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## Preliminary results of geochemistry, Sm–Nd and Rb–Sr studies of post-Karoo carbonatite complexes in Southern Africa\*

by U.R.F. Ziegler<sup>1</sup>

### Abstract

The preliminary results presented in this article show that the major and trace element composition of most of the analysed post-Karoo carbonatite complexes of Namibia (Kalkfeld), Zambia (Kaluwe, Chasweta), Malawi (Kangankunde) and Tanzania (Mbeya) is in good agreement with the expected composition for the respective carbonatite types. The chondrite normalized REE patterns of all the analysed carbonatites show a strong LREE/HREE enrichment and the absence of significant anomalies. K–Ar age determinations of the Eisenberg carbonatite (Kalkfeld complex) yielded ages between 153.6 and 172.8 Ma. Rb–Sr and Sm–Nd studies indicate depleted mantle reservoirs for the Kalkfeld, Kaluwe and Kangankunde carbonatites while the Mbeya complex seems to have a Rb-depleted, Nd-enriched reservoir. The study of the Chasweta is not conclusive with respect to its mantle source as the results show a bimodal sample distribution which either indicates different mantle sources or severe contamination/mixing for the Chasweta magmas.

*Keywords:* Geochemistry, isotope geochemistry, carbonatites, post-Karoo complex, southern Africa.

### 1. Introduction

During the late Triassic the initial rifting of the South Atlantic triggered the separation of Africa from Antarctica and South America. Intracontinental stretching accompanying the opening of the South Atlantic and the South Indian Ocean led to a multitude of anorogenic magmatic events in southern Africa. During the early to late Jurassic the magmatism of the Karoo igneous province (ERLANK, 1984) was the characteristic and volumetrically most important type of magmatism in southern Africa. Old lines of weakness near the eastern end of Atlantic-related transform fault zones extending far inland (e.g. in Angola and Namibia) and intracontinental regions such as the Chilwa province in Malawi (e.g. WOOLLEY, 1991), the Rufunsa province in Zambia (BAILEY, 1966; TURNER, 1988) and the Mbeya area

in southern Tanzania (VAN STRAATEN, 1989) where lineaments and/or fault systems occur and partly transect each other were the place of subsequent late Jurassic to early Cretaceous (ca. 165 to 100 Ma) ultra-alkalic and carbonatitic magmatism in southern Africa (KAMPUNZU and POPOFF, 1991). Within the last few years several studies on African carbonatites (e.g. BELL and BLENKINSOP, 1989; KINNAIRD and BOWDEN, 1991) have shown that the majority of African carbonatites have relatively smooth and steep REE patterns and that the source regions of the so far analysed African carbonatite complexes lie within the subcontinental mantle which must be inhomogeneous with respect to its Sr and Nd isotopic composition.

As no Rb–Sr, Sm–Nd, REE and age data exist on many of the major carbonatite complexes of southern Africa (e.g. the Kalkfeld complex in Namibia and the Rufunsa carbonatites of Zam-

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bia) while the isotope and trace element characteristics of the carbonatites of eastern Africa and the Republic of South Africa are partly well known there exists a major gap in the knowledge on the mechanisms and sources of the post-Karoo magmatism in these areas. The aim of the present study is thus to gain more information on these subjects on a regional scale by the analysis of the REE- and isotope systematics of various post-Karoo carbonatite complexes of southern Africa. This report summarises the first preliminary results of this ongoing study.

## 2. Sample description

The analysed samples cover all the major structural and tectonic settings in which Mesozoic carbonatites occur in southern Africa. They were collected in the following areas:

The Rufunsa province is located at the triple junction of the NE–SW Luangwa rift with the middle and lower Zambesi rifts (Fig. 1A). This province formed close to the northeastward extension of the (reactivated) Proterozoic Mwembeshi shear zone (DALY, 1988). Carbonatites occur in a group of four complexes emplaced into a sequence of Upper Karoo sandstones (BAILEY, 1966; TURNER and REX, in press). Detailed descriptions of the Rufunsa carbonatites which are not associated with any silicic magmatic rocks may be found in BAILEY (1960 and 1966), TURNER (1988). K–Ar age determinations of TURNER and REX (in press) yielded ages between 101 and 113 Ma for the Kaluwe complex. The samples which were analysed during this study derive from the northernmost Kaluwe and the southernmost Chasweta complexes. The Kaluwe samples Z19, Z20 and Z21 are dark grey, fine-grained sövites. The Chasweta samples Z1, Z4, Z12 are dark brown, fine-grained ferrocarnatites while Z17 is a brownish, fine-grained sövite.

The Kalkfeld province (Fig. 1B) of central western Namibia is situated on the southwest-northeast trending lineament of the Damaraland province (PRINS, 1981) which represents an Atlantic related transform fault zone. The three carbonatite complexes of the Kalkfeld province (Kalkfeld, Ondurakorume, Osongombo) which have been described in detail by VERWOERD (1967) intruded the country rock of pan-African age amidst (on a regional scale) a large number of alkaline ring complexes. The analysed fine-grained biotite sövite samples N15 and N33 were collected on the central Eisenberg plug of the Kalkfeld complex. The large (up to 3 cm in diameter), partly chloritized biotites (N36 I – N36 IV)

used for the K–Ar age determinations of this study derive from the biotite sövites of the summit area of Eisenberg.

The Chilwa alkaline province (Fig. 1C) of southern Malawi is situated at the junction of the north-south trending East African Rift and the east-west trending Zambezi rift. Seventeen carbonatite centres of a wide compositional range are known from this area (GARSON, 1965). K–Ar age determinations of SNELLING (1965) and CAHEN and SNELLING (1966) on the Kangankunde, Tundulu and Chilwa island complexes yielded ages of  $123 \pm 6$  Ma,  $133 \pm 7$  Ma and  $136 \pm 7$  Ma, respectively. The analysed samples M5, M7 and M8 are dark brown, fine-grained, monazite rich magnesiocarbonatites from Kangankunde Hill which is (besides some alnöitic dykes and some carbonated nephelinite) free of associated silicate rocks.

The Mbeya (Panda Hill) province is located in southwestern Tanzania south of the Tanzania craton along strike of the East African Rift (Fig. 1D). K–Ar age determinations of SNELLING (1965) and MILLER and BROWN (1963) yielded ages between  $96 \pm 9$  Ma and  $113 \pm 6$  Ma for the four Mesozoic carbonatites of southwestern Tanzania occurring in this area. The analysed samples EH12 and EH13 are creamy white to grey, fine-grained sövites from the Panda Hill complex close to the city of Mbeya.

## 3. Methods

The major and REE elements of the samples N15, N33, Z1, Z4, Z12, Z17, Z19, Z20, Z21, M5 and M7 were determined at CRPG, Nancy, France using inductively coupled plasma atomic emission spectrometry while the REE composition of the samples EH12 and EH13 was determined by neutron activation at Bondar Clegg Ltd., Ottawa, Canada. CO<sub>2</sub> was coulometrically determined at CRPG in Nancy. All the isotopic measurements were carried out at the Laboratory for Isotope Geology of the University of Bern. The Rb–Sr concentrations and the Sr isotopic compositions were determined using the isotope dilution method as described by JAEGER (1979). The Sm and Nd concentrations as well as the Nd isotopic composition were determined according to the method described by STOESEL and ZIEGLER (1989) using a two column element separation procedure. The Rb analyses were carried out on an "Ion Instruments" solid source mass spectrometer. Elemental Sr, Sm, and Nd measurements were carried out on a "VG Sector" thermal ionisation mass spectrometer by single and triple filament

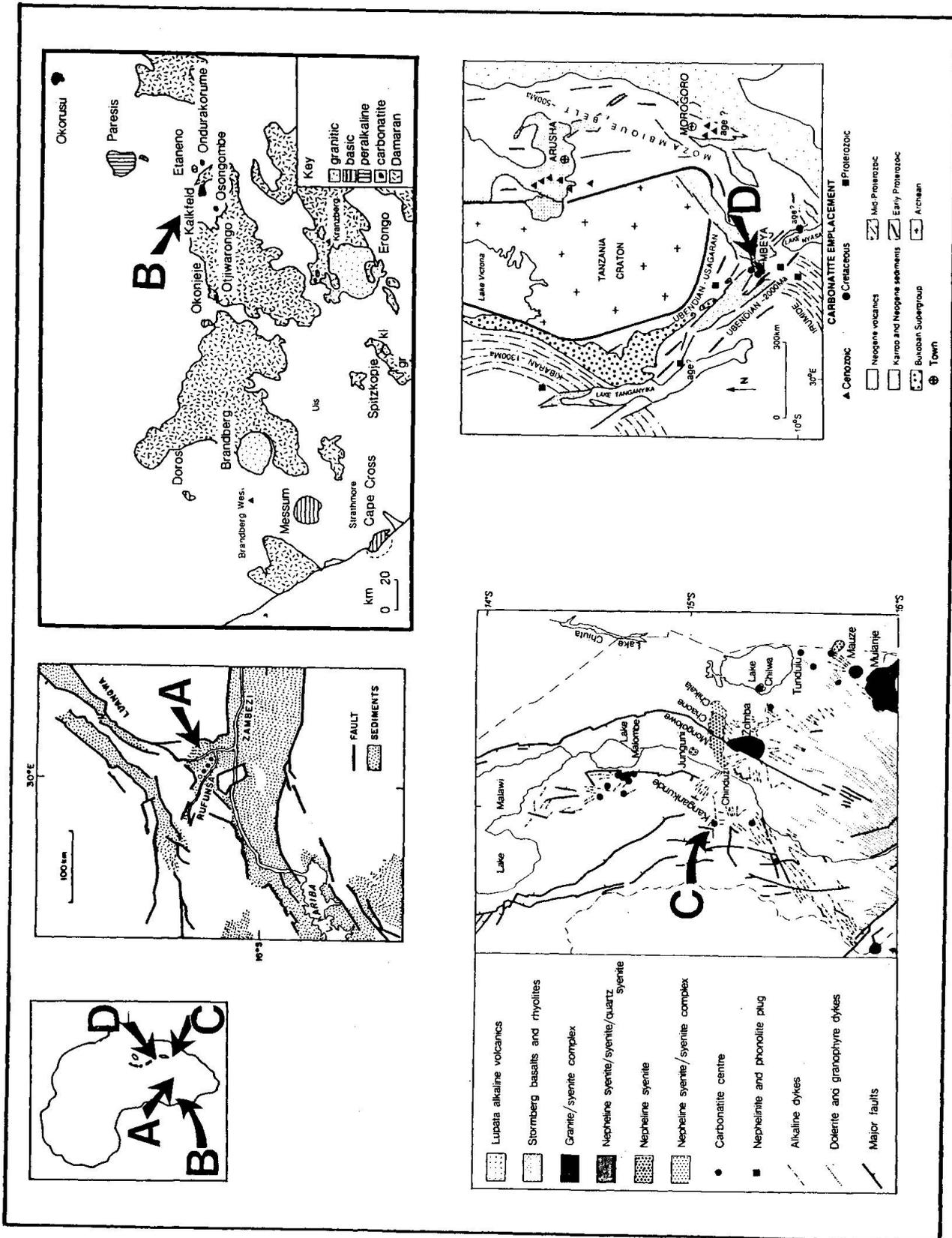


Fig. 1. Location map of the analysed complexes: A) Rufsusa area (Zambia) after BAILEY (1989); B) Kalkfeld province (Namibia) after KINNAIRD and BOWDEN (1991); C) Chilwa alkaline province (Malawi) after WOOLLEY (1991); D) Carbonatite areas of Tanzania after VAN STRAATEN (1989).

Tab. 1 Major, trace and rare earth element concentrations of the analysed samples.

Complex	Kalkfeld Namibia			Chasweta Zambia			Kaluwe Zambia			Kangankunde Malawi		Mbeya Tanzania	
Sample	N15	N33	Z1	Z4	Z12	Z17	Z19	Z20	Z21	M5	M7	EH12	EH13
Major Elements (wt%):													
SiO <sub>2</sub>	0.79	25.67	1.53	3.11	1.63	1.51	0.75	5.74	0.14	5.99	4.99		
Al <sub>2</sub> O <sub>3</sub>	0.13	9.31	0.71	1.45	0.78	0.44	0.08	1.58	0.07	1.56	1.41		
Fe <sub>2</sub> O <sub>3</sub>	3.72	9.71	11.69	11.94	11.35	3.69	1.45	2.15	0.48	4.76	10.64		
MnO	0.91	0.56	1.67	1.01	2.02	0.51	0.16	0.51	0.48	1.64	2.51		
MgO	0.21	5.75	8.21	4.25	5.05	0.48	0.86	0.88	0.27	12.03	11.71		
CaO	51.82	21.2	31.43	38.37	37.26	51.61	53.75	48.76	55.75	21.66	26.87		
Na <sub>2</sub> O	0.07	0.61	0.03	0.03	0.04	0.03	0.06	0.06	tr	0.05	0.02		
K <sub>2</sub> O	tr	3.47	tr	0.11	tr	0.03	0.03	0.89	tr	0.14	tr		
TiO <sub>2</sub>	tr	2.38	0.11	0.07	0.06	0.11	0.02	0.08	tr	0.02	0.02		
P <sub>2</sub> O <sub>5</sub>	2.22	1.20	1.18	1.29	3.00	1.35	3.45	0.86	1.41	2.84	1.08		
CO <sub>2</sub>	37.44	13.93	34.93	32.39	31.76	37.21	37.31	35.27	40.91	33.93	35.58		
Trace Elements (ppm):													
Ba	434	>5000	>5000	>5000	>5000	>5000	1119	>5000	1278	3586	>5000	650	1500
Be	2	8	7	10	10	5	1	5	2	8	3		
Co	19	31	42	69	53	21	19	18	11	32	22	14	17
Cr	13	362	27	26	23	18	12	18	8	17	21	46	23
Cu	49	53	155	57	96	13	26	22	19	42	31		
Ga	54	16	35	32	41	20	19	21	19	163	79		
Nb	189	170	>1000	460	609	546	962	379	362	170	23		
Ni	16	86	19	157	40	15	14	15	10	25	13		
Rb	1	66	<1	6	<1	4	2	22	1	2	1	6	<1
Sc	26	32	24	26	42	35	16	17	20	39	28	5	4
Sr	8064	5844	1830	1663	1737	723	5272	992	748	90258	27260	13278	3910
Th	252	301	216	329	433	109	71	99	55	822	326	4	214
V	25	148	151	369	201	159	75	168	104	43	49		
Y	333	86	141	266	197	90	62	96	74	80	46		
Zn	86	127	510	395	202	142	26	168	45	>1000	>1000		
Zr	37	275	105	375	123	104	53	76	32	153	66		
Rare earth elements (ppm):													
La	2967	183	2456	1825	2892	513	243	657	402	14525	5625	612	306
Ce	5193	285	3743	2945	4195	876	496	1045	724	23261	9012	1120	610
Nd	2897	180	1582	1267	1507	374	239	439	294	8130	3129	391	222
Sm	335	35.7	177	161	177	57.1	36.8	63.1	43.9	477	216	46.9	31.9
Eu	75.8	9.7	38.2	41.7	46.9	19.1	8.31	20.5	10.0	90	53	10	7
Gd	212	23.7	114	127	146	63.3	23.6	60.8	28.3	318	144		
Dy	113	13.2	61.5	77.5	85.0	43.0	11.3	45.8	15.0	111	65		
Er	47.6	7.1	27.6	40.3	38.8	24.4	4.71	23.1	6.4	53	58		
Yb	23.9	6.1	17.0	29.7	26.7	15.9	1.93	17.2	2.8	23	20	9	7
Lu	3.9	1.1	2.9	5.5	5.0	3.0	0.33	3.0	0.4	5	4	0.9	<0.2

modes, respectively. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are normalized to  $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$  while the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios are normalized to a  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio of 0.72190. Total blanks were  $< 1$  ng for Sm, 0.01–0.1 ng for Nd and  $< 10$  ng for Sr. K was analysed by flame photometry from an aliquot of the sample. The isotopic composition and the concentration of Ar were determined on a VG MM1200 solid source mass spectrometer following the extraction and purification in a Pyrex glass line and the addition of 99.997% pure  $^{38}\text{Ar}$  spike.

#### 4. Results and discussion

The results of the major, trace and rare earth element analyses are listed in table 1 while those

of the isotopic analyses are compiled in tables 2–4.

The K–Ar ages of the analysed Eisenberg samples range between 153.6 and 172.8 Ma and thus confirm the classification of the Kalkfeld carbonatites as post-Karoo complexes.

Figure 2 shows a general classification of the analysed samples according to the propositions of WOOLLEY and KEMPE (1988). A comparison with the data in WOOLLEY and KEMPE (1988) shows, with the exception of N33, that the major and trace element geochemistry of the samples is (although certain trace elements are in cases slightly enriched compared to the literature data) generally in good agreement with the expected range for the respective carbonatite types. The abnormal composition of N33 is due to the presence of biotite, chlorite, vermiculite, augite and some

Tab. 2 Tabulation of the Rb and Sr results. Constants used are:  $^{87}\text{Rb}$  decay constant =  $1.42 \cdot 10^{-11} \text{a}^{-1}$  (STEIGER and JAEGER, 1977),  $^{85}\text{Rb}/^{87}\text{Rb} = 2.59265$ ,  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ ,  $^{84}\text{Sr}/^{86}\text{Sr} = 0.056584$  (STEIGER and JAEGER, 1977),  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{Uniform Reservoir UR}} = 0.7045$  (e.g. DE PAOLO, 1988),  $^{87}\text{Rb}/^{86}\text{Sr}_{\text{UR}} = 0.0827$  (e.g. DE PAOLO, 1988).

Sample	Rb ppm	Sr ppm	$^{87}\text{Sr}/^{86}\text{Sr}$	+/-	$^{87}\text{Rb}/^{86}\text{Sr}$	+/-	Epsilon Sr(T)
<b>Kalkfeld</b>							
<b>Namibia</b>							
N15	0.57	8064	0.703669	10	0.000206	0.000002	-9.1
N33	65.53	5844	0.703918	12	0.032432	0.000324	-6.6
<b>Chasweta</b>							
<b>Zambia</b>							
Z1	0.32	1830	0.707739	9	0.000498	0.000005	47.9
Z4	6.19	1663	0.705736	7	0.010769	0.000108	19.2
Z12	0.41	1737	0.706338	11	0.000683	0.000007	28.0
Z17	3.68	723	0.703836	8	0.014702	0.000147	-7.9
<b>Kaluwe</b>							
<b>Zambia</b>							
Z19	2.18	5272	0.703286	9	0.001195	0.000012	-15.4
Z20	22.89	992	0.704240	11	0.066747	0.000667	-3.3
Z21	1.08	748	0.703747	8	0.004169	0.000042	-8.9
<b>Kangankunde</b>							
<b>Malawi</b>							
M5	1.82	90258	0.703016	5	0.000059	0.000001	-19.0
M7	0.81	27260	0.703067	7	0.000086	0.000001	-18.3
M8	0.59	39367	0.703033	9	0.000043	0.000001	-18.7
<b>Mbeya</b>							
<b>Tanzania</b>							
EH12	5.69	13279	0.703876	7	0.001238	0.000012	-7.2
EH13	0.61	3910	0.703407	8	0.000449	0.000004	-13.9

K-feldspar besides carbonates and limonite. Figure 3 shows the results of the REE analyses in chondrite normalized abundance patterns. All the REE abundance patterns are very steep and smooth due to very high light REE abundances and the absence of pronounced anomalies both of which are typical features of carbonatites. The  $\epsilon\text{Nd}_{(T)}$  values calculated for the respective intrusion ages of the analysed complexes from the measured  $^{143}\text{Nd}/^{144}\text{Nd}$  data range between -5.3 and +5.5. The Kangankunde, Kaluwe and Eisenberg samples all have positive  $\epsilon\text{Nd}_{(T)}$  values while those of the Mbeya and Chasweta samples are at least partially negative. With the exception of Chasweta all the  $\epsilon\text{Sr}_{(T)}$  values range between -19.0 and -3.3. The  $\epsilon\text{Sr}_{(T)}$  values of the Chasweta samples are between -7.9 and +47.9.

Figure 4 shows the results of the isotopic measurements in an  $\epsilon\text{Nd}_{(T)}$  v.  $\epsilon\text{Sr}_{(T)}$  diagram. All the Kaluwe, Eisenberg and Kangankunde samples as well as one Chasweta data point scatter within the upper left (depleted) quadrant. This indicates that

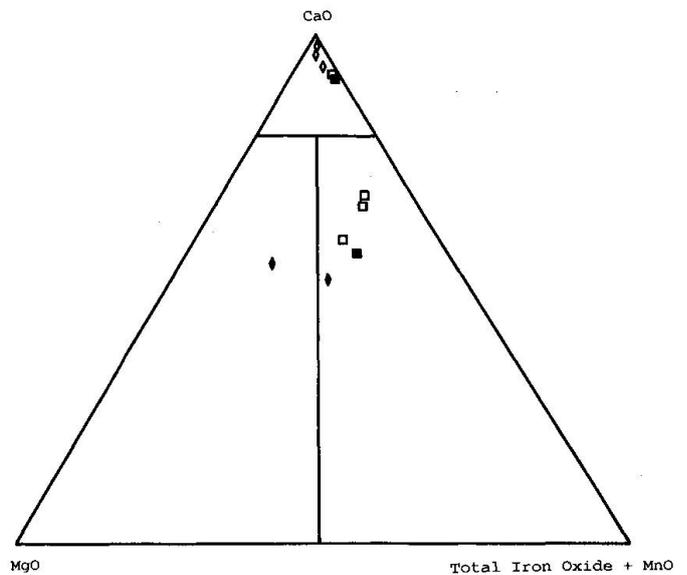


Fig. 2 CaO-MgO-Total Iron Oxide + MnO plot of the analysed carbonatites (same symbols as in Fig. 4).

Tab. 3 Tabulation of the Sm and Nd results. Constants used are:  $^{147}\text{Sm}$  decay constant =  $0.00654 \text{ b.y.}^{-1}$  (LUGMAIR and MARTI, 1978),  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{Chondritic Uniform Reservoir CHUR}}(t=0) = 0.51264$ ,  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{Depleted Mantle DM}(0)} = 0.51316$ ,  $^{147}\text{Sm}/^{144}\text{Nd}_{\text{CHUR}} = 0.1967$ ,  $^{147}\text{Sm}/^{144}\text{Nd}_{\text{DM}} = 0.2136$ .

Sample	Sm ppm	Nd ppm	$^{143}\text{Nd}/^{144}\text{Nd}$ +/-	$^{147}\text{Sm}/^{144}\text{Nd}$ +/-	Epsilon Nd(T)	
<b>Kalkfeld</b>						
<b>Namibia</b>						
N15	334.65	2897.8	0.512575	2 0.0698	0.0007	1.3
N33	35.74	180.06	0.512580	3 0.1200	0.0012	0.4
<b>Chasweta</b>						
<b>Zambia</b>						
Z1	177.00	1582.1	0.512442	2 0.0676	0.0007	-2.1
Z4		1267.0				-2.8
Z12	176.95	1506.9	0.512280	5 0.0710	0.0007	-5.3
Z17	57.12	374.48	0.512849	16 0.0922	0.0009	5.5
<b>Kaluwe</b>						
<b>Zambia</b>						
Z19	36.83	238.88	0.512737	18 0.0932	0.0009	3.3
Z20	63.07	439.67	0.512694	3 0.0867	0.0009	2.6
Z21	43.95	293.51	0.512750	3 0.0905	0.0009	3.6
<b>Kangankunde</b>						
<b>Malawi</b>						
M5	477.18	8129.6	0.512679	2 0.0355	0.0004	3.3
M7	216.33	3129.3	0.512694	3 0.0418	0.0004	3.5
M8	189.05	2950.3	0.512669	2 0.0387	0.0004	3.0
<b>Mbeya</b>						
<b>Tanzania</b>						
EH12	46.88	390.76	0.512511	3 0.072523	0.0007	-1.0
EH13	31.85	222.00	0.512506	5 0.086734	0.0009	-1.3

Tab. 4 Tabulation of the K-Ar results. Constants used are:  $^{40}\text{K} = 5.543 \cdot 10^{-10} \text{ a}^{-1}$  (total  $^{40}\text{K}$  decay constant),  $^{40}\text{K}^e = 0.581 \cdot 10^{-10} \text{ a}^{-1}$  (STEIGER and JAEGER, 1977),  $^{40}\text{Ar}/^{36}\text{Ar}_{\text{atm}} = 295.5$ ,  $^{38}\text{Ar}/^{36}\text{Ar}_{\text{atm}} = 0.1869$  (STEIGER and JAEGER, 1977).

Sample	K (wt%)	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{K}/^{36}\text{Ar}$	Age (Ma)
N36 I	1.41	1243.8	94898	164.3
N36 II	2.44	1069.5	78984	161.3
N36 III	3.37	3620.4	315562	172.8
N36 IV	2.58	6144.8	627735	153.6

these carbonatites derive from reservoirs depleted in Large Ion Lithophile Elements (LILE) relative to bulk Earth while the Mbeya samples seem to derive from a mantle source with lower Sm/Nd and Rb/Sr ratios relative to the bulk Earth. Three of the four Chasweta samples plot within the enriched quadrant. A comparison with literature data taken from a compilation of BELL and BLENKINSOP (1989) shows that the majority of the samples plots in the areas of known carbonatite compositions although some of them do not follow the East African carbonatite line of BELL

and BLENKINSOP (1989). The high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of the three enriched Chasweta samples are somewhat puzzling as they plot far away from known carbonatite compositions. The fact that the fourth Chasweta sample (Z17) as well as all the Kaluwe samples do not show such aberrant isotopic compositions raises even more questions on the genesis of these Rufunsa carbonatites. The only conclusions that can be drawn from the present data are the following: The Kaluwe samples as well as Z17 seem to have their origins in a mantle reservoir depleted in LILE and their isotopic composition remained more or less unchanged during formation, ascent and emplacement of the carbonatite magmas. If the sövitic Z17 and the three enriched ferrocarnatitic Chasweta samples which show a certain tendency towards Group II kimberlites (data from GURNEY et al., 1991) do not have the same origins then the aberrant samples must either derive from a comparatively enriched mantle source or they must have had a strong crustal component in their

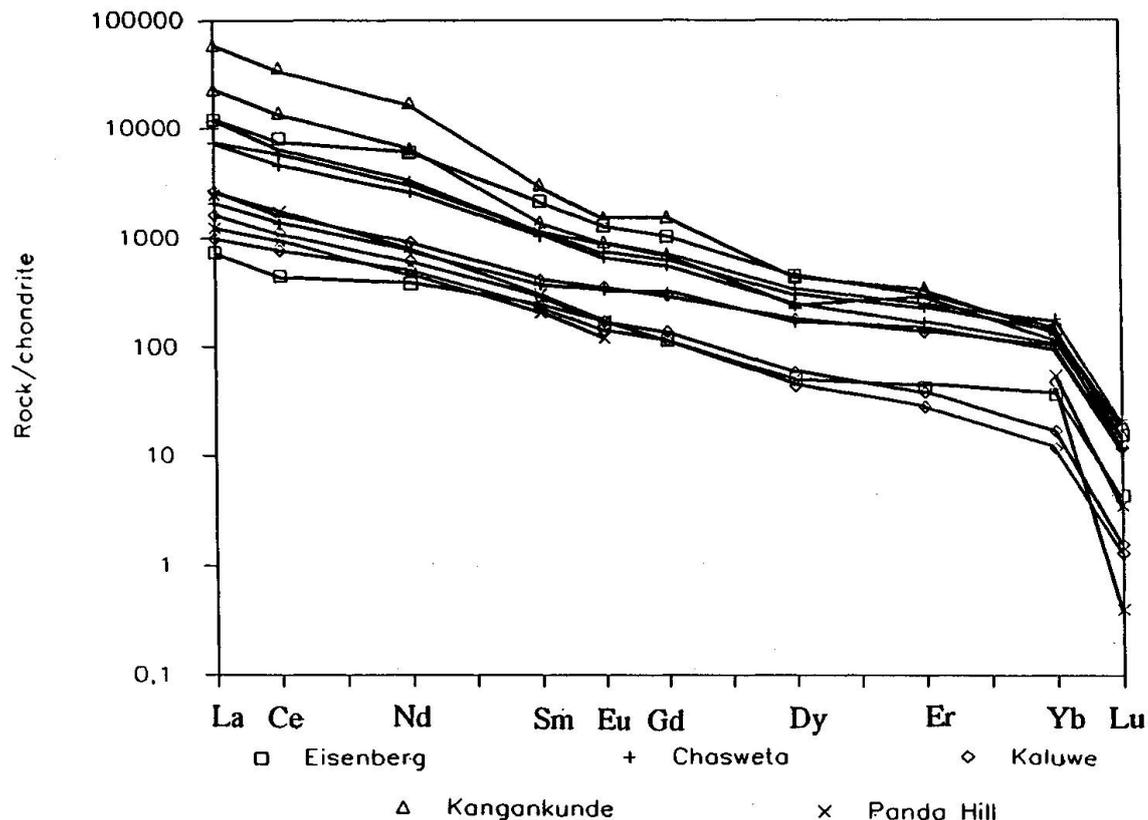


Fig. 3 Chondrite normalized REE plot for the analysed carbonatites.

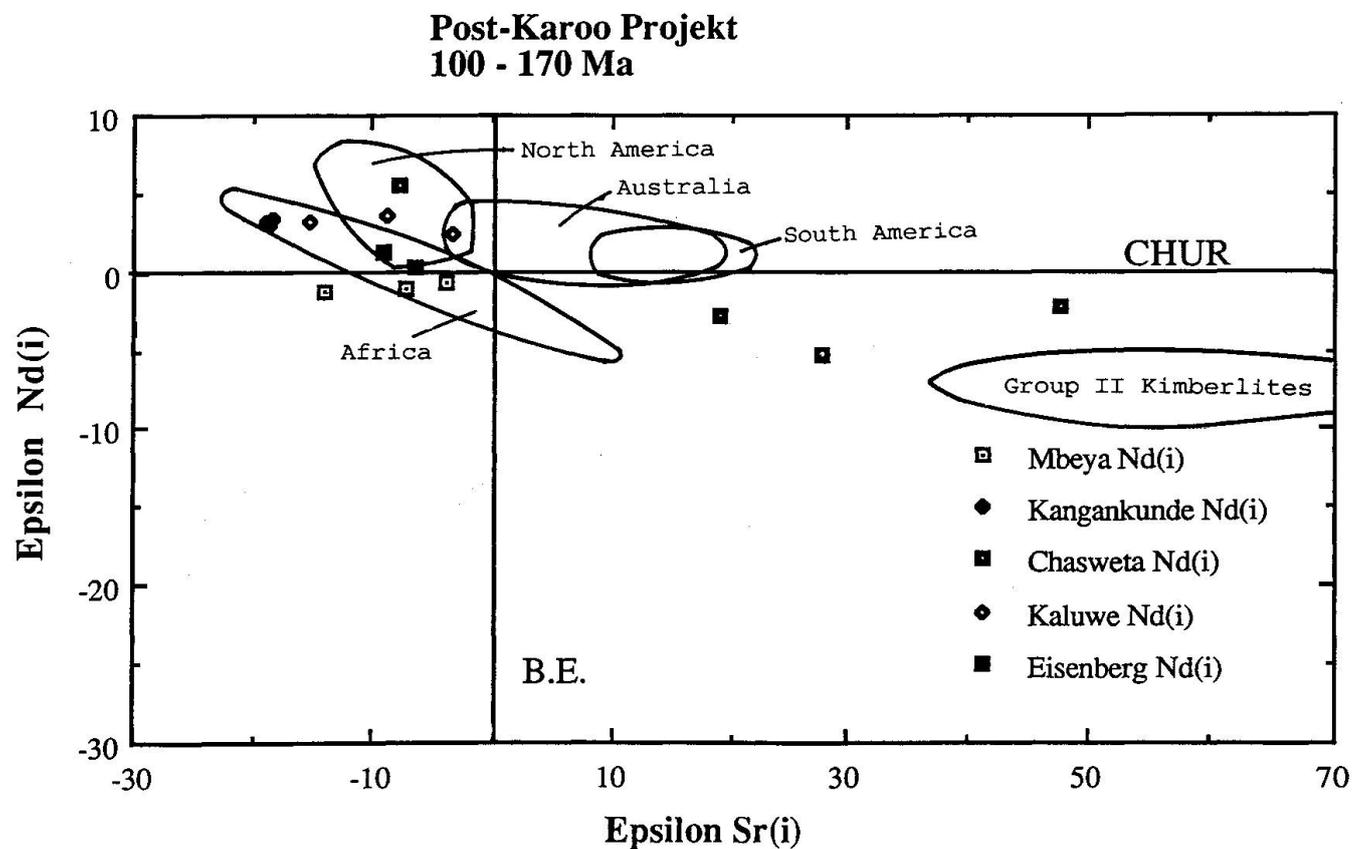


Fig. 4 Plot of  $\epsilon_{Nd(T)}$  versus  $\epsilon_{Sr(T)}$  for the analysed samples. Data for comparison are taken from the compilation of BELL and BLENKINSOP (1989).

source area while Z17 derives from a depleted source. If, however, they have common origins then certain parts of the Chasweta magma must have been subject to mixing processes including the assimilation of continental crust material. The first interpretation is supported up to a certain degree by the considerations of BAILEY (1989) who identified magnesio-chromite-bearing pyroclasts in part of the Chasweta carbonatites which thus indicate a certain kimberlite affinity of these pyroclastic carbonatites. As magnesio-chromite is only present in the pyroclastic carbonatites and is absent in the coarse grained intrusive carbonatites BAILEY (1989) also stated that the Rufunsa carbonatites must derive from various origins; a conclusion which would also support the first interpretation. However, only further detailed field and laboratory work can help to find a solution to this Rufunsa problem.

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