

## RARE EARTH CONTENTS IN CARBONATITES

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Received 14 June 1971

Revised version received 6 January 1972

Mass spectrometric measurements of rare earth elements have been made by isotope dilution in several carbonatites. The results show a great enrichment of total rare earth content and a large fractionation between heavy and light rare earths. The patterns observed permit an easy distinction between limestones and carbonatites. This result suggests that in the carbonatite process the gas phase might play an important role.

## 1. Introduction

During recent years, rare earth elements (REE) have attracted the attention of many groups in geochemistry [1–5], using activation analysis or mass spectrometry and isotope dilution. The normalised chondrite diagram of Masuda and Coryell et al. [6] made it possible to express REE distribution patterns efficiently and to compare measured and calculated patterns easily. The carbonatites, which are known for their enrichment in rare earth elements, have drawn only limited attention [1, 7]. Our interest in these rocks was aroused by the hypothesis that gas–magma interaction, which takes place in normal magmatic processes, plays a predominant role in the process of carbonatite formation. The evidence provided by  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  measurements in our laboratory [8] is in favour of this hypothesis. Information on REE fractionation resulting from gas–magma interaction is virtually not available. By studying REE abundances in carbonatites we may extend our knowledge of REE fractionation on this point.

## 2. Analytical techniques

The REE measuring technique used in this investigation is similar to the one used by Schnetzler et al. [9]. The sample was dissolved in HCl and spikes were

added. The residue of this first dissolution was dissolved in HF. The chemical separation of rare earth elements was achieved by cationic exchange using Dowex 50  $\times$  8 (200–400 mesh) in a glass column, 25 cm long and 18 mm in diameter. The column was washed with 600 ml of 6 N HCl, and subsequently calibrated with 2 N HCl. The sample was added in 0.5 N HCl and the solution eluted with 8  $\times$  20 ml by 6 N HCl. Eight fractions of 20 ml each were obtained and the fractions 2, 4, 6 were chosen which contain respectively (Dy, Er, Yb, Lu) (Nd, Sm, Eu, Gd) (La, Ce). The 8th fraction contains relatively pure La and was sometimes used.

Three separate mass spectrometer runs were made. The nitrate forms were mounted on a prebaked single Ta filament and introduced into a 30 cm mass spectrometer. This mass spectrometer is equipped with an electron multiplier and a Faraday-cup with  $10^{11}\Omega$  and  $10^{10}\Omega$  resistors. In each case heating was done in steps to resolve several minor interferences which are not completely suppressed by chemical separation. Each rare earth element was run at several intensities to check the appearance of interferences. The shunts and linearity of recorder were calibrated from time to time. All chemical preparations were made in a clean laboratory equipped with filtered air, in teflon vessels, with Merck 'Suprapur' reagents. The blanks were less than 0.02 ng and are negligible for this work.

Gast et al. [10] have pointed out that spike cali-

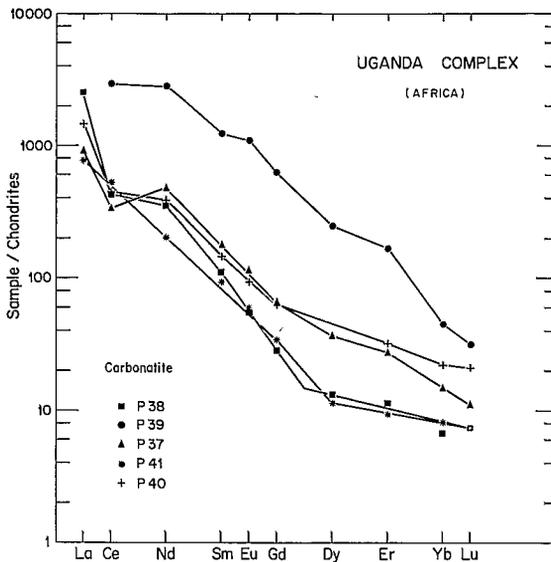


Fig. 1. Chondrite-normalized rare earth concentration in five carbonatites of the Uganda complex, Africa.

bration for the rare earths is a serious problem because the normal suprapure standards contain  $\text{CO}_2$  or  $\text{H}_2\text{O}$ . Our calibrated spikes were baked at high temperature in order to get rid of the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the carbonates of the REE. After this treatment, standard solution can be prepared gravimetrically with Merck reagents. The spikes were calibrated three times, and the results agreed reasonably well to within  $\pm 2\%$ . The spiking was done gravimetrically with a correction for evaporation during the spiking time.

The total error of our determination is  $\pm 3\%$  except for La. In this case, the error could be as much as 10% because of a correction for cerium interference. However we have frequently had runs in which the cerium interference was only minimal.

### 3. Results and comments

In the first part of this investigation, we studied ten carbonatites from Uganda, (Africa), Fen (Norway), Angola and Congo (Africa). The analytical results are given in table 1 and in figs. 1, 2 and 3.  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  isotope ratios for the same samples have been reported by Pineau and Javoy [8].

The Uganda complexes are situated in Eastern

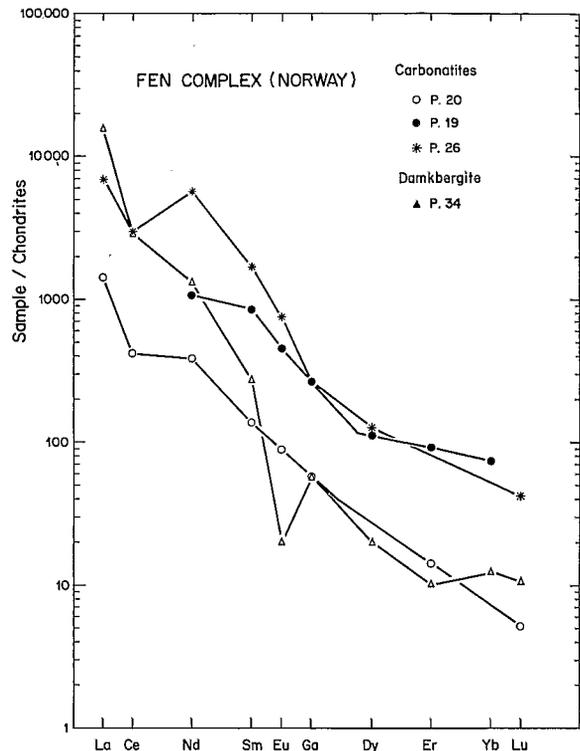


Fig. 2. Chondrite-normalized rare earth concentration in three carbonatites and one dankjernite (P30) of the Fen complex, Norway.

Uganda, North of Lake Victoria, they belong to the well known carbonatitic and alkaline complexes associated with the African rift. They cross-cut the Precambrian gneissic and granitic basement.

Geologically, we may distinguish old and young complexes [11]. The old complexes are probably Cretaceous or younger, the ages increasing from south to north. The young complexes are situated in the north, and these are probably Tertiary or younger. Our samples range in time from Sukulu to Lukopoi Napak. They all are associated with alkaline rocks, principally ijolites and nepheline syenites. The mineralogy of the samples is given in Appendix 1.

The REE abundances clearly show a large enrichment when compared with the other terrestrial rocks and a big fractionation between the light and the heavy REE (LREE and HREE) (fig. 1).

The HREE concentrations are comparable to those of basalts (both alkaline basalts and tholeiites), but

Table 1  
Rare earth abundances in the different samples analysed (ppm).

$\delta^{18}\text{O}_{\text{SMOW}}$	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu	
Uganda											
8.15	270	290	287	46.5	8.5	21.3	12.2	6.20	2.65	0.37	P37
11.8	850	362	190	21.3	4.00	9.26	4.30	2.34	1.15	0.22	P38
14.25	884	2460	1913	272	90.4	143	74.6	31.8	8.0	0.85	P39
9.4	512	372	233	33.7	7.31	20.3		7.30	3.60	0.63	P40
7.2	216	424	116	19.9	4.30	8.37	3.93	2.16	1.30	0.223	P41
Fen											
10.6		( 200)	614	184	34.1	85.7	34.1	20.4	13.0		P19
7.05	423	338	227	28.6	6.5	14.5	8.0	2.91		0.165	P20
8.2	(2500)	2100	3367	357	60.2	85	43.2	20.8		2.22	P26
	4371	1850	745	59.45	1.63	19.7	6.50	2.20	2.42	0.355	P30
Angola											
17.3		588	585	82.0	23.1	51.3	48.3	30	12.2	1.25	P114
8.1	1500	1170	498	64.8	14.8	37.5	18.7	11.1	6.25	0.9	P117
Metamorphic limestones											
21.1	7.4	3.8	2.6	0.45	0.093	0.34		0.25		0.025	P34
Kirumba											
12.3	9	26	16.9	3.42	1.74		3.26	1.36	0.86		P35
Atlantic Islands											
8.2		237	150	23	7.9	14.2	12.7	8.5	5.7	0.698	P50
7.8		49.1	92.7	20.1	4.60	14.6	12.9	12.5	8.06	1.13	P62
Chondrites (reference)											
	0.30	0.84	0.58	0.21	0.076	0.32	0.31	0.31	0.17	0.031	

the LREE are enriched by a factor of 100 to 200 relative to basalts (i.e., a factor 1000 to 3000 relative to chondrites). All our samples except the oldest one from the Sukulu complex have negative cerium anomaly. No europium anomaly was found.

The Fen complex (Norway) is well known in carbonatite petrology [12]. The age of this complex is about Permian. Petrographically, the carbonatitic rocks are divided into sövite, rauhaugites and rödbergites. We have studied two rauhaugites and one rödbergite. Their mineralogy is described in Appendix 1.

The REE results are similar to those of the Uganda complex (fig. 2): LREE enrichment, a smaller HREE enrichment and a negative Ce anomaly. In samples P19 and P26 the HREE are relatively enriched compared with the other carbonatites, including the

Uganda carbonatites. The rauhaugite rocks are cut by 'kimberlitic' dykes. We have studied the REE in one of these dikes (sample P30). The abundances are similar to those of the rauhaugite, except that there is no cerium anomaly and a large negative europium anomaly.

In the case of the Angola samples [13], the abundances are very much like those of the samples above discussed (fig. 3).

We also studied the Kirumba carbonatite (sample P35) geologically described by Denaeyer [14]. This carbonatite, which is probably very altered as indicated by the  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$  ratios [8], is also anomalous in its REE abundances. These are very low for a carbonatite, but the pattern is not destroyed.

In summary, these carbonatites have an extremely high REE content (between 1000 to 10 000 ppm) and

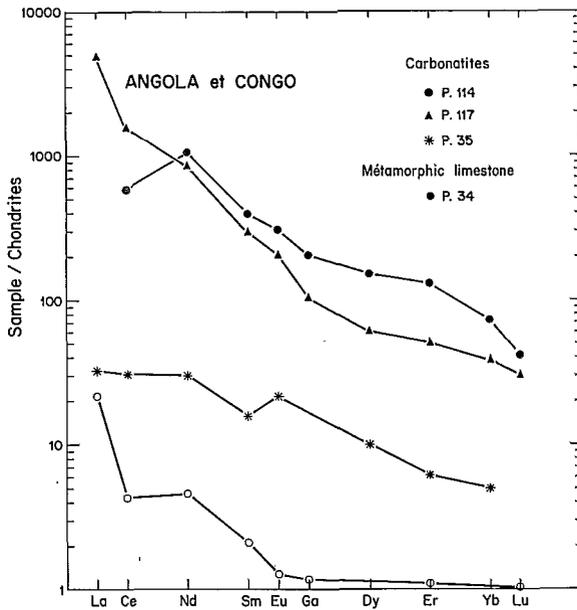


Fig. 3. Chondrite-normalized rare earth concentration of three carbonatites and one metamorphic limestone (P34) of Angola and Congo.

are perhaps the most enriched rocks known at the surface of the earth. They display a fractionation between the LREE and HREE which is also large. The conventional ratio of La/Yb varies between 60 to 740. These rocks have no Eu anomaly but a negative Ce anomaly is quite common.

#### 4. Discussion on the origin and the formation of carbonatites

##### 4.1. Limestones and carbonatites

The question of whether carbonatites have a limestone origin or a magmatic origin has been debated for some time. Chemically this question has been investigated by means of tracers [15–17].

Taylor et al. [17] defined a region in the  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$  diagram within which magmatic carbonatites plot. However, some cases have been found which plot outside the Taylor et al. [17] quadrangle and which do not have a limestone origin. Such cases should be seriously discussed before definitive conclusions can be drawn. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio has also been used to separate carbonatites from limestones.

But this feature does not solve the problem completely; it allows at best the elimination of recent limestones as source material for carbonatites. We tried to investigate this problem studying REE data. To determine the influence metamorphism has on the REE distribution, we measured one strongly metamorphosed Precambrian limestone (sample P34). Our results for this case are similar to the results of Haskin et al. [19] for unmetamorphosed limestones, which are drastically different from carbonatites in this respect (fig. 4). The case of the Kirumba complex (sample P35) is different. This carbonatite is probably very altered. The abnormal REE pattern can represent one product of alteration or a step of evolution not as developed as in the other complexes. The fact that this pattern does not display a Ce anomaly favours this interpretation.

The fact that limestones and carbonatites are different in REE concentration is not a priori a definitive proof that these two rock types are completely unrelated. But if carbonatites are remobilized limestones, one has to devise a geological process which could produce such a distinct REE pattern for carbonatites, without transitional stages. The  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  data and the REE results are more easily explained by a magmatic origin for carbonatites [8, 18].

The samples which plot within the  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$  carbonatite quadrangle defined by Taylor et al. [17] have the typical REE carbonatite pattern. The samples which plot outside it, but are on the gas magma evolution line defined by Javoy et al. [18] also have the REE carbonatite pattern. The samples which are outside the carbonatite quadrangle and off the magmatic evolution line do not have the normal REE pattern.

We have applied this criterion to check carbonatite occurrences on Atlantic islands. Our measurements of REE concentrations in 'carbonatitic' rocks from the Cape Verde and Canary Islands, show a pattern [20] which is typical for carbonatites with a large enrichment in REE and which displays a Ce anomaly. However the ratio LREE/HREE is smaller, as in some other carbonatites.

##### 4.2. Magmatic process related to carbonatite formation

In agreement with the majority of people who work

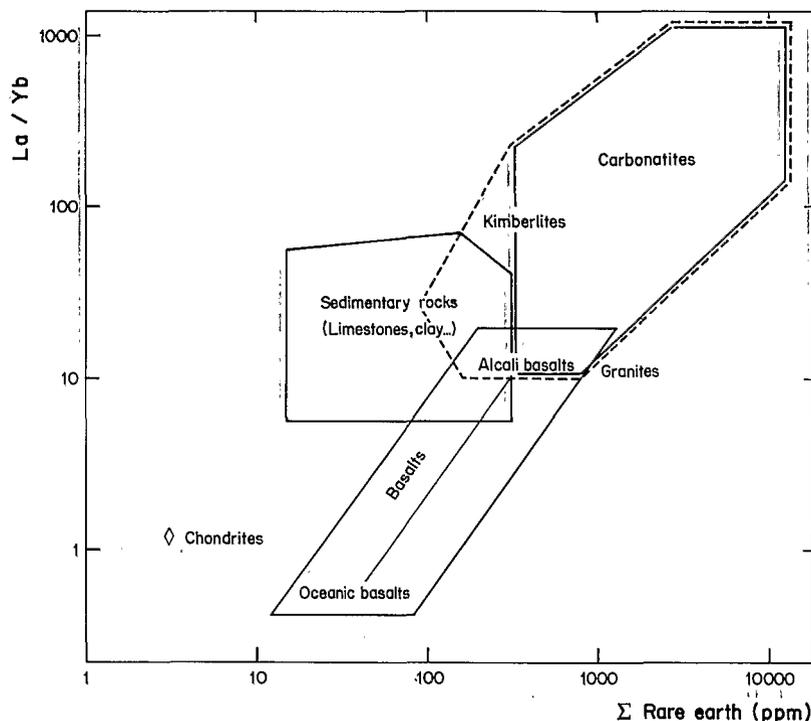


Fig. 4. La/Yb ratio plotted against total REE showing progressive transition in the different types of volcanic rocks. Carbonatites and kimberlites look very much like highly differentiated rocks.

on carbonatite problems, we assume a magmatic origin for carbonatites. In this hypothesis we must explain the origin of the characteristic REE pattern. The two most important features of REE carbonatite pattern are the LREE/HREE ratio and total REE enrichments. We have used, as is commonly done, the La/Yb ratio to characterise the LREE–HREE fractionation (fig. 4).

A plot of the La/Yb ratio versus total REE for different types of volcanic rocks shows a gradual transition between oceanic tholeiites and carbonatite via alkali basalts and kimberlites. There is a positive correlation between the La/Yb ratio and REE content. This kind of relation was explained by Gast [21] and afterwards by some others as being a result of partial melting. Gast argued that the degree of partial melting decreases in going from tholeiites to alkali basalts and kimberlites; this will cause a large La/Yb fractionation in kimberlites produced by partial melting of a garnet lherzolite mantle and could explain REE concentrations in some kimberlites. The REE in carbon-

atites which have a pattern similar to kimberlites may be explained in similar fashion. But the mineralogy for both kimberlites and carbonatites can not be explained in this way. Gast [21] pointed out that with a garnet lherzolite mantle we can not explain alkali basalt genesis; *we have found no important discontinuity between kimberlite and enriched alkali basalts as far as their REE are concerned*. If the partial melting hypothesis is correct, then the second process which is responsible for the mineralogy of kimberlites and carbonatites should not much alter the primary REE pattern produced by such a partial melting.

Crystal settling may also produce large REE fractionations. The only minerals which can give big LREE/HREE fractionations are the pyroxenes, but to reproduce the observed La/Yb ratio for kimberlites and carbonatites, the proportion of pyroxene which must precipitate is extremely large, as has been pointed out by Gast [21].

The gas phase plays an important role in the genesis of carbonatites and kimberlites, which fact is evi-

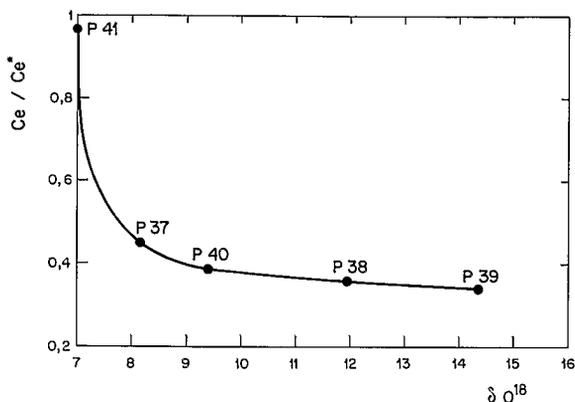


Fig. 5. Evolution in the Uganda suite of the Ce anomaly plotted against  $^{18}\text{O}$  chosen as an index of the magmatic evolution. Ce is the actual concentration of the sample. Ce\* is the virtual cerium concentration corresponding to the absence of anomaly.

dent from many experimental and geological observations. The large amounts of excess argon [22] found in carbonatites also point in this direction. This gas phase will contain  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (rare gases) but also some HF, HCl etc [23].

A study of the  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$  relationships in several carbonatite suites has demonstrated that the observed relationships can be explained with a model in which gas—magma interaction is expressed as a Rayleigh distillation process [8, 18]. It was shown that  $\delta^{18}\text{O}$  is a good index for the carbonatite magma evolution. We have compared the evidence obtained from  $\delta^{18}\text{O}$  values with that of the REE. The only suite for which we have enough samples is from the Uganda complexes. There is a clear correlation between  $\delta^{18}\text{O}$  and the total REE content. For the other complexes this correlation may also be valid, but unfortunately we have only two samples from each complex to test this hypothesis (two rauhaugites from Fen P19–P20, and two carbonatites from Angola). In each case  $\delta^{18}\text{O}$  and the REE vary sympathetically.

Therefore, we propose as a working hypothesis that in the gaseous or supercritical fluid solutions in contact with a basaltic magma there are complexes which are responsible for the enrichments in alkali metals and REE in kimberlites and carbonatites. It has been pointed out by Balashov et al. [24] that HREE carbonate complexes are more stable than LREE car-

bonate complexes. Therefore, we may suppose that after the gaseous or supercritical phase has been separated from the basaltic magma, and carbonate precipitation from it occurs, the precipitated carbonate will have a larger LREE/HREE ratio than the basaltic source.

In this sense, we think that it would be possible to find some rocks in non-altered carbonatite complexes rich in HREE, as they exist in granitic aplites (Balashov et al. [24]).

### 3. Cerium anomaly and comparison with kimberlites

We have pointed out above that a negative Ce anomaly is frequently found in carbonatites. A negative Eu anomaly may also occur in kimberlites, for example in the Dutoitspan kimberlite [1] and a dankjernite from Fen (P30). In the Uganda samples, we have studied the evolution of the Ce anomaly, taking  $^{18}\text{O}$  as an index of magmatic evolution (fig. 5). The pattern seems to indicate that the medium becomes more and more oxidizing as the differentiation proceeds,  $\text{Ce}^{3+}$  is oxidized into  $\text{Ce}^{4+}$  and is thus separated from the other ions which remain in the 3+ state.

The presence of the europium anomaly may indicate a change of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  under reducing conditions. This can be interpreted in two ways, if one accepts the general relationship between carbonatites and kimberlites.

(i) Carbonatites are derived from kimberlites while continuous increase in the oxidizing conditions occurs ( $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ ), ( $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ ).

(ii) Kimberlites and carbonatites are derived independently from a common magma source in response to different redox conditions. It is of interest to note that the carbon is in  $\text{CO}_3^{2-}$  form in carbonatite and partly in C form (diamond) in kimberlites, in agreement with our two different redox conditions hypothesis.

### Acknowledgements

Samples were provided by Dr. S. Machado, Torre d'Assunção Mendes, M. Denayer, F. Pineau. This cooperation was greatly appreciated. Y. Bottinga re-

viewed the manuscripts with great care, and S. Panigel typed the several repetitive versions. The mass spectrometer was maintained in operation with the cooperation of M. Girard. A reviewer for this journal made some useful comments on the original version.

## Appendix 1

Name, origin and mineralogic composition of the samples.

Uganda		
P37	Sövite of Tororo Hill	80% carbonates – magmatite and hematite
P38	Sövite of Tororo	Almost pure calcite
P39	Sövite of Lukopöi Napak	Carbonates (90% calcite) – 10% magnetite
P40	Sövite of Busumbu Quarry	Carbonates (90% calcite) – 10% magnetite
P41	Sövite of Tororo Sukulu Hill	Almost pure calcite
Fen		
P19	Rauhaugite	Calcite 42% Dolomite 38%
P20	Rauhaugite	Calcite 10% Dolomite 80%
P26	Rödbergite	Alkali feldspaths 2% – Apatite 8% carbonatite with hematite traces
P30	Dankjernite	Variety of kimberlite

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*Reprinted from:*

# EARTH AND PLANETARY SCIENCE LETTERS

A LETTER JOURNAL DEVOTED TO THE DEVELOPMENT IN TIME OF THE EARTH AND PLANETARY SYSTEM

Volume 14, No. 2, March 1972

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pp. 226 – 232

11 DEC. 1972

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