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Carbonatite Bombs, Lapillus, Pisolites And Ashes In Semi-Unconsolidated Conglomerate Of Early Pleistocene From Thiruvalangadu, Tamil Nadu, India

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ABSTRACT

Occurrence of sediments hosted smooth surfaced flat / discoid black and pink coloured bimodal carbonatite bombs, lapillus, pisolites and ashes in semi-unconsolidated conglomerate covering an area of 90 sq.km is reported from Thiruvalangadu (13°10'36"N-76°44'38"E) area situated 60 km WNW of Chennai. The carbonatite materials are uniformly composed of flow-oriented fine-grained calcites <0.02 mm with vesicles < 1mm dimensions filled with recrystallized relatively coarse-grained calcites (~0.1mm). These rocks are essentially composed of calcite with accessories of apatite, augite, hornblende, biotite, wollastonite, skeletal sanidine, sodic oligoclase and corroded quartz. These rocks have significant amount of silica and alumina. Their Fe^{3+}/Fe^{2+} is greater than 1. The pink variety contains $K_2O > Na_2O$. Mafic minerals are alkalic in nature. The low values of $\partial^{13}C_{PDB}$ (from -8.2 to -5.5‰) in black carbonatite and in pink carbonatite (from -5.2 to 0.10‰) and high values of $\partial^{18}O_{SMOW}$ (from 23.1 to 23.7‰) for block carbonatites and (from 24.4 to 27.63‰) for pink carbonatites indicate extensive degassing and loss of volatiles and alkalies by exhalative eruption of these lavas.

Keywords – Carbonatite bombs, Pyroclasts, Early Pleistocene bimodal carbonatite eruptions, Thiruvalangadu, Tamil Nadu

I. INTRODUCTION

Carbonatite volcanism in Quaternary Period has plate tectonic significance [1]. The occurrences of black and pink coloured bimodal carbonatite lava materials in a semi-unconsolidated conglomerate lying between Mio-Pliocene sandstone and Pleistocene boulder bed in some well sections around Thiruvalangadu village (13°10'36"N-76°44'38"E) located about 60 km WNW of Chennai City has significance in stratigraphic correlation of sedimentary sequences of Tamil Nadu and Peninsular India. Though carbonatite floats were reported from several places of Tamil Nadu from Kudangulam, Manappadu, Podupatti, Sivamalai, Alampadi, and Dharagambadi, age relationships of these carbonatite lava materials are not clearly known, though they appear to be belonged to the Quaternary Period [2,3,4, 5}. The occurrence of carbonatitic lava materials in Thiruvalangadu area has remarkable identity of its age relationship with its host rocks.

II. FIELD INVESTIGATION

The Upper Cretaceous shale is a source rock for a large clay deposits occurring in and out of Chennai City. During clay investigation, extensive traverses were made to map the clay deposit when the author was worked as a geologist in the Tamil Nadu State Department of Geology and Mining, Chennai during 1998-1999. He has collected floats of very fine-grained carbonate materials of varying in sizes from grit to boulder size. On detailed investigations by petrographic and geochemical studies, it is known that these carbonate materials are volcanic-rocks with characteristic carbonatitic affinities. From the studies on the 4 wall-sections of several wells, it is known that these volcanic materials occur in a conglomerate bed (Fig. 1, 2 and 3) lying between Mio-Pliocene sandstone (equivalent to Cuddalore Sandstone Formation) and boulder bed belonging to Pleistocene Period [6]. Figure 2 shows carbonatite

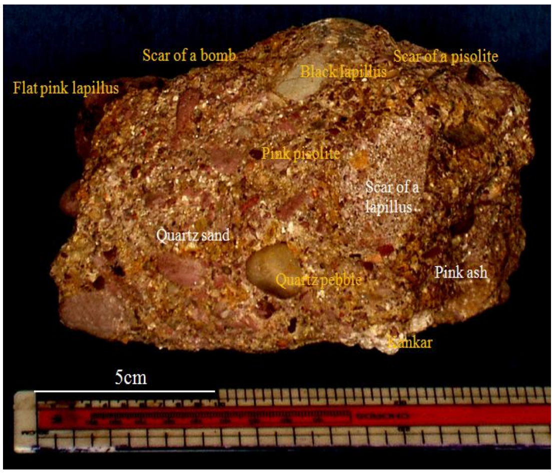


Figure 1 Conglomerate like calcareous sandstone composed of pyroclastic materials of carbonatitic lapillus, pisolites and ash materials together with quartzite pebble.

lapillus from the conglomerates. Pyroclastic materials of bombs, lapillus, pisolites and ashes are oblate and discoid in shape. They are more flat in shape as their sizes reduce to < 2 cm and their thickness reduces from 4 mm to 2 mm. They have very smooth outer surfaces. They have very thin outer skin of chilled margins. They are very fine-grained and by naked eye, it is impossible to identify any mineral grains. They do not have any concentric layers around any nuclei

Figure 2 Grey and pink coloured carbonatite lapillus in various shape and sizes

The broken materials have very sharp edges. They are compact and exhibit conchoidal fractures. Sometimes small vesicles or voids are seen. Some lapillus contain vesicles incorporating clayey materials of Upper Cretaceous Shale [7] as xenoliths and a halo bleached zone is seen around the vesicle and the clay.

Figure 3. carbonatite lapillus, pisolites and ash bearing conglomerate sample size 15X12X 7 cm

Inside the vesicle the xenolithic shale was found oxidized to reddish brown and stained along its peripheral portions. Just 2 km west of Thiruvalangadu, the conglomerate directly overlies above pink-granite gneiss which exposed at a depths of 7 to 10m below the ground level. The hornblende granite gneiss exposed at the well section was partially epidotized and kaolinized. Upper Cretaceous shale (Fig 4 and 5) is a very fine-grained rock with well defined fissility oriented parallel to its bedding plane and along its bedding plane; it is intercalated with 1-5% of grits, pebbles, cobbles or boulders of very fine-grained quartzites. The drainage pattern of this area reveals a maar like structure, a characteristic feature for many complexes. In the field large quantities of quartzite pebbles and boulders are strewn. They can be easily distinguished by their higher hardness from carbonatite materials. Unfossiliferous Miopliocene calcareous sandstone overlies the Upper Cretaceous shale. The lower portion of sandstone is highly indurate and compact in nature. Some places, it directly overlies above Nagari quartzites of Proterozoic age. The upper horizon of the sandstone incorporates some detritus quartzite pebbles derived from the shale formation. The colour of shale, quartzite and sandstone varies widely from dirty white, pale yellow, yellow and reddish brown to purple in places. The upper horizon of sandstone is partially lateritized to reddish brown colour. The rock is composed of 10 to 15% coarse-grained sand particles. The mean grain-size of sand particle of the conglomerate admixed with the pyroclastic material is around 0.7 mm. However, coarse-grained sand grains exceeding over 2 mm

Figure 4 Google Earth Image of Thiruvalangadu

A maar like structure is marked with red line.

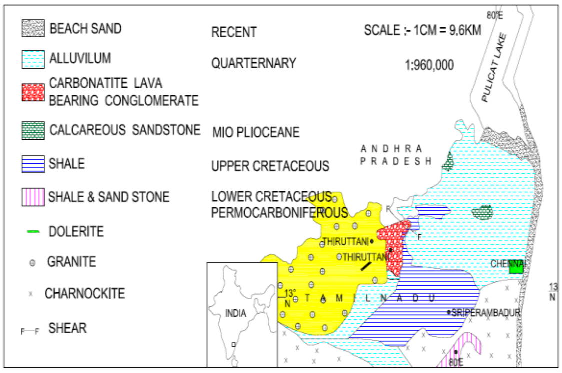


Figure 5 Geological map of Thiruvalangadu area

exceeds over 10% of its total volume. About 5% volume of soft clay acts as cementing media. The ash material altered to lime material also form as cementing media. However it is loosely packed. The pyroclastic material easily peals out from the conglomerate and scars are left where the pyroclastic materials fell-down. In addition to pyroclastic materials, detritus grits of quartz and rock fragments are also seen in the conglomerate. Grey coloured and pink coloured carbonatitic pyroclastic material of varying in sizes from bombs, lapillus, pisolites and ashes are seen together in a single specimen (Fig. 1.). This feature indicates that the conglomerate was formed after the eruption of both black and pink pyroclastic materials. The geological map with its staratigraphical sequence is also given (Fig. 5). The conglomerate is composed of carbonatitic pyroclastic materials, detritus quartz, fragments of quartzite, granite gneiss, amphibolite, dolerite, trachyte and basalt.

III. METHODOLOGY

Thin sections of the rock samples~0.03 mm thicknesses were prepared and examined under polarizing micro-scope. Wet gravimetric analyses were carried out for 4 samples. Carbon and oxygen isotope studies and Energy Dispersive X-ray Micro Analyzer (EDAX probe) were carried out to study geochemical variations of the rock types. The analyses were carried out by using Micronsperpixy 0031 attached with an EDAX probe of high resolution SEM in the Metallurgical and Material Science Laboratory, Indian Institute of Technology, Madras, Chennai-36. Mineral phases were indentified by petrographic examination, back-scattered images and also by EDAX analyses. Carbon and oxygen isotopes $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ were determined for the black and pink carbonatite lavas. The carbonatite lava samples were examined under high resolution scanning electron microscope at 10000X. The scanning microscope attached with EDAX Probe analyzer. The pyroclasts in the conglomerate have well developed euhedral crystals of calcites and they appear to be very fresh without any weathering features.

IV. PETROGRAPHY

The pyroclastic materials are very fine-grained and compact rock. They exhibit conchoidal fractures. The sizes of these pyroclastic materials vary from ash particles to boulder size exceeding over 30 cm in diameter. More frequently occurring sizes vary between pisolites (2-18mm) to lapillus. (18-64mm). Lapillus exhibits vesicles/vacuoles rarely. Halo of a bleached zone is present in some vesicles. Very thin chilled margins are present in some lapillus. Homogeneous mosaics of very fine-grained rhombohedral calcites (<0.02 mm) are seen under polarizing microscope. An array of vesicles containing apatite, sodic oligoclase, iron oxides and re-crystallized calcites (0.05mm) are seen along the inner periphery of the vesicles, similar to the carbonatite tuff of Fort Portal, Uganda [8]. Flow orientation of calcites, vesicles, cracks and weak planes are not uncommon. Among very fine-grained calcite matrix, patches of loosely packed, re-crystallized, slightly coarse grained freely grown calcite grains are seen along the cracks and weak planes. However, no glassy carbonate material has been noticed. Spherules of radiating microlites of calcites are seen along the inner peripheral portions of vesicles under polarizing microscope. Minute equate grains of iron oxides, microlites of phlogopite and euhedral to subhedral grains (0.1 x 0.05 mm) to large phenocrysts of sodic oligoclase (0.7 x 0.5mm) are present together with K-feldspar with very weak birefringence (Ist order grey sanidine?) rimmed with sodic oligoclase. Hollow crystals of potash feldspars are present. Some potash feldspars are extensively sericitized and kaolinized. Along periphery of some potash feldspars, phlogopite is oxidized to iron oxides. Some potash feldspars contain core of nearly isotropic or very weak birefringence materials (leucite?) with distinct cleavage and negative relief. Submicroscopic fine-gaseous inclusions of vacuoles are seen among fine-grained calcite. Large phenocrysts of calcite are also present. Some phenocrysts of biotite, hornblende and clinopyroxenes are completely replaced by calcite. Anhedral to subhedral grains of very fine-grained magnetite; apatite, rutile and perovskite are present as accessories. Quartz is found with corroded outline. Minute prism of wollastonite is also seen. Xenolithic fragments of quartz are also seen. The rock is composed of calcite 75-98%, vesicles 5-1%, sodic oligoclase 7-2%, K-feldspar 4-1%, magnetite 3-1%, phlogopite 3-1%, hornblende 0.5%, augite 0.5%, apatite 1% and other accessories 1% (by vol.%). Hornblende granite gneiss exposed at the contact of the conglomerate is partially epidotized and kaolinized. It is essentially composed of oligoclase, microcline and quartz with accessories of hornblende, biotite and magnetite. Quartzite occurs as detritus material derived from the Upper Cretaceous shale. It is hard and compact rock, well rounded with smooth outer surface. The Upper Cretaceous shale occurring in this area is a very fine-gained rock with well defined fissility parallel to its bedding plane. It is intercalated with well rounded grits, pebbles, cobbles and boulders of quartzite. The quartzite is composed of fine-grained mosaics of quartz grains. The sandstone formation equivalent to Cuddalore sandstone of Mio-Pliocene age shows wide variation in its chemical composition, structural and textural features. Gritty calcareous sandstone without any pyroclastic materials is also found as one of the facial variant of the sandstone formation. The pyroclasts bearing conglomerate is loosely packed generally found above the sandstone formation. The pyroclastic materials are cemented with coarse-grained sands admixed with clay and calcareous materials. About 10 to 30% pyroclastic materials are seen in this rock. Both black coloured and pink coloured pyroclastic materials are seen together in this rock. The pyroclastic materials are very fresh and fine-grained. Quartzite pebbles have higher degree of sphericity (0.5-0.3) and roundness (0.90 to 0.95) than the carbonatitic pyroclastic materials having lower degree of sphericity (0.30-0.10) and roundness (0.70-0.85). As the size of pyroclastic material increases from ash to bombs, sphericity and roundness increases and the flatness decreases. Bombs are more spherical and round in shape. Pisolites are more flat in shape with low sphericity and roundness. However, their shapes are modified by teir as content, fluidity /viscosity, temperature and composition of erupted fragments of pyroclastic materials thrown into the air. During spray of highly fluid pyroclastic carbonatitic lava materials thrown into the air from deep seated source, the high fluidity of the lava induced flatness of the materials. The pyroclastic bearing conglomerate is overlain by Pleistocene boulder bed, alluvial and recent soil overburden.

V. GEOCHEMICAL CHARACTERISTICS

Wet-gravimetric analyses of carbonatite lapillus indicate that they are enriched in silica and alumina. Their Fe_2O_3/FeO ratio is greater than 1 or approaches 1 (Table 2). They have significant amount of K_2O. In pink variety K_2O is greater than Na_2O. They have excessive molecules of CO_2 after normative estimation of calcite. Their chemical composition is very similar to the chemical compositions of carbonatite tuff of Fort Portal area in western Uganda [9] and the atypical carbonatite tuffs from other places of Tamil Nadu [5]. The low values of ∂^{13} C_{PDB} (from -8.2 to -5.5 ‰ in black carbonatite tuff and in pink carbonatite tuff from -5.2 to 0.10‰ and high values of ∂^{18} O_{SMOW} (from 23.1 to 23.7 ‰ for black carbonatite

Table 1 ∂^{13} C_{PDB} and ∂^{18} O_{SMOW} isotope distributions in the carbonatite lava samples

S.No	Particulars	∂^{13} CPDB	∂^{18} OSMOW
1	Black carbonatite lava	-8.20	23.10
2	Black carbonatite lava	-5.50	23.70
1	Pink carbonatite lava	-5.20	24.40
2	Pink carbonatite lava	+0.10	27.63

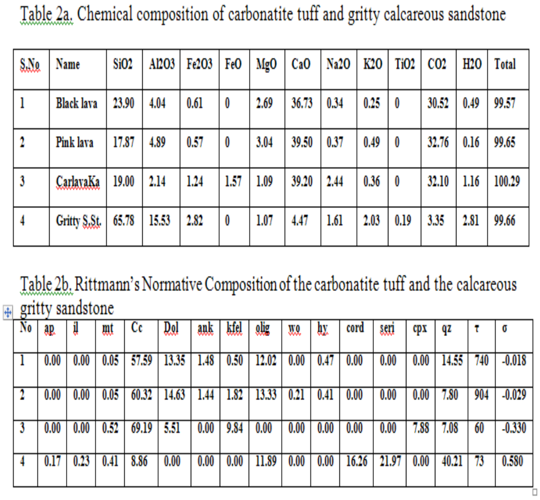


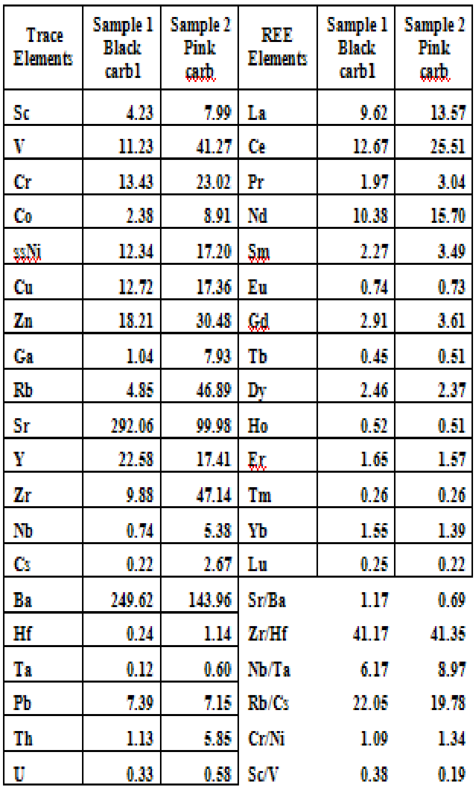
Table 2a. Chemical composition of carbonatite tuff and gritty calcareous sandstone

S.No	Name	SiO2	Al2O3	Fe2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	CO2	H2O	Total
1	Black lava	23.90	4.04	0.61	0	2.69	36.73	0.34	0.25	0	30.52	0.49	99.57
2	Pink lava	17.87	4.89	0.57	0	3.04	39.50	0.37	0.49	0	32.76	0.16	99.65
3	CarlavaKa	19.00	2.14	1.24	1.57	1.09	39.20	2.44	0.36	0	32.10	1.16	100.29
4	Gritty S.St.	65.78	15.53	2.82	0	1.07	4.47	1.61	2.03	0.19	3.35	2.81	99.66

Table 2b. Rittmann's Normative Composition of the carbonatite tuff and the calcareous gritty sandstone

No	ap	il	mt	Cc	Dol	ank	kfel	olig	wo	hy	cord	seri	cpx	qz	τ	σ
1	0.00	0.00	0.05	57.59	13.35	1.48	0.50	12.02	0.00	0.47	0.00	0.00	0.00	14.55	740	-0.018
2	0.00	0.00	0.05	60.32	14.63	1.44	1.82	13.33	0.21	0.41	0.00	0.00	0.00	7.80	904	-0.029
3	0.00	0.00	0.52	69.19	5.51	0.00	9.84	0.00	0.00	0.00	0.00	0.00	7.88	7.08	60	-0.330
4	0.17	0.23	0.41	8.86	0.00	0.00	0.00	11.89	0.00	0.00	16.26	21.97	0.00	40.21	73	0.580

Table 3 Trace element compositions of carbonati



Trace Elements	Sample 1 Black carb1	Sample 2 Pink carb	REE Elements	Sample 1 Black carb1	Sample 2 Pink carb
Sc	4.23	7.99	La	9.62	13.57
V	11.23	41.27	Ce	12.67	25.51
Cr	13.43	23.02	Pr	1.97	3.04
Co	2.38	8.91	Nd	10.38	15.70
ssNi	12.34	17.20	Sm	2.27	3.49
Cu	12.72	17.36	Eu	0.74	0.73
Zn	18.21	30.48	Gd	2.91	3.61
Ga	1.04	7.93	Tb	0.45	0.51
Rb	4.85	46.89	Dy	2.46	2.37
Sr	292.06	99.98	Ho	0.52	0.51
Y	22.58	17.41	Er	1.65	1.57
Zr	9.88	47.14	Tm	0.26	0.26
Nb	0.74	5.38	Yb	1.55	1.39
Cs	0.22	2.67	Lu	0.25	0.22
Ba	249.62	143.96	Sr/Ba	1.17	0.69
Hf	0.24	1.14	Zr/Hf	41.17	41.35
Ta	0.12	0.60	Nb/Ta	6.17	8.97
Pb	7.39	7.15	Rb/Cs	22.05	19.78
Th	1.13	5.85	Cr/Ni	1.09	1.34
U	0.33	0.58	Sc/V	0.38	0.19

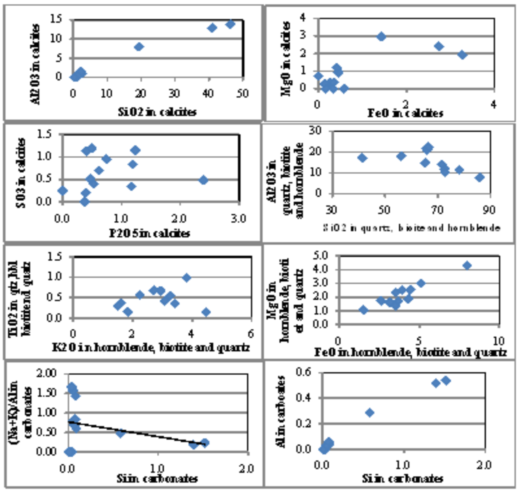


Figure 6 Geochemical variations in pyroclastic minerals

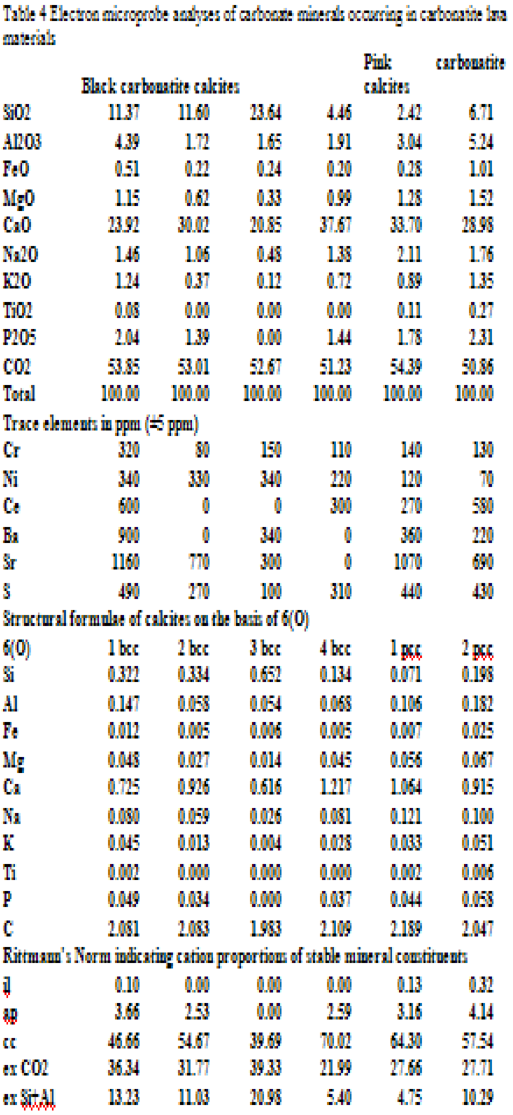


Table 4 Electron microprobe analyses of carbonate minerals occurring in carbonatite lava materials

					Pink	carbonatite
	Black carbonatite calcites				calcites	
SiO2	11.37	11.60	23.64	4.46	2.42	6.71
Al2O3	4.39	1.72	1.65	1.91	3.04	5.24
FeO	0.51	0.22	0.24	0.20	0.28	1.01
MgO	1.15	0.62	0.33	0.99	1.28	1.52
CaO	23.92	30.02	20.85	37.67	33.70	28.98
Na2O	1.46	1.06	0.48	1.38	2.11	1.76
K2O	1.24	0.37	0.12	0.72	0.89	1.35
TiO2	0.08	0.00	0.00	0.00	0.11	0.27
P2O5	2.04	1.39	0.00	1.44	1.78	2.31
CO2	53.85	53.01	52.67	51.23	54.39	50.86
Total	100.00	100.00	100.00	100.00	100.00	100.00
Trace elements in ppm (±5 ppm)						
Cr	320	80	150	110	140	130
Ni	340	330	340	220	120	70
Ce	600	0	0	300	270	580
Ba	900	0	340	0	360	220
Sr	1160	770	300	0	1070	690
S	490	270	100	310	440	430
Structural formulae of calcites on the basis of 6(O)						
6(O)	1 bcc	2 bcc	3 bcc	4 bcc	1 pcc	2 pcc
Si	0.322	0.334	0.652	0.134	0.071	0.198
Al	0.147	0.058	0.054	0.068	0.106	0.182
Fe	0.012	0.005	0.006	0.005	0.007	0.025
Mg	0.048	0.027	0.014	0.045	0.056	0.067
Ca	0.725	0.926	0.616	1.217	1.064	0.915
Na	0.080	0.059	0.026	0.081	0.121	0.100
K	0.045	0.013	0.004	0.028	0.033	0.051
Ti	0.002	0.000	0.000	0.000	0.002	0.006
P	0.049	0.034	0.000	0.037	0.044	0.058
C	2.081	2.083	1.983	2.109	2.189	2.047
Rittmann's Norm indicating cation proportions of stable mineral constituents						
il	0.10	0.00	0.00	0.00	0.13	0.32
ap	3.66	2.53	0.00	2.59	3.16	4.14
cc	46.66	54.67	39.69	70.02	64.30	57.54
ex CO2	36.34	31.77	39.33	21.99	27.66	27.71
ex Si+Al	13.23	11.03	20.98	5.40	4.75	10.29

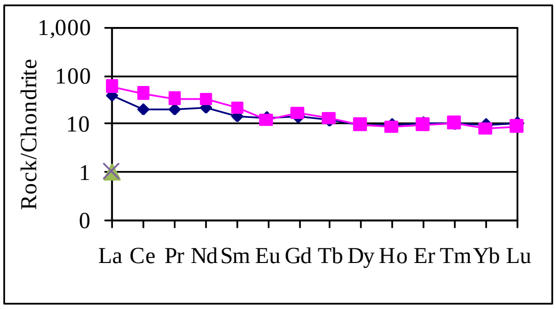


Figure 7. Chondradite normalized REE pattern for lapillus. Diamond– Black lapillus; Square –Pink lapillus

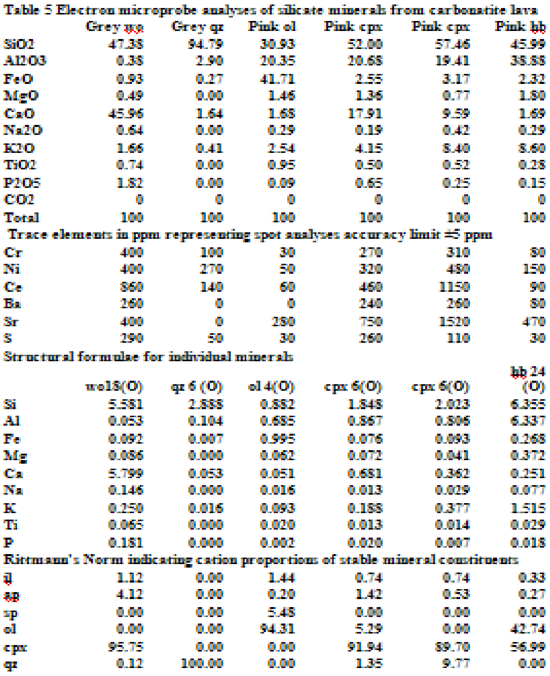


Table 5 Electron microprobe analyses of silicate minerals from carbonatite lava

	Grey wo	Grey qz	Pink ol	Pink cpx	Pink cpx	Pink hb
SiO2	47.38	94.79	30.93	52.00	57.46	45.99
Al2O3	0.38	2.90	20.35	20.68	19.41	38.88
FeO	0.93	0.27	41.71	2.55	3.17	2.32
MgO	0.49	0.00	1.46	1.36	0.77	1.80
CaO	45.96	1.64	1.68	17.91	9.59	1.69
Na2O	0.64	0.00	0.29	0.19	0.42	0.29
K2O	1.66	0.41	2.54	4.15	8.40	8.60
TiO2	0.74	0.00	0.95	0.50	0.52	0.28
P2O5	1.82	0.00	0.09	0.65	0.25	0.15
CO2	0	0	0	0	0	0
Total	100	100	100	100	100	100
Trace elements in ppm representing spot analyses accuracy limit ±5 ppm						
Cr	400	100	30	270	310	80
Ni	400	270	50	320	480	150
Ce	860	140	60	460	1150	90
Ba	260	0	0	240	260	80
Sr	400	0	280	750	1520	470
S	290	50	30	260	110	30
Structural formulae for individual minerals						
	wo18(O)	qz 6 (O)	ol 4(O)	cpx 6(O)	cpx 6(O)	hb 24 (O)
Si	5.581	2.888	0.882	1.848	2.023	6.355
Al	0.053	0.104	0.685	0.867	0.806	6.337
Fe	0.092	0.007	0.995	0.076	0.093	0.268
Mg	0.086	0.000	0.062	0.072	0.041	0.372
Ca	5.799	0.053	0.051	0.681	0.362	0.251
Na	0.146	0.000	0.016	0.013	0.029	0.077
K	0.250	0.016	0.093	0.188	0.377	1.515
Ti	0.065	0.000	0.020	0.013	0.014	0.029
P	0.181	0.000	0.002	0.020	0.007	0.018
Rittmann's Norm indicating cation proportions of stable mineral constituents						
il	1.12	0.00	1.44	0.74	0.74	0.33
ap	4.12	0.00	0.20	1.42	0.53	0.27
sp	0.00	0.00	5.48	0.00	0.00	0.00
ol	0.00	0.00	94.31	5.29	0.00	42.74
cpx	95.75	0.00	0.00	91.94	89.70	56.99
qz	0.12	100.00	0.00	1.35	9.77	0.00

Table 6 Chemical compositions of some minerals from carbonatite lapillus

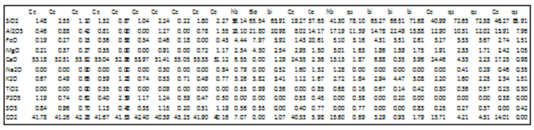


Table 7 Structural formulae for the minerals

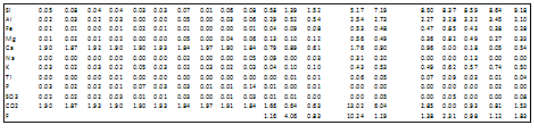
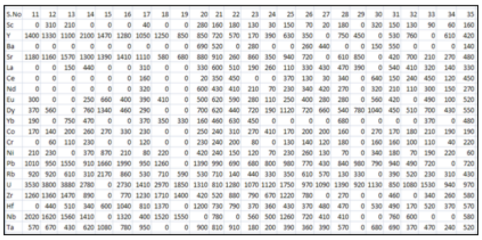


Table 8 Trace element compositions of carbonatite lapillus



tuff and for pink carbonatite tuff 24.4 to 27.63‰ (Table 1) indicate extensive degassing and loss of volatiles and alkalies by exhalative eruption of carbonatite lava [10,11] and during Early Pleistocene Period. Rittmann's Tao values (τ = (Al2O3-Na2O)/TiO2) and negative Row values (σ = (K2O+Na2O)/ SiO2-43) indicate (Table 2a and 2b) that these carbonatites belong to alkaline suite and the pink variety is subjected to greater degree of loss of alkalies with enrichment of alumina [12]. Pink carbonatite lapillus contains higher Al_2O_3/SiO_2 and lower H_2O/CO_2 ratios than the blacks indicating greater degree of loss of volatile constituents from the magma. It contains higher values of MgO, K_2O and K_2O/SiO_2 which indicate that it might be erupted from deeper source than the black lapillus [13]. About 10% of $MgCO_3$ enter in the calcite lattice indicating its temperature of formation around 660^{o}C [14]. EDAX chemical compositions of various mineral grains are given in Table 4, 5, 6 and 7. Structural formulae of these minerals are also given. Trace elemental compositions of these rocks and minerals are given in the Table 8. Significant enrichments of HREE, U, Pb, Zr, and Nb are characteristic for this volcanic complex. The depletion of LREE relative to HREE might be due to escape of volatile constituents carrying lighter elements during the course of higher level ascent and effusion of lava. The relative enrichment of Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Zr, Nb, Cs, Hf, Ta, Th, U, La, Ce, Pr, N, Sm, Gd, Tb, Zr/Hf, Nb/Ta and Cr/Ni in pink carbonatite lapillus over the black lapillus indicates that the former is highly degassed from common parent melt (Table 3, 8). Further lower values of Sr/Ba, Rb/Cs and Sc/V indicate that the black lapillus is older than the pink lapillus. SEM EDAX analyses indicate (Fig. 6) co-existing mineral assemblages of hornblende, biotite, quartz, calcite and wollastonite in black and pink lapillus. The calcites in the lapillus indicate enrichments of both Al_2O_3 and SiO_2; MgO and FeO; SO_3 and P_2O_5 towards the course differentiation. Similar trends are also seen between Al_2O_3 and SiO_2; TiO_2 an K_2O and MgO and FeO in the bulk compositions of quartz, biotite and hornblende present in the lapillus. (Na+K)/Al or Al in the structural formulae of calcites against Si show in increasing trends of differentiation. In Figure 7, chondrite normalized REE pattern shows enrichment of LREE in pink lapillus, slowly merging with HREE of black lapillus with a parallel trend of carbonatites. The wollastonite ($Si_{5.58}Al_{0.05}Ti_{0.07}$ $Fe_{0.09}$ $Mg_{0.09}Ca_{5.80}$ $Na_{0.15}$ $K_{0.25}P_{0.18}$) is highly deficient in tetrahedral site and it could not be compensated by entry of Ti, Al, Fe, and Mg and the co-existing quartz is also highly deficient in tetrahedral site is compensated by entry of Al, Fe^{3+}, Fe, Mg, Ca and K. Both quartz and wollastonite are enriched in Cr, Ni, Ba and Ce . The average composition of calcite from black and pink lapillus is $Ca_{0.87}Mg_{0.22}Fe_{0.01}$ $NaK_{0.08}Si_{0.36}Al_{0.08}$ $Ti_{0.00}P_{0.03}C_{2.06}$ $Ca_{0.99}Mg_{0.06}$ $Fe_{0.02}$ $NaK_{0.15}$ $Si_{0.13}Al_{0.14}Ti_{0.004}P_{0.051}C_{2.12}$. The olivine in pink lapillus is composed of $Fe_{1.00}Mg_{0.06}Ca_{0.05}$ $Al^{vi}0.59$ $Na_{0.02}$ $K_{0.09}$ $Si_{0.88}$ $Al^{iv}_{0.10}$ $Ti_{0.02}$ $P_{0.002}$. The olivine is deficient in its tetrahedral site and is compensated by $Ti_{0.02}$ $Al^{iv}_{0.10}$ ions. Olivine is significantly enriched with fayalite molecule. Two aegirine augite is composed of $Si_{1.85;2.02}Ti_{0.01;0.01}$ $Al_{0.87;0.81}$ $Fe_{0.08;0.09}Mg_{0.07;0.04}Ca_{0.68;0.36}$ $Na_{0.01;0.03}$ $K_{0.19;0.38}$. The breakdown of feldspars and clinopyroxene in carbonatite magma leads to crystallization of amphibole rich in alkalies and alumina and quartz.

$(NaK)AlSi_3O_8+CaAl_2Si_2O_8+CaMgSi_2O_8+Mg_2FeSi_3O_9+H_2O \longleftrightarrow NaCa_2Mg_3FeAl_3Si_6O_{22}(OH)_{2}+4SiO_2$

Since the degree of oxidation is very high, it appears that the amphibole is devoid of ferrous iron and it is completely enriched with ferric iron. At this condition exchange of MgAl $\longleftrightarrow$ $Fe^{2+}Fe^{3+}$ and $MgSi_2$ $\longleftrightarrow$ (NaK)Al are possible. Thus, significant amount Fe^{3+}, (Na,K) and Al enter to replace Mg and Si. Si deficiency in the tetrahedral site is compensated by Al^{iv} for about 1.61 ions. The composition of alkali bearing amphibole is $Si_{6.36}Ti_{0.03}Al^{iv}_{1.61}Al^{vi}_{4.73}{}^{Fe}{}_{0.27}Mg_{0.37}Ca_{0.25}Na_{0.08}K_{1.52}P_{0.02}$. The amphibole belongs to K-rich magnesio katophorite. Both calcites and silicate mineral are enriched with P and S. The calcite composed of low proportion of dolomite and ankerite molecules.

VI. DISCUSSION

Unlike magmatic differentiation under plutonic condition, the course of differentiation under volcanic stage is rather different. Under volcanic state, the viscosity / fluidity, temperature, chemical composition, time series, polymerization of mineral constituents, and fluid-pressure play critical role in the chemical variation of lava materials erupted at late stages of volcanic eruptions. Degassing of volatile materials is one of the major factors which cause change in the composition of lava materials. The chemical composition of lava materials and structural components of mineral constituents indicate their chemical differentiation due to magmatic degassing and rapid consolidation of the lava materials [8, 15, 16, 17]. The flat shape of ash materials, pisolites and discoid shape of lapillus and bombs indicate that they were juvenile fractions tend to occur spherical / discoid pyroclastic materials [15} associated with phreatomagmatic phases developed in diatremes cross-cutting nearby surface aquifers just prior to eruption. The roundness of the lapillus developed along the direction of blown up and falling down of the material. Carbonatite lavas are generally very fluid in nature. Therefore they attain flat shape before falling down. Sprays of low viscous carbonatite lava fractions thrown from deep-seated source into the air quickly attain flat shapes [16, 17]. The co-existing mineral assemblages of calcite-wollastonite-quartz are also reported in many igneous rocks [18], though they are commonly found in skarn rocks or in impure metasomatic limestone. The above assemblages are considered to be a geothermometers, indicating their high temperature of formation above 700°C [14] by $CaCO_3$+SiO_2 $CaSiO_3$+SiO_2 the reaction. Leucite and quartz may associate together in volcanic rocks. Xenolithic quartz reacts with carbonatite magma producing wollastonite. Co-existing leucite, wollastonite, calcite and xenocrysts of quartz were reported in some volcanic rocks from the Central Apennines, Italy [18]. Chondradite normalized REE of the bulk composition of black and pink carbonatite lapillus show steep gradients logarithmic variations indicating their carbonatitic affinity (Fig,7). Scannig electron microscopic back-scattered images of black and pink lapillus show well developed crystal forms of the calcites (Fig. 8).

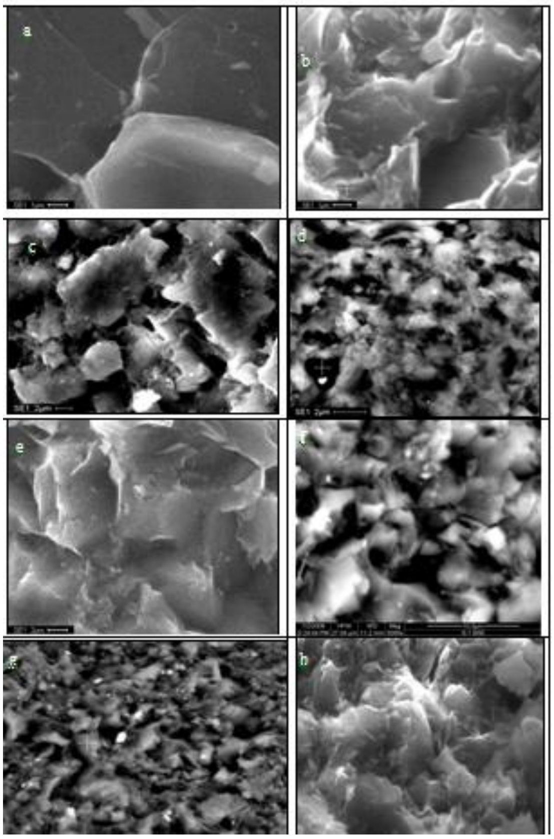


Figure 8 Scanning electron micrographs of (a-d) represent black lapillus and (e-h) represents pink lapillus. Calcites have crystalline forms. Vesicles (2 - 8µm) formed by escape of volatiles from lava.

Carbonatite bearing ultramafic alkaline complexes generally exhibit chaotic mineral assemblages by their explosive metasomatic alteration and high activity of volatile materials. Table 3 indicates excessive CO_2 in the lattice of carbonate minerals. The enrichment of Si and Al in all these minerals indicates oversaturation of Si and Al due to degassing of volatiles just prior to eruption. Abnormal enrichments of traces of Cr, Ni, Ce, Ba, Sr and S their silica undersaturated ultra-alkaline parentage from mantle horizon. The Great Ep-Archaean unconformity lies between the conglomerate and the hornblende granite gneiss derived from charnockite. In places, grey and pink ashy carbonatitic pyroclastic materials are altered to lime and act as cementing media in the conglomerate.

VII. CONCLUSION

The present study reveals that the very fine-grained lapillus, pisolites and ashes present in the conglomerate are not caliches but of volcanic materials belonging to carbonatite lava. Field and petrographical studies indicate that the grey coloured carbonatite pyroclastic materials were erupted initially followed by pink pyroclastic materials. The materials were deposited together in a conglomerate during the period of Early Pleistocene. The paper documents carbonatitic volcanic activities in the staratigraphical records of Tamil Nadu, Peninsular India. However, radiometric dating of the lapillus is essential to confirm the bimodal volcanism in this area.

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