

Features of Mineral and Chemical Composition of the Khamambettu Carbonatites, Tamil Nadu

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Abstract: The paper presents mineralogical features and EPMA results of the Khamambettu carbonatites. The mineralogical data suggest that these rocks have been generated in magmatic and hydrothermal stages. Mineral geothermometer for carbonatite give temperatures of 790°-980°C. Fluid inclusion measurements in monazite (hydrothermal stage) give temperatures of 220°-290°C. One of the features of the carbonatites is high content of magnesia that is defined by the presence of dolomite, olivine, spinel, phlogopite, Mg-rich ilmenite. Chloritization, serpentinization, amphibolization, silicification processes and occurrence of barite, monazite-(Ce), strontianite, celestine are related to hydrothermal stage. Hydrothermal minerals at the Khamambettu were formed by recrystallization of primary carbonatite minerals in the presence of Ba, $(SO_4)^{2-}$, REE and Si carried in solution by the hydrothermal fluid.

Keywords: Carbonatite, EPMA, Hydrothermal mineralization, Recrystallization, Monazite, Carbonates of REE and strontium, Khamambettu, Tamil Nadu.

INTRODUCTION

The Khamambettu carbonatite is interesting because of its moderately high magnesian composition (up to 6.88 wt. % MgO) (Table 1), in contrast to most world carbonatite occurrences which are predominantly Ca-rich and Mg-poor (average MgO content of 1.80 wt.%) (Woolley and Kempe, 1989). Phlogopite-carbonate-bearing peridotite can be expected to produce more magnesian melt compositions with increasing pressure (Olafsson and Eggler, 1983). The Khamambettu occurrence may be regarded as a candidate for direct, partial melt from the mantle.

Field and textural observations of carbonatites indicate that the associated mineralization in many cases is hydrothermal (Mariano, 1989). Hydrothermal REE mineralization in carbonatites are known, including occurrences at Kangankunde, Malawi (Wall and Mariano, 1996), Barra do Itapirapua, Brasil (Andrade et al. 1999). It is still unclear whether the REE minerals precipitated directly from hydrothermal solutions or formed during the replacement of the primary minerals in the carbonatites.

In this paper, we report the results of our mineralogical study of the hydrothermally altered carbonatites at Khamambettu, and present data obtained from mineral

geothermometers and thermometric determinations. This carbonatite complex provides comparisons of primary and hydrothermally altered carbonatite that contains about 5 % secondary minerals, such as monazite-(Ce), dolomite, amphibole, magnetite, strontianite, barite, celestine and carbonates of REE and strontium [carbocernaite and ancyllite-(Ce)]. In addition to our presentation of new data on the primary and hydrothermal minerals at Khamambettu, we speculate on the behavior of various elements of interest during hydrothermal activity.

ANALYTICAL METHODS

Most of the mineral analyses were carried out in the laboratories of Geological Institute SB RAS (Ulan-Ude, Russia). The minerals were analyzed using electron probe micro-analysis (EPMA): a MAR-3 WDS microprobe with an accelerating voltage of 20 kV, beam current of 40 nA, a 20 s counting time and beam size of 2 μm . In order to obtain a meaningful average composition several parallel analyses were made around each point.

Microstructural features of minerals were carried out using LEO-1430 scanning electron microscope with an

IncaEnergy-300 energy-dispersive system (SEM-EDS).

Major and trace elements in the carbonatites are defined by X-ray fluorescence at the Mineralogical-Petrography Institut, Hamburg University (Germany), and REE by neutron activation analysis at the Bhabha Atomic Research Centre, Trombay, Mumbai. Inclusions were studied in polished wafers up to 0.3 mm thick, using optical and thermometric methods. Primary and secondary inclusions were distinguished using textural criteria formulated by (Roedder, 1983). Inclusions that clustered along randomly orientated surface tracing healed microcracks were considered as secondary. Random, solitary inclusions were considered as primary. Heating of inclusions in minerals was carried out by using microscope Olympus BX51 with the high-temperature chamber "Lincam 1500". The rate of sample heating varied, on average, within 15°C/min. The investigations were carried out in the Institute of Geochemistry of A.P. Vinogradov (Irkutsk).

The $\delta^{13}\text{C}$ PDB and $\delta^{18}\text{O}$ SMOW values were analyzed in the isotope laboratory of the Analytical Center FESC RAS (Vladivostok, Russia) using a Finnigan MAT 253 sensitive mass-spectrometer. The techniques of sample preparation and their analysis is enumerated in Ignatev and Velivetsky (2005). The method is calibrated by international (NBS-28, NBS-30) and laboratory standards. Reproducibility of analyses for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for calcite and apatite was $\pm 0.1\text{--}0.3\text{\textperthousand}$ at 95% confidence level.

GEOLOGICAL SETTINGS OF THE OCCURRENCE AND CHEMICAL COMPOSITION OF THE CARBONATITES

The Khamambettu carbonatites are located 5 km to the west of Khamambettu village, in the Teni district in the Neo-Proterozoic granulite terrain of Tamil Nadu, bordering the Kerala state (Fig. 1). The Khamambettu occurrence is associated with the Late Proterozoic gneisses and migmatites. Quartzites, charnockites and granulites also occur in this area. Small massifs of pyroxenites and syenites are also known from these parts. Metamorphic rocks are cut by carbonatite dyke 50 m wide, that can be followed for 0.5 km. The age of the carbonatites and the related silicic magmatic rocks has not been determined.

The carbonatites are composed of medium to coarse-grained calcite containing disseminations and segregations of apatite, olivine, dolomite, pyroxene, magnetite and phlogopite. Ilmenite, spinel, pyrochlore, carbocernaite and ancyllite-(Ce) are accessory minerals. A late hydrothermal overprint has led to the replacement of pyroxene by amphiboles and chlorites, olivine by serpentine are noted

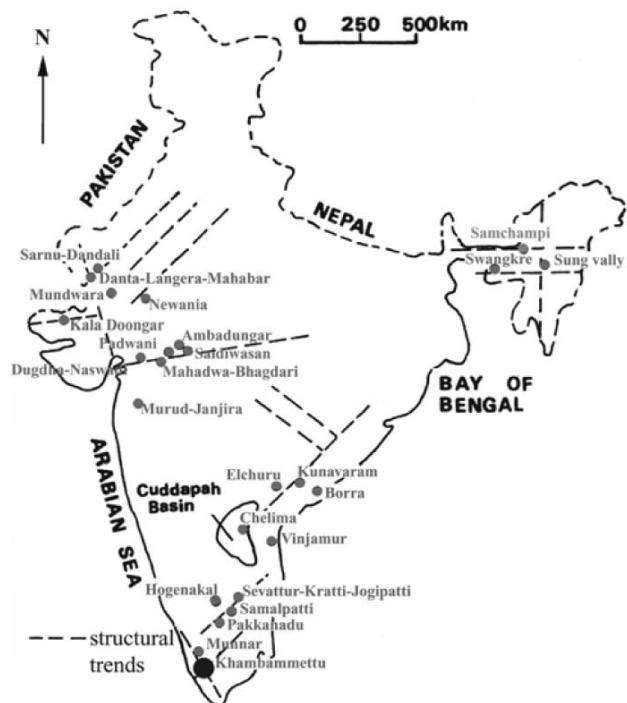


Fig.1. Tectonic setting of the Khamambettu carbonatites (according to Srivastava and Hall, 1995).

in some places in carbonatites. Among the minerals of the later generation include barite, monazite-(Ce), celestine, strontianite and quartz.

The chemical composition of the rocks (Table 1) corresponds to calcite carbonatite. However, concentration of MgO in them is 2-2.5 times higher than the average calcite carbonatite of Woolley and Kempe (1989). It is apparently related to the presence of olivine, phlogopite, spinel, pyroxene, dolomite, which were formed at an early stage of the carbonatite crystallization. The rocks are also characterized essentially by higher amount of phosphorus and barium (1.5-2 times) than in average carbonatites. There are widespread disseminations of barite. There is an irregular distribution of barium in the rocks (Table 1), and its greatest concentration (up to 1.5 wt.% BaO) is noted in samples with high contents of silica (up to 8.47 wt.% SiO₂).

The presence of strontianite and celestine, high amount of strontium in calcite, fluorapatite, ancyllite-(Ce), carbocernaite and monazite-(Ce) account for the higher strontium content of the rocks.

Primitive-mantle-normalized plots of the Khamambettu carbonatite and magnesio-carbonatite (Woolley and Kempe, 1989) are very similar (Fig. 2). A comparison of the chemical features with average magnesio-carbonatite reveals the lower Th, V, Zr and Nb in the Khamambettu carbonatites. The carbonatites are depleted in HREE, Mg, V relative to primitive mantle and characterized by a strong

Table 1. Chemical composition of the Khamambettu carbonatites

	KMB1	KMB2	KMB3	KMB4	KMB5
Weight percent					
SiO ₂	8.47	8.27	0.29	0.24	3.78
TiO ₂	0.17	0.08	0.08	0.05	0.07
Al ₂ O ₃	0.10	3.20	0.00	0.00	1.70
FeO t.	5.72	5.84	3.34	2.51	2.99
MnO	0.10	0.14	0.13	0.13	0.09
MgO	0.68	6.88	3.87	4.24	4.10
CaO	45.48	38.67	47.16	47.05	44.86
Na ₂ O	0.11	0.02	0.09	0.08	0.03
K ₂ O	0.04	1.52	0.01	0.01	0.62
P ₂ O ₅	4.15	5.28	4.69	3.41	2.42
CO ₂	32.10	29.60	36.75	39.33	37.40
Total	97.12	99.50	96.41	97.05	98.06
ppm					
Ba	10397	15029	6679	7074	23441
Sr	4473	6328	28668	29081	4168
Y	132	85	44	38	51
Zr	10	68	5	5	15
Nb	30	35	3	5	15
Th	5	5	10	3	5
Pb	42	51	104	103	18
Cu	144	18	76	31	12
V	5	5	9	2	2
U	5	5	10	15	5
La	1050	1045	928	880	1855
Ce	2053	2027	1863	2070	3887
Sm	124	120	116	160	190
Eu	28.4	27.8	26.5	37.7	46.5
Tb	9.9	9.2	9.2	13.8	15.0
Yb	5.7	6.2	5.3	8.4	8.9
Lu	0.8	0.9	0.9	1.1	1.1

enrichment in Ba, Sr, LREE, with an average La/Yb = 168 (Fig. 2).

Biotite-K-feldspar aggregates found in the carbonatites have sharp borders. Barite and calcite are also present here. Feldspar from these aggregates is characterized by high concentration of barium (Table 2) characteristic of

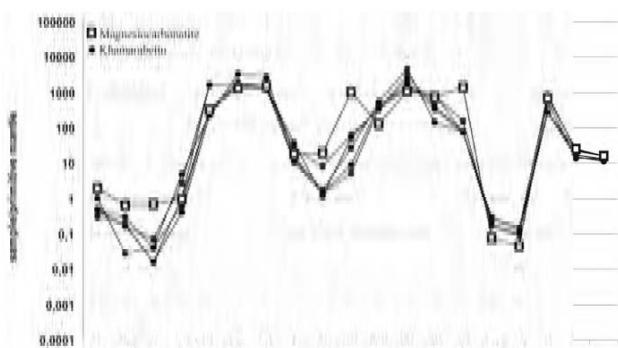


Fig.2. Trace elements in the Khamambettu carbonatites, normalized against primitive mantle (McDonough and Sun, 1995). Average magnesio-carbonatite values are from Woolley and Kempe (1989).

hyalophane. High-titanium (3.5-5.0 wt.% TiO₂) biotite (Table 2) forms inclusions within feldspar grains. It is also enriched in barium (2.8- 3.3 wt.% BaO).

MINERAL COMPOSITION OF THE CARBONATITES

About 20 minerals are recorded in the carbonatites which were generated at magmatic and hydrothermal stages. Calcite is the main mineral; fluorapatite, dolomite, olivine, phlogopite and magnetite are minor minerals. Pyrochlore, monazite-(Ce), ancyllite-(Ce), carbocernaite are accessory phases.

Minerals of the Magmatic Stage

Calcite is characterized by an irregular shape and high amount of strontium (up to 5 wt.% SrO), and a high level 2-3 wt.% MgO (Table 3). Strontianite forms (Figs. 3, 4) disseminations within calcite. It is usually observed near sites with superimposed hydrothermal mineralization. In such cases a heterogeneous distribution of Sr in calcite is observed. An appreciable amount is observed under scanning electron microscope and fixed by light and dark sites. In altered calcite content of SrO and FeO decreases and MnO increases (Table 3, analysis 6 to 9). The isotope compositions of oxygen (7.8 ‰ δ¹⁸O SMOW) and carbon (-6.4 ‰ δ¹³C PDB) of the primary calcite are identical to the compositions of primary igneous carbonatites from other regions (Taylor et al. 1967).

Dolomite which accompanies olivine, pyroxene, spinel, magnetite, commonly forms a rim around these mineral grains (Figs. 5, 6). Dolomite has low amount of iron (1.1-6.0 wt. % FeO). Content of Sr is much less than calcite (Table 3, analysis 10-16).

Fluorapatite occurs as rounded grains and segregations (Fig. 4, 5). Like calcite, it is also enriched in strontium (on the average 3 wt.% SrO), and the TR₂O₃ content of rare-earth elements reaches up to 2.6 wt.% (Table 4). The light rare-earth elements are predominant. The average Ce/La, Ce/Nd and La/Nd values are 2.5, 2.1 and 0.9, respectively. The amount of REE in fluorapatite is distinctly correlated with the sodium content. The heterogeneity of trace-element distribution in apatite is a consequence of secondary processes. In such cases a decrease REE and strontium content is marked. Disseminations of monazite along microcracks and edges of apatite grains (Fig. 2-b) were formed as result of this process. The apatite – biotite geothermometer (Ludington, 1993) yielded temperatures in the range of 790°-980°C. The δ¹⁸O VSMOW values for apatite from carbonatites vary over the range of +4.5 to +6.5‰ (Alberti et al. 1999; Doroshkevich et al. 2007; Santos

Table 2. Chemical composition of silicate minerals from the Khamambettu carbonatites, wt.%.

No.	Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	BaO	MgO	CaO	K ₂ O	Na ₂ O	F	Total
Pyroxene												
1	3/1	53.91	0.06	1.29	7.13	<0.09	13.98	22.58	<0.03	1.03	<0.22	100.21
2	3/2	52.96	0.07	1.33	7.53	<0.09	13.75	22.40	<0.03	1.11	<0.22	99.33
3	3/3	53.72	<0.05	1.30	7.33	<0.09	13.56	22.23	<0.03	1.13	<0.22	99.48
Amphibole												
4	42/1	46.84	0.26	8.31	4.78	<0.09	19.81	12.84	<0.03	2.87	1.05	97.02
5	42/2	43.81	0.37	11.45	5.39	<0.09	18.55	12.86	<0.03	3.03	1.31	95.47
6	4/7	44.58	<0.05	8.46	4.22	<0.09	20.67	13.38	<0.03	1.38	1.13	93.14
7	4/5	58.44	<0.05	<0.04	2.02	<0.09	24.35	13.10	<0.03	<0.11	<0.22	99.05
8	42/11	58.87	<0.05	<0.04	1.93	<0.09	24.00	13.57	<0.03	<0.11	<0.22	99.29
9	42/13	58.94	<0.05	<0.04	1.95	<0.09	23.82	13.48	<0.03	<0.11	<0.22	98.18
10	16/1	58.55	<0.05	<0.04	1.54	<0.09	23.47	13.19	<0.03	<0.11	<0.22	96.74
Phlogopite												
11	1 / 2-1	39.55	0.16	15.98	2.30	1.03	26.46	<0.03	7.13	2.47	0.50	100.06
12	1 / 3 -2	39.12	0.16	16.97	2.71	1.31	25.43	<0.03	6.85	2.60	0.54	100.19
13	1/4	39.43	0.13	16.71	2.44	1.24	25.87	<0.03	7.12	2.63	0.53	100.60
14	1/5	39.46	0.14	16.70	2.74	1.15	25.77	<0.03	7.16	2.63	0.41	100.61
15	1/1 -1	39.83	0.12	16.48	2.38	1.16	25.81	<0.03	6.51	2.96	0.55	100.34
16	2/1 -1	39.34	0.11	16.96	2.46	1.15	25.92	<0.03	6.77	2.79	0.31	100.37
17	2/2 -1	38.33	0.13	18.11	2.50	1.81	25.38	<0.03	6.28	2.88	0.41	100.33
18	1 -8	36.78	<0.05	17.32	3.49	1.78	24.98	<0.03	6.62	2.13	<0.22	97.59
19	2 -3	37.54	<0.05	18.06	2.69	2.33	25.11	<0.03	5.72	2.93	<0.22	98.89
20	4-2-8	38.66	<0.05	17.62	3.21	1.89	25.14	<0.03	6.77	2.44	<0.22	98.22
Biotite*												
21	7/3	37.97	3.78	13.61	11.77	2.81	18.16	<0.03	10.09	<0.11	<0.22	98.18
22	7/6	37.51	4.86	13.49	12.04	2.84	17.23	<0.03	9.66	<0.11	<0.22	97.62
23	72/5	36.66	5.06	13.68	12.23	2.97	16.21	<0.03	9.65	<0.11	<0.22	96.45
24	72/6	38.05	3.90	13.66	11.14	3.35	18.18	<0.03	9.92	<0.11	<0.22	98.21
Feldspar*												
25	7/2	55.57	<0.05	20.63	<0.09	11.41	<0.03	0.24	11.98	0.74	<0.22	100.58
26	7/4	55.97	<0.05	19.44	<0.09	9.39	<0.03	<0.03	12.67	0.64	<0.22	98.11
27	72/1	55.22	<0.05	21.20	<0.09	11.90	<0.03	<0.03	11.67	0.81	<0.22	100.80
28	72/2	57.09	<0.05	19.83	<0.09	9.38	<0.03	<0.03	12.75	0.69	<0.22	99.74
29	73/3	58.50	<0.05	20.17	<0.09	8.73	<0.03	<0.03	13.64	0.61	<0.22	101.65
30	72/4	58.65	<0.05	20.14	<0.09	6.91	<0.03	<0.03	14.73	0.71	<0.22	101.14

Note: *Biotite and feldspar are from xenoliths (?). The high value of sodium caused by the presence of the preiswerkite component.

and Clayton, 1995). $\delta^{18}\text{O}$ VSMOW for apatite from Khamambettu is considerably enriched by a heavy isotope ($\delta^{18}\text{O} = 8.2\ \text{\textperthousand}$). It is caused most possibly by low-temperature isotopic exchange between a mineral and a fluid in the process or after cooling of the system.

Forsteritic olivine occurs as single grains in calcite matrix and contains less than 10% of fayalite component (8-9 wt.% FeO). It is associated with phenocrysts of pyroxene and dolomite (Fig. 6). Olivine is converted to serpentine along the edges and microcracks.

Magnetite occurs as isometric (Fig. 5) and skeletal grains in calcite. It is in solid solution with ilmenite, whereas inclusions of spinel, fluorapatite, dolomite, pyrochlore, Mg-rich ilmenite are found in the mineral. Magnetite contains titanium (up to 1.7 wt% TiO₂), magnesium (up to 3.5 wt.% MgO), manganese (up to 0.61 wt.% MnO) and in some cases

aluminum (up to 0.7 wt.% Al₂O₃) (Table 5). The average Fe³⁺/Fe²⁺ ratio is 2.1.

Phlogopite occurs as single tabular grains or aggregates in the calcite matrix. It is light green and associated with magnetite. It is poor in F (up to 0.5 wt.% F), Ti (less than 0.15 wt.% TiO₂) but enriched in magnesium (Table 2). Low contents of potassium in it are compensated by the preiswerkite (0.3-0.4 formula coefficient Na) and kinoshitalite (1.0-2.3 wt. % BaO) components. The Fe³⁺/Fe²⁺ ratios vary from 1.5 to 2.1.

Spinel forms solid inclusions in magnetite (Fig. 5). The mineral has 10-18 % of hercynite and higher amount of MnO and ZnO (Table 5). A Mg-rich ilmenite-geikielite is associated with spinel (Fig. 7).

Ilmenite forms plates in magnetite (solid solutions) and a rim around of spinel inclusions (Fig. 7). The most important

Table 3. Chemical composition of the carbonate minerals from the Khamambettu carbonatites, wt.%

No.	Sample	FeO	MnO	MgO	CaO	SrO	Na ₂ O	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	SiO ₂	Total
*Calcite													
1	7/2	0.71	<0.07	1.21	45.62	5.05	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	52.59
2	7/1	0.54	<0.07	0.84	46.52	5.12	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	53.02
3	2/8	0.46	<0.07	0.83	47.79	5.61	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	54.69
4	1/5	0.35	<0.07	0.56	48.39	3.42	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	52.72
5	4/9	0.47	<0.07	0.67	47.51	3.44	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	52.09
6	2/9	0.42	<0.07	0.35	52.21	0.53	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	53.51
7	3/7	0.33	0.13	2.39	51.69	0.79	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	55.33
8	3/8	0.30	0.15	1.96	51.78	0.85	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	55.04
9	1/6-2	0.09	0.11	1.74	52.82	0.50	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	55.26
**Dolomite													
10	4/2	1.33	<0.07	18.50	28.15	1.84	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	49.82
11	13/7	1.36	0.31	19.06	28.98	1.64	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	51.35
12	1/6	1.13	<0.07	19.85	29.91	1.61	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	52.50
13	12/7	1.01	<0.07	18.49	28.93	1.59	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	50.02
14	3/6	3.77	<0.07	16.91	32.54	0.94	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	54.16
15	5/7	6.28	0.34	16.30	29.08	0.67	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	52.67
16	6/2	5.58	<0.07	17.13	29.44	0.71	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	52.86
17	42/10	0.43	<0.07	17.45	32.38	0.61	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	50.87
18	3-1	0.56	<0.07	19.19	29.36	<0.2	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	49.11
19	1-2	0.28	<0.07	18.97	28.75	<0.2	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	48.00
Strontianite													
20	1/4	<0.09	<0.07	<0.03	6.30	58.57	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	64.87
21	2/4	<0.09	<0.07	<0.03	11.26	56.79	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	68.05
22	3/3	<0.09	<0.07	<0.03	10.41	54.28	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	64.69
23	4/5	<0.09	<0.07	<0.03	5.15	59.40	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	64.55
24	6/4	<0.09	<0.07	<0.03	4.16	61.06	<0.11	<0.18	<0.16	<0.28	<0.28	<0.06	65.22
Ancylite - (Ce)													
25	5-1	<0.09	<0.07	3.02	2.03	17.22	<0.11	14.22	24.40	1.36	6.88	3.41	72.54
26	5-2	<0.09	<0.07	2.28	1.94	16.75	<0.11	13.78	23.51	<0.28	6.72	2.66	67.64
Carbocernaite													
27	2-3-2	<0.09	<0.07	<0.03	12.42	13.67	5.23	9.88	18.63	1.23	4.35	<0.06	65.41
28	2-3-3	<0.09	<0.07	<0.03	11.71	13.49	3.55	8.92	18.91	1.82	5.93	<0.06	64.33

Note. Total is without CO₂, * 1-5 are unaltered calcite, 6-9 – altered calcite, ** 10-16 – early generation of dolomite, 17-19 – late generation of dolomite.

feature of the mineral is high concentration of magnesium (up to 20 wt.% MgO) (Table 5). There is 13-16 % pyrophanite mineral in it with some geikielite component (to 64 %). Its composition is distinct from the ilmenite from carbonatites, and it is close to ilmenite from the Jacupiranga massif (Haggerty, 1991).

Pyroxene occurs as single grain and is associated with olivine and dolomite (Fig. 6). It is diopside with low amounts of aluminum, iron and sodium (Table 2). Fe³⁺ is predominant over Fe²⁺. It is replaced by tremolite and chlorite along microcracks and edges of grains.

Pyrochlore forms small (less than 10 µm) grains with irregular shapes and occurs in two types. The first type has high amount of tantalum, thorium and REE (Table 6, analysis 1, 2) and associated with magnetite, phlogopite and chlorite and the second type (Table 6, analysis 3-5) forms inclusions in magnetite and is associated with spinel and ilmenite. It is

characterized by high contents of titanium, iron, zirconium and fluorine.

Minerals of the Post-magmatic Stage

Monazite-(Ce) occurs in two generations. The first forms fine disseminations along cleavages, rims and microcracks of apatite grains (Fig. 4b). The average Ce/La, Ce/Nd and La/Nd values are 1.7, 3.3 and 2, respectively. The second, on the other hand, is associated with quartz, barite, celestine, strontianite. Such monazites are more coarse-grained (Fig. 4a) and forms irregular shaped veinlets. The average Ce/La, Ce/Nd and La/Nd values are 1.5, 4.5 and 3.1, respectively. This shows that during the hydrothermal process there was an increase in Nd.

Apart from light lanthanides, strontium and sulfur are present in monazite. The highest concentrations of SrO (up to 4 wt. %) and up to 2.8 wt. % SO₃ (Table 4) are determined

Table 4. Chemical composition of fluorapatite and monazite-(Ce) from the Khamambettu carbonatites, wt.%

	Fluorapatite							Monazite-(Ce)						
	2/10	2/9	2/10	2/6	2/10	2/7	3/4	3/4-2	12/4	4/4	42/5	4/2	13/6	12/3
SiO ₂	<0.06	0.10	0.13	0.07	<0.06	0.21	0.14	0.70	0.71	0.96	<0.06	1.00	<0.06	
CaO	49.85	50.56	50.35	51.33	50.07	51.80	51.94	52.61	0.71	0.32	0.54	<0.03	1.01	5.25
Na ₂ O	0.42	0.33	0.38	0.34	0.40	0.31	0.23	0.21	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
SrO	2.95	3.30	3.24	2.87	3.49	3.07	2.03	1.86	<0.2	1.05	1.17	0.72	1.08	4.65
Ce ₂ O ₃	1.33	0.88	1.12	0.89	1.19	0.84	0.55	0.61	34.34	34.66	35.41	34.19	34.14	29.05
La ₂ O ₃	0.47	0.44	0.47	0.37	0.59	0.31	0.23	<0.18	20.43	20.99	21.73	26.17	21.61	16.12
Pr ₂ O ₃	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	3.27	3.71	2.83	2.12	3.82	3.24
Nd ₂ O ₃	0.73	0.39	0.59	0.40	0.61	<0.28	0.30	<0.28	10.58	9.27	8.10	6.70	8.69	8.32
P ₂ O ₅	40.42	41.17	40.02	41.01	40.05	41.42	40.56	40.89	29.08	27.95	27.91	29.22	27.35	30.44
SO ₃	0.23	0.31	0.27	0.28	0.36	0.18	0.35	0.47	0.95	0.79	1.36	<0.1	1.29	2.81
Cl	<0.06	<0.06	<0.06	0.07	0.11	0.13	0.35	0.26	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
F	3.18	3.62	3.18	3.28	2.88	3.29	3.32	3.85	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22
Total	99.72	100.79	99.74	100.84	99.75	101.43	100.09	100.96	100.06	99.45	100.01	99.10	99.99	99.88
F = - O	1.34	1.52	1.34	1.38	1.21	1.39	1.40	1.62						
Ce/La	2.83	2.00	2.38	2.39	2.04	2.67	2.40	3.41	1.68	1.70	1.63	1.31	1.58	1.80
Ce/Nd	1.75	2.26	1.90	2.22	1.95	2.81	1.81	1.95	3.25	3.74	3.95	5.10	3.93	3.49
La/Nd	0.64	1.13	0.80	0.93	0.95	1.05	0.75	0.57	1.93	2.26	2.44	3.30	2.49	1.94

Table 5. Chemical composition of oxide minerals from the Khamambettu carbonatites, wt.%

No.	Samples	TiO ₂	Al ₂ O ₃	FeO t.	MnO	MgO	ZnO	Sc ₂ O ₃	Total	FeTiO ₃	MgTiO ₃	MnTiO ₃
Ilmenite												
1	4/2	59.79	<0.04	16.62	7.41	17.02	<0.1	0.40	101.24	0.30	0.57	0.13
2	03/8	59.20	<0.04	13.82	8.05	18.12	<0.1	0.40	100.22	0.25	0.60	0.15
3	32/7	59.65	<0.04	13.38	8.10	18.20	<0.1	0.40	99.73	0.25	0.61	0.14
4	32/8	59.50	<0.04	14.18	8.68	16.80	<0.1	0.20	100.42	0.27	0.57	0.16
5	32/7	59.80	<0.04	13.55	8.16	18.47	<0.1	0.50	100.40	0.25	0.61	0.14
6	33/8	60.50	<0.04	11.78	8.27	20.08	<0.1	0.30	100.90	0.21	0.64	0.15
Spinel												
7	03/10	<0.05	66.99	9.56	0.18	22.81	1.61	<0.1	99.55			
8	03/4	<0.05	66.00	7.51	0.36	23.41	1.62	<0.1	98.89			
9	32/3	<0.05	66.84	7.74	0.22	23.38	1.58	<0.1	98.91			
10	32/4	<0.05	67.46	6.81	0.25	24.58	1.18	<0.1	100.29			
11	32/5	<0.05	67.03	6.65	<0.07	24.12	1.52	<0.1	98.70			
12	32/6	<0.05	68.85	5.76	0.29	25.18	1.26	<0.1	101.34			
13	03/5	<0.05	66.87	8.36	0.28	23.06	1.47	<0.1	100.03			
14	33/2	<0.05	66.40	8.79	<0.07	22.86	1.51	<0.1	98.74			
15	33/3	<0.05	67.35	7.58	<0.07	23.98	1.52	<0.1	100.44			
16	33/4	<0.05	66.80	6.75	<0.07	25.20	1.10	<0.1	100.55			
*Magnetite												
17	1/8-1	1.23	0.25	89.32	0.56	2.52	<0.1	<0.1	94.07			
18	1/8-2	1.44	0.64	89.13	0.43	2.44	<0.1	<0.1	94.08			
19	1/8-1	1.37	<0.04	88.92	0.54	2.17	<0.1	<0.1	93.27			
20	1-2-9	1.13	0.72	90.56	0.42	1.89	<0.1	<0.1	94.30			
21	2/3-1	1.74	0.57	87.74	0.59	3.54	<0.1	<0.1	94.36			
22	2-2-5	0.91	<0.04	89.43	0.57	3.10	<0.1	<0.1	94.02			
23	2-6-1	<0.05	<0.04	93.59	<0.07	<0.03	<0.1	<0.1	93.59			
24	3/10	0.09	<0.04	91.86	0.60	1.70	<0.1	<0.1	94.01			

Note. *17-22 – early generation of magnetite, 23 – 24 – magnetite, formed at serpentinization of olivine

in inclusions of monazite in apatite. In monazite from veinlets, contents of La is appreciably higher than in inclusions in apatite (20-23 and 15-17 wt.% respectively). The mineral contains fluid inclusions composed of gas (up to 5%), undiagnosed solid phase (up to 80%) and fluid. The size of inclusions range from 8 to 14 µm. A thermometric study of the fluid inclusions had shown their

homogenization temperatures in the range of 220°-290°C.

Dolomite formed at a postmagmatic stage, occurs as small isometric grains in calcite, and also as disseminations and microveinlets in the matrix. It is associated with hematite as irregular shaped grains. It is depleted in Sr and Fe compared to the early generation of dolomite (Table 3, analysis 17-19).

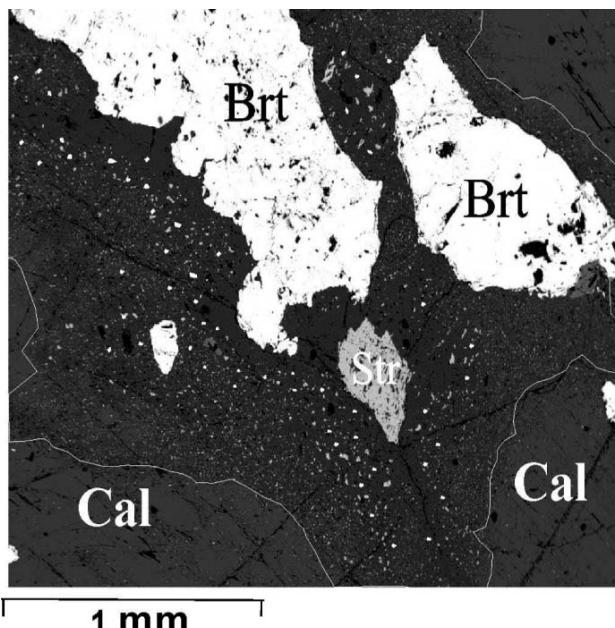


Fig.3. The area of strontianite (Str) disseminations in calcite (Cal) near barite (Brt) microvein.

Amphibole occurs in two types. One of them is tremolite, which replaced the early dolomite. It also forms microveinlets in pyroxene and olivine. The mineral is enriched in Mg, depleted in Fe, Al and F which are below detection limit (Table 2, analysis 7-10). $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios vary from 2.3 to 2.7. The composition of the secondary amphibole (Table 2, analysis 4-6) corresponds to magnesio-hornblende. It also occurs as a replacement product of pyroxene and dolomite. The mineral contains more aluminium and fluorine compared to tremolite.

Table 6. Chemical composition of pyrochlore from the Khamambettu carbonatites, wt.-%.

	1	2	3	4	5
	1-2-1	1-2-2	2-2-3	2-2-4	4-2-4
Na_2O	3.63	3.70	6.42	5.34	5.77
CaO	13.36	13.41	14.92	15.18	14.88
TiO_2	4.35	3.45	7.82	9.80	4.60
FeO	1.31	1.53	3.49	3.82	6.72
Nb_2O_5	50.81	46.66	48.24	47.38	48.86
Ta_2O_5	8.36	14.87	7.75	7.74	9.44
WO_3	<0.20	1.50	1.42	1.65	<0.20
ZrO_2	<0.15	<0.15	4.27	5.19	<0.15
ThO_2	3.42	2.56	<0.12	<0.12	2.15
La_2O_3	2.02	1.36	<0.18	<0.18	<0.18
Ce_2O_3	7.50	5.86	<0.16	<0.16	2.41
Nd_2O_3	1.67	1.14	<0.28	<0.28	<0.28
SiO_2	1.85	1.74	<0.06	<0.06	1.81
F	<0.22	<0.22	4.88	3.91	3.35
Total	98.28	97.78	99.21	100.01	99.99
$\text{F}=\text{O}_2$			2.05	1.64	1.41

Note: 1, 2 are the first type, 3-5 – the second type

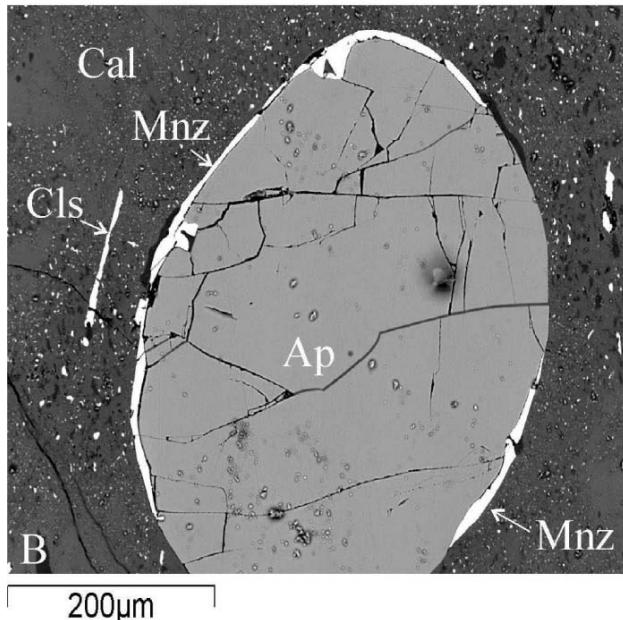
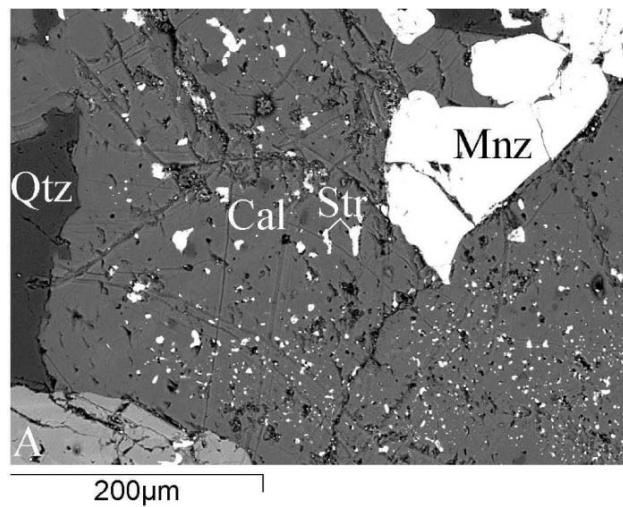


Fig.4. The features of strontianite (Str) and monazite-(Ce) (Mnz) distribution within hydrothermally modified carbonatites. Cal – calcite, Qtz – quartz, Ap – fluorapatite, Cls – celestine.

Magnetite of the second generation occurs as irregular shaped grains (Fig. 6). Amount of titanium is below detection limit, and MgO content does not exceed 1.5 wt. %. The average $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (2.6), in comparison with magnetite of magmatic stage is higher.

Strontianite forms fine disseminations in calcite. The mineral is associated with barite, monazite-(Ce), celestine and quartz (Fig. 4). It has higher amount of NaO , ranging from 4 to 11.2 wt. %.

Barite with monazite-(Ce), celestine and quartz form microveinlets, small nodular assemblages (Fig. 3). The mineral contains 2 to 5.5 wt.% of SrO (Table 7).

Celestine is a rare mineral. It is associated with

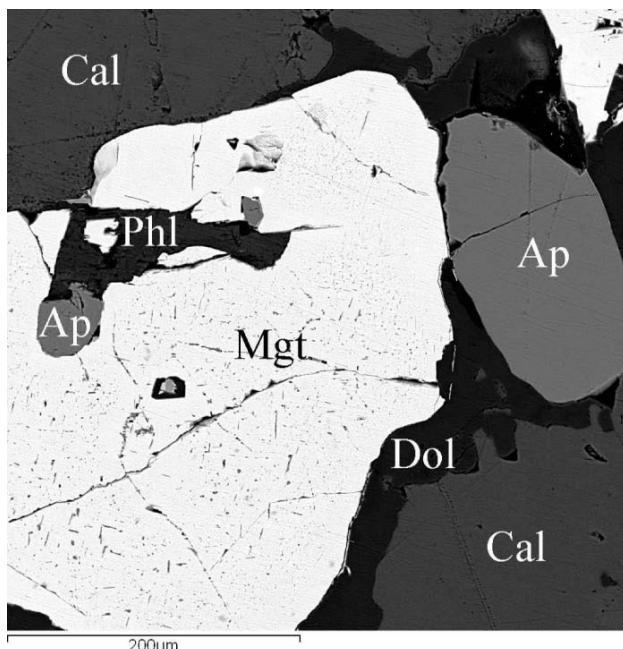


Fig.5. Rims of early dolomite (Dol) around of magnetite (Mgt) and fluorapatite (Ap) grains; Cal – calcite. There are inclusions of fluorapatite and phlogopite (Phl) in magnetite.

monazite-(Ce), barite. It contains 12-14 wt.% BaO (Table 7).

Carbonates of REE and strontium are also detected in the carbonatites. They occur as single disseminations in interstices of calcite grains. The compositions of the minerals are close to carbocernaite and ancylite-(Ce) (Table 3).

DISCUSSION

The mineral composition of the Khamambettu rocks is in accordance with carbonatite paragenesis. Its evolutionary history is a combination of magmatic assemblages and a later hydrothermal stage.

Minerals of the magmatic stage dominate with more than 95 % of the volume of the rocks. With essential calcite composition of the rocks, the prevalence of magnesium-bearing minerals is characteristic for this stage. Along with olivine, dolomite, spinel, phlogopite, Mg-rich ilmenite-geikielite occur in these carbonatites. Even magnetite, calcite

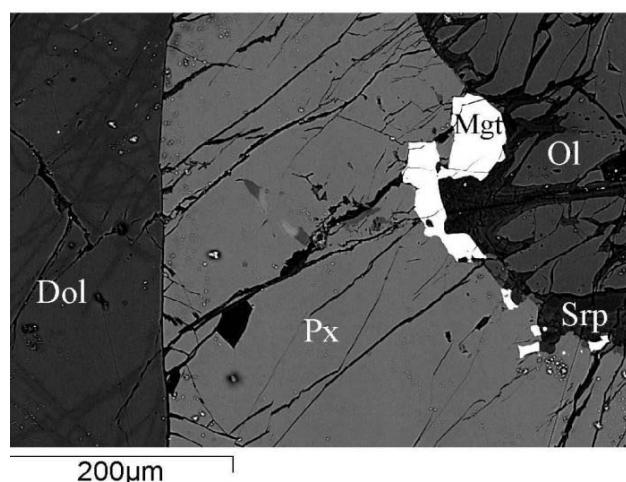


Fig.6. Association of olivine (Ol), pyroxene (Px) and early dolomite (Dol). Serpentization (Srp) of olivine along of microcracks. White is late magnetite (Mgt).

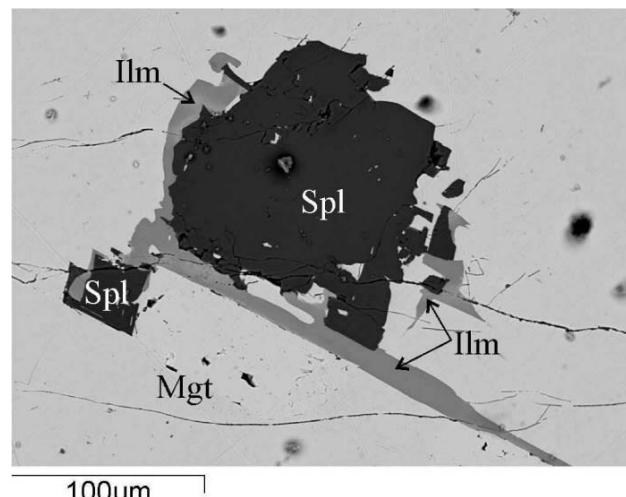


Fig.7. Spinel (Spl) and Mg-rich ilmenite-geikielite (Ilm) inclusions in magnetite (Mgt). It is clearly visible that ilmenite is later than spinel.

and pyroxene have higher magnesium contents. Most of the listed minerals have been formed at the initial stage of the carbonatite crystallization. The temperature of the magmatic stage is more than 790°C, according to apatite-biotite geothermometer. The mineralogical data indicate that the Khamambettu carbonatites have been formed under fairly oxidizing conditions. The oxidation state is embodied in the composition of phlogopite, pyroxene and magnetite that have higher Fe³⁺ content. The isotopic composition of O and C in the carbonatites confirms their primary magmatic origin. The isotopic compositions of O in apatite ($\delta^{18}\text{O} = 8.2\text{‰}$) despite being heavy, nevertheless is close to mantle values. Its isotopic content is most possibly related to interaction with hydrothermal fluids.

Table 7 Chemical composition of barite and celestine from the Khamambettu carbonatites, wt.%

No.	SrO	BaO	CaO	SO ₃	Total
1-3	5.53	59.16	0.22	34.76	99.67
2-7	4.32	61.89	0.22	34.67	101.1
7-5	5.12	59.34	<0.03	34.63	99.09
4-1	3.95	59.64	<0.03	33.88	97.47
4-3	41.69	14.06	<0.03	40.97	96.72
2-3	43.63	12.05	<0.03	43.10	98.78

The products of a post-magmatic stage occur in close proximity to sites of rocks that are tectonically crumpled. The temperature of this stage is inferred to be 220-290°C. The average $\text{Fe}^{3+}/\text{Fe}^{2+}$ values in amphibole and magnetite indicates that oxygen fugacity increased during a post-magmatic stage of the Khamambettu carbonatite evolution. Serpentization of olivine, replacement of pyroxene and dolomite by amphibole, chloritization of pyroxene, amphibole, formation of barite, monazite-(Ce), strontianite, celestine and quartz microveinlets are connected with this stage. According to mineral associations, it is possible to assume a variable source of solutions. One source induced serpentization, amphibole formation and chloritization, whereas the other led to the formation of monazite-(Ce), barite, strontianite, and celestine.

Replacements of calcite and apatite from admixtures are related to the late post-magmatic processes. Along the hydrothermal microveinlets (Fig. 4), assemblages of strontianite disseminations are fixed in the host calcite, as a rule. Away from such veinlets, the size of strontianite grains consistently decreases and then they disappear. The amount of strontium in such calcite is lower than in the unaltered types (less than 1 wt. % SrO). A decreasing in the amount of magnesium also is noted in calcite. As a result numerous small dolomite grains have formed within calcite.

Replacement of apatite led to the formation of strontium-bearing monazite grains within apatite. Thus REE content has decreased in apatite.

One of the features of Khamambettu is also low concentration of fluorine in minerals. Fluorine either is not found, or is present in rather small amounts in phlogopite, which normally contains this element in a much greater amount.

The mineral association of quartz, strontianite, barite and monazite is typical of overprinted carbonatites which is related to high activity of $\text{Ba, } (\text{SO}_4)^{2-}$, REE and Si in the

fluid and in particular the increasing of the role Nd among REE.

We observe that there were two important ways for formation of hydrothermal minerals at Khamambettu: (1) re-equilibration and recrystallization of the primary minerals, such as fluorapatite, calcite, releasing elements to form secondary minerals like strontianite, monazite and celestine, and (2) introduction of key elements from hydrothermal solution into the carbonatites to form quartz, barite.

Another possible example of replacement of a primary mineral to form secondary minerals at Khamambettu involves the re-equilibration and recrystallization of calcite with the formation of strontianite, where strontium is liberated from the primary calcite. Part of the strontium probably was introduced by hydrothermal solutions.

CONCLUSIONS

This investigation shows, that:

- 1 The temperature of magmatic stage of the carbonatite was 790-980°C;
- 2 Hydrothermal minerals were generated in the range of 220° to 290°C;
- 3 They were formed by recrystallization of primary carbonatite minerals, with elements introduced by hydrothermal solution;
- 4 There is evidence that $\text{Ba, } (\text{SO}_4)^{2-}$, REE and Si were important components of hydrothermal fluid;
- 5 Oxygen fugacity was higher during evolution of the Khamambettu carbonatite.

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Government of India Ministry of Mines

NOMINATIONS FOR NATIONAL GEOSCIENCE AWARDS - 2012

The Ministry of Mines invites nominations from the individuals / team of geo-scientists / engineers /technologists/academicians in order to recognize their meritorious contributions in the field of fundamental or applied geosciences, mining and allied areas with a view to provide them an incentive for striving towards excellence. The awards will be given each year.

Nature of Awards

The National Geoscience Awards are of three categories:

- (A) **National Geoscience Award For Excellence:** Award for Excellence is made to one outstanding geo-scientists / engineers / technologists/academicians for his lifetime achievements and significant contribution in any field(s) of Geosciences. The award carries a cash prize of Rs. 500,000/-, a certificate, a citation and a trophy.
- (B) **National Geoscience Awards:** Nineteen awards are given to geo-scientists / engineers /technologists/academicians individually or to team(s) in recognition of meritorious contribution in any of the following fields; Discovery & exploration for minerals, coal, lignite & coal bed methane, oil, natural gas & gas hydrates and, groundwater, mining technology, mineral beneficiation (including mineral economics), sustainable mineral development, stratigraphy, structural geology, paleontology, geomorphology, Economic Geology, Geodynamics, petrology and geochemistry, applied geology, geophysics / applied geophysics, geo-environmental studies, disaster management, ocean development, geo-information system and Glaciology and Antarctic Research. Each award carries a cash prize of Rs. 200,000/-, a certificate, a citation and a trophy.
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Any citizen of India who is a professionally qualified geo-scientists / engineers /technologists/academicians with significant contribution in any of the field specified in Clause 3 of the Regulation shall be eligible for the National Geoscience Awards.

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The nominations (**in the prescribed nomination formonly**) for the *National Geoscience Award for Excellence - 2012* and the *National Geoscience Awards – 2012 and one Young Researcher Award-2012* are invited from individuals through designated sponsoring organisations as mentioned in Clause 9 of the Regulations.

The last date of receipt of nominations will be 31st May, 2013

Nominations received beyond the stipulated date or incomplete or nominations made in any format other than the prescribed **will be rejected**. **The Regulations along with nomination form can be downloaded from the website: www.mines.nic.in**

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