Geology of the Kamthai Rare Earth Deposit

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Abstract : A wide spectrum of calciocarbonatites and associated alkaline rocks are exposed around Kamthai, Rajasthan. The mineralogical studies exhibit a bimodal distribution of REE minerals. The southeastern block has carbocernaite and the eastern block has bastnaesite \pm ancylite / synchysite as the dominant REE minerals followed by parisite and other accessory minerals. Calcite is the most abundant of the gangue phase, followed by biotite, albite, k-feldspar and iron oxide / hydroxide. Minor and trace gangue phases include pyrite, ilmenite, apatite, siderite, ankerite, amphibole, pyroxene, strontianite, barite, ilmenite / pyrophanite, celestine, clay minerals, sphalerite, pyrochlore, fluorite and Mn-rich phases including hollandite and Mn-Fe oxides. Calciocarbonatite occuring as intrusive veins, sills/dykes and plug, is perhaps a product of crystallization of a primary carbonatite melt generated at upper mantle. The first phase magmatic calciocarbonatite is alvikite type, rich in carbocernaite whereas second hydrothermal phase, sovite type, is enriched in bastnaesite. The absence of supergene activity and minerals (crandalite, florencite, gorceixite) indicate minor role of secondary enrichment. A rift-related mechanism, thermal equivalent to Deccan flood basalt (65±2 Ma), invoking "Reunion plume - continental hot spot" might have triggered Tertiary alkaline magmatism.

Keywords: Carbonatites, Mineralogy, REE, Kamthai, Rajasthan.

INTRODUCTION

The rare earth group of lanthanides has fifteen elements in the periodic table with atomic numbers from 57 to 71 namely from La to Lu. The light rare earth elements (LREE) have atomic number from 57 to 63 (La, Ce, Pr, Nd, Pm, Sm $&Eu$), whereas heavy rare earth elements (HREE) are those with atomic numbers from 64 to 71 (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). *Senso stricto* there are only fourteen REE, Pm being scarce due to highly unstable and radioactive nature. There is another term in the financial market called 'critical rare earths', which includes Nd, Tb, Dy, Eu and Er. REE are high field strength elements (HFSE) and display lithophile character since they occur in silicate mineral.

The REE are characterised by high melting point, conductivity and thermal conductance. Due to their unique magnetic, fluorescent and chemical properties, REE are key components in hybrid rechargeable batteries, catalyst converter, glass, polishing, magnets, laser, components of colour TV, superconductors, ceramics and high end defence systems.

The REE minerals are hosted by magmatic carbonatites or as hydrothermal deposits formed by replacement and even supergene enrichment of in-situ weathering of carbonatite bodies (Le Bas, 1999). The other rocks hosting either LREE or HREE minerals are pegmatites, alkali syenite, phonolite, bauxite, laterites, metamorphic rocks, phosphorite, clay, placers and heavy mineral beach sands. The major REE bearing minerals are bastnaesite, ion-adsorption clays, monazite, xenotime and laporite, the last mineral occurs either in nepheline syenite or replacement of perovskite in carbonatite.

Monazite (Ce,La,Th,Y) $PO₄$, rare earth phosphate and bastnaesite (Ce,La) $FCO₃$: a rare earth flurocarbonate are two principal commercial rare earth ore minerals. Monazite is present in beach sands around the coastal belts of India, Brazil, Australia, South Africa and USA. Boatou Mianning and Weishan deposits in China and Mountain Pass, California, USA are the most significant bastnaesite deposits. Bastnaesite contains 75% combined rare earth oxides and minor amount of Yttrium. (Kim et al., 2010). 60-70% of rare earth oxides $(Re₂O3)$ in world are extracted from bastnaesite (Ren et al., 1997).

Carbonatite occur as magmatic, intrusive or extrusive, hydrothermal or replacement bodies which contain more than 50% by volume, primary igneous carbonate minerals derived from, carbonatite magma (Streckeisen, 1980, Woolley 1982). Calciocarbonatites are either coarse grained Sovite (C1) or medium to fine grained alvikite (C2) type (LeBas, 1999). According to Tuttle and Gittins (1966),

carbonatite complexes are always associated with ijolites, nephelinites and other alkaline rocks indicating origin of carbonatites from an alkaline magma.

Globally there are 527 carbonatite occurrences, (Woolley and Church 2005; Woolley and Kjarsgaard, 2008), with 49 of these being extrusive, ranging in age from Archean to present. The oldest dated carbonatite 3007 ma old, is localed in Tupertalik, Greenland (Downes et al., 2012.). Most of the extrusive carbonatites are pyroclastic in nature. (Bailey and Kearns, 2012). According to Jaireth et al ., (2014) there are 140 REE deposits being explored out of which only 12 deposits have $> 1\%$ rare earth oxide (REO).

In India, REE are of endogenic as well as exogenic origin. The endogenic type includes carbonatite pegmatite and metamorphic - metasomatic veins. The exogenic variant includes coastal or beach placers and offshore placers. Monazite is the principal ore mineral occuring in beach placers along west as well as east coast of India. India has estimated reserve of 5 MT of monazite and xenotime, 70- 75% occur in beach placers and the rest in the inland and offshore. Monazite concentration of beach sands may be upto 11% where REO content may exceed 60%.

Krishnamurthy (1988) compiled carbonatite occurrences of India including Sung valley in Meghalaya, Samalpatti, Pakkanadu, Hogenekal, Savattur and Khambammettu in Tamil Nadu, Ambadongar in Gujarat, Niwania, Sarnu Dandali, Mundwara in Rajasthan, and Borra, Elechuru, and Kunavaram in Andhra Pradesh. Woolley and Kjarsgaard (2008) complied carbonatite occurrences of the world and recorded 29 locations from India. While compiling carbonatites of Rajasthan (Niwania, Mundwara, Kamthai and Bhamni), Viladkar (1998) opined that Kamthai carbonatite exhibits very high concentration of REE.

Regarding REE content from Indian carbonatites, Schleicher (1998) reported 3.22% and 8.2% REE from carbonatites of Pakkanadu and Samalpatti respectively from Tamil Nadu.The average lower rare earth oxides (LREO) of carbonatites from Ambadongar does not exceed 0.25% (Viladkar and Dulski (1986). However Bhushan and Kumar (2013) recorded 19.39 % LREO from Kamthai carbonatites.

The Tertiary Alkaline Complex (TAC) of Sarnu-Dandhali; Rajasthan was first reported by Narayan Das (1973) followed by Udas et al., (1974), Chaube et al., (1974), Wall et al., (1993). Chandrasekharan, 1987 and Chandrasekharan et al., (1990), described ultramafic alkaline rocks including ijolites, melanephelenite, phonolite, alkali basalt and carbonatites of the area. Srivastava et al., (1993), Simonetti et al., (1998), Bell (2001), Ernst and Bell (2010). Bhushan and Chandrasekharan (2002) gave detailed account of geology and geochemistry of the TAC rocks. Bhushan

and Kumar (2013) reported the first carbonatite hosted LREE deposit from India, the geological, major, trace and REE geochemistry along with resource estimation has been carried out. A revised resource of 7.36 mt with average grade 1.62% REO, is expected from Kamthai carbonatite.

GEOLOGICAL SETUP

The TAC of Sarnu-Dandali comprises of ultrabasic alkaline rocks, ijolite, nepheline syenite, phonolite and carbonatite. The TAC is intrusive into the Neoproterozoic Malani rhyolites and lower Cretaceous sandstone, (Chandrashekaran et al., 1990). Around Kamthai (Fig.1A.) the Malani rhyolite occuring as basement rock is seen towards, south, west and eastern side, whereas in north, nepheline syenite pluton of TAC intrude through the rhyolites. This is intruded by ijolite plug having intrusive relationship with the adjacent Malani rhyolite and foidal syenite. The first influx of calciocarbonatite, alivikite type, occured as thin to thick E-W trendings intrusives through the ijolite. The second and strong Ba $&$ Sr bearing calciocarbonatite phase, sovite type, (Fig.1C) pierced through the ijolite plug resulting in concentration of high grade bastnaesite (> 8% REE) with small amount of either synchysite or ancylite. In the LV section of the SE block, the 12 boreholes exhibits 2D configuration of carbocernaite rich fine grained alvikite type calciocarbonatite (Fig.1B). This calciocarbonatite ore is dominated by carbocernaite (low grade REE upto 5%). The carbonatite samples studied are of two types: TYPE (1) Banded and brecciated rocks consisting of a melanocratic and leucocratic component, the latter hosts the bulk of the REE mineralization. Both components are calcite carbonatites. The calcite in these differ in texture and composition. The calcite in the melanocratic component is Mn-bearing (up to 4 wt.% MnO) and characterized by alteration to small patches of Ca-Fe-Mn-carbonates set in Mn-poor calcite. The overall appearance of this component results from oxidation and alteration of Fe- and Mn-bearing carbonates to diverse amorphous Fe- and Mn-oxides. In some instances, phlogopite (fenite) mica and magnetite are present, together with minor amounts of pyrochlore and niobian rutile. REE-minerals when present are commonly enriched in La relative to Ce.

The leucocratic component consists principally of colourless Mn-poor $(< 0.5 \text{ wt.} %$ MnO) anhedral calcite crystals with interstitial REE-carbonates associated with barite and cerianite. Barite abundance varies greatly within and between samples, with leucocratic zones in sample containing the most barite (c. 20 vol. %). Cerianite-(Ce) is developed as a secondary mineral on pre-existing REE-

Fig.1A. Geological map of carbonatite/ijolite plug (based on pit and surface geology), Kamthai, Barmer district, Rajasthan.

carbonates. Cerianite is not considered to be a supergene phase as it is not present in the associated melanocratic phases. REE-carbonates in the leucocratic zones are typically enriched in La relative to Ce. The abundances and character of the principal REE carbonate vary widely. Evidently at least two different styles of REE-mineralization are present in these leucocratic components. Trace amounts of phlogopite, Sr-REE-bearing apatite and magnetite are present as anhedral crystals. Daqingshanite and britholite are not present.

TYPE (2) A fine grained grey calcite carbonatite that is rich in Sr as indicated by the presence of abundant carbocernaite-(Ce), Sr-bearing calcite with lesser strontianite and abundant celestine carbocernaite-(Ce) commonly intergrown with bastnaesite-(La) and daqingshanite-(Ce), bastnaesite-(Ce). Calcite in this sample also exhibits pronounced exsolution textures of ancylite-like phases set in a Sr-rich calcite matrix. Barite occurs intergrown with ancylite/carbocernaite. Phlogopite, pyrite, and pyrophanite are also present. Type 2 carbonatites represent a distinct phase of Sr-rich REE- minerali-zation.This mineral assemblage of carbonatite intruding through the ijolite has been subjected to extensive fenitization through alkali metasomatism.

MINERAL CHEMISTRY

Prior to drilling for REE bearing minerals, surface samples were studied by Electron Probe Micro Analysis (EPMA) and Back Scattered Electron Image (BSE) at EPMA laboratory of Geological Survey of India, Faridabad. Ten samples were studied by Prof. Roger Mitchell of Almaz Petrology, Canada. XRD strudies on surface samples were undertaken at MINTEK Laboratory, South Africa. After detailed grid pattern pitting and trenching, drilling at 25m intervals was carried out to study the REE minerals occurring as veins, dykes and plug in the host rock ijolite. The core samples of SE block (Fig.1.A) have been mineralogically studied by ANSTO Minerals, NSW, Australia, whereas for the eastern block, the EPMA has been carried out by Earth Science Solutions (ESS), Faridabad, India. All the samples have been collected and studied from the calciocarbonatite occurring as veins, bands, dykes and plug (Fig.2 $A & B$).

RMML, EXPLORATION, SINDHARI
DATE : 11.04.2014 -50 -20 -30 -10 110 $\begin{array}{c}\n \bullet \\
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 \bullet\n \end{array}$ mRL (Mts) 100 $\overline{9}$ \rm{g} \mathcal{O} 80 \mathcal{S} \overline{Q} 50 20 \overline{a} \otimes **FOCT** $\overline{1}$ Ē $\frac{1}{2}$ 3.71%x0.61m
3.11%x0.26m 0.67%x0.30m
0.63%x1.57m
0.73%x0.43m 91%x7.70m .52%x0.33m 0.92%x0.64m 32%x17.15m 1.85%x6.80m 147%x0.64n **K4%vn** 24m 0.56%x2.57m **BOX** VT 64 87%x0.64n **BO%x0.64r** 114.14 Mts (149.00 Mts) BHK002 25 54%x1.62m %x0.64m 146.10 MIS) 1.21%x2.05m .13%x23.7 01%x1.1 BHK001 $\frac{1}{3}$ 111.92 Mts (14
3.99%x1.34m
3.69%x1.28m
0.54%x0.64m \circ - 8.12%x0.81m 04%x8.0m 1.02%x2.02m 86%x4.58m 0.56%x0.57m 135.97 Mts (177.50 Mts) 1.94%x3.75m 5.87%x5.96 **DS%17 BHK003** 25 \approx 132.53 Mts (173.00 Mts) 31%×0.66 BHK004 50 **REAL PROPERTY** 1%×0.64m 17%x9.50m 174.40 Mts (228.00 Mts) **BHK005** 75 0.56%x0.53m
1.12%x0.37m
0.57%x0.54m 32%x0.77m 16%x0.64m 17%x20.79m 51%x0.64m 1.13%x11.19m 1,57%x0.67m 62%x0.32m $0.57%x1.23m <$ ENTRANGEMENT 100 66%x1.28m 146.10 Mts (191.00 Mts) 144.57 Mts (189.00 Mts) **BHK007 B** 125 **DYSK1.16m** 1.13%x0.64m 2%x0.64m 1.22%x2.57m 0.89%x1.28m 1.72%x3.15m 51%x0.64m 424-715m 1.50%x1.03m 1.85%x0.64m 3%x12 84m .02%x7.19m 1.23%x6 42m 76%x1 28m

0.5%x1 38m

0.5%x1 64m
 \sim Band Av. Lnee_% x Band True Width(m)
0.51% x 4.49m **BHK008** 150 61%x0.31m 78%x0.51m R2%xR 72m 73%x0.59m 0.78%x0.49m
1.25%x0.81m 175 0.80%x3.21m 0.96%x1.28m <
0.79%x0.61m -
0.81%x2.45m < 0.79%x2.44m BH Lree Band 2.72%x0.19m 2.13%x0.90m 1.03%x0.77m 0.63%x1.22m 61%x2.02m 117.8 Mts (153.80 Mts) BHK008 200 (> 80 % Dyke (No samp **SYENITE** $(FC > 50 % with CC)$ (FC with <80 % Dyke) $(CC > 50%$ with FC (CC with < 80 % Dyke) (FC>100 % (Pum Fi **THO CODE** $(96.09<20)$ NEPHELINE S $\frac{1}{\bullet}$ BARITE F
Rhyolia 225 TON
SINE I 1.05%x1.83m 0.64%x1.93m 0.71%x1.93m 1.01%x1.93m 0.50%x0.64m 0.80%x3.85m $+ 6 + 6$ 0.53%x0.64m 0.57%x0.64m $\frac{100}{245}$ 1.64%x5.28m 1.82%x0.64m 1.51%x0.84m 1.03%x1.28m 0.61%x0.64m 1.57%x2.57m 0.71%x0.64m mRL(Mts) 110 50 100 90 80 $\overline{27}$ **GO** Q_{+} 30 20 $\frac{1}{2}$ $\rm ^{\rm 8}$ -10 -20 -30 -50

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Fig.1B. L.V. Section of drillholes of Kamthai area, Barmer district, Rajasthan.

Fig.1B. L.V. Section of drillholes of Kamthai area, Barmer district, Rajasthan.

Fig.1C. Photograph showing carbocernaite rich alvikite veins formed due to hydrothermal alternation cross cutting magmatic bastnaesite rich bands and aggregates within iron rich carbonatite, Kamthai.

The calciocarbonatite differ in their mineralogical assemblage and exhibit bimodal distribution. The SE block has carbocernaite as dominant rare earth mineral (+80%) where as eastern block has voluminous bastnaesite with small amount of ancylite or syncisite. Quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) was carried out using a Quanta 650 electron XFlash 5030 energy dispersive detectors, controlled by iDiscover and iMeasure image analysis hardware/software. The dominant REE containing mineral in the sample is a Sr and Ca rich REE carbonate (11.9 wt\%) , whose chemical composition best matches with the mineral carbocernaite $((Ca, Na)$ (Sr, REE, Ba)CO₃)₂). Parisite is the next most abundant mineral containing REE (0.92%). All the REE containing minerals have a significant proportion of calcite, which is the dominant gangue mineral. Significant proportion of minor and trace REE minerals are associted with other REE mineral, which indicates intergrowth of these REE minerals. The other minerals are ankerite, pyroxene, amphiboles, sphalerite, pyrochlore, fluorite and clay minerals.

Carbocernaite is well-liberated (Fig.3a). Almost 90% (89.2%) of the carbocernaite in the sample has a degree of liberation of greater than 50%. Parisite, the second most abundant mineral containing REE has a significantly lower degree of liberation than carbocernaite. While 48.2% of the parisite in the sample has little or no contact with the

Fig.2. (A) Carbonatite dyke injecting through ijolite plug. **(B)** Panther skin type exsolution between light grey calcite and dark grey REE minerals. **(C-D)** BSE image taken at successively higher magnifications showing **(C)** a large particle comprised predominantly of carbocernaite, with some associated ancylite and gangue minerals celestine, siderite and calcite. **(D)** a carbocernaite particle containing synchysite and bastnaesite, as well as the gangue minerals calcite and fluorite. **(E)** A particle comprised of needle/lath shaped parisite with some associated bastnaesite. **(F)** BSE images showing a particle predominantly comprised of ancylite, with some associated bastnaesite, strontianite, apatite and calcite.

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outer surface of particles (0-10% degree of liberation), only 14.3% exhibit a 30-40% degree of liberation. The other trace REE containing minerals bastnaesite, ancylite, synchysite, monazite, cerianite in the sample are, in general, poorly liberated.

REE minerals that are present in the composite sample in trace amounts include bastnaesite, ancylite, synchysite, monazite and cerianite. These trace constituents are typically associated with each other, or with the major REE containing particles. Some gangue minerals such as apatite and barite are found as small inclusions in the carbocernaite (Fig. 2C). The large carbocernaite particle contains numerous inclusions of gangue phase such as albite, K-feldspar, barite, pyrite, strontianite and biotite. Typical EDS spectra from the carbocernaite particles are presented in Fig. 3c. BSE images taken at successively higher magnifictions show a large particle predominantly comprised of carbocernaite with some associated ancylite and gangue minerals celestine, siderite and calcite. An EDS spectrum from the ancylite is shown in Fig. 2F and Fig.3b along with the normalized elemental composition.

The EMPA studies were carried out for eastern block by ESS, first by an Energy Dispersive Spectrometry (EDS) attached to Scanning Electron Microscope (SEM). This study, though indicated the presence of barite, ancyllite (hydrous Sr Ce carbonate), bastnaesite, kukherenkoite (Ba-Ce carbonate with fluorine), parisite (Ce-La Ca carbonate) and synchysite (Ba-parisite) along with ilmenite, Fe-oxides, sphalerite, titanomagnetite, latrappite (Nb bearing Ca-Na-Fe oxide), apatite, yet it was not possible to properly identify the REE phases. Electron Probe Micro Analyzer (EPMA) was thereafter used to characterize some of these phases.

In Back Scattered Electron (BSE) image barite occurs with an exsolution texture of La-Ce bastnaesite (Table 1 - 16, 17 & 18) and synchysite (lower half of Fig. 3d, Table 1 - 19 & 21). Synchysite and bastnaesite contain >50% total REE but there is higher Ca in synchysite. Commonly the exsolved REE carbonates together are in the size range of approximately 50-100 micron meter. This is also the common size of barite. Besides the fibrous and acicular exsolution (Fig. 2E), the REE carbonates also show a zonation with the margin being made of synchysite. Barite also contains approximately 3-4% of Ce_2O_3 (Table 1). There is a well formed large silicate phase yielding $~65\%$ SiO₂ (Table 1- 25).

In another sample barite occurs as relatively fine sized equant grains within a matrix of carbonate and fibrous minerals (Table 1 - 20, 22 and 23). The texture is inequigranular with the matrix filled by larger sized calcite. Barite shows high relief and fibrous/acicular development is of local nature. Barite constitutes \sim 15-20% of this rock and its size varies from 50-1300 micron meter. Corona (generally few hundred micron meter thick) development around barite is common. The bright grey tone is barite and around it Sr-REE carbonate corona is developed close to the centre. The REE rich carbonate locally show exsloved

| DataSet/Point | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SrO | 2.35 | 1.24 | 0.49 | 0.39 | 0.34 | 0.98 | 0.57 | 0.11 | 0.04 | 0.00 | 16.78 | 16.56 | 17.41 | 1.75 | 0.90 |
| SiO ₂ | 0.35 | 0.84 | 1.24 | 0.66 | 0.03 | 0.74 | 0.02 | 0.00 | 0.06 | 64.42 | 0.10 | 0.13 | 0.08 | 0.04 | 0.10 |
| P_2O_5 | 0.00 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 | 0.04 | 0.00 | 0.01 | 0.00 | 0.01 | 0.03 | 0.00 | 0.05 | 0.10 |
| C1 | 0.01 | 0.07 | 0.04 | 0.04 | 0.00 | 0.02 | 0.01 | 0.00 | 0.01 | 0.06 | 0.00 | 0.03 | 0.06 | 0.00 | 0.00 |
| CaO | 2.91 | 2.86 | 5.51 | 10.61 | 0.03 | 16.24 | 0.13 | 0.03 | 52.95 | 0.00 | 0.83 | 0.44 | 0.54 | 0.80 | 1.73 |
| TiO ₂ | 0.00 | 0.09 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 |
| FeO | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.27 | 0.02 | 0.00 | 1.86 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.97 |
| BaO | 7.36 | 2.42 | 0.06 | 0.14 | 65.92 | 0.26 | 65.32 | 63.33 | 0.00 | 0.00 | 0.00 | 0.00 | 0.21 | 0.01 | 0.00 |
| La ₂ O ₃ | 23.00 | 20.76 | 26.30 | 20.12 | 0.05 | 17.42 | 0.00 | 0.03 | 0.00 | 0.00 | 21.35 | 22.09 | 21.67 | 26.44 | 25.86 |
| Ce ₂ O ₃ | 23.56 | 31.72 | 22.73 | 22.52 | 3.93 | 23.75 | 3.84 | 3.80 | 0.15 | 0.00 | 24.08 | 23.57 | 25.70 | 30.84 | 30.71 |
| Pr ₂ O ₃ | 1.82 | 1.41 | 2.10 | 2.04 | 0.19 | 1.48 | 0.00 | 0.00 | 0.00 | 0.18 | 1.41 | 1.84 | 1.93 | 2.00 | 2.39 |
| Nd ₂ O ₃ | 4.86 | 4.49 | 5.04 | 4.54 | 0.04 | 4.94 | 0.06 | 0.00 | 0.20 | 0.00 | 3.57 | 3.71 | 3.52 | 5.58 | 5.71 |
| SmO | 0.04 | 0.00 | 0.11 | 0.12 | 0.00 | 0.23 | 0.00 | 0.00 | 0.10 | 0.11 | 0.38 | 0.00 | 0.42 | 0.32 | 0.16 |
| EuO | 0.22 | 0.27 | 0.50 | 0.24 | 0.00 | 0.43 | 0.00 | 0.00 | 0.29 | 0.00 | 0.31 | 0.35 | 0.02 | 0.05 | 0.20 |
| Gd_2O_3 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | 0.18 | 0.00 | 0.00 | 0.06 | 0.16 | 0.00 | 0.00 |
| Dy_2O_3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.21 | 0.00 | 0.00 | 0.00 | 0.34 | 0.09 | 0.00 |
| ThO ₂ | 0.08 | 0.11 | 0.00 | 0.17 | 0.11 | 0.00 | 0.03 | 0.00 | 0.21 | 0.00 | 0.09 | 0.04 | 0.16 | 0.00 | 0.00 |
| UO ₂ | 0.00 | 0.00 | 0.30 | 0.00 | 0.14 | 0.28 | 0.08 | 0.13 | 0.06 | 5.01 | 0.13 | 0.00 | 0.10 | 0.00 | 0.52 |
| SO_{3} | 0.00 | 0.00 | 0.03 | 0.09 | 27.98 | 0.00 | 26.57 | 27.57 | 0.00 | 0.02 | 0.04 | 0.00 | 0.01 | 0.00 | 0.01 |
| Total | 66.57 | 66.27 | 64.45 | 61.82 | 98.75 | 67.11 | 96.68 | 95.00 | 56.32 | 69.82 | 69.10 | 68.83 | 72.34 | 67.98 | 69.34 |
| Point# | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Comment | bas | bas | bas | syn | ba | syn | ba | ba | cal | sil | anc | anc | anc | bas | bas |

Table 1. EPMA of REE minerals from Eastern Block, Kamthai, Rajasthan

bas- bastanasite; syn- synchysite; ba- barite; cal; calcite; sil- unidentified silicate; cc- carboceranite; anc- ancyllite; ilm- ilmenite; ap- apatite; ol- olivine?

Fig.3. (a) A typical EDS spectrum from the carbocernaite particle shown in Fig.2C. (**b)** An EDS spectrum from the ancylite in the particle shown in Fig.2 C & F. (**c)** An EDS spectrum from the synchysite in the particle shown in Figs D & E. (**d)** An EDS spectrum from the bastnaesite in the particle shown in Figs 2D, E & F.

phases in the form of La-Ce ancyllite and La-Ce bastanasite (Fig. 2D; Table 1). In this rock it is estimated that barite constitutes ~20%, while ancyllite and bastnaesite make up around 30% volume of the rock, the remaining being mainly calcite and other accessory minerals (Fig. 2F).

The mineralogical study reveals that many of the samples contain significant amounts of REE- bearing minerals. The most important of these include: bastnaesite-(La); bastnaesite-(Ce); synchysite-(Ce); carbocernaite-(Ce); cerianite-(Ce). Other minerals less commonly present include: daqingshanite-(Ce);, britholite-(Ce). Minor-to-trace amounts of monazite and REE-bearing apatite are present. Secondary REE-minerals such as crandallite, florencite, gorceixite and fluorite and/or quartz are absent in the REEmineralized rocks.

DISCUSSION

The origin of carbonatites have been summarized in recent reviews by Le Bas (1987), Gittins (1989) and Bailey (1993). The generation of carbonatite magma is highly debated.Three main theories are proposed for the genesis :

1 Residual melts of fractionated carbonated nephelinite or melilite (Gittins and Jago, 1998; Gittins 1989).

- 2 Immiscible melts fractions of CO_2 saturated silicate melts. (Kjarsgaard and Peterson, 1991; Lee and Wyllie, 1997; Kjarsgaard and Hamilton 1989; Brooker and Hamilton 1990; Church and Jones, 1995; Moore, 2012.).
- 3 Primary mantle melts generated through partial melting of CO₂ bearing peridotite (Harmer 1998; Sweeney, 1994; Wallace and Green,1988).

The radiogenic and stable isotopic studies indicate that the parental magmas area derived from mantle melts. The carbonatite magma are produced as a (1) derivative magma from a silicate meltt through differentiation or through liquid immiscibility (2) or directly as primary melts from carbonated mantle peridotite (Le Bas, 1987; Gittins, 1989). According to Gittins (1989) and Bailey(1993), the calciocarbonatites are derived from primary carbonatite magma. The association of barite, strontianite and REE flourocarbonates (bastnaesite, parisite-synchisite), indicates strongly overprinted carbonatite (Doroshkevich et al., 2009).

Carbonatite melts represent extreme enrichment in REE and some orthomagmatic and magmatic hydrothermal deposits of REE are related to carbonatite. The large ionic radii of the REE limits significant substitution of the elements into minerals. However the presence of hydrothermal deposits of REE indicates relative mobility of these elements is hydrothermal fluids (Jaireth et al., 2014). According to Le Bas (1981), the presence of barite, strontianite with REE mineralisation indicates generation of magmatic carbonatite with high content of incompatible elements (Sr, Ba, REE).

The mineralization at Kamthai is interpreted to have formed in two stages. The first stage witnessed magmatic fluids rich in calciocarbonatite dominated by carbocernaite rare earth mineral, pierce through ijolites. This stage which occur like panther skin type (Fig.2A), highly enriched in LREE, occur as low angle intrusive sheets, plug and E-W trending dykes. The second stage with voluminous bastnaesite intruded as structurally controlled hydrothermal veins and dykes (Fig 1.C.)

Temporal and spatial relationships between these two diverse calciocarbonatites is not clear. The enrichment in Mn and Fe might suggest that some of the melanocratic carbonatites are late differentiates of the parental magma. Such late stage ferrocarbonatites are common in other carbonatite complexes. In this case the calcite carbonates would represent crystallization from a less evolved magma with their formation as flotation or rheological cumulates. The latter being subsequently invaded by the carbohydrothermal fluids which formed the interstitial Laenriched REE-carbonate assemblages.

The presence of La-enriched carbonates in association with cerianite-(Ce) is unusual. The presence of the latter mineral is commonly considered to indicate occurrence of supergene processes and might be the cause of the REEenrichment of the carbonatite. However, if this were so then cerianite would be present in all the rocks examined and especially in the melanocratic carbonatites. The absence of such typical supergene minerals as crandallite, florencite and gorceixite does not support supergene enrichment for this deposit. Geochemically Kamthai carbonatites have greater abundance of incompatible elements (Ba, Rb) and depletion in compatible elements (Hf, Zr, Ti). This together with their silica under-saturated composition supports their formation by low degree of partial melting. According to Le Bas (1981) the extensive fenitization generated by injection of hydrothermal solutions has altered the host ijolite and alterations consisting of metasomatic halos containing albite, arfvedsonite along with apatite, barite, strontianite and pyrite in the wall rock alterations are observed. In Fig.4, the chondrite normalized values, (after Nakamura, 1974), indicates a very strong decline from La to Eu, steep depletion from Gd to Dy and flat Ho to Lu. Such pattern is common with the REE minerals of magmatic origin, occurring in

Fig.4. Chondrite normalized REE pattern of Kamthai. Normalisation values after Nakamura (1974). *Symbols:* Circle, plus, polygon, cross and inverted triangle in order of decreasing abundance of total REE.

carbonatites. Steep slope of LREE/HREE point to fractionation during evolution of this carbonatite magma. Based on REE chemistry and the La/Lu ratio suggest a magmatic origin of these carbonatite (Srivastava et al., 1995). The enrichment of large-ion lithophtile elements (LILE), Sr, P & REE in carbonatites results by fractionation of a mantle derived undersaturated magma by liquid immiscibility (Freestone and Hamilton 1980; Deines 1989). Magmatic REE mineralization formed in the first phase could have been remobalised by hydrothermal fluids during the second phase. This bimodal calciocarbonatite bearing REE mineralisation may be formed in carbonate rich magma with heavy influx of volatiles and strongly enriched in Ba, Sr and LREE. The Kamthai deposit has strong similarity to Khanneshin LREE deposit of Afganistan as described by Tucker et al., (2012).

Carbonatites occur within stable, intraplate setting, half of them being in Africa, (Carmody, 2012). The confinement of carbonatites to continental lithosphere indicates that the lithosphere played a vital role in the genesis of carbonatite magma. (Bell and Blenkvisop, 1987), since isotopic evidence suggests the derivation of these melts from asthenospheric depths (Nelson et al., 1988).The Nd, Pb & Sr isotope data on carbonatites and other alkaline rocks adjacent to Kamthai area have been attributed to mantle source through plume-lithosphere interaction (Simonetti et al., 1998). Ray and Ramesh (1999) carried out stable carbon and oxygen isotope studies on the Kamthai carbonatites and concluded formation by fractional crystallization from CO_2 - rich carbonate magma derived from parent carbonated

silicate magma. Ray et al. (2000) suggested derivation of Kamthai carbonatite from isotopically average mantle composition. According to Krishnamurthy (1988) most of the carbonatites associated with alkaline suites in India have been generated from upper mantle source with or without contamination or mantle metasomatism. The fenitization process resulted due to presence of meteoric-hydrothermal fluids. Ernst and Bell (2010) suggested a sub-lithospheric mantle source for Kamthai carbonatites, consistent with the plume / asthenosphere upwelling origin as described from large igneous provinces (LIPs). The temporal and spatital relationship of Kamthai with Deccan flood basalt (~65 ma), support the hypothesis of reunion plume origin (Ray et al., 2000). Therefore carbonatite as well as host ijolite plug of Kamthai can be attributed to mantle 'hot spot' activity coeval with the Deccan volcanism.

Acknowledgements: The author is grateful to the management of MSPL and RMML, specially to Mr. Narendra Kumar A Baldota, Chairman and Managing Director, Baldota Group of Companies for encouragement and support during the field work, drilling and analysis. I express thanks to Prof. Roger Mitchell, A. Lombard of MINTEK S.A, B. Young and KE Prince of Ansto Minerals, Australia for their mineralogical and XRD studies. Sincere thanks are also due to S/s O P Somani, Siddu Kalagudi, P.Ravichandra Gowd, Amit Kumar and Parthasarathy for their assistance during the finalisation of manuscript.

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(Received: 20 January 2014; Revised form accepted: 2 January 2015)