

Noble gases in South Indian carbonatites: Trapped and in situ components

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Abstract

We have studied noble gases in carbonates and apatites from three carbonatites of South India, namely Hogenakal (2400 Ma), Sevattur (770 Ma) and Khambamettuu (523 Ma) by vacuum crushing. Apatite has also been analysed by pyrolysis. Vacuum crushing mostly releases the trapped gas components. The ratios $^{21}\text{Ne}/^{20}\text{Ne}$, $^{22}\text{Ne}/^{20}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ increase with progressive crushing due to preservation of different composition gases in smaller inclusions released in later steps. This heterogeneity of isotopic composition of fluid inclusions is a consequence of the involvement of magmas carrying different noble gas signatures. The inclusions with lower ratios suggest the presence of a subducted atmospheric component, while the higher $^{21}\text{Ne}/^{20}\text{Ne}$, $^{22}\text{Ne}/^{20}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ can be attributed to the presence of an enriched lithospheric mantle component. In addition, very minor trapped gases from less degassed, deeper mantle may also be present but overprinted by lithospheric and/or nucleogenic components. We propose that these carbonatites were generated only in an advanced stage of magmatism when this lithospheric component overwhelmed any contribution from the deeper mantle source. The lithospheric mantle underwent enrichment during an ancient subduction process through mantle metasomatism manifested in nucleogenic/radiogenic isotopic ratios of $^{21}\text{Ne}/^{20}\text{Ne}$, $^{22}\text{Ne}/^{20}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$. The apatites analysed by pyrolysis clearly show nucleogenic ^{21}Ne from $^{18}\text{O}(\alpha, n)$ reaction. We have demonstrated the potential of using U, Th– ^{21}Ne systematics as a thermo-chronometer in conjunction with the established U, Th– ^4He and U– ^{136}Xe clocks. While for Hogenakal, the U, Th– ^{21}Ne age of 845 ± 127 Ma is in agreement with the age of emplacement of other adjacent younger carbonatites, syenites and alkali granites, for the Sevattur apatite (738 ± 111 Ma) it indicates the crystallisation age.

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1. Introduction

The paucity of noble gas data in carbonatites lies in the very low noble gas concentration in these rocks and their overprinting by atmospheric contamination. Carbonatites have been reported from both depleted and enriched reservoirs of the mantle (Bell and Blekinshop, 1989; Kwon et al., 1989). A study of noble gases in carbonatites can

be useful to trace the contribution from the plume-like, deeper, less degassed mantle from the MORB-like shallow degassed mantle. So far, the only carbonatites for which detailed noble gas studies are reported are the Kola, Canadian and Brazilian carbonatites, all of which suggest a deep mantle source (Marty et al., 1998; Tolstikhin et al., 2002; Sasada et al., 1997). For Kola, a plume source with a trapped $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of ~ 4000 , $^{21}\text{Ne}/^{22}\text{Ne}$ ratio of ~ 0.045 and $^3\text{He}/^4\text{He}$ ratio of $\sim 24R/R_A$ have been observed (Marty et al., 1998; Tolstikhin et al., 2002). The studied Brazilian and Canadian carbonatites have a trapped $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of ~ 6400 and show the presence of excess ^{129}Xe (Sasada et al., 1997). Noble gas results from Sung

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Valley and Ambadongar also show excess ^{129}Xe (Basu and Murty, 2006). The $^{21}\text{Ne}/^{22}\text{Ne}$ ratios in the range of 0.031–0.069 for Sung Valley and 0.030–0.054 for Ambadongar are consistent with the presence of a MORB component admixed with crustal noble gases introduced into the lithospheric mantle by subduction (Basu and Murty, 2006). Thus, no unique source region in the mantle can be ascribed to the carbonatites. The present contribution discusses the results obtained from noble gas analyses of carbonatites from Hogenakal, Sevattur and Khambamettu and their implications towards understanding their mantle source region.

2. Geological settings and earlier studies

The Hogenakal carbonatitic complex was emplaced into a series of deep NNE to NE trending fracture zones in the southern Indian craton as seen in Fig. 1 and occurs as discontinuous lensoid bodies (Grady, 1971). Both Rb–Sr and Sm–Nd isochron ages for the Hogenakal carbonatite indicates its emplacement into the crust at 2.4 Ga (Kumar et al., 1998). The Sevattur carbonatite, which occurs as arcuate bodies bordering a large syenitic stock, is spatially associated with the Hogenakal carbonatite and located only 70 km ENE of it (Fig. 1). However, it is much younger than the Hogenakal complex and its age is 0.77 Ga based on mica-whole rock Rb–Sr isochrons for the carbonatites

(Kumar et al., 1998). The Sr–Nd isotopic data are compatible with an enriched mantle source for the Sevattur carbonatites (Kumar et al., 1998; Pandit et al., 2002).

The carbonatites from Khambamettu are associated with the Western Ghat faults and occur as minor occurrences in the form of dykes and veins (Krishnamurthy, 1988). However, this carbonatite still needs to be analyzed for various isotopes and dated precisely. To date, the only available age obtained for this carbonatite is 523 Ma using Rb–Sr and Sm–Nd dating techniques (Kumar, unpublished data).

3. Sample characterisation and experimental procedures

Only fresh and unaltered samples have been used in this study. All noble gases were determined from coarse-grained (mm sized) carbonate and apatite. Mineral identification was confirmed using X-ray diffraction (XRD) studies. The minerals have also been analysed for K, Na and Fe by atomic absorption spectroscopy (AAS) and Ca and Mg by Inductively-Coupled-Plasma-Atomic-Emission-Spectroscopy (ICPAES). The carbonates are predominantly calcitic, with Mg and Fe both <0.5% except for SE-C3 where Mg(1.8%) and Fe(1.0%) are slightly higher. Thin section studies were used to distinguish between early and late stages of carbonatites and those showing late stage phases (quartz, zeolite, fluorite, chlorite, rutile and

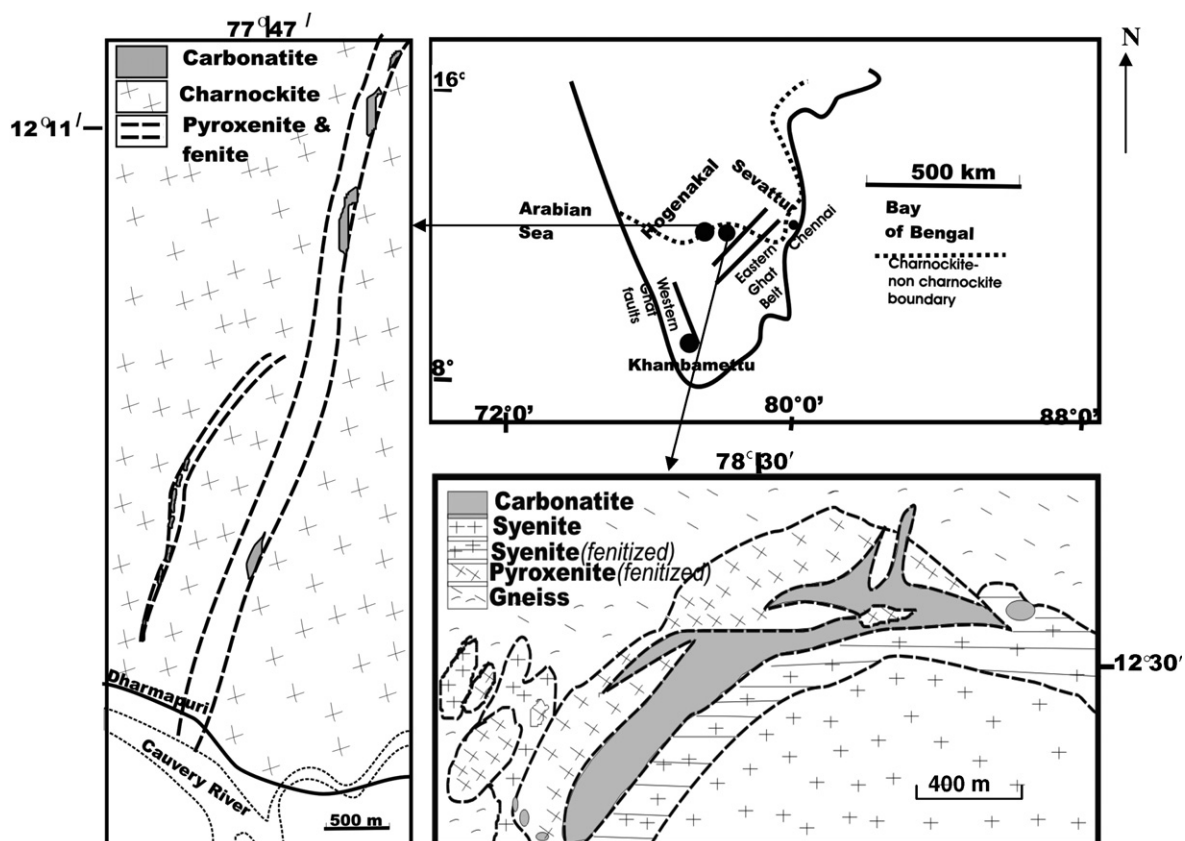


Fig. 1. Sketch map of India showing the approximate locations of the carbonatitic complexes of Hogenakal, Sevattur and Khambamettu.

haematite) as well as recrystallization textures were not used in this study.

The samples analysed in this study are abbreviated as follows: H, Hogenakal; SE, Sevattur and K, Khambamettu; the letters C and A are used for calcite and apatite respectively. The numbers indicate different samples while different letters (e.g. A, B and C) after the numbers indicate different aliquots.

3.1. Noble gas extraction procedures

While apatite was analysed by both stepwise pyrolysis and vacuum crushing (VC), the carbonates and magnetites were analysed only by vacuum crushing. VC releases the trapped gases from the fluid inclusions with minimal contribution from the *in situ* matrix component. It would be difficult to analyse the carbonates by pyrolysis because of the huge amount of CO₂ that would be released on melting. Subsequent to gas extraction by either VC or pyrolysis, all noble gases were analysed following the procedures described in Murty (1997). For pyrolysis, the apatite was wrapped in Al foil and mounted in the sample line. The system was evacuated and baked up to ~150 °C under vacuum. Initially the sample was introduced into a double-walled quartz finger where it was combusted at 400 °C in the presence of O₂ (at 2 torr pressure) to get rid of any surficial contaminants that may be present. It was then directly dropped into a Mo crucible where it was heated from 600 °C in small incremental steps of 200–250 °C up to melting to ensure the complete release of gases.

For VC, about a gram of sample was loaded in a stainless steel crusher with a magnetic piston and baked overnight under vacuum at 150 °C. The sample gas was extracted by crushing the sample with the piston that was activated using an external solenoid. During crushing, a sequence of three steps of 15, 300 and 300 strokes for carbonates, and 15, 500 and 500 strokes for the apatites were used to evaluate any possible change in the composition of the released gases with progressive crushing. The initial step was used to rupture the larger inclusions that may contain a greater fraction of atmospheric gases as observed from previous studies (Sarda et al., 1988; Jambon et al., 1985). The second step was the main extraction step while the third step enabled complete release of the gases from the samples.

After extraction, the noble gas mixture was purified and separated into individual noble gases using the standard procedures. He and Ne were separated from the other noble gases using a charcoal trap held at liquid nitrogen temperature to trap the heavier noble gases. The gases were purified using Ti–Zr/Ti getters. While a glass extraction system was used for pyrolysis, a metal system has been used in case of the VC.

Routinely blanks were performed in identical fashion to the sample steps both for VC and pyrolysis (and combustion) and the data acquired is corrected for blanks. Blank compositions were almost atmospheric for all the noble

gases. Typical blank concentrations (in 10^{–12} cc STP) for VC are 20(⁴He), 4.4(²⁰Ne), 0.8(³⁶Ar), 1(⁸⁴Kr) and 0.3(¹³²Xe), and for pyrolysis at 1800 °C are 600(⁴He), 230(²⁰Ne), 2.2(³⁶Ar), 0.6(⁸⁴Kr) and 0.1(¹³²Xe). Blank concentrations for ⁴He are negligible and do not normally exceed 10% for other noble gases.

The isotopic compositions and the elemental abundances for the gases were determined using a VG 1200 mass spectrometer with resolution of ~170. It is difficult to detect ³He in the samples even if present due to the tailing effect of a large ⁴He peak. Contributions from H₂¹⁸O⁺ and ⁴⁰Ar⁺⁺ at mass 20 and ¹²C¹⁶O₂⁺⁺ at mass 22 can lead to interference effects for Ne. To minimise these mass interferences, a liquid nitrogen trap is constantly maintained on the SSM (stainless-steel-mesh) finger open to the mass spectrometer during He–Ne analyses. The Ne data is therefore routinely corrected for these background contributions from the measured peak heights of the masses 18, 40 and 44 and the ¹⁸O/¹⁶O (normal isotopic ratios), and the abundance ratios of 40⁺⁺/40⁺ and 44⁺⁺/44⁺ that are periodically determined for the operating conditions of the mass spectrometer. The ranges of 40⁺ and 44⁺ observed during Ne analyses remained relatively constant within a factor of 2 and typical values of 40⁺⁺/40⁺ and 44⁺⁺/44⁺ are 0.06(±10%) and 0.01(±10%), respectively. The mass spectrometer is calibrated for sensitivity and mass discrimination using a known amount of air. The final data reported here has been corrected for blanks, background and instrument mass discrimination, and the errors evaluated.

4. Results

The noble gas concentrations and isotopic ratios are listed in Table 1 for the different samples. Kr was not analysed for its isotopic composition. ³⁸Ar/³⁶Ar ratios are air-like and are not listed. For Xe, only the ¹²⁹Xe/¹³²Xe ratio has been listed for all samples (Table 1) and those of heavy Xe isotopes for the pyrolysis of apatites (Table 2). The full data set for Xe will be discussed elsewhere (manuscript in preparation). For Ne data, isotope ²⁰Ne has been used for normalisation, rather than the conventional ²²Ne so that any excess ²¹Ne or ²²Ne above trapped values may be identified clearly. The VC results from the carbonates indicate that the ⁴He concentration (10^{–6} cc STP/g) is highly variable among the samples analysed (1.5–301). In general, it is higher in the apatites compared to their corresponding carbonates separated from the same hand specimen e.g. 193 vs. 30 (Hogenakal) and 54 vs. 1.5 (Sevattur). However, the ⁴He concentrations of the Khambamettu apatites are comparable with those of the carbonates. On the other hand the concentration ranges are much more limited for ²⁰Ne (4.4–22)10^{–10} cc STP/g, ³⁶Ar (7.2–33)10^{–10} cc STP/g and ¹³²Xe (1.4–19)10^{–12} cc STP/g. The concentrations of ²⁰Ne, ³⁶Ar and ¹³²Xe for the apatites from Hogenakal and Sevattur lie within the range for carbonates although they are lower for both the Khambamettu apatites.

Table 1
He, Ne, Ar and Xe abundances and isotopic ratios of all samples

No. of strokes (VC) or °C (P)	⁴ He (10 ⁻⁶)	²⁰ Ne (10 ⁻¹⁰)	³⁶ Ar (10 ⁻¹⁰)	¹³² Xe (10 ⁻¹²)	²¹ Ne/ ²⁰ Ne	²² Ne/ ²⁰ Ne	⁴⁰ Ar/ ³⁶ Ar	¹²⁹ Xe/ ¹³² Xe
<i>Hogenakal</i>								
H-C1A(VC)(1.0128g)								
50	12.0	7.2	22.7	2.5	0.0042 .0002	0.1032 .0003	6415 63	1.11 .01
300	18.1	3.2	1.6	2.0	0.0056 .0002	0.1182 .0014	14641 127	1.03 .01
800	BL	BL	2.8	BL			18323 157	
Total	30.1	10.4	27.1	4.5	0.0046 .0002	0.1078 .0006	8131 76	1.07 .01
H-C2(VC)(1.6637g)								
25	4.5	5.00	7.7	1.1	0.0039 .0001	0.1084 .0038	8806 84	0.99 .02
500	68.8	9.8	12.3	2.2	0.0042 .0002	0.0799 .0073	17927 17	0.98 .09
500	BL	BL	1.8	BL			19886 18	
Total	73.3	14.8	21.8	3.3	0.0041 0.0002	0.0895 0.0061	14867 41	0.99 .01
H-C1B(VC)(1.7386g)								
15	3.2	2.4	7.7	NA	0.0056 .0001	0.1020 .0007	5879 54	
300	18.8	5.0	12.2	NA	0.0051 .0002	0.1028 .0005	14063 131	
300	BL	BL	1.4	NA			18597 148	
Total	22.0	7.4	21.3		0.0052 .0001	0.1026 .0006	11392 104	
H-C4(VC)(1.9537g)								
15	BL	BL	6.3	2.8			6609 61	1.14 .02
300	BL	BL	23.1	6.6			8183 77	1.14 .02
300	BL	BL	3.9	BL			10700 94	
Total			33.3	9.4			8095 75	1.14 .02
H-A(VC)(0.8246g)								
15	14.8	0.9	1.6	BL	0.0228 .0015	0.3136 .0178	3359 25	
300	57.8	1.0	6.8	3.4	0.0625 .0053	0.9540 .0717	4986 41	1.11 .01
300	40.4	0.7	BL	BL	0.0718 .0070	1.035 .0973		
800	79.9	4.3	BL	BL	0.0262 .0016	0.4112 .0212		
Total	192.9	6.9	8.4		0.0319 .0017	0.4881 .0216	4679 38	
H-A(P)(0.1752g)								
400	69.5	159.9	BL	BL	0.0032 .0001	0.1005 .0002		
600	1247	76.3	1.4	BL	0.0041 .0001	0.1264 .0014	4015 15	

(continued on next page)

Table 1 (continued)

No. of strokes (VC) or °C (P)	^4He (10^{-6})	^{20}Ne (10^{-10})	^{36}Ar (10^{-10})	^{132}Xe (10^{-12})	$^{21}\text{Ne}/^{20}\text{Ne}$	$^{22}\text{Ne}/^{20}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{129}\text{Xe}/^{132}\text{Xe}$
950	600.4	74.1	0.9	BL	0.0100 .0001	0.2896 .0025	4322 36	
1200	56.7	10.9	BL	BL	0.0655 .0047	1.549 .1113		
1400	0.6	5.9	2.5	BL	0.0986 .0061	1.951 .1202	1373 6	
1600	0.7	46.3	9.1	BL	0.0083 .0001	0.2116 .0017	664 1	
1800	0.8	38.8	10.9	3.4	0.0181 .0002	0.4196 .0023	4595 7	
Total	1976	412.2	24.8		0.0096 .0001	0.2469 .0021	2787 6	0.03 .002
<i>Sevattur</i>								
SE-A1(VC)(1.9554g)								
15	3.9	7.5	15.4	2.8	0.0039 .0001	0.1013 .0016	1913 18	0.98 .01
500	32.8	4.1	9.6	3.2	0.0076 .0002	0.1261 .0013	5719 53	1.09 .01
500	17.4	0.9	0.9	BL	0.0132 .0010	0.1199 .0076	8463 64	
Total	54.1	12.5	25.9	6.0	0.0058 .0002	0.1108 .0019	3549 33	1.04 .01
SE-C1(VC)(1.62g)								
25	BL	BL	18.1	1.8			1116 11	1.04 .01
500	1.5	6.7	6.5	0.9	0.0052 .0003	0.1089 .0086	3125 30	1.02 .01
Total	1.5	6.7	24.6	2.7	0.0052 .0003	0.1089 .0086	1647 16	1.04 .01
SE-C2(VC)(1.63g)								
25	BL	BL	9.4	0.8			1631 16	1.00 .01
500	2.6	5.4	5.3	0.6	0.0061 .0003	0.0952 .0068	3484 34	1.04 .02
500	BL	BL	1.2	BL			3114 29	
Total	2.6	5.4	15.9	1.4	0.0061 .0003	0.0952 .0068	2357 23	1.01 .02
SE-C3A(VC)(1.93g)								
25	BL	BL	9.5	NA			946 9	
500	4.5	5.7	7.6	NA	0.0056 .0002	0.1164 .0022	2249 22	
500	BL	BL	0.8	NA			3197 26	
Total	4.5	5.7	17.9		0.0056 .0002	0.1164 .0022	1598 15	
SE-C3B(VC)(1.7591g)								
15	1.1	5.0	6.0	BL	0.0044 .0003	0.1045 .0020	549 5	
300	5.0	5.9	6.3	1.1	0.0052 .0002	0.1073 .0011	1048 10	1.04 .01
Total	7.1	10.9	12.3	1.8	0.0048 .0002	0.1060 .0015	805 8	1.04 .01

Table 1 (continued)

No. of strokes (VC) or °C (P)	^4He (10^{-6})	^{20}Ne (10^{-10})	^{36}Ar (10^{-10})	^{132}Xe (10^{-12})	$^{21}\text{Ne}/^{20}\text{Ne}$	$^{22}\text{Ne}/^{20}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{129}\text{Xe}/^{132}\text{Xe}$
SE-C5(VC)(1.7747g)								
15	NA	NA	2.8	0.9			3081 28	1.03 .01
300	NA	NA	4.1	2.6			8667 81	1.04 .01
300	NA	NA	0.3	BL			16678 115	
Total			7.2	3.5			6859 62	1.04 .01
SE-C6(VC)(1.7372g)								
15	73.4	9.3	9.1	6.1	0.0043 .0002	0.0982 .0009	5093 49	1.04 .01
300	227.3	11.4	6.9	10.1	0.0048 .0004	0.1025 .0066	14366 136	1.05 .01
Total	300.7	22.1	16.0	16.2	0.0046 .0003	0.1006 .0040	9092 87	1.04 .01
SE-C7(VC)(1.4293g)								
15	12.6	NA	20.3	3.8			2750 26	0.99 .01
300	20.4	NA	8.9	4.3			9584 88	1.12 .01
300	3.00	NA	0.7	BL			16064 111	
Total	36.0		29.9	8.1			5115 46	1.06 .01
SE-A2(P)(0.4554g)								
400	53.5	119.5	BL	BL	0.0031 .0001	0.1003 .0001		
600	54.8	41.2	1.2	BL	0.0044 .0001	0.1054 .0010	5121 82	
950	1012	58.4	1.4	BL	0.0061 .0002	0.1522 .0023	7051 9	
1200	155.8	6.8	BL	BL	0.0147 .0019	0.2538 .0056		
1400	104.9	11.6	2.9	BL	0.0164 .0003	0.3060 .0019	671 2	
1600	43.2	24.2	BL	BL	0.0113 .0002	0.1851 .0007		
1800	10.3	18.2	1.0	BL	0.0108 .0001	0.2021 .0010	3967 11	
Total	1435	279.9	6.5		0.0060 .0001	0.1380 .0008	3350 6	
<i>Khambamettu</i>								
K-C-1 (VC)(2.09g)								
15	BL	BL	8.6	0.9			3045 29	0.98 .01
500	26.9	3.5	4.5	0.7	0.0044 .0001	0.1191 .0029	10051 96	0.97 .01
Total	26.9	3.5	13.1	1.6	0.0044 .0001	0.1191 .0029	5452 52	0.98 .01
K-C-2(VC)(1.5130g)								
15	NA	NA	5.2	NA			3516 32	

(continued on next page)

Table 1 (continued)

No. of strokes (VC) or °C (P)	^4He (10^{-6})	^{20}Ne (10^{-10})	^{36}Ar (10^{-10})	^{132}Xe (10^{-12})	$^{21}\text{Ne}/^{20}\text{Ne}$	$^{22}\text{Ne}/^{20}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{129}\text{Xe}/^{132}\text{Xe}$
300	NA	NA	2.6	NA			12806	
							109	
Total			7.9				6613	
							58	
K-C-3(VC)(1.43g)								
15	BL	BL	7.3				3334	
							32	
300	258.3	4.4	15.7	1	0.0059	0.1189	2858	1.06
					.0005	.0090	27	.03
300	BL	BL	0.5				16000	
							116	
Total	258.3	4.4	23.5		0.0059	0.1189	3304	
					.0005	.0090	31	
K-A2 (VC)(0.6984g)								
15	8.8	1.5	2.6	BL	0.0074	0.0916	2545	
					.0007	.0015	20	
500	13.0	0.3	1.4	BL	0.0340	0.2114	7967	
					.0035	.0103	55	
Total	21.8	1.8	4.0		0.0119	0.1120	4468	
					.0011	.0025	32	
K-A2 (P) (0.3096g)								
400	4.0	221.9	BL	BL	0.0076	0.1024		
					.0001	.0003		
950	39.2	BL	0.6	BL			3512	
							27	
1400	13.6	BL	BL	BL				
1800	2.5	105.5	1.1	BL	0.0046	0.0783	1748	
					.0001	.0001	11	
Total	59.3	337.4	1.7		0.0064	0.0918	2347	
					.0001	.0002	16	
K-A1 (VC)(1.7015g)								
15	1.8	0.8	1.7	BL	0.0094	0.1090	673	
					.0003	.0013	6	
500	10.1	0.7	2.8	BL	0.0273	0.4105	1235	
					.0009	.0112	9	
Total	11.9	1.5	4.5		0.0178	0.2497	1021	
					.0006	.0059	8	
K-A1 (P) (0.3625g)								
400	20.8	18.1		BL	0.0053	0.0941		
					.0001	.0010		
950	1265	27.6		BL	0.0275	0.4389		
					.0001	.0142		
1300	74.0	5.0		BL	0.2546	4.3056		
					.0008	.0120		
1500	0.2	22.3		BL	0.0470	0.8430		
					.0002	.0054		
1800	—	17.6		7.8	0.0351	—		0.27
					.0002			.01
Total	1360	90.6		7.8	0.0420	0.6001		0.27
					.0002	.0065		.01

Concentrations are in cc STP/g. Errors in concentrations are $\pm 10\%$. Errors in isotopic ratios are at 95% confidence level. (BL, blank level; NA, not analysed).

Table 2
Xe abundances and isotopic ratios for apatites during pyrolysis

Sample	^{132}Xe (10^{-12} cc STP/g)	$^{129}\text{Xe}/^{132}\text{Xe}$	$^{131}\text{Xe}/^{132}\text{Xe}$	$^{134}\text{Xe}/^{132}\text{Xe}$	$^{136}\text{Xe}/^{132}\text{Xe}$
H-A	13.0	$0.03 \pm .002$	$0.21 \pm .01$	$1.30 \pm .04$	$1.61 \pm .04$
SE-A2	165.8	1.05	0.80	0.40	0.34
		.01	.01	.01	.01
K-A1	7.8	0.27	0.38	1.10	1.25
		.01	.01	.01	.01
$^{238}\text{U}_{\text{sf}}$ ^a		<0.003	0.13	1.40	1.68
Air ^a		0.98	0.78	0.38	0.32

Errors in conc. are $\pm 15\%$, and errors in isotopic ratios represent 95% confidence limits.

^a Ozima and Podosek (2002).

Table 3

Ages (in Ma) obtained from U,Th and different noble gas systematics of apatites (from Hogenakal, Sevattur and Khambamettu) from this work and from Brazilian and Canadian carbonatites (PRAP, BOAP and POAP) from Sasada et al. (1997)

Sample	U (ppm)	Th (ppm)	Age (Ma)	^4He (10^{-6} cc STP/g)	$^{21}\text{Ne}_n$ (10^{-10}) (cc STP/g)	$^{136}\text{Xe}_{\text{sf}}$ (10^{-12}) (cc STP/g)	U,Th- ^4He age (Ma)	U,Th- ^{21}Ne age (Ma)	U- ^{136}Xe age (Ma)	Retentivity (%)		
										^4He	^{21}Ne	^{136}Xe
H-A	25.4	189	2400	1976	2.7	20.8	234 ± 35	845 ± 127	1370 ± 205	8.5	33	52.5
SE-A1	7.1	84.6	770	1435	0.9	–	437 ± 66	738 ± 111		54	96	
K-A1	44.9	83	523	1360	3.5	9.0	175 ± 26	>Age ^a	367 ± 55	33	>100 ^a	69
K-A2	0.78	6.2	523	59.3	1.2	–	220 ± 33	>Age ^a		42	>100 ^a	
PRAP	196	172	1030	26000	18.2	170	850 ± 128^a	>Age ^a	1442 ± 216^a	81	>100 ^a	>100 ^a
BOAP	1.35	14.0	1870	76	0.5	2.9	136 ± 20	2215 ± 333	3123 ± 468	6	80	>100 ^a
POAP	22.5	163	2700	2400	0.7	46	326 ± 49	271 ± 41	2994 ± 450	10	9	>100 ^a

^a Apparent ages greater than the crystallization ages and >100% retentivities indicate excess ^4He , ^{21}Ne and ^{136}Xe due to lithospheric component. All concentrations are in cc STP/g.

The $^{21}\text{Ne}/^{20}\text{Ne}$ ratios vary mostly between 0.0041 ± 0.0002 and 0.0061 ± 0.0003 and the $^{22}\text{Ne}/^{20}\text{Ne}$ ratios ranges between 0.0895 ± 0.0061 and 0.1089 ± 0.0086 . However, if we consider individual crushing steps for the carbonates both $^{21}\text{Ne}/^{20}\text{Ne}$ as well as the $^{22}\text{Ne}/^{20}\text{Ne}$ ratios can be higher in the samples. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are also observed to be higher in the individual crushing steps compared to the total. While the total $^{40}\text{Ar}/^{36}\text{Ar}$ of the samples vary between 715 ± 7 to 14311 ± 40 , the $^{40}\text{Ar}/^{36}\text{Ar}$ of the individual steps are up to 19886 ± 180 for Hogenakal, 16678 ± 115 for Sevattur and 16000 ± 116 for Khambamettu. The $^{129}\text{Xe}/^{132}\text{Xe}$ show clear excess above air ratios, except for H-C2 and K-C1A where they are air-like.

The Ar and Xe isotopic ratios between the carbonates and apatites are very different. Both $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios are higher for the apatites than their carbonates e.g. 0.0319 ± 0.0017 and $0.4881 \pm .0216$ for H-A, $0.0119 \pm .0011$ and $0.1120 \pm .0020$ for K-A2 and $0.0178 \pm .0006$ and $0.2497 \pm .0056$ for K-A1. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, although higher than air, are lower than the carbonates e.g. 4679 ± 38 (H-A), 3549 ± 33 (SE-A1), 4468 ± 32 (K-A2) and 1235 ± 9 (K-A1). Like the carbonates, they also show some heterogeneity among the individual crushing steps for both Ne and Ar isotopic ratios. The $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios may be as high as $0.0718 \pm .0070$ and $1.035 \pm .0973$ (H-A), $0.0340 \pm .0035$ and $0.2114 \pm .0103$ (K-A2) and $0.0273 \pm .0009$ and $0.4105 \pm .0112$ (K-A1) in the later crushing steps. The

$^{40}\text{Ar}/^{36}\text{Ar}$ ratios are observed to be as high as 8463 ± 64 (SE-A1) and 7967 ± 55 (K-A2). While in the Khambamettu apatites the Xe concentration is too low for measurement, for both H-A and SE-A1 the $^{129}\text{Xe}/^{132}\text{Xe}$ ratios are clearly above the atmospheric value.

If we compare VC and pyrolysis, there is a clear indication of release of *in situ* gases during P from the higher $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios. Fission Xe is also observed during pyrolysis from the extremely low $^{129}\text{Xe}/^{132}\text{Xe}$ ratios of $0.03 \pm .002$ and $0.27 \pm .01$ in H-A and K-A1 respectively. Fissionogenic contribution is also evident from the $^{131}\text{Xe}/^{132}\text{Xe}$, $^{134}\text{Xe}/^{132}\text{Xe}$ and $^{136}\text{Xe}/^{132}\text{Xe}$ ratios (listed in Table 2).

It should be mentioned that the K contents of both the carbonates and the apatites determined by AAS are too low to significantly contribute any radiogenic ^{40}Ar to the samples. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are in fact lower in the case of pyrolysis than VC. U and Th have been determined in the apatites by ICPMS (see Table 3).

5. Discussion

5.1. Trapped components: Enriched lithospheric, subducted and deep mantle components

Models for the generation of carbonatites often prefer the role of lithosphere, based on the Sr isotopes (Bell et al., 1982). Often, carbonatite generation is believed to

be induced by metasomatism of the lithosphere by the incursions of carbonated-silicate melts (Meen et al., 1989). However, Nelson et al. (1988) suggested an asthenospheric origin for the carbonatites on the basis of geochemical and Sr, Nd, Pb, O and C isotopic data in conjunction from worldwide carbonatites. But, many of the carbonate–alkaline complexes are temporally and spatially associated with major continental flood basalt provinces leading to the hypothesis of plume origin for these complexes (Ray et al., 1999). Direct evidence of a plume contribution for the carbonatite magmatism comes from Nd, Pb and Sr isotopic compositions of the East African carbonatites (Bell and Tilton, 2001). Also, plume contribution for the carbonatites from Kola has been advocated on the basis of noble gases (Marty et al., 1998; Tolstikhin et al., 2002).

Carbonatites generation is often envisaged as a two stage process involving an upwelling plume that metasomatizes the overlying lithosphere inducing its melting as inferred from Nd, Pb and Sr isotopes of Oldoinyo Lengai and other East African carbonatites (Bell and Simonetti, 1996). Evidences for such plume lithosphere interaction also come for the Indian carbonatites of Ambadongar (Simonetti et al., 1998). Based on geochemical and Nd, Pb and Sr isotopic data, it was inferred that the early stages were dominated by plume component, but gradually replaced by larger lithospheric imprint (Simonetti et al., 1998). There are also evidences of dilution of asthenospheric (MORB-like) signatures in the Indian carbonatites of Ambadongar and Sung Valley gradually by increasing lithospheric contribution from Nd, Pb and Sr isotopes as well as noble gases (Simonetti et al., 1998; Basu and Murty, 2006).

To account for the huge amount of C in carbonatites, the role of subduction is often considered important during carbonatite magmatism. Direct evidences of subduction in the source lithospheric mantle of Sung Valley carbonatites comes from C isotopes and also supported by noble gases (Ray et al., 1999; Basu and Murty, 2006).

In the sequential crushing steps, the earlier steps tend to be of atmospheric composition while both $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios are higher than atmospheric in the later crushing steps. This is clearly observed for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios that show an increase with progressive crushing. Although release of some *in situ* components during VC cannot be entirely ruled out, we do not attribute this observed trend to release of more *in situ* gases progressively because the K content in the samples is too low to produce significant ^{40}Ar so as to alter the trapped $^{40}\text{Ar}/^{36}\text{Ar}$ ratios. Rather, we attribute this trend to heterogeneity in the fluid inclusion composition of the samples that also indicates the possible presence of more than one noble gas component in them. Also, F concentration in carbonates would be too low to produce any excess ^{22}Ne . Independent F determination by spectrophotometric methods rules out presence of any F in the carbonates. The presence of included grains of apatite and fluorite in the carbonates may contribute towards the production of nucleogenic ^{22}Ne , but so far,

we are not aware of any reports of presence of fluorite in these carbonatites. However, apatite commonly occurs as minor or important accessory mineral. To account for the excess ^{22}Ne observed during VC, the amount of apatite that should be present in the carbonates may be estimated on the basis of ^{22}Ne released during VC of the apatite itself. For example, for H-C1A to account for the observed excess $^{22}\text{Ne} \sim 0.06 \times 10^{-10}$ cc STP/g in the final crushing step, about 2% of apatite (H-A separated from the same hand specimen), with excess $^{22}\text{Ne} \sim 2.7 \times 10^{-10}$ cc STP/g, should be present in the carbonate separates. XRD on the same aliquot does not show any apatite in the separates.

In a volatile saturated magma, inclusions grow with time due to a combination of decompression and diffusion processes. Individual inclusions of different sizes nucleating at different times from the evolving magma will preserve the volatile composition of the magma from which they evolved (Burnard, 1999). Studies of He and Ar from Atlantic MORB glasses have shown that inclusions of different sizes formed from different batches of magma that preserve their distinct isotopic identity as observed from their $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (Jambon et al., 1985). Such isotopic heterogeneity for $^{40}\text{Ar}/^{36}\text{Ar}$ and $^3\text{He}/^4\text{He}$ has also been observed in mantle xenoliths between shrinkage bubbles and melt inclusions (Yamamoto et al., 2004). For carbonatites, the study of fluid inclusions in apatites and calcites of Ambadongar have revealed that fluids of different compositions that progressively evolved from the magma were trapped at different *P–T* conditions indicating the history of fluid evolution (Williams-Jones and Palmer, 2002). For Kola carbonatites also, it has been seen that the smaller fluid inclusions preferentially host trapped ^3He (Tolstikhin et al., 2002). *In situ* Sr isotopic compositions of coexisting apatite and carbonate from the carbonatites of Sarfartoq alkaline complex, Greenland, show considerable isotopic variability even within individual hand specimens, attributed to heterogeneous mantle source or mixing between different magma components (Bizzarro et al., 2003).

A plausible scenario that may be envisaged for the preservation of different $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in inclusions of different sizes could be the involvement of two batches of magma suggested by Jambon et al. (1985) for Atlantic MORBs. The first batch may involve volatiles derived from a component with lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratio that could be atmospheric gases introduced into the magma via subduction, or interaction of the melt with fluids (e.g. hydrothermal) bearing atmospheric gases. Our coupled study of N and Ar (Basu and Murty, 2005) support subduction. A new batch of magma may have been subsequently introduced into the chamber from which inclusions with higher $^{40}\text{Ar}/^{36}\text{Ar}$ ratios evolved. A similar scenario involving both recycled and mantle components has been proposed for MORBs by Sarda (2004). There also, the difference in the isotopic ratios between vesicles of different sizes, and therefore formed at different time, had been attributed to melt from two components, namely the subducted and MORB components. If the process of melting is accompanied by

the volatiles getting physically separated from the melt, it would prevent complete mixing between the different noble gas components. So, while the vesicles generated later have more of the MORB component, the earlier formed vesicles that have more time to grow have a larger fraction of air component released during early melting of subducted matter. From recent study on polycrystalline diamonds, it has been proposed that noble gases, including Ne are added to the mantle during subduction processes (Honda et al., 2003). Here, we propose that the melting of the subducted slab must have occurred at considerably shallow depths as subduction of atmospheric Ne to the very deep mantle is unlikely. Evidences of subduction into the mantle with low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios have been seen using Pb and N as tracers (Sarda et al., 1999; Mohapatra and Murty, 2000). The subducted component in these carbonatites can be more easily traced using $\delta^{15}\text{N}$ in conjunction with $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (manuscript in preparation).

The presence of two components in the samples is also indicated by the Ne isotopic data. In a plot of $^{21}\text{Ne}/^{20}\text{Ne}$ vs. $1/^{20}\text{Ne}$ (Fig. 2) for the carbonatites studied from Hogenakal and Sevattur, the presence of a component with enriched $^{21}\text{Ne}/^{20}\text{Ne}$ can be observed.

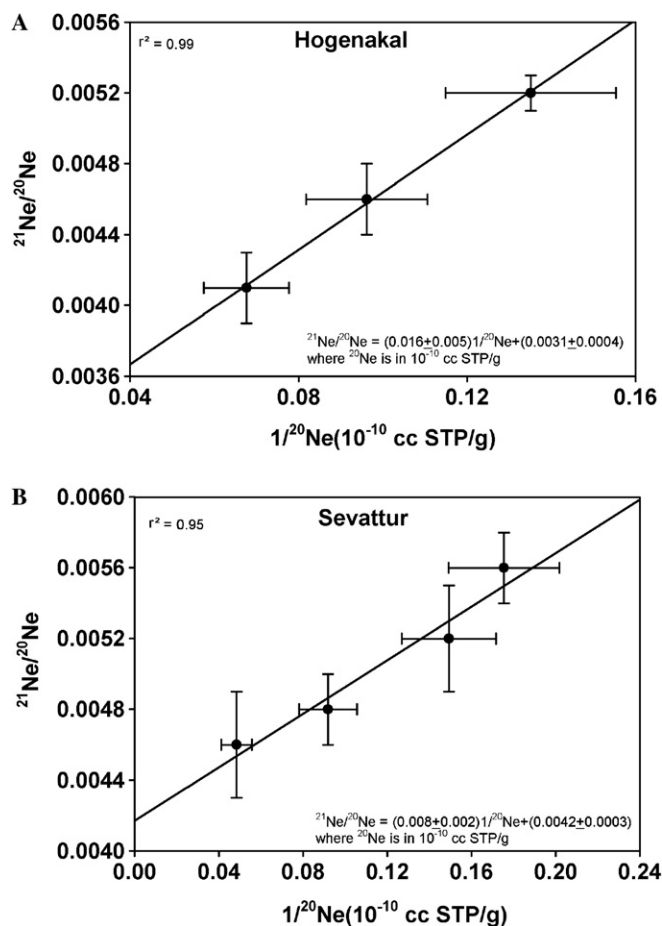


Fig. 2. Plot of $1/^{20}\text{Ne}$ vs. $^{21}\text{Ne}/^{20}\text{Ne}$ suggests two component mixing between trapped and enriched lithospheric mantle gases for (A) Hogenakal and (B) Sevattur. Intercept from the plots indicate an air-like trapped component for Hogenakal and a deeper mantle component for Sevattur. For discussion see text.

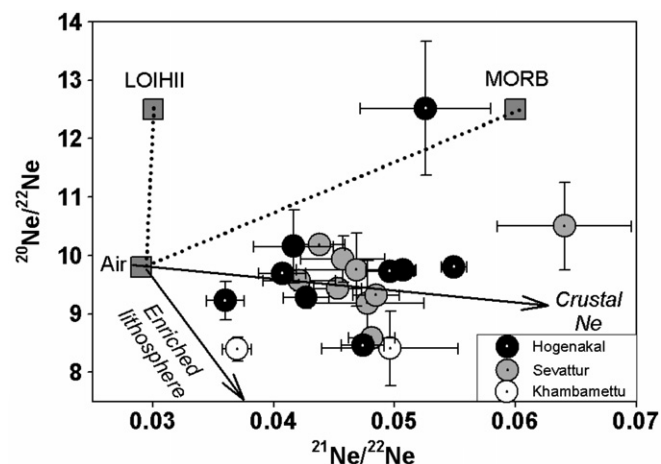


Fig. 3. Ne 3-isotope plot for Hogenakal (black), Sevattur (grey) and Khambamettu (white) carbonatites. Dotted symbols represent individual crushing steps while filled symbols indicate totals. The trends for mixing between Air + MORB and Air + LOIHI are shown. The trend for crustal addition is also shown (Kennedy et al., 1990). The plot clearly indicates the presence of an enriched lithospheric mantle component (The trend for the presence of enriched lithospheric component is indicated only as a guide. The actual slope of the line depends on the O/F ratio and U, Th contents).

Fig. 3, the usual Ne three isotope plot shows that the samples do not plot on the standard MORB or LOIHI trend. As seen from Fig. 3, it is difficult also to attribute all the data to addition of crustal noble gases entrained by the uprising magma.

The possibility of crustal contamination is greatly reduced for the carbonatites owing to the low density and low viscosity of carbonatitic melts that enables them to move rapidly through the crust. Also, low temperatures of 600–770 °C of the carbonatitic melts prevent fusion and incorporation of the wall rocks by the uprising magma (Secher and Larson, 1980). Earlier studies have indicated that the C and O isotopic compositions of both Hogenakal and Sevattur lie well within the range expected for mantle derived carbonatitic magma (Kumar et al., 1998). For Sevattur, additionally it is seen that major, minor and trace element compositions of these carbonatites are comparable to typical carbonatitic abundances (Krishnamurthy, 1988), and identical Sr ratios for both early formed pyroxenites and later formed carbonatites rule out progressive and variable crustal contamination of the magma during differentiation in a crustal magma chamber (Kumar and Gopalan, 1991). The possibility of late incorporation of noble gases during crustal residence of carbonatites is also quite unlikely, since it has not been observed from any of the carbonatites of different ages that have been studied. Also, based on Hf isotopes, it has been proved that the residence period of carbonatitic melts in the crust is extremely brief (Bizimis et al., 2003), thus reducing the possibility of crustal contamination.

Earlier studies of crustal composition from gas fields and ground water where the highest excesses of ^{21}Ne and

^{22}Ne were found have shown that at the most $^{40}\text{Ar}/^{36}\text{Ar}$ ratios were up to ~ 6000 , although these reservoirs sample relatively older portion of the crust >250 Ma (Bottomley et al., 1984; Kennedy et al., 1990; Hiyagon and Kennedy, 1992). This is considerably lower than the ratios of up to $\sim 20,000$ observed here, whereas the crust formed was just 150 Ma at Hogenakal at the time of carbonatitic emplacement. Therefore, the high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios cannot be explained by contribution from crustal sources.

Following discussion by Porcelli and Ballentine (2002), the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio obtained for unidirectional degassing from a single solid Earth reservoir represented by the MORB source region (assuming a well mixed mantle and degassing at a constant rate without any return flux by subduction) would be ~ 5000 for Hogenakal, significantly lower than that observed in the samples. Thus the observed high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in the samples cannot be accounted by a contribution from MORB in agreement with observations from Ne (Fig. 3).

Very often, fossil subducted slabs are believed to have penetrated great depths in the mantle creating a compositionally distinct layer at depths of about 1600 km to the core-mantle boundary (Kellogg et al., 1999; Rudnick et al., 2000). Theoretically, such a deep-seated layer, rich in K, U and Th could be an environment with elevated $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{21}\text{Ne}/^{20}\text{Ne}$ ratios and a region for plume origin. But, so far there have been no direct evidences of mantle plumes with elevated noble gas ratios. For Hogenakal and Sevattur, based on Sr–Nd isotopic data on carbonatites and associated alkaline silicate rocks, a lithospheric mantle source enriched in alkali metals and LREE have been suggested (Kumar et al., 1998; Pandit et al., 2002). So, in the present case, it seems more likely that the observed higher ratios of $^{40}\text{Ar}/^{36}\text{Ar}$, $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ are due to the presence of an enriched lithospheric mantle component. Very high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios up to 53070 ± 2871 have been observed in Jwaneng diamonds (Honda et al., 2003). The consistency in halogen and noble gas abundances between diamonds (including those from Jwaneng) and MORB samples have led Johnson et al. (2000) to suggest MORB-like mantle source for the lithospheric volatiles. It is therefore not surprising that such high MORB-like ratios may be generated in the subcontinental lithosphere. Since the subcontinental lithosphere is a long-life conservative reservoir, mobilisation and homogenisation would be very slow (Kramers, 1991). Thus, the time interval between the enrichment process and the mobilization of parent carbonatitic magma could be variable but long enough to generate enriched isotopic signatures as have been observed for the 370 Ma Kola carbonatites where the metasomatic event has been estimated to have occurred between 450–750 Ma (Tolstikhin et al., 2002). For Hogenakal and Sevattur, Sr and Nd isotopic data suggest that the source may have formed at 2.5–2.6 Ga, indicating that the enrichment must have been shortly before the generation of Hogenakal magmas (Kumar et al., 1998). This period is marked by major crustal generation,

magmatism and metamorphism in this region (Friend and Nutman, 1991; Peucat et al., 1993). The activity probably occurred along the southern edge of the Dharwar craton marked by subduction of sediments along the convergent margin (Kumar et al., 1998). Such an enrichment event can account for the observed elevated $^{40}\text{Ar}/^{36}\text{Ar}$, $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios in the samples. It is noteworthy that the average F concentration in the mantle is much lower than that of the crust while their O abundances are comparable resulting in O/F ratio of the mantle to be $\sim 28,000$ (Leya and Wieler, 1999). The present results call for an enrichment of F concentration in the lithospheric mantle.

Although we observe that the samples are mainly dominated by volatiles from the enriched lithospheric mantle source region along with the subducted gases, some contribution from the deeper mantle volatiles cannot be entirely ruled out. For K–Al(P), from the trend in Fig. 4, for mantle $^{22}\text{Ne}/^{20}\text{Ne}$ ratio of 0.08, the corresponding $^{21}\text{Ne}/^{20}\text{Ne}$ ratio obtained is 0.0043 ± 0.0002 , lower than the value of 0.0056 expected for MORB that implies contribution of volatiles from the less degassed, deep mantle. This component could also be decoupled for K–A2(P) where at the 1800°C step, a mantle $^{22}\text{Ne}/^{20}\text{Ne}$ ratio of 0.0783 ± 0.0001 is accompanied by $^{21}\text{Ne}/^{20}\text{Ne}$ ratio of 0.0046 ± 0.0001 . It is also possible that the ancient source of the MORBs had been the source of these volatiles when the reservoir had a $^{21}\text{Ne}/^{20}\text{Ne}$ ratio similar to 0.0043. But noble gas evolutionary (degassing) models show that the $^{21}\text{Ne}/^{20}\text{Ne}$ ratio of the depleted mantle exceed the value of 0.0043 post 3Ga (Tolstikhin and Marty, 1998) and thus a contribution from the deep mantle is more likely.

While the early stages of magmatism may be dominated by the deep mantle volatiles, progressively there may be an increased heating of the continental lithosphere resulting in a larger degree of partial melting and increased input of lithospheric isotopic signal. The presence of deep mantle component (from a plume) in the lithospheric mantle in south-eastern Australia has been reported from the study of Ne isotopes in apatites from lherzolite xenoliths, while the other coexisting mineral phases were dominated by MORB signatures (Matsumoto et al., 1997). The plume signatures in the apatites had been attributed to metasomatic fluids. In the present study also it is possible that the upwelling deep mantle component has induced melting of the overlying shallow subducted component and the enriched lithospheric mantle. If apatite growth occurs over an extended period, the growing apatite crystals will entrap volatiles at different times in the inclusions. In that case, apatite will have trapped volatiles from the deep mantle in the early stages while progressively there is greater contribution of other volatiles as melting progressed. Similar trend has been observed in Amba Dongar from fluid inclusion studies where it has been seen that the apatites trap inclusions earlier and at greater depths than the carbonates over a sufficiently larger interval of time recorded by five fluid inclusion types

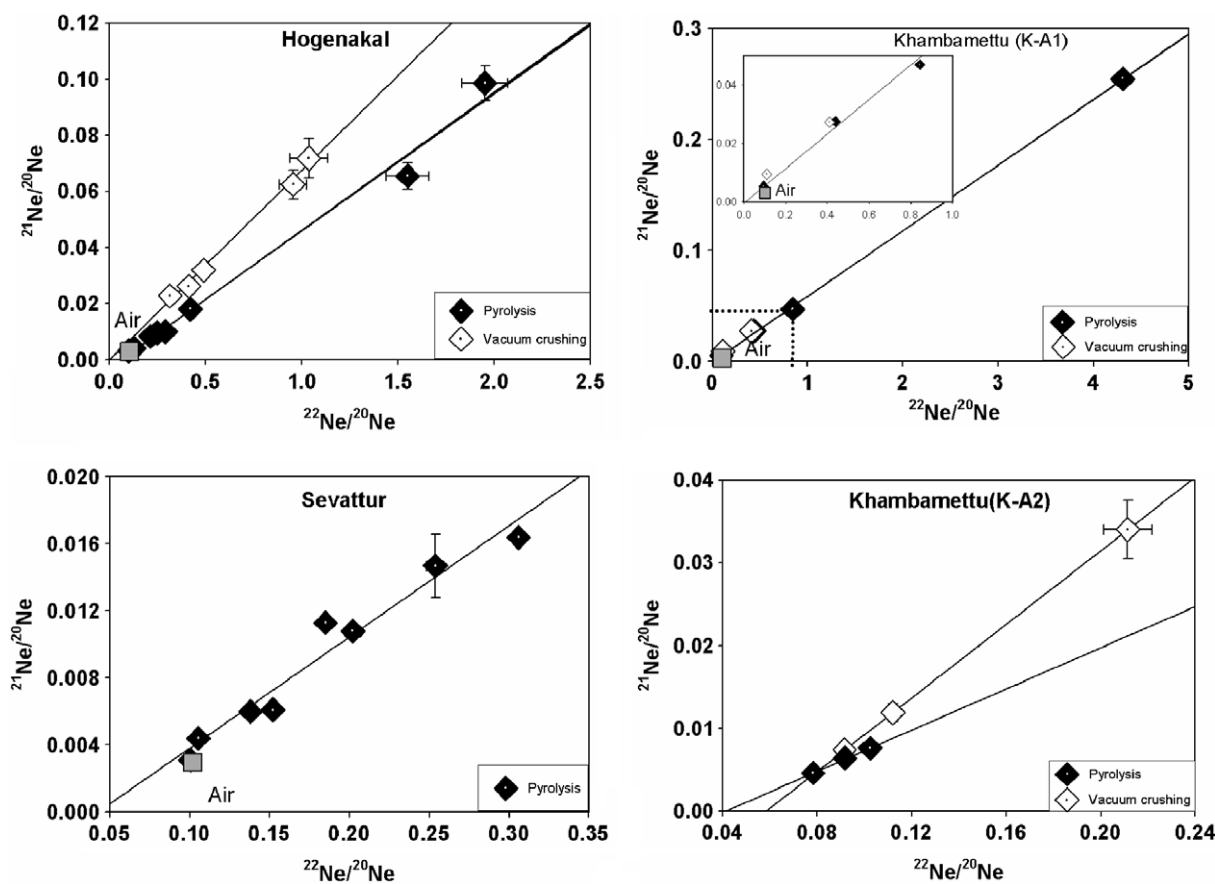


Fig. 4. Plot of $^{21}\text{Ne}/^{20}\text{Ne}$ vs. $^{22}\text{Ne}/^{20}\text{Ne}$ for apatites from Hogenakal (H-A), Sevattur (SE-A2) and Khambamettu (K-A1 and K-A2). Higher ratios above that of air indicate the addition of a nucleogenic component. The slope of the trend corresponds to nucleogenic $^{21}\text{Ne}/^{22}\text{Ne}$ ratios that translate into the O/F ratio of the samples. For discussion, see the text. Black represents pyrolysis while open symbols indicate vacuum crushing. Individual crushing steps are represented by a dot in the centre of the symbols while filled ones indicate totals.

(Williams-Jones and Palmer, 2002). If carbonate growth occurred over a shorter period of time, it is possible that they would be mostly dominated by volatiles from the enriched lithospheric mantle and the subducted component bearing air-like gases. Thus the deeper mantle component can be overprinted by contribution from the recycled and lithospheric mantle sources, as well as nucleogenic Ne for the apatite.

Presence of deep mantle volatiles may also account for the lower $^{40}\text{Ar}/^{36}\text{Ar}$ accompanied by high $^{129}\text{Xe}/^{132}\text{Xe}$ ratios in the apatites (H-A, SE-A1) and many carbonates (SE-C1, SE-C2, SE-C3B), although the possibility of the addition of a fractionated atmospheric component cannot be ruled out. Contribution of deep mantle fluids is also observed from Fig. 2B from the intercept indicating a trapped $^{21}\text{Ne}/^{20}\text{Ne}$ ratio of 0.0042 ± 0.0003 .

Some *in situ* contribution during VC can account for the high $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios in the apatites. From Fig. 4 in a plot of $^{21}\text{Ne}/^{20}\text{Ne}$ vs. $^{22}\text{Ne}/^{20}\text{Ne}$ the slope of the trend defines the nucleogenic $^{21}\text{Ne}/^{22}\text{Ne}$ ratio that may be translated into O/F ratios using the equation of Hunemohr (1989). The O/F ratios of ~ 13 (H-A), 17 (SE-A2) and 15 (K-A1) during pyrolysis are in the range of values observed for the apatites, indicating

in situ contribution of nucleogenic ^{21}Ne and ^{22}Ne in the samples. However, as seen in Fig. 4, while K-A1 defines the same trend in such a plot for both VC and pyrolysis, the trend defined is different for H-A and K-A2 between pyrolysis and VC indicating that the entire excess of ^{21}Ne and ^{22}Ne during VC may not be accounted for by *in situ* contribution and in turn suggesting the presence of an enriched lithospheric mantle component. In fact, for K-A2 the O/F ratio obtained from the trends are ~ 31 and 54 for pyrolysis and VC respectively, much higher than that expected for the apatite.

5.2. *In situ* components and gas retention ages

The *in situ* noble gases produced in the apatites after their crystallization have been released from the samples during their pyrolysis. In U, Th rich apatites, ^{238}U decay produces alpha particles (α) and Xe (^{136}Xe) by spontaneous fission. The *in situ* produced ^4He and fission Xe are potential thermo-chronometers, due to their differing temperature sensitivities for loss by diffusion. Since the closure temperature of He for apatite is $\sim 70^\circ\text{C}$, it is now established that U–Th/He ages of apatite record cooling histories (Farley, 2000). However, fractional loss of He is also

controlled by crystal size (Reiners and Farley, 2001). Considering the mean stopping distance of 19.7 μm of α particles in apatites, meaningful He ages can be obtained for larger crystals (Farley et al., 1996). In the present study, cylindrical, mm sized grains were analyzed so that corrections for α stopping distances are insignificant and the gas retention was efficient.

Fissionogenic Xe has been seen to survive greenschist facies metamorphic conditions ($T \approx 350^\circ\text{C}$ and $P \approx 0.4\text{ GPa}$), and in pitchblendes it also indicate the formation age (Eikenberg et al., 1989; Meshik et al., 2000). Thus U–Xe age should either correspond to the formation age of the mineral or indicate resetting by a geological event, with temperature and pressure conditions greater than those of greenschist metamorphism.

5.2.1. U, Th– ^{21}Ne dating

The α particles, that have energies between 4.01 and 8.75 MeV induce various (α, n) reactions with low threshold energies in the samples during their slowing down and interaction with the surrounding atoms (Wetherill, 1954). However, these nuclear reactions only occur with light elements such as O, F and Mg that have low threshold energies. Since the fluence of α particles inducing the nuclear reaction $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ depends on the age of the samples and U, Th concentration in the mineral, the ^{21}Ne ($^{21}\text{Ne}_n$) so produced will also depend on the age of the samples along with target element (O) and U, Th concentrations of the mineral. In fluorapatite, (which is the most common form of apatite in carbonatites) the target element O for the reaction $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ is abundant ($\sim 38\%$) and the cross sections is high ($\sim 300\text{--}650$ millibarns). We attempted here for the first time to check the potential of U, Th– $^{21}\text{Ne}_n$ systematic as a dating tool along with the established U, Th– ^4He and U– ^{136}Xe tools. We have also evaluated the applicability of these dating methods using the data from the apatites analysed from the Canadian carbonatites and syenites, ranging in age from 2700 to 1300 Ma, published by Sasada et al., 1997.

5.2.2. Calculation of *in situ* noble gas component

For U, Th rich minerals such as apatite, it is not unreasonable to consider the entire ^4He measured ($^4\text{He}_m$) to be radiogenic. However, for Ne and Xe it is necessary to decouple the trapped and *in situ* components. As seen from Figs. 4 and 5, Ne and Xe in the samples are a mixture of trapped and nucleogenic/fissionogenic components. The *in situ* noble gas content in the samples can be estimated after correcting the total gas released for trapped contribution. The trapped component in the samples is a mixture of atmospheric and mantle components. From two component mixing between trapped and nucleogenic gases, one can obtain the nucleogenic ^{21}Ne ($^{21}\text{Ne}_n$) from the equation

$$^{21}\text{Ne}_n = ^{20}\text{Ne}_m [(^{21}\text{Ne}/^{20}\text{Ne})_m - (^{21}\text{Ne}/^{20}\text{Ne})_t]$$

where m, t and n stand for measured, trapped and nucleogenic, respectively, and all ^{20}Ne present is of trapped origin. The fissionogenic ^{136}Xe can be estimated by considering

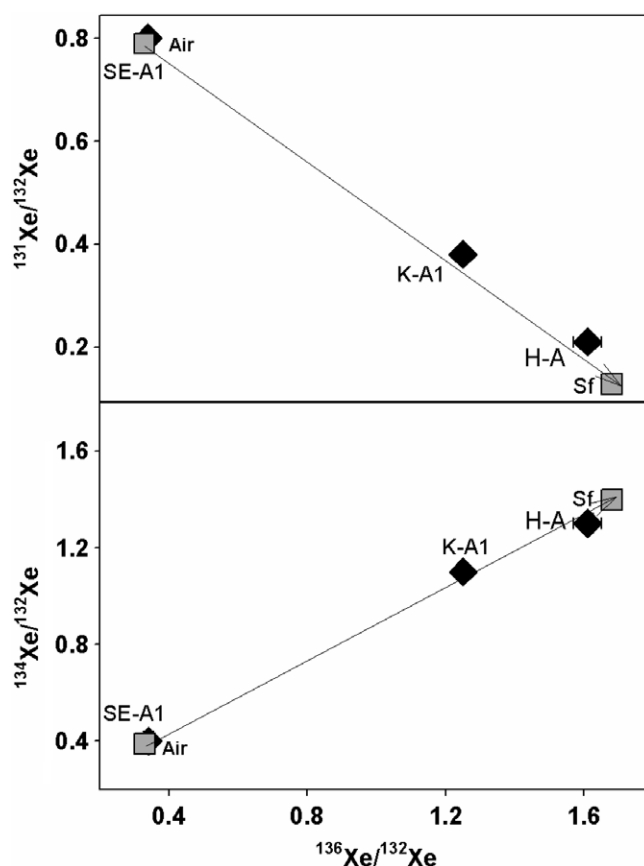


Fig. 5. Plot of $^{131}\text{Xe}/^{132}\text{Xe}$ and $^{134}\text{Xe}/^{132}\text{Xe}$ vs. $^{136}\text{Xe}/^{132}\text{Xe}$ for the three apatites H-A, K-A1 and SE-A1 indicate mixing between air and fissionogenic Xe. While the fission component is dominant in H-A, trapped gases dominate in SE-A1.

all ^{129}Xe to be trapped. Table 3 lists the concentration of *in situ* ^4He , ^{21}Ne and ^{136}Xe determined for the samples. For the Canadian carbonatites the *in situ* ^4He and ^{136}Xe are listed as given by Sasada et al. (1997).

5.2.3. U, Th– ^4He , U, Th– ^{21}Ne , U, Th– ^{22}Ne , and U– ^{136}Xe as dating tools

The radiogenic ^4He expected in the samples behaving as closed system can be estimated using Eq. (1)

$$\sum \alpha = U [7.942(e^{2238t} - 1) + 0.0504(e^{2235t} - 1) + 6\{(\text{Th}/\text{U}) \times (e^{2232t} - 1)\}] \quad (1)$$

where $\sum \alpha$ is the α particle fluence over the crystallization age (t) of the sample

For nucleogenic Ne ($^{21}\text{Ne}_n$), using the production rates estimated for apatite (Leya and Wieler, 1999)

$$^{21}\text{Ne}_n (10^{-10} \text{ cc STP/g}) = 0.0963 \times \sum \alpha \times [\text{X}/\text{Y}] \quad (2)$$

where

$$\text{X} = \{5.62 + 1.91(\text{Th}/\text{U})\}$$

$$\text{Y} = \{21.29 + 4.87(\text{Th}/\text{U})\}$$

W(O) = 0.38 and U is expressed in ppm. Fissionogenic ^{136}Xe can be estimated using Eq. (3)

$$^{136}\text{Xe}_f = [\{(^{238}\text{U} \times iY_{sf} \times \lambda_{sf})/\lambda_{238}\}(e^{\lambda_{238}t} - 1)] \quad (3)$$

where $iY_{sf} \times \lambda_{sf} = 5.7 \times 10^{-18} \text{ y}^{-1}$ (Eikenberg et al., 1993) and λ_{238} is the decay constant of ^{238}U .

5.2.4. Release pattern and retentivity of different noble gas isotopes

For the apatites analyzed by pyrolysis, most of the ^4He is released at 600–950°C (Table 1). The $^{21}\text{Ne}/^{20}\text{Ne}$ ratio suggests that the nucleogenic component is mostly released at higher temperature of 1200–1400 °C. For ^{132}Xe , almost all the gas is released during the melting step. The difference in the release pattern for the different *in situ* gases reflects the different diffusion rates for each of the gas species in the apatite. The release pattern is similar to that observed for the apatites analysed from the Canadian and Brazilian carbonatites (Sasada et al., 1997).

The difference in diffusional characteristics of the three noble gas isotopes is also reflected in their retentivity defined as the fraction of the gas presently retained in the sample (corresponding to the measured concentration after correction for trapped component), to the amount that should be actually present in the sample since formation had there been no loss of volatiles (Table 3). The expected concentration of any particular *in situ* isotope in a given sample can be obtained from the equations discussed earlier and the measured U, Th concentration in the samples. As expected, the retention of the lightest gas isotope ^4He is the least, followed by ^{21}Ne and ^{136}Xe is retained the maximum. For example, in Hogenakal apatite the retention of *in situ* ^4He , ^{21}Ne and ^{136}Xe (in %) are 8.5, 33, and 52.5, respectively. Thus an event that may not reset Xe in the sample can reset both He and Ne. However, a subsequent lower temperature event may be able to further reset only the He systematics in which case the imprint of the earlier event is only recorded by the U,Th- ^{21}Ne geological clock.

5.2.5. Age estimation from *in situ* ^4He , ^{21}Ne , and ^{136}Xe

The ages estimated using Eqs. (1)–(3) are given in Table 3. The U,Th- ^4He age of $234 \pm 35\text{Ma}$ for Hogenakal represents the age when this provenance was exhumed to the upper 2–4 km of the earth's crust corresponding to the closure temperature of $75 \pm 5^\circ\text{C}$. The U,Th- ^4He age of Sevattur is $437 \pm 66\text{Ma}$. For the two Khambamettu apatites analyzed the U,Th- ^4He ages of 175 ± 26 and $220 \pm 33\text{Ma}$ are in agreement within errors and should also represent the exhumation ages of these samples. Similarly, the younger U,Th- ^4He ages of the Canadian carbonatites should actually represent the exhumation ages for these rocks assuming that the apatites analysed were of the appropriate shape and size and completely retained the gases after their closure.

The U- ^{136}Xe ages of the Canadian carbonatites reflect that the system is highly retentive and may also correspond to the formation ages of the apatites as observed for the sample POAP. The U- ^{136}Xe age of $1370 \pm 205\text{Ma}$ for Hogenakal is however lower than the crystallisation age of the

apatite. In Peninsular India, besides the peak granulite metamorphism at 2.5 Ga before the formation of the carbonatite, there are reports of further granulite metamorphism at $\approx 1.6 \pm 0.2$ and $0.9 \pm 0.1\text{Ga}$ related to Indo-Antarctic collision, followed by a younger event at $0.55 \pm 0.10\text{Ga}$ (Kale, 1998). Thus, the observed U- ^{136}Xe age for Hogenakal may be a partial reset age of granulite metamorphism.

The U,Th- ^{21}Ne age of 738 ± 111 for the Sevattur apatite is very close to its crystallisation age of 770 Ma indicating the high retentivity of this mineral. The U,Th- ^{21}Ne age of 2215 ± 333 for the sample BOAP is also within error very close to its crystallisation age. For Hogenakal, the U,Th- ^{21}Ne age of 845 ± 127 is in agreement with the age of emplacement of other adjacent younger carbonatites, syenites and alkali granites and is coeval with rifting and alkaline magmatism in other continental blocks related to the break up of Rodinia (Basu et al., 2005). Overprinting of 700–800 Ma thermal event is demonstrated by the Ar age spectrum of single plagioclase grains from dolerite dykes in the same Dharampuri region (Radhakrishna et al., 1999). But, for the sample PRAP, like the U- ^{136}Xe age, the U,Th- ^{21}Ne age may also reflect excess implanted ^{21}Ne (Sasada et al., 1997). In the present study, no low temperature release of excess ^{21}Ne or ^{136}Xe have been observed from the pyrolysis of apatites. This fact makes it clear that implantation of nucleogenic ^{21}Ne and fissionogenic ^{136}Xe components from U, Th rich minerals onto apatite surface are negligible. Hence, for the Khambamettu apatites, in addition to trapped air-like Ne, the samples are likely to contain nucleogenic Ne from enriched lithospheric mantle also accounting for the overestimation of U,Th- ^{21}Ne ages. This is also seen in Fig. 3 for K-A2 where the slope of the trend suggests contribution from enriched lithosphere.

The different ages from the three systematics are likely to be related to the closure temperature of ^4He , ^{21}Ne and ^{136}Xe in apatites. In future if closure temperature of U,Th- ^{21}Ne and U- ^{136}Xe in apatites are determined, in conjunction with the established U,Th- ^4He clock, these three systems may be used for unravelling the cooling history of a terrain. They may be applied to other U,Th rich minerals like monazite and zircon as well. In fact, this is also demonstrated from some recent studies of magmatic Archaean zircons from Greenland showing good retention of nucleogenic ^{21}Ne (Honda et al., 2004).

6. Conclusions

Noble gas studies in the three spatially and temporally different carbonatites from South India suggest an enriched lithospheric mantle source region. Additionally, isotopic heterogeneity of fluid inclusion composition indicates contribution of subducted air-like component. It is likely that a minor deep mantle component is also present but is only discernible when not overprinted by the lithospheric and/or nucleogenic components, depending on the timing of entrapment of the volatiles by the mineral inclusions. So, a multi stage process can be envisaged for carbonatitic melt

generation where upwelling deeper mantle fluids induce melting of the overlying air-like volatile bearing subducted component and enriched lithosphere. Probably melting involved different batches of magma with continuous separation of the volatiles from the melt. This prevented complete homogenisation between the different volatile components enabling their identification from inclusions of different sizes. While in the initial stages of magmatism, the deep mantle component is dominant as in the case of Kola, progressively with increasing degree of melting of the lithospheric mantle it is the later stage fluids from the lithosphere that dominate these South Indian carbonatites. In the absence of any specific distinction in noble gas data for the temporally varied Hogenakal and Sevattur carbonatites, we assume a common enrichment process in the source region probably as early as 2.5 Ga. when subduction of sediments and altered oceanic crust along the convergent margin of Dharwar craton could have provided the necessary enrichment (Kumar et al., 1998).

For the first time, we have demonstrated that U,Th-²¹Ne serves as a potential dating tool in conjunction with the established systematics. For Hogenakal, the U,Th-²¹Ne age of 845 ± 127 is in agreement with the age of emplacement of other adjacent younger carbonatites, syenites and alkali granites (Basu et al., 2005). The U,Th-²¹Ne age of 738 ± 111 for the Sevattur apatite and 2215 ± 333 for BOAP (apatite from Canadian carbonatite) within errors are also very close to their crystallisation ages. If the closure temperatures for U,Th-²¹Ne and U-¹³⁶Xe are obtained in apatites and other U,Th rich minerals, along with U,Th-⁴He systematics they can be used for understanding the terrain cooling histories.

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