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Rare Earth Element Geochemistry of the Munnar Carbonatite, Central Kerala

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Abstract

Rare earth element abundance in carbonatite associated with the 740 Ma old alkaline complex of Munnar is reported. High values of La (up to 232 ppm) and Ce (up to 261 ppm), moderate Sm (up to 11 ppm), with low Tb (up to 1.1 ppm), Yb (up to 3 ppm) and Lu (up to 0.6 ppm) are observed, comparable with similar values for carbonatites from other regions. The chondrite normalised patterns exhibit a steep slope from LREE to HREE, with $(La/Lu)_{cn}$ ranging up to 191. A genetic model involving CO_2 degassing from the mantle and ion exchange reactions with deep crustal rocks is envisaged, with the carbonatites probably representing a late immiscible fraction that separated from a polymerized alkali silicate melt. REE geochemistry of the carbonatite substantiates the view of a Late Precambrian alkaline magmatic regime in this part of the Indian Shield.

INTRODUCTION

The alkaline complex of Munnar in Central Kerala comprises of an alkali granite pluton with minor patches of syenite and carbonatite emplaced within Precambrian gneisses (Nair *et al*, 1983, 1984). The complex is spatially related to the intersection zone of the NE-SW trending Attur lineament and the NW-SE trending Idamalayar lineament (Fig. 1). The rocks occur along the Madurai and Kerala aulacogenes made up of the NE Palni arm, NS Cardamom arm and the NW Anamalai arm. Katz (1978) considered a triple point junction developed at the aulacogene stage, probably manifesting as a hot-spot formed as a resultant tensional wedge due to NE dextral/NW sinistral interaction. The alkali granite of the complex has been dated at 740 ± 30 m.y. (Odom, 1982).

We report here the rare earth element abundance in the carbonatite and, based on the REE distribution patterns, the genesis of the carbonatite is evaluated.

THE CARBONATITE

The carbonatites of Munnar include two types. The coarse-grained holocrystalline variety has yellowish calcite crystals constituting 90% of the rock, with pyroxene, apatite and magnetite corresponding to sovitic composition. The second variety which contains highly coarse calcite crystals and associated minor dolomite with mafic minerals up to 30% and corresponding to alvikite. The sovite exhibits an interlocking crystal mosaic of calcite in thin section where individual crystals sporadically show exsolution blebs of dolomite (Nair *et al*, 1984). The major mafic component in both the varieties is aegirine augite, which forms euhedral to subhedral laths. The opaque phase is dominantly magnetite. Rarely, phlogopite,

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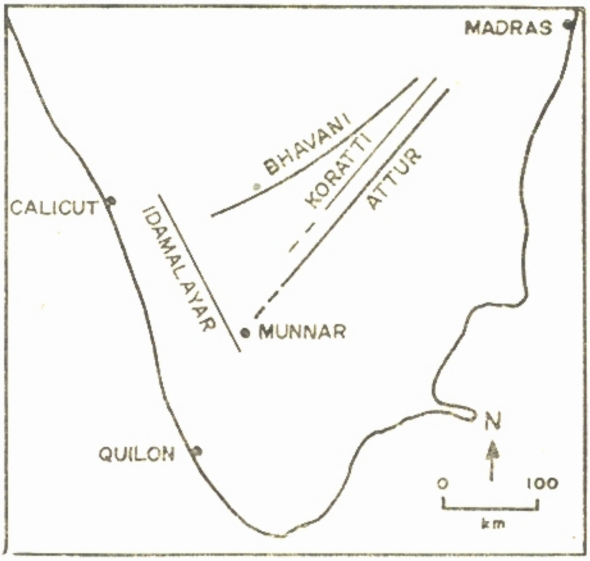

Figure 1. Location of Munnar alkaline complex and its spatial relationship with regional lineaments.

biotite and minor laths of albite are also noted. Small crystals of euhedral apatite are found occluded in the calcite grains.

General geochemical features of the carbonatites (Table I) include high SiO_2 (av. 15.3), Al_2O_3 (av. 2.95) and CaO (av. 47.04), whereas TiO_2 (av. 0.11), Fe_2O_3 (av. 0.06), MgO (av. 1.10) and P_2O_5 (av. 0.06) show low levels. In the CaO-MgO-$FeO^t + MnO$ triangle (Fig. 2), the plots of the carbonatites fall in a restricted spectrum, within the field of sovite/alvikite. The trace element concentrations are comparable with those of sovites and alvikites and fall within the spectrum of typical carbonatites. Higher contents of Co (av. 20.8 ppm), Cr (av. 88.5 ppm), Ni (av. 54.3 ppm) and Pb (av. 56 ppm) than that of sedimentary carbonates (0.1, 11, 20 and 9 ppm respectively); (Turekian and Wedepohl, 1961) are characteristic. The Ba (av. 122.8 ppm) and Sr (av. 268 ppm) values are, however, low. Nair *et al* (1984) attributed this to the petrogenetic history of the alkaline complex.

REE GEOCHEMISTRY

Instrumental neutron activation analyses of rare earth elements and U and Th in four representative samples of the Munnar carbonatites are presented in Table II. The analytical techniques, precision and accuracy are the same as those reported in Vasconcellos and Luna (1978) and Iyer *et al* (1984). The generally high values of La (up to 232 ppm) and Ce (up to 261 ppm) are comparable with similar values for carbonatites from other regions, such as those of Alno complex, which show averages of 250 and 340 ppm of La and Ce respectively (Moller *et al*, 1980, Table I). Sukheswala and Viladkar (1978) reported a range of 100–4000 ppm of (La + Ce) values in carbonatites from India. Higher abundance of La and Ce in late ankerites of Amba Dongar were correlated with the presence of monazite. Sm (up to 11 ppm), Tb (up to 1.1 ppm) Yb (up to 3 ppm) and Lu (up to 0.6 ppm) values are

TABLE I. Major and trace element data of carbonatites from Munnar (after Nair *et al* 1984).

	M-15	M-18	M-39	M-43
	Major elements wt%			
SiO_2	17.21	9.99	17.33	16.68
Al_2O_3	2.60	2.55	3.06	3.57
TiO_2	0.11	0.08	0.17	0.09
Fe_2O_3	0.08	0.04	0.03	0.04
FeO	0.72	1.08	0.93	1.08
Mno	0.03	0.04	0.04	0.04
Mgo	0.80	0.80	1.60	1.20
CaO	49.28	50.40	43.69	44.80
Na_2O	0.50	0.23	0.25	0.31
K_2O	0.58	0 01	0.57	0.02
P_2O_5	0.09	0.09	0.04	0.02
Moisture	0 09	0.13	0.21	0.09
L.O.I.	27.87	34.41	31.61	31.70
	Trace Elements, ppm			
Ag	5	4	3	11
B	160	190	90	100
Ba	164	78	233	16
Bi	50	62	43	51
Co	23	22	19	19
Cr	57	83	120	94
Cu	8	10	8	3
Li	4	4	4	6
Ni	33	64	59	61
Pb	68	62	43	51
Rb	10	11	37	38
Sr	107	553	105	307
Y	17	17	19	19
Zn	26	26	22	21
Zr	30	37	21	29

also comparable (20, 1.9, 3.7 and 0.5 ppm respectively; Moller *et al,* 1980). The generally high Th values (up to 83 ppm) are characteristic of carbonatites. Sample M-30 shows a lower abundance of REE as compared to other samples. REE abundance studies in carbonatites and their calcite separates indicate that the rare earth elements are generally concentrated in accessory phases other than calcite (cf. Moller *et al,* 1980). The REE content in the sample correlates with the lower modal abundance of accessory minerals.

The range of REE in Munnar is 58–634 ppm (Table III), falling within the 72–15515 ppm range for carbonatites (Cullers and Graft, 1984). The $(La/Lu)_{cn}$ range from 12.3 to 191 and correlates with the 7.1–1240 range for carbonatites. Even though Eu and Sm have not been analysed, their values can be extrapolated from REE distribution curves (e.g. Cullers and Graft, 1984). $(Eu/Sm_{cn}$ values range from 0.26 to 0.29, comparable with 0.15–0.50 range for carbonatites.

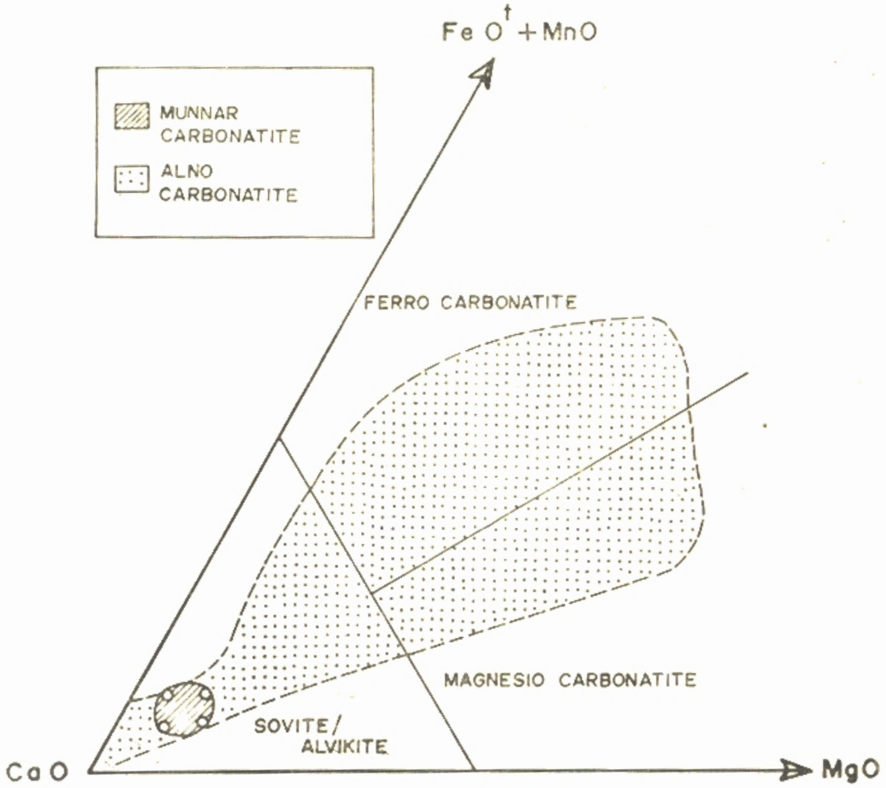

Figure 2. FeO^t + MnO – CaO – MgO plots of Munnar carbonatites. The classification boundaries and field of Alno carbonatites are after Woolley (1982).

TABLE II. Rare Earth and U, Th analysis of carbonatites of Munnar (all abundances in ppm).

Rock	La	Ce	Sm	Tb	Yb	Lu	U	Th
M – 15	232	261	11.0	0.97	1.1	0.26	1.7	9.2
M – 18	87	149	8.5	1.1	1.5	0.6	4.4	78.0
M – 32	85	151	9.4	0.9	3.0	0.5	4.1	83.0
M – 40	10.1	26.9	1.8	0.2	1.1	0.084	0.6	3.8
Chondrite *	0.315	0.813	0.192	0.047	0.208	0.0323		

Analyst: Dra. Marina B. A. Vasconcellos

Method: Instrumental neutron activation analysis

* Chondrite: Values used are from Jahn *et al* (1980), where the values are based on (Leedy Chondrite/1.2).

TABLE 3. REE characteristics of Munnar carbonatites compared with other carbonatites.

	M – 15	M – 18	M – 39	M – 40	Carbonatites
REE	634	300	290	58	72 – 15515
(La/Lu) cn	92	149	191	123	7.1 – 1240
(Eu/Sm) cn	0.26	0.29	0.29	0.28	0.15 – 0.50

M – 15 to M – 40: Munnar carbonatites; Range for other carbonatites, as compiled by Cullers and Graft (1984, Table 7.1).

Chondrite normalised REE distribution patterns of the carbonatites are shown in Fig. 3. The patterns exhibit a steep slope from La to Lu, depicting a sharp decrease from LREE to HREE.

DISCUSSION

The pronounced enrichment of LREE relative to HREE is characteristic of undersaturated alkaline rocks in general (Hermann, 1968). The Munnar carbonatites show high $(La/Lu)_{cn}$ values (up to 191) and steep REE distribution patterns. The REE distribution patterns of the Munnar carbonatites (excluding sample M-30, which shows relatively low concentration) are compared with those of carbonatites from other regions in Figure 4, where they define similar trends.

The processes of melting, crystallization and volatile transport are the major factors that affect REE distribution patterns in carbonatites. (Dawson, 1967; Frey *et al,* 1977; Cullers and Graft, 1984). Cullers and Medaris (1977) proposed a basaltic parent melt produced from a garnet peridotite source, with subsequent fractional crystallization for varied silicate-carbonate rock associations. However, there are no direct evidences for the occurrence of such a parent melt in the complex. They also proposed fractional crystallization of minerals from a presumed alkali basalt parent at varied pressures to explain the REE patterns in associated silicate complexes. However, the large degree of fractional crystallization to produce the required REE contents in such models may be unrealistic (Cullers and Graft, 1984).

Moller *et al* (1980) proposed a different model involving a sequence of chemical reactions beginning with CO_2 emanation from the mantle. Chemically reactive, CO_2-rich volatiles cannot remain in thermodynamic equilibrium with deep crustal rocks (cf. Newton and Sharp, 1975), which would result in partial melting and production of a carbonate-rich magma. When the reaction olivine + diopside + CO_2 giving rise to carbonate melt + pyroxene occurs, LREE would be enriched in the melt due to the selective enrichment of HREE in subcalcic pyroxenes (Moller *et al,* 1980). When such a carbonate-rich liquid penetrates the overlying alkali-rich deep crustal rocks, metasomatic reactions are triggered, leading to further REE enrichment. By the process of Ca-metasomatism, the carbonate melt becomes enriched in alkali metals at the expense of alkaline-earth metals. Introduction of alkali metals into the carbonate liquid leads to an enhancement of CO_2 partial pressure. Excess of CO_2 polymerizes silicate anions in the melt. This acts as the

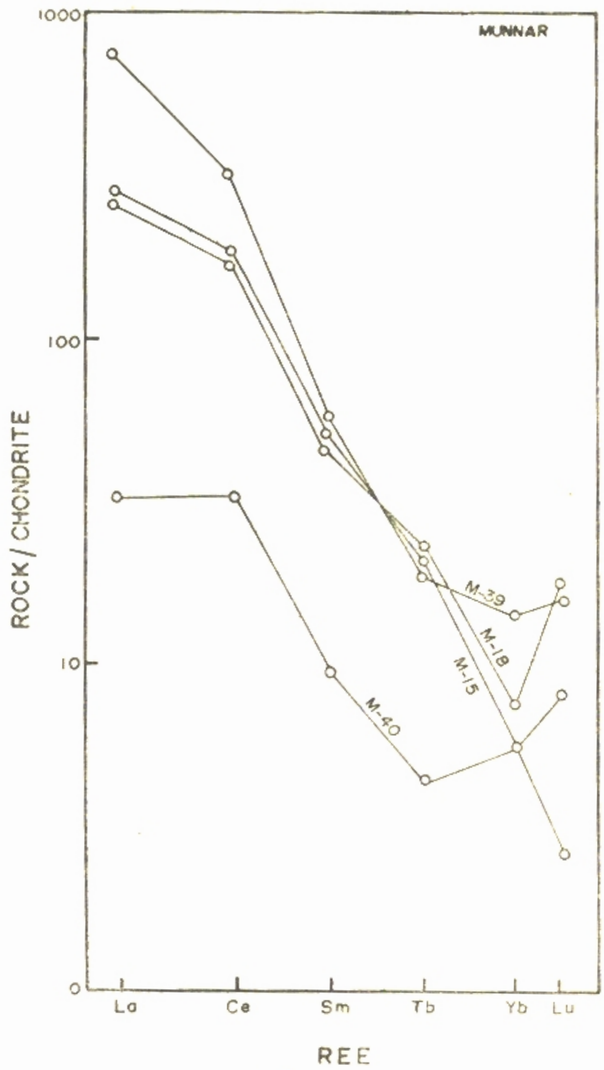

Figure 3.
Chondrite normalised REE plots of Munnar carbonatites.

pre-requisite for the immiscibility between silicate-saturated carbonate liquid and associated carbonate saturated silicate melt. REE distribution in the two resulting fractions is controlled by the availability of octahedral coordination sites. Enrichment of REE in the carbonate-rich fraction is due to the higher capacity for complex formation in this medium. Several other workers have also proposed liquid immiscibility as an important process which controls the REE distribution of presumably cogenetic magmas (e.g. Eby, 1975; Cullers and Medaris, 1977). The alkali granite-syenite-carbonatite association may represent an event of late immiscible separation of silicate-rich and carbonate-rich fractions. However, since the volume of syenite and carbonate is very less as compared to the granite pluton, we

Figure 4. REE distribution patterns of Munnar carbonatites compared with those from other regions.

would interpret that this process could have played only a minor role, that too, during the late stages.

The volatile transport of REE in CO_2-rich fluids is an important mechanism in the petrogenesis of carbonatites and associated alkaline rocks (Loubet *et al*, 1972). Extreme LREE enrichment in the soviitic carbonatites of Fen, Norway, is attributed to the volatile transport of LREE (Mitchell and Brunfelt, 1975). Wendlandt and Harrison (1979) showed that REE, particularly LREE, partition strongly into CO_2 vapor. Pure CO_2 has a high partition coefficient of LREE (about 50) and thus could effectively scavenge the LREE from a magma. Fluid inclusion studies in the Munnar alkali granite (Santosh, 1984) show the presence of CO_2-rich fluids, indicating a CO_2-dominated regime during the granite petrogenesis.

The Idamalayar and Attur lineaments with which the Munnar carbonatite is spatially related, are possible deep-seated taphrogenic lineaments (cf. Nair *et al*, 1983, 1984). Crustal warping and distension is envisaged to have triggered mantle degassing, resulting in the liberation of volatiles enriched with CO_2 (cf. Bailey, 1974). Since large volumes of undersaturated alkaline rocks are not associated with the Munnar complex, the degree of mantle melting would have been too low. The CO_2-rich volatiles caused partial melting at deeper crustal levels and ion exchange reactions resulted, producing a carbonate-rich silicate liquid. The increasing concentration of alkalies and CO_2 towards the late stage in the melt led to the immiscibility, with enrichment of REE in the carbonate-rich fraction. The concentration and distribution patterns of REE in the carbonatites and the unique alkaline rock association in Munnar support an alkaline magmatic regime related to distensional tectonics during Late Precambrian.

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References

Bailey, D. K., (1974) Continental rifting and alkaline magmatism. *In:* H. Sorensen (Ed.). The alkaline rocks. John Wiley—Interscience, New York, pp. 148-159.

Cullers, R. L. and Graft, J. L., (1984) Rare earth elements in igneous rocks of the continental crust: predominantly basic and ultrabasic rocks. *In:* P. Henderson (Ed.). Rare earth element geochemistry, Elsevier, Amsterdam, pp. 237-274.

Cullers, R. L. and Medaris, L. G., (1977) Rare earth elements in carbonatite and cogenetic alkaline rocks: Examples from Seabrook Lake and Calender Bay, Ontario. Contrib. Mineral. Petrol., v. 65, pp. 143-153.

Dawson, J. B., (1967) Geochemistry and the origin of kimberlite. *In:* P. C. Wyllie (Ed.). Ultramafic and related rocks. John Wiley, New York.

Eby, G. N., (1975) Abundance and distribution of the rare earth elements and Yttrium in the rocks and minerals in the Oka carbonatite complex, Quebec. Geochim. Cosmochim. Acta, v. 39, pp. 597-620.

Frey, F. A., Ferguson, I. and Chappell, B. W., (1977) Petrogenesis of South African and Australian kimherlite suites. Second Intern. Kimberlite Conf., Santa Fe, N. Mexico (U.S.A.).

Hermann, A. G., (1968) Die Verteilung der Lanthaniden in basaltschen Gesteinen. Contrib. Mineral. Petrol., v. 17, pp. 275-314.

Iyer, S. S., Chaudhuri, A., Cordani, U .G. and Vasconcellos, M. B. A., (1984) Radioactive element distribution on the Archaean granulite terrane of Jequie Bahia, Brazil. Contrib. Mineral. Petrol., v. 85, pp. 95-101.

Jahn, B. M., Auvray, B., Blais, S., Capdevila, R., Cornichet., Vidal, F. and Hameurt, J., (1980) Trace element geochemistry and petrogenesis of Finnish greenstone belts. Jour. Petrol., v. 21, pp. 201-244.

Katz, M., (1978) Tectonic evolution of the Archaean granulite facies belt of Sri Lanka and south India. Jour. Soc. India, v. 19, pp. 185-205.

Loubet, M., Bernat, M., Javoy, M. and Allegre, C. J., (1972) Rare earth contents in carbonatites. Earth Planet. Sci. Lett., v. 14, pp. 222-232.

Mitchel, R. H. and Brunfelt, A. O., (1974) Rare earth element geochemistry of kimberlites. Phys. Chem. Earth, v. 9, pp. 671-686.

Moller, F., Morteani, G. and Schley, F., (1980) Discussion of REE distribution patterns of carbonatites and alkalic rocks. Lithos, v. 13, pp. 171-179.

NEWTON, R. C. and SHARP, W. E., (1975) Stability of fosterite + CO_2 and its bearing on the role of CO_2 in the mantle. Earth Planet. Sci. Lett., v. 26, pp. 239-244.

NAIR, N. G. K., SANTOSH, M. and THAMPI, P. K., (1983) Geochemistry and petrogenesis of the alkali granite of Munnar, Kerala (India) and its bearing on rift tectonics. Neues Jb. Miner. Abh., v. 148, pp. 223-232.

——— (1984) Alkali granite-syenite carbonatite association in Munnar, Kerala, India: implications for rifting, alkaline magmatism and liquid immiscibility. Proc. Indian Acad. Sci. (Earth Planet Sci.), v. 93, pp. 149-158.

ODOM, A. L., (1982) Isotope age determinations of rock and mineral samples from Kerala, India. Final Rep. U.N. Case No. 81-10084, 10 pp.

SANTOSH, M., (1984) Silicate-carbonate fluid immiscibility as recorded by fluid inclusions in quartz from Munnar alkali granite, Kerala. *In* Nat. Sem. on Scientific and Industrial Application of Fluid inclusions. Dehra Dun (Abstr.).

SUKHESWALA, R. N. and VILADKAR, S., (1978) Carbonatites of India. Proc. First Int. Symp on carbonatites, Brazil, pp. 277-293.

TUREKIAN, K. K. and WEDEPOHL, K. H., (1961) Distribution of elements in some major units of the earth's crust. Bull. Geol. Soc. America, v. 72, p. 175.

VASCONCELLOS, M. B. A. and LUNA, F. W. J., (1978) Activation analysis of alkaline rocks—A comparison between destructive and non-destructive methods. Jour. Radioanal. Chem., v. 44, pp. 55-81.

WENDLANDT, R. F. and HARRISON, W. J., (1979) Rare earth partitioning between immiscible carbonate and silicate liquids and CO_2 vapor: results and implications for the formation of light rare earth enriched rocks. Contrib. Mineral. Petrol., v. 69, pp. 409-419.

WOOLLEY, A. R., (1982) A discussion of carbonatite evolution and nomenclature and the generation of sodic and potassic fenites. Mineral. Mag., v. 46, pp. 13-18.

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