

## Occurrence of REE mineralization in the layered Gabbros of Phenai Mata Igneous Complex, Gujarat, India

Among the magmatic rocks, carbonatites are known to possess the highest concentration of rare earth elements ( $\Sigma\text{REE} = 72\text{--}15,515$  ppm), and they have the best REE mineral resources<sup>1-3</sup>. Rare earth deposits in igneous rocks have been grouped into five distinct categories differing in the provenance and evolution of magma and in the rock types hosting mineralization<sup>4</sup>, viz.: (i) carbonatites, (ii) peralkaline silica-undersaturated rocks, (iii) peralkaline granites and pegmatites, (iv) pegmatites associated with sub- to metaluminous granites, and (v) Fe oxide-phosphate deposits. Occurrence of REE minerals in rocks other than those mentioned above, especially mafic and ultramafic rocks is scantily documented; only recently, they were looked upon as hosts of REE-mineralization<sup>5</sup>.

Some of the recent reports of REE-mineralization in rocks excluding carbonatites include the following: the REE-Th-U in microlite-pyroxenite-albite in Ajmer and Nagaur districts of Rajasthan<sup>6</sup>; britholite and chevkinite in tuffs of Jemez volcanic field, New Mexico<sup>7</sup>; Nacerniobsite and britholite in peralkaline granites from Morro Redondo complex, Graciosa Province, Southern Brazil<sup>8</sup>; britholite and allanite in the A-type granite boulder incorporated in the Pieniny Klippen, Western Carpathians, Slovakia<sup>9</sup>; ultrapotassic melasyenite<sup>10</sup>; calcite-amphibole-clinopyroxene rock from Afrikanda complex, Kola Peninsula, Russia<sup>11</sup>; and kakortokite (nepheline syenite) in the agpaite complexes<sup>12</sup>. In addition, REE-mineralization has been recorded in metamorphic rocks<sup>13,14</sup>. Therefore, in general, the following types of paragenesis are known for REE minerals: (i) primary magmatic mineralization (typical of carbonatites); (ii) hydrothermal processes (with or without relation to late-stage fluid activity in the carbonatite complexes); (iii) weathering processes (remobilization of REEs); (iv) metasomatism of country rocks (most commonly associated with carbonatites, but also common in pegmatites) and (v) metamorphism of pre-existing minerals.

More than 200 minerals containing essential or significant REE minerals have been known to occur in carbonatite complexes<sup>15</sup>, the majority of which occur

in carbonatites<sup>1</sup>. REE minerals can be conventionally classified by anion groups such as halides, carbonates, phosphates, silicates, etc.<sup>16</sup>; or structurally, according to the geometry of anion groups such as triangular, tetrahedral, octahedral, etc.<sup>17</sup>. The commonest of REE mineral groups are halides, carbonates (and fluoro-carbonates), phosphates, niobates and tantalates, and silicates<sup>15</sup>. Distribution of REE minerals in mafic-ultramafic rocks is relatively less well known; however, recent reviews by Lesnov<sup>5,18</sup> provided a systematic study of REE minerals in mafic and ultramafic rocks.

In this paper we report occurrence of REE-rich apatite (britholite), epidote (allanite) and an independent REE-carbonate synchysite (Ce) in the alkali gabbro of Phenai Mata Igneous Complex (PMIC). Although REE-rich minerals britholite and chevkinite are known to occur in Ambadongar<sup>19</sup>, this is the first time that an REE-mineralization has been reported from PMIC. This study has significance because PGE-mineralization

was also recently reported from gabbros of PMIC<sup>20</sup>.

The Phenai Mata Igneous Complex (Figure 1) is profusely composed of basaltic lava flows (nearly 2/3rd of the total area<sup>21-23</sup>). The remaining (1/3rd) portion is occupied by layered gabbros, syenites and granophyre; intruded by dykes and sills of varying composition<sup>19,20</sup>. Gabbros have been distinguished in three categories, viz. tholeiitic gabbro, alkali gabbro<sup>23</sup> and orthopyroxene gabbro<sup>24</sup>. The former is intimately associated with tholeiitic basalt and acid differentiates and the latter in close association with syenitic rocks occurring in the northeastern part of the Phenai Mata hill. Rhythmic layering and cumulates of pyroxene and olivine accentuates cumulus texture to these rocks<sup>21,22,25,26</sup>. Tholeiitic and alkali gabbros exhibit a variety of texture, and as noted by Kumar<sup>23</sup>, the mineral assemblage in both gabbros is same but differs in modal mineral proportion. Sukheswala *et al.*<sup>27</sup> considered gabbro and anorthosite of the Phenai Mata area to be gravity differentiates

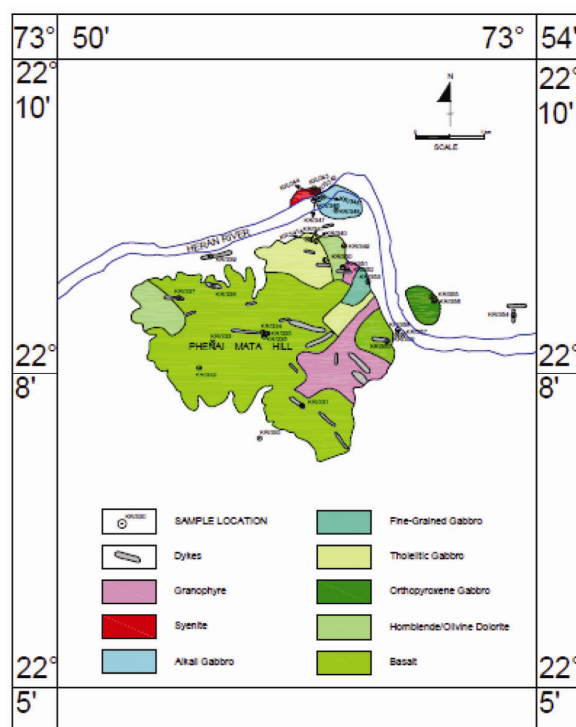


Figure 1. Geological map of the Phenai Mata area (ref. 40).

# SCIENTIFIC CORRESPONDENCE

**Table 1.** Chemical analysis of REE bearing mineral phases britholite (Ce), synchysite (Ce) and allanite.

Mineral	Britholite (Ce)						Synchysite (Ce)		Allanite		
	1/1	23/1	28/1	29/1	32/1	33/1	2/1	Formula	4/1	7/1	
CaO	28.800	28.970	22.180	14.620	16.600	24.440	12.710	SiO <sub>2</sub>	33.620	34.310	
Na <sub>2</sub> O	0.000	0.000	0.000	0.000	0.020	0.000	0.000	TiO <sub>2</sub>	0.060	0.120	
FeO	0.000	0.130	0.000	0.000	0.380	0.100	0.150	ThO <sub>2</sub>	1.300	0.740	
MnO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	Al <sub>2</sub> O <sub>3</sub>	16.750	17.680	
MgO	0.010	0.000	0.000	0.000	0.090	0.020	0.030	Ce <sub>2</sub> O <sub>3</sub>	6.350	5.870	
La <sub>2</sub> O <sub>3</sub>	9.530	9.330	13.650	15.170	11.670	10.780	11.330	La <sub>2</sub> O <sub>3</sub>	3.970	3.890	
Ce <sub>2</sub> O <sub>3</sub>	18.100	17.330	21.610	26.940	22.800	19.280	24.440	Nd <sub>2</sub> O <sub>3</sub>	1.030	1.360	
Pr <sub>2</sub> O <sub>3</sub>	1.830	1.740	1.860	2.700	2.390	1.740	2.590	FeOT	14.330	14.570	
Nd <sub>2</sub> O <sub>3</sub>	4.640	4.680	4.350	5.930	5.810	3.830	7.300	MnO	0.550	0.380	
SmO	1.330	1.461	1.046	2.071	2.572	0.719	2.202	MgO	0.170	0.190	
Gd <sub>2</sub> O <sub>3</sub>	2.190	2.010	2.260	3.060	2.790	2.150	2.990	CaO	16.990	17.220	
Y <sub>2</sub> O <sub>3</sub>	1.410	1.400	2.100	1.960	2.100	1.860	1.330	Total	95.120	96.330	
ThO <sub>2</sub>	3.506	3.281	3.666	4.907	3.910	4.258	1.175	Fe <sub>2</sub> O <sub>3</sub>	4.736	4.290	
P <sub>2</sub> O <sub>5</sub>	13.610	14.340	7.370	0.470	5.150	10.230	0.140	FeO	2.088	2.010	
SiO <sub>2</sub>	15.050	14.740	18.630	22.070	19.980	16.080	1.690	Total	95.594	96.760	
Total	100.006	99.412	98.722	99.898	96.262	95.487	68.077				
	Calculated on the basis of 25 (O, OH, F, Cl)						3 (CO <sub>3</sub> , F)		12.5 (O)		
Ca	3.437	3.440	2.867	2.083	2.272	3.159	3.664	Si	3.238	3.247	
Na	0.000	0.000	0.000	0.000	0.005	0.000	0.000	Ti	0.004	0.009	
Fe	0.000	0.012	0.000	0.000	0.041	0.010	0.034	Th	0.028	0.016	
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	Al	1.901	1.972	
Mg	0.002	0.000	0.000	0.000	0.017	0.004	0.012	Ce	0.224	0.203	
La	0.391	0.381	0.607	0.744	0.550	0.480	1.125	La	0.141	0.136	
Ce	0.738	0.703	0.954	1.312	1.066	0.851	2.408	Nd	0.035	0.046	
Pr	0.074	0.070	0.082	0.131	0.111	0.076	0.254	Fe + 3	0.343	0.306	
Nd	0.185	0.185	0.187	0.282	0.265	0.165	0.702	Fe + 2	0.168	0.159	
Sm	0.051	0.056	0.044	0.095	0.113	0.030	0.204	Mn	0.045	0.030	
Gd	0.081	0.074	0.090	0.135	0.118	0.086	0.267	Mg	0.024	0.027	
Y	0.084	0.083	0.135	0.139	0.143	0.119	0.190	Ca	1.753	1.746	
Th	0.095	0.088	0.107	0.158	0.121	0.124	0.077	Total	7.907	7.897	
P	1.283	1.346	0.753	0.053	0.557	1.045	0.032	TREE	0.400	0.385	
Si	1.676	1.634	2.248	2.935	2.552	1.940	0.455				
Total	8.597	8.572	8.574	8.567	8.431	8.589	9.923				
TREE	1.604	1.552	2.100	2.837	2.366	1.808	5.149				
Ca + REE	5.041	4.992	4.966	4.920	4.638	4.966	8.814				
Si + P	2.960	2.979	3.000	2.988	3.109	2.985	0.487				

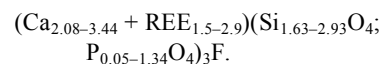
thus indicating their common parentage. More recently, Hari *et al.*<sup>24</sup> considered orthopyroxene gabbro to be a separate variety with ~8% orthopyroxene in the rock composed of plagioclase and clinopyroxene.

During the present work, EPMA studies were conducted at NCEGR Laboratory, Geological Survey of India, Bengaluru, using CAMECA SX-100 wavelength dispersive spectrometry (WDS). A special programme was made for identification of rare earths and other elements including Na, Si, Mg, Al, P, S, Mn, Fe, Y, La, Ce, Ba, Pr, Nd, Sm, Eu, Gd, Tb, and Dy at an accelerating current of 20 keV and 20 nA with a beam size of 1 µm. Calibration standards for mineral phases were Na on jadeite, Si and Ca on wollastonite, Mg on olivine, Al on co-

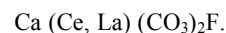
rundum, P on apatite, S on pyrite, Mn on rhodonite, Fe on hematite, Y on YAG, Ba on barite and La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy on the glasses with 10% corresponding elements. The raw electron microprobe data were processed using peak sight GEOQUANTA software, which uses standard ZAF correction algorithms. These data are presented in Table 1.

The PMIC gabbros (both tholeiitic and alkaline) contain apatite in variable proportions; however, alkaline gabbros show significant concentration of zoned apatite crystals. We observed that several apatite crystals were rimmed by REE-rich britholite (Figures 2 and 3) although independent crystals of apatite as well as britholite also occur (Figures 2 and 3 b). The general chemical formula for fluor-britholite is written as: (Ca, REE)<sub>5</sub>(SiO<sub>4</sub>,

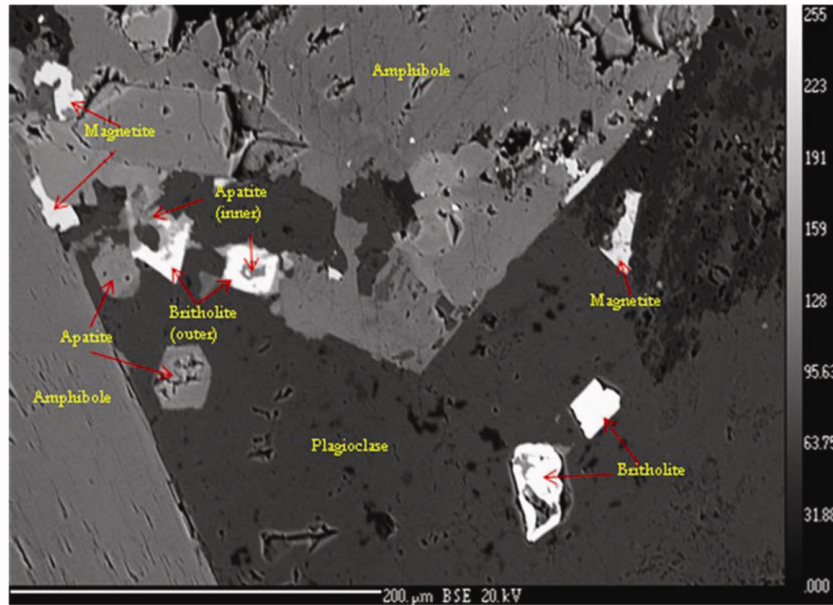
PO<sub>4</sub>)<sub>3</sub>F<sup>28</sup>. The britholites of PMIC are rich in Ce, followed by La and Nd. Therefore, britholite may be designated as Ce-Britholite in the present case. The general formula is



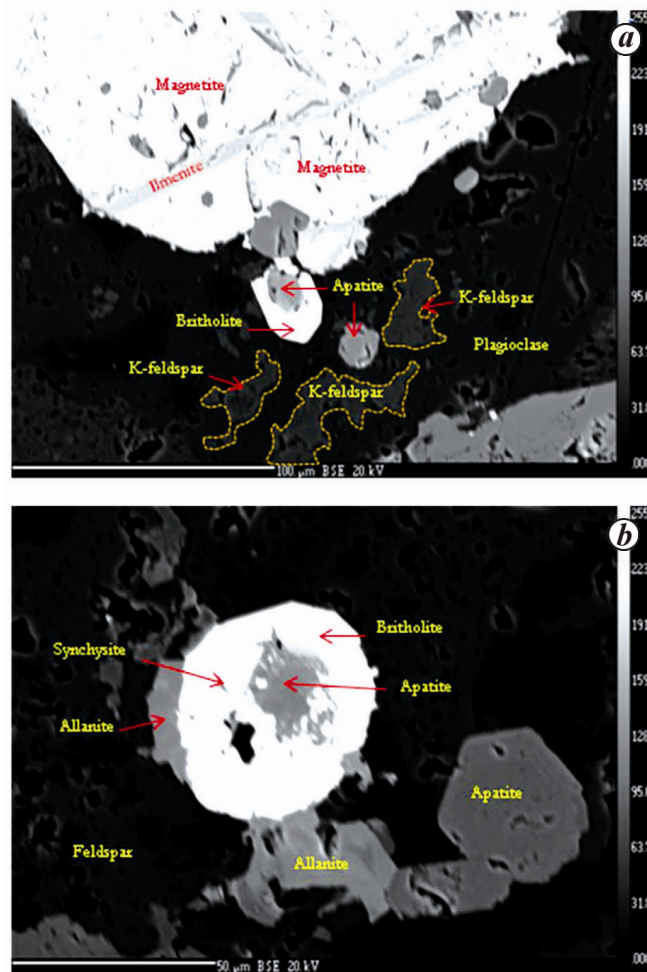
A small crystal of REE carbonate mineral has been identified as 'Synchysite' (Figure 3 b). It is relatively a less common mineral occurring in late-stage hydrothermal mineral in granitic and alkali syenites. The general formula for this mineral<sup>15,29</sup> is



Within the limitation of absence of fluorine and strontium from data and



**Figure 2.** Apatite and britholite in alkaline gabbro (KR/346). Note apatite cores and britholite rims. Independent crystals of apatite and britholite are also seen.



**Figure 3.** *a*, Apatite and britholite along with other minerals (KR/346). Towards upper part of the photograph relatively big magnetite crystal with exsolution lamelli of ilmenite is present. Towards the bottom plagioclase and potassic feldspars form subsolvus exsolution. *b*, An REE mineral Synchysite can be seen within britholite. Apatite core is surrounded by britholite rim. Towards left and lower side this mineral allanite is developed.

instrumental limitation for carbon analysis by EPMA, a 100% total could not be obtained; moreover Nd as well as other REEs also occur in abundance (Table 1). Our calculations of the data based on cation percentages (Table 1) indicate that this mineral is synchysite<sup>30</sup>. The recalculated formula assuming ideal site occupancies for synchysite and REEs is expressed as total REEs instead of La and Ce alone, as follows



Ca + TREE value is 2.06, which is close to ideal cation occupancy, though there is little deficiency in Ca and almost equivalent excess in total REEs. We see possibility of matrix effect while analysing this tiny grain; alternatively substitution between Ca and REEs cannot be ruled out.

Allanite occurs in alkaline gabbro (KR-346), in close association of britholite (Figure 3 b). Chemical (EPMA) analysis indicates reasonably high proportion of REEs ( $\text{Ca}_2\text{O}_{33.89-3.97}$ ,  $\text{Ce}_2\text{O}_{35.87-6.35}$ ,  $\text{Nd}_2\text{O}_{31.03-1.36}$ ,  $\text{Gd}_2\text{O}_{30.61-0.67}$  and  $\text{Y}_2\text{O}_{30.11}$ ) as well as radioactive elements ( $\text{ThO}_{20.74-1.3}$ ,  $\text{UO}_{20.05}$ ). However, metamictization is a major problem in assigning a proper species name for REE bearing epidote group minerals<sup>31</sup>. Metamict samples tend to be more reactive than well-crystallized minerals and exhibit anion and cation-exchange properties. There is no sharp borderline between a completely X-ray amorphous substance (due to metamictization) and a mineral with a well-ordered crystal lattice. Subsequent heat-treatment under inert condition to re-establish an ordered crystal lattice seems to be questionable if the resulting mineral adopts a composition that is characteristic of a partly ion-exchanged poorly crystalline (metastable) substance, but not of the original mineral<sup>31,32</sup>.

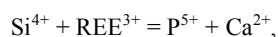
In the formula of allanite of PMIC (KR/346), there is an observed excess of cations at A (especially Ca) and Z (especially Si) sites, whereas there is considerable deficiency at M (Ti, Al,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , Mg) site. Such excess and deficiencies could result due to the presence of considerable amount of thorium (0.74–1.3 apfu) or due to interference of similar cations due to matrix effect during analysis<sup>20</sup>.

The REE-bearing minerals (britholite + synchysite + allanite) observed in alkaline gabbros of PMIC are also known to occur in different localities and host

rocks. Britholite is usually considered to have been formed by post-magmatic hydrothermal alteration of pre-existing apatite<sup>9,11,13</sup>. It is commonly observed that britholite either forms a rim around apatite or get completely converted forming independent crystals. However, sometimes, retrograde relationship is observed where apatite is formed by alteration of britholite<sup>33</sup>. They are also known to have been formed by crystallization of magmatic rocks, e.g. peralkaline granites<sup>8</sup> and high-grade fluid-triggered metasomatism of pre-existing fluorapatite<sup>13</sup>.

Epidote occurs in many basic and ultrabasic rocks; however, it is considered to be of metamorphic origin, whereas allanite occurs much less commonly but formed due to magmatic processes. Smith and Henderson<sup>34</sup> proposed a model of formation of allanite by reaction of hedenbergite and anorthite with REE- and Th-bearing fluids during cooling of high-salinity, late magmatic fluids. Much similar association of britholite and allanite was observed by Ondrejka<sup>9</sup> in A-type granite in West Carpathians (Slovakia) where the post-magmatic alteration and breakdown of primary magmatic accessory fluorapatite and allanite (-Ce) produce unique assemblage of minerals such as britholite (-Y), flourbritholite (-Y) and fluorcalciobritholite. In addition, secondary monazite, REE carbonates and few other minerals were also observed. In the case of PMIC we observed that britholite rims over apatite, whereas allanite grains are mostly anhedral and surround apatite-britholite crystals. This clearly indicates that REE carrier minerals britholite, allanite, and synchysite (which occurs with britholite), are secondary in origin. In all probability, this is due to post-magmatic hydrothermal alteration of apatite and epidote by REE-rich meteoric-hydrothermal fluid.

Harlov *et al.*<sup>13</sup> indicated that the fluid triggered metasomatism of apatite can initiate leaching of Si and/or Na from apatite structure without coupled removal of Y + REE, the resulting charge imbalance, are due primarily to coupled substitution reactions of the following types, can induce (Y + REE) to contribute to the nucleation growth of other minerals either as inclusions or individual grains on the surface of apatite



Late-stage pervasive hydrothermal activity is known in the Amba Dongar and surrounding areas<sup>35,36</sup>, which also resulted in the formation of huge deposit of fluorite at Amba Dongar<sup>37,38</sup>. Imprints of such late-stage fluids have resulted in formation of very unusual rocks in the surrounding areas<sup>39,40</sup>. Phenai Mata gabbros were also influenced by such late-stage hydrothermal fluids, rich in REE, carbonates and fluorine. These fluids were probably responsible for the formation of REE-rich mineral phases in the PMIC gabbros.

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