacuum for one hour. About 0.5 mg dried sample was reacted with 100%  $\text{H}_3\text{PO}_4$  at 50°C in an on-line  $\text{CO}_2$  extraction system. Evolved  $\text{CO}_2$  gas, thoroughly cleaned of water vapour, was analysed in a VG Micromass 602D mass spectrometer for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  (ref. 7). Precision of measurement based on the replicate analysis of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of internal laboratory standards Z-carrara and MAKARB is  $< \pm 0.1\text{‰}$  (refs. 7, 8). Data for  $\delta^{13}\text{C}$  (against PDB standard) and  $\delta^{18}\text{O}$  (against SMOW standard) are given in Table 1 and plotted in Figure 1. The  $\delta^{13}\text{C}$  values range from -6.4‰ (in sovite) to -1.1‰ (in ferrocarnatite), i.e. a spread of ~5‰. The  $\delta^{18}\text{O}$  spread, on the other hand, is much larger. It ranges from a sovite value of +6.1‰ to +28.2‰ in the ferrocarnatite. A distinct grouping can be seen in the isotope values. The sovites are the most depleted and the ferrocarnatites the most enriched in  $^{18}\text{O}$  and  $^{13}\text{C}$ , with the alvikite values intermediate between sovite and ferrocarnatite. The sovite samples and a set of alvikite samples show strong correlation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  (see line AA' in Figure 1). We attribute this

Table 1. Oxygen and carbon-isotope data for Rajasthan carbonatites

Sample	Locality	Rock type	$\delta^{18}\text{O}^*$ (‰)	$\delta^{13}\text{C}^\dagger$ (‰)
M-1	Mundwara	Sovite	+7.9	-5.2
M-2	Mundwara	Sovite	+6.1	-6.4
C-143	Barmer (S)	Alvikite	+8.2	-5.4
C-254	Barmer (D)	Alvikite	+10.9	-4.4
C-291	Barmer (D)	Alvikite	+22.75	-6.1
M-119	Mundwara	Alvikite	+9.15	-4.75
C-255	Barmer (D)	Alvikite	+16.35	-3.6
C-124	Barmer (S)	Alvikite	+16.7	-2.0
M-149	Mundwara	Alvikite	+25.2	-5.2
C-290	Barmer (D)	Alvikite	+13.95	-5.65
C-94	Barmer (S)	Alvikite	+18.7	-2.7
M-3	Mundwara	Alvikite	+21.55	-3.8
A-841	West of Barmer town	Alvikite	+17.0	-1.60
121-M	West of Barmer town	Alvikite	+16.2	-1.2
C-177	Barmer (S)	Ferrocarnatite	+28.2	-1.4
A-161	West of Barmer town	Ferrocarnatite	+21.2	-1.6
A-805	West of Barmer town	Ferrocarnatite	+25.4	-1.6
A-807	West of Barmer town	Ferrocarnatite	+27.5	-1.1
A-18	West of Barmer town	Carbonated orthoclase	+24.35	-3.45
A-800	West of Barmer town	Carbonated orthoclase	+24.35	-2.05

S denotes village Sarnu; D, village Dandali.

Data are with respect to \*SMOW standard, †PDB standard.

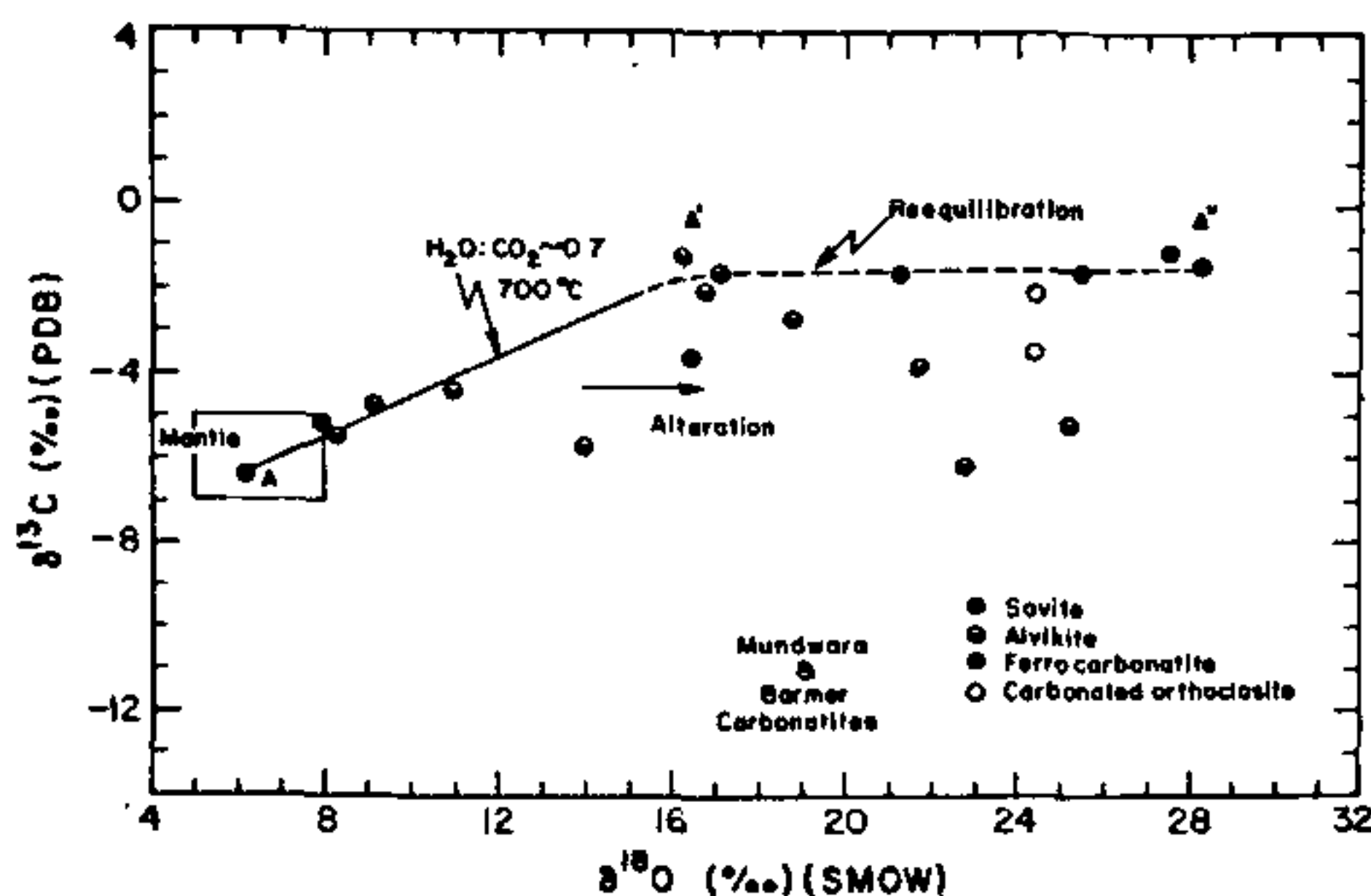


Figure 1. Plot of  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  of the Rajasthan carbonatites.

positive correlation to the fractionation of an original carbonatite magma, as found earlier in the case of near-surface (volcanic) carbonatites<sup>9,10</sup>. The ferrocarnatites show positive shifts in  $\delta^{18}\text{O}$  relative to the final composition defined by A'. Some alvikites and orthoclase samples also lie below the lines AA' and A'A'' (Figure 1).

The net fractionation trend in these carbonatites is sovite-alvikite-ferrocarnatite, which is also supported by their major- and trace-element chemistries (R. K. Srivastava, personal communication). The exact mechanism of fractionation is, however, somewhat complicated. Carbonatite magma is a complex solution of  $\text{CaCO}_3$ - $\text{CO}_2$ - $\text{H}_2\text{O}$ , in which the relative amounts of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  play an important role<sup>3</sup>. Pineau *et al.*<sup>4</sup> suggested a model where the Rayleigh fractionation of carbon and oxygen isotopes between crystallizing calcite and the

coexisting vapour phase is responsible for the simultaneous enrichment in both. The basic assumptions in their model are that the calcites form a continuous crystallization sequence and the coexisting vapour phase is the main source of oxygen. From a starting composition of  $\delta^{13}\text{C} = -4\text{‰}$  and  $\delta^{18}\text{O} = +7\text{‰}$ , they calculated the path of Rayleigh fractionation at  $700^\circ\text{C}$  in a closed system. The slope of the path is determined by the  $\text{H}_2\text{O}/\text{CO}_2$  mole ratio. The solid line AA' in Figure 1 represents the fractionation path for the Mundwara and Barmer carbonatites and is computed on the basis of Pineau *et al.*'s<sup>4</sup> model using a temperature of  $700^\circ\text{C}$  and a  $\text{H}_2\text{O}/\text{CO}_2$  mole ratio of  $\sim 0.7$ . We have taken an initial composition of  $\delta^{18}\text{O} = +6.1\text{‰}$  and  $\delta^{13}\text{C} = -6.4\text{‰}$ , which corresponds to the unfractionated, deep-seated and probably the most pristine (sovite) carbonatite. This becomes evident when these values are compared with the available mantle composition. The box in Figure 1 shows the probable mantle composition of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  based on the analysis of trapped  $\text{CO}_2$  in MORB glasses and diamonds from various parts of the world<sup>2,11</sup>. Note that only the sovites fall within the range of mantle carbon and oxygen values, and represent the first calcites crystallized from a residual carbothermal liquid derived by the fractional crystallization of an original basanitic magma<sup>5</sup>. Therefore the mantle (source) carbon ( $\delta^{13}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotopes below the Indian crust can be assigned values of  $-6.4\text{‰}$  and  $+6.1\text{‰}$  respectively. Interestingly, recent measurements on Deccan basalt flows from Mahabaleshwar section show that the pristine composition of their mantle source also has a  $\delta^{18}\text{O}$  value of  $+6\text{‰}$  (SMOW)<sup>12</sup>.

However, it is difficult to generate the heavy-oxygen-

isotope ratios in ferrocarnatites only by the Raleigh fractionation of a liquid. The maximum positive shift in ferrocarnatite  $\delta^{18}\text{O}$  is  $\sim 12\%$  with respect to A'. Loss of isotopically lighter water by pressure release during successive emplacements has been suggested as a cause of such enrichment<sup>10</sup>. Petrological and geochemical evidences indicate that these carbonatites formed from a liquid that was charged with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  till the last stage<sup>5</sup>. Hence we rule out any significant water loss in the process. We therefore propose that the highly enriched ferrocarnatites were generated by reequilibration of the end-stage calcites (with composition similar to that of the alvikites at A' stage) with the magmatic water at low temperature. This proposition is consistent with the picture that the ferrocarnatites were emplaced at a shallower level subsequent to their formation. The carbon-isotope fractionation factor between calcite and  $\text{CO}_2$ , i.e.  $\alpha_{\text{H}_2\text{O}}^{\text{CaCO}_3}$ , shows a very small change of  $\sim 2\%$  in the temperature range of 100–700°C, with the calcite being depleted in heavy isotope<sup>13</sup>. In contrast,  $\alpha_{\text{H}_2\text{O}}^{\text{CaCO}_3}$  for oxygen in this range exhibits a large change of  $\sim 15\%$ , with the calcite enriched in heavy isotope<sup>14</sup>. Hence a reequilibration of the ferrocarnatites at lower temperature would show a large enrichment (positive shift) in  $\delta^{18}\text{O}$  but not in  $\delta^{13}\text{C}$ . The line A'A" in Figure 1 represents the postulated reequilibration path for ferrocarnatites.

Six alvikites and one orthoclase sample lie below the line AA'–A'A", indicating enrichment in  $^{18}\text{O}$  by variable amounts along with some depletion in  $^{13}\text{C}$ . The maximum enrichment in  $^{18}\text{O}$  is up to 17% while the  $^{13}\text{C}$  depletion is up to 5%. There may be two reasons for this: (i) interaction of carbonatite magma with atmospheric  $\text{CO}_2$ , (ii) alteration by meteoric water. A complete exchange with atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C} = -7\%$  PDB) either during the aerial exposure of the magma or through the dissolved  $\text{CO}_2$  in ground water might produce the  $\delta^{13}\text{C}$  depletion. We do not consider this mechanism to be responsible for the isotopic shifts, firstly because the alvikites show well-developed calcite crystals and not the chilling effect one would expect from a complete exposure to atmosphere, and, secondly, the total amount of carbon available, either through an exposure to the atmosphere or in the dissolved state (as bicarbonate in ground water), is quite small for changing the carbonatite carbon-isotope value. Consequently we attribute the shifts to variable amount of alteration (through dissolution–reprecipitation) by meteoric water. We suggest that these alvikites (and orthoclase) exchanged their original oxygen with the meteoric water at low temperature, thereby increasing their  $^{18}\text{O}$  content. The magnitude of such enrichment can be as high as +28% if it takes place at near-surface temperature ( $\sim 25^\circ\text{C}$ ) (considering the  $\alpha_{\text{H}_2\text{O}}^{\text{CaCO}_3}$  at  $25^\circ\text{C}$  of  $\sim 1.0283$ , ref. 15). Such post-crystallization alteration by meteoric water and large

enrichment in  $^{18}\text{O}$  have earlier been reported by Taylor<sup>15</sup>. Since meteoric water has very little carbon, the  $\delta^{13}\text{C}$  change in this process is expected to be negligible. Hence we think that these values were generated from the line AA' by positive shift in  $\delta^{18}\text{O}$  (but no change in  $\delta^{13}\text{C}$ ). The course of this shift (and alteration) is shown by the arrow in Figure 1.

To summarize: The Mundwara and Barmer carbonatites show a Raleigh fractionation trend of an original carbonatite magma at 700°C, resulting in a progressive enrichment in both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . The net fractionation trend in the carbonatites is sovite–alvikite–ferrocarnatite. Of these, ferrocarnatites show reequilibration with magmatic water at a low temperature and are highly enriched in  $\delta^{18}\text{O}$ . Some alvikites and an orthoclase also show post-crystallization meteoric-water alteration, exhibiting variable enrichment in  $\delta^{18}\text{O}$ . Sovies, by far, are the most unfractured and pristine carbonatite and hence their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  (most depleted) values can be taken to represent the mantle values. The study therefore indicates that it is necessary to trace out the undifferentiated carbonatite to retrieve the juvenile carbon- and oxygen-isotope values. It seems that the juvenile carbon and oxygen are globally homogeneous in composition.

1. Faure, G., *Principles of Isotope Geology*, (John Wiley & Sons), New York, 1986, pp. 589.
2. Deines, P. and Gold, D. P., *Geochim. Cosmochim. Acta*, 1973, 37, 1709.
3. Samoilov, V. S and Plyusnin, G. S., *Geokhimiya*, 1982, 9, 1230
4. Pineau, F., Javoy, M and Allègre, C. J., *Earth Planet. Sci. Lett.*, 1976, 29, 413.
5. Subramanyam, N. P. and Rao, G. V. U., *J. Geol. Soc. India*, 1977, 18, 306
6. Krishnamurthy, P., *J. Geol. Soc. India*, 1977, 18, 265.
7. Sarkar, A and Bhattacharya, S. K., Proceedings of the 4th National Symposium on Mass Spectrometry, Bangalore, 1988.
8. Sarkar, A., Ramesh, R. and Bhattacharya, S. K., *Terra Nova*, 1990, 2, 489.
9. Suwa, K., Oana, S., Wanda, H. and Osaki, S., *Phys. Chem. Earth*, 1975, 9, 735.
10. Nielsen, T. F. D. and Buchardt, B., *Chem. Geol.*, 1985, 53, 207.
11. Nelson, D. R., Chivas, A. R., Chappel, B. W. and McCulloch, M. T., *Geochim. Cosmochim. Acta*, 1988, 52, 1.
12. Matsuhisa, Y., Bhattacharya, S. K., Gopalan, K., Mahoney, J., and Macdougall, J. D., *Terra Cognita*, 1986, 6, 181.
13. Robinson, B. W., *Geochem. J.*, 1975, 9, 43.
14. Taylor, H. P., *Econ. Geol.*, 1974, 69, 843
15. Taylor, H. P., Frechen, J. and Degens, E. T., *Geochim. Cosmochim. Acta*, 1967, 31, 407.

ACKNOWLEDGEMENT We thank Prof. R. K. Srivastava of Rajasthan University for providing the Mundwara and Barmer carbonatite samples and Prof. B. L. K. Somayajulu, S. Krishnaswami and K. Gopalan for encouragement.

Received 30 April 1991; revised accepted 30 April 1991