

Anomalous REE concentration in carbonate–phosphate bearing phases from Narasimharajapuram area, Visakhapatnam district, Andhra Pradesh

Apatite–magnetite veins of varying dimensions along with vermiculite, biotite, calcite and other minerals occur as fracture fillings hosted within Precambrian Eastern Ghat Group of rocks in Kasipatnam area and are well known since the early forties¹. These steeply dipping veins (NW–SE trend; dipping southwest) occur within charnockites, exhibit sharp contact and are almost perpendicular to the regional strike of the area. These veins are observed in an en echelon pattern with pinch and swell structure with widths varying from a few centimetres to 2.50 m. Six phases of mineral association as phosphate (apatite), oxides (magnetite, ilmenite, martite, spinel), silicate (salite, biotite, vermiculite, zircon, allanite, actinolite, chert), sulphate (barite), sulphide (pyrite, chalcopyrite, pyrhotite, chalcocite, covellite, galena) and carbonate (calcite, malachite) have been reported from these apatite–magnetite veins^{2,3}.

Earlier works on the apatite–magnetite veins reflect the economic significance^{1,4}, occurrence and disposition⁵, characterization of apatite⁶ and recognition of paragenetic sequence². Possible affinity to carbonatitic complexes^{7,8} and alkali syenitic association³ for these apatite magnetite veins have been indicated from mineralogical and geochemical characters. However, the data on rare earth elements (REEs) in phosphate (apatite) and carbonate (calcite) phases of these veins are limited. Presence of rare earths (qualitative) in fluoro-apatite⁶ and higher concentration of Ce_2O_3 (1.35–3.10%) as well as Y_2O_3 (0.025–0.082%) from phosphate-bearing rocks based on XRF analysis have been reported from Kasipatnam apatite veins⁹. In addition, REE oxides in allanite (Ce + La + Nd: 24.60%) and fluoroapatite (REE: ~5000 ppm) from these veins have been reported^{2,10}. Till date, no attempt has been made to study the concentration and distribution of individual REEs in these phosphate (apatite) and carbonate (calcite) phases, which are being presently mined at Narasimharajapuram (NR Puram) area (18°15'45.6"N; 83°08'15.2"E), Visakhapatnam district, Andhra Pradesh –

a part of the Kasipatnam apatite–magnetite mineralization area (Figure 1). In the NR Puram mine pit, sharply defined distinct zones of calciferous pyroxene, vermiculite/biotite, magnetite and apatite are visible from wall to the core of these veins. Apatite, vermiculite/biotite, magnetite and calcite are coarse-grained with well-developed crystal faces. In this correspondence, preliminary results on the subsurface samples are presented which bring out the anomalous concentration of REEs in apatite and calcite mineral phases.

Thirteen samples from phosphate (apatite) and two samples from carbonate (calcite) phase were collected from development mining faces. Apatite samples (sample nos 1–13) were collected from the central zone and calcite samples (sample nos 14 and 15) from the outer zone adjoining the host rock. All samples

were analysed chemically for their individual REE content; the results are given in Table 1. Quantitative analysis indicates that all these samples contain substantial amount of REEs (La–Lu + Y: 10,938–23,531 ppm). REE (La–Lu + Y) content indicates the predominance of LREE (La–Sm; 10,938–22,167 ppm) component (95.85% to 96.77%) over HREE (Eu–Lu + Y; 453–807 ppm) component (3.23% to 4.15%) for phosphate phase. Similar trend has also been noticed for carbonate phase (LREE: 20,164–23,531 ppm; 97.54% to 97.61% and HREE: 482–580 ppm; 2.39% to 2.46%). A relatively higher distribution of HREE (2.39% to 4.15%) within REE is noteworthy and a REE distribution of $Ce > La > Nd > Pr > Sm > Y > Gd > Eu > Dy$ has been consistently observed for all these samples. XRD analysis indicates the presence of barite, ancyllite [Sr(La, Ce)-

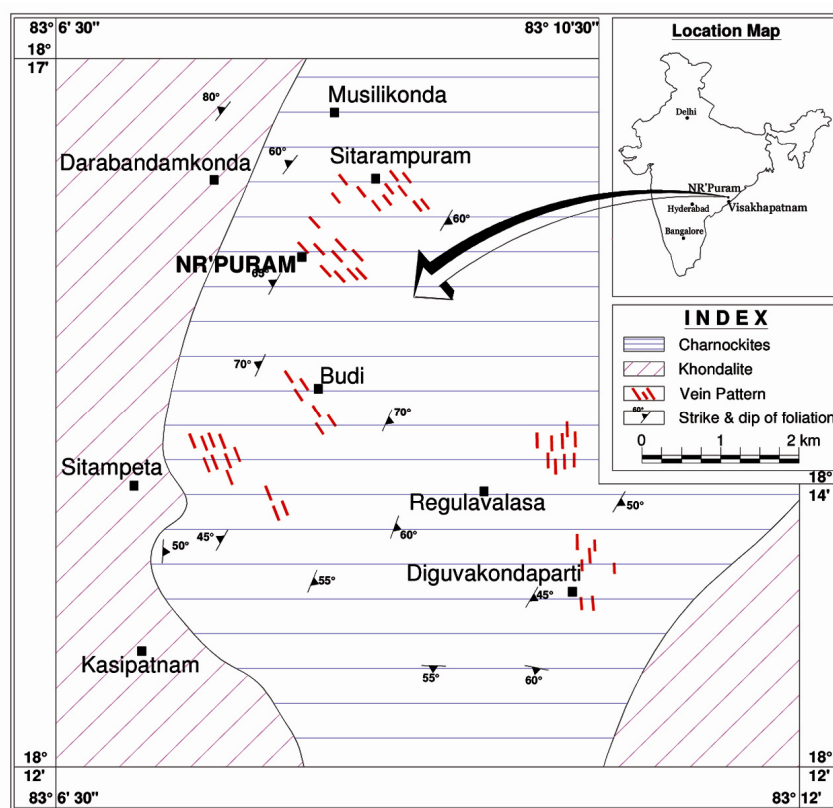


Figure 1. Location and vein pattern of the apatite–magnetite deposits near Kasipatnam, Visakhapatnam district, Andhra Pradesh².

Table 1. REE concentration (ppm) in phosphate and carbonate phases of NR Puram, Visakhapatnam district, Andhra Pradesh

Sample no.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Y	REE (La-Lu + Y)	LREE (La-Sm)	HREE (Eu-Lu + Y)	Distribution			Mineralogy
																	LREE%	HREE%	HREE%	
1	3200	6197	730	3223	492	90	182	18	56	10	34	7	200	14439	13842	597	95.87	4.13	4.13	Apatite
2	4837	8690	1010	4250	639	117	233	27	78	14	27	12	296	20230	19426	804	96.03	3.97	3.97	Apatite
3	3605	6836	827	3533	538	99	200	22	62	12	19	10	236	15999	15339	660	95.87	4.13	4.13	Apatite
4	4250	7712	900	3880	592	109	220	24	69	12	21	10	216	18015	17334	681	96.22	3.78	3.78	Apatite
5	3730	6990	840	3637	557	100	208	22	60	12	20	9	230	16415	15754	661	95.97	4.03	4.03	Apatite
6	4394	7405	840	3474	511	94	185	20	57	10	19	8	230	17247	16624	623	96.39	3.61	3.61	Apatite
7	3528	6620	798	3475	528	98	202	22	60	9	19	8	230	15597	14949	648	95.85	4.15	4.15	Apatite
8	2556	4683	548	2332	366	67	142	16	40	8	13	7	160	10938	10485	453	95.86	4.14	4.14	Apatite
9	3500	6528	767	3350	504	92	190	20	57	11	18	8	212	15257	14649	608	96.01	3.99	3.99	Apatite
10	4475	9525	1088	3906	478	105	208	8	69	17	24	2	214	20123	19472	651	96.76	3.24	3.24	Apatite
11	4688	10631	1194	4306	541	118	245	9	79	19	29	3	299	22167	21360	807	96.36	3.64	3.64	Apatite
12	3469	7638	869	3113	388	87	179	6	55	14	21	2	189	16034	15477	557	96.53	3.47	3.47	Apatite
13	4944	10575	1163	4250	517	113	225	8	72	18	27	3	246	22166	21449	717	96.77	3.23	3.23	Apatite
14	7384	10305	1000	3784	478	84	170	17	49	10	24	10	216	23531	22951	580	97.54	2.46	2.46	Calcite
15	6264	8810	874	3310	424	77	140	16	40	8	14	7	180	20164	19682	482	97.61	2.39	2.39	Calcite
Minimum	2556	4683	548	2332	366	67	140	6	40	8	13	2	160	10938	10485	453	95.85	2.39	2.39	-
Maximum	7384	10631	1194	4306	639	118	245	27	79	19	34	12	299	23531	22951	807	97.61	4.15	4.15	-
Average	4322	7943	897	3588	504	97	195	17	60	12	22	7	224	17888	17253	635	96.38	3.62	3.62	-

Note: Tm and Lu in all the samples analysed were <5 ppm.

Table 2. Comparison of rare earth oxides distribution (%)

REE oxides	Mt Weld, Australia	Bayan Obo, China	Kamthai, Rajasthan	NR Puram, AP
La ₂ O ₃	25.50	25.70	37.71	23.37
Ce ₂ O ₃	46.70	51.30	47.70	46.12
Pr ₂ O ₃	5.30	5.40	3.91	4.99
Nd ₂ O ₃	18.50	15.70	9.87	19.30
Sm ₂ O ₃	2.30	1.10	0.66	2.69
LREE	98.30	99.20	99.85	96.47
Eu ₂ O ₃	0.44	0.19	0.15	0.52
HREE	1.26*	0.61*	0.00*	3.01
Grade	14.80	5–8	2.97	2.14

*Data not available. Data reflected by subtracting total available REE oxides from 100.

(CO₃)₂(OH)], hydroxyl-bastnasite [Ce(CO₃)(OH)], baddeleyite (ZrO₂) and anatase (TiO₂) minerals in calcite (sample nos 14 and 15) and monazite, fluorapatite and traces of calcite in apatite samples (sample nos 1 and 5).

Various suggestions have been put forth for the possible source of Kasipatnam apatite–magnetite veins. A fracture-filling metasomatic skarn deposit displaying pegmatitic fabric has been cited for the genesis of these veins from the mineralogical study². Similarly, a pegmatitic origin is fairly well established in view of coarse-grained size, symmetrical and asymmetrical zoning of mineral assemblages. Based on the characteristic mineral assemblages of sulphides, barites, calcite, enrichment of strontium and REEs, a possible carbonatite source or an alkali/alkaline affinity source has also been considered^{3,7,8}. The present study has brought to light the presence of additional mineral association of ancylite, hydroxyl-bastnasite (carbonates), baddeleyite, anatase (oxides) and monazite (phosphate) as well as the anomalous concentration of REEs in calcite and apatite. Carbonatites are typically composed of calcite, dolomite, apatite, phlogopite, magnetite, aegirine–augite, pyrochlore, arfvedsonite, fluorite, barite, strontianite, bastnasite, ancylite, parisite, monazite, zircon and baddeleyite minerals^{11,12}. The presently identified mineral associations along with earlier reported mineralogy are typical mineralogical evidences found in carbonatites. The imprints/signatures of mineralogy akin to carbonatites within pegmatitic veins assume significance. This association may be

explained for a probable source of alkali/alkaline affinity (?) that might have differentiated at depths and enrichment of Ba, Sr, Zr and REEs followed by their emplacement along fractures for which carbonatitic mineralogy is imprinted on a pegmatitic phase. The pegmatitic veins that have emplaced along NW–SE fractures within charnockites are surface expression of such differentiation and mixing/contamination.

In majority of the known REE deposits of the world, LREE are far more abundant than HREE and typically constitute 98–99% of the total REE. In Bayan Obo (China) and Mt Weld deposits (Western Australia), LREE accounts for 99.20% and 98.30% respectively (Table 2). Similarly, LREE accounts for 99.85% of total REE oxides hosted in carbonatite of Kamthai area, Rajasthan¹². A relatively higher HREE distribution is noticed in NR Puram area compared to other deposits as mentioned earlier. In this scenario, the present report of high concentration of REE in apatite and calcite in pegmatitic veins with comparatively high HREE in India is significant and of great economic importance. Detailed petrological and geochemical study of these veins which establish probable alkali/alkaline affinity source (?) that does not have any surface expression though their signatures are imprinted on pegmatitic phase needs to be investigated followed by subsurface exploration. The occurrence seems to be unique and the geochemical signatures observed in the course of limited subsurface sampling carried out in these calcite–apatite-bearing veins suggest vast potential for REEs.

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ACKNOWLEDGEMENT. Analytical support from the Chemistry and XRD Laboratory, AMD is acknowledged. We thank Andhra Phosphate Pvt Ltd for help to visit the mining area and in sampling.

Received 12 January 2015; accepted 16 July 2015

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