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A deep mantle source for carbonatite magmatism: evidence from the nephelinites and carbonatites of the Buhera district, SE Zimbabwe

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Abstract

In the Buhera district of SE Zimbabwe the Dorowa and Shawa complexes are composed of dolomitic carbonatites with MgO and Mg# values comparable to those anticipated for mantle melts. These carbonatites are associated with olivine-bearing nephelinitic plugs and dykes which are correlatives of the picritic and nephelinitic lavas of the basal Karoo volcanic succession in the Nuanetsi–North Lebombo (NNL) region. The NNL volcanics are isotopically anomalous. Previous detailed Sr, Nd, Pb and Os isotopic studies indicate that the anomalous signatures result from mixing between enriched lithospheric mantle and deep mantle plume material. New geochemical and isotopic data are presented which reveal that the Buhera nephelinites have signatures similar to, but more enriched, than those of the NNL attaining ϵ_{Nd} values of -22 to -15 at ϵ_{Sr} of $+8$ to $+20$. By contrast the Shawa carbonatites are not isotopically anomalous with ϵ_{Nd} (0 to $+1$) and ϵ_{Sr} ($+3$ to $+6$) comparable to the ‘mildly depleted mantle’ signature typical of carbonatites globally. A single analysis of a Dorowa carbonatite has an intermediate signature ($\epsilon_{Sr} + 7$; $\epsilon_{Nd} - 10$). These relationships provide unequivocal evidence that the Buhera nephelinites and carbonatites were derived from discrete, unrelated parental magmas derived from different sub-cratonic mantle segments. Clearly, the source of the Shawa carbonatites must lie below the zone of ancient LREE enriched lithosphere sampled by the Buhera and NNL silicate magmas and their isotopic signatures more closely approximate the asthenospheric component identified in the NNL picrites. As such these results require the existence of discrete carbonatite magmas at mantle depths in excess of those producing nephelinitic magmatism. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years a substantial body of evidence has accumulated in support of the existence of carbonatitic magmas in the mantle. High pressure experimental studies have demonstrated that magnesian

carbonate liquids are produced as near-solidus melts of carbonated peridotite at pressures above 21 kbar [1–4]. On ascent, these liquids will be extinguished through reaction if they remain in equilibrium with enclosing mantle peridotite. The results of these carbonatite–peridotite reactions have been identified in many mantle nodule suites [5–8] providing additional, indirect evidence for the existence of carbonatite magmas at mantle depths. Carbonate melts are

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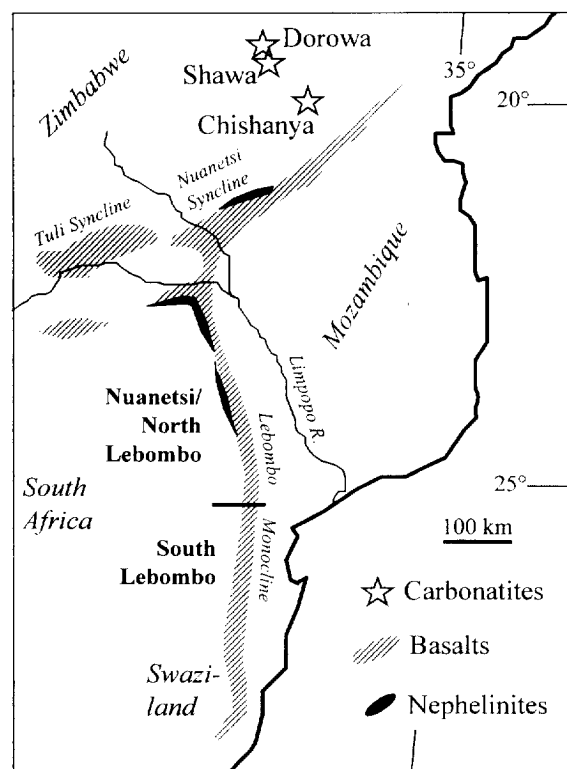


Fig. 1. Locality map showing the positions of the Buhera carbonatites relative to areas of outcrop of Karoo volcanics. The North Lebombo–Nuanetsi and South Lebombo distinction is after Hawkesworth et al. [18].

very efficient agents of mantle metasomatism in that they are mobile in the upper mantle at pressures of 2 GPa and above and have the ability to transport and precipitate substantial quantities of incompatible elements [9,10]. Existence of carbonatite-like liquids at extreme lithospheric depths has been invoked to explain the enriched trace element signatures found in harzburgitic mineral inclusions in Archaean diamonds [11]. Carbonatites have very limited ranges in $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ composition; more restricted than the range reported for oceanic basalts despite the fact that they penetrate crustal lithospheres of widely different ages and complexities (e.g. [12]). It has been argued that the generally high Nd and Sr contents of carbonatites would buffer them to a large extent against the effects of crustal interaction and so preserve their original (mantle) signatures: as such they have been extensively used as ‘probes’ of the sub-continental mantle (e.g. [12] and references therein; [13]).

Despite these various lines of evidence, however, many petrologists still prefer to consider carbonatites as secondary magma types derived at low (crustal) pressures through liquid immiscibility from parental silicate magmas of nephelinitic affinity [14–17].

Resolution of the depth at which surface carbonatites are derived will thus provide important constraints not only on the petrogenesis of carbonatite magmatism but also contribute to the understanding of mantle enrichment processes. In this paper we present new geochemical and isotopic data for Karoo-aged nephelinitic and carbonatitic intrusives of the Buhera district, SE Zimbabwe (see Fig. 1). Previous studies of Karoo volcanic rocks from the North Lebombo–Nuanetsi area provide evidence about the composition of the sub-continental lithospheric upper mantle in this region and this allows unambiguous constraints to be placed on the source of these nephelinite and carbonatite magmas. Relevant aspects of the Karoo data are first discussed followed by presentation and discussion of the Buhera data.

2. The sub-cratonic lithospheric mantle of SE Africa as revealed by Karoo volcanics: a review

Isotopic variability in the ca. 185 Ma Karoo volcanics of southern Africa was documented by Hawkesworth and co-workers [18] who showed that a correlation existed between geographic location within the Karoo magmatic province and degree and style of isotopic enrichment (summarised in Fig. 2). Basaltic and nephelinitic volcanics from the northern Lebombo and Nuanetsi (NNL) regions of northeastern South Africa and southeastern Zimbabwe (see Fig. 1) are characterised by highly negative ϵ_{Nd} values at only moderately enriched ϵ_{Sr} values indicating derivation from a source which had experienced an ancient enrichment in LREE. Ellam and Cox [19] analysed a carefully selected suite of high Mg# picrite samples from the Nuanetsi area and the $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ and Pb isotopic data for these samples correspond well with the previously published data for the NNL mafic volcanics (Fig. 2). The high Mg# chemistry of these samples indicate that they represent direct mantle melts unmodified by crustal contamination. It was concluded [20] that the enriched isotopic signatures in the NNL volcanics cannot be due to con-

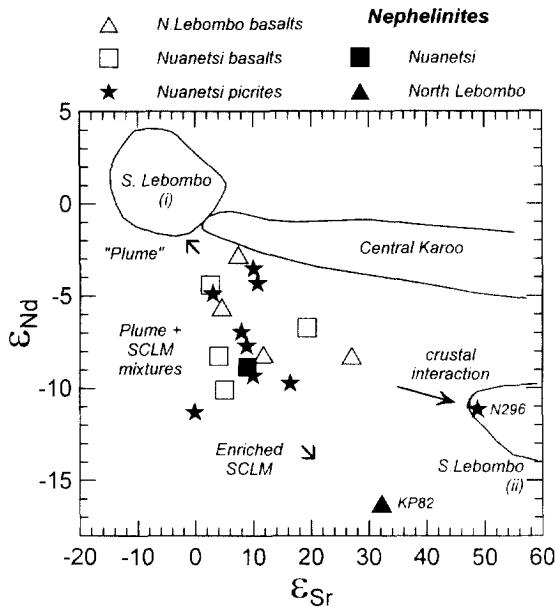


Fig. 2. $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ plot of data from volcanics of the Nuanetsi–North Lebonbo region shown in comparison to data from the South Lebonbo and central areas of Karoo volcanics [18,19]. Vectors indicate approximate positions of isotopic reservoirs sampled by the NNL volcanics and are after Ellam and Cox [20] and Ellam et al. [21]. SCLM = sub-continental lithospheric mantle. Sample KP82 is a Mashikiri nephelinite [18] and sample N296 is a picrite which shows evidence of crustal interaction [19].

tinental contamination but were derived from melting of enriched sub-continental lithospheric mantle (SCLM). Further study [21] showed that the picrite $^{143}\text{Nd}/^{144}\text{Nd}$ values were positively correlated with $^{187}\text{Os}/^{188}\text{Os}$. Crustal rocks have high Re/Os values (which hence develop high $^{187}\text{Os}/^{188}\text{Os}$ with time) and so these data confirmed that the low $^{143}\text{Nd}/^{144}\text{Nd}$ (negative ϵ_{Nd}) signature in the NNL rocks cannot be due to the incorporation of crustal material. Instead, it was concluded [21] that the isotopic compositions of the NNL volcanics are ‘most readily explained as mixtures between enriched SCLM and sub-lithospheric material, most probably derived from a mantle plume’, as annotated in Fig. 2.

One sample which carried clear geochemical evidence of crustal contamination (N296) was included in the above data set [19]: this sample has substantially higher ϵ_{Sr} (see Fig. 2), $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ (see Section 5.2) values than the remainder of the picrites and provides a useful indicator of the isotopic influence of continental crust.

3. General geology and geochemistry of the Buhera carbonatite complexes and nephelinites

3.1. General geology

The carbonatites and alkaline rocks of the Buhera district in southeastern Zimbabwe intrude Precambrian basement gneisses some 200 km north of the Nuanetsi area (see Fig. 1) and are the time equivalents of the Mashikiri nephelinitic volcanics which initiated the Karoo magmatism in the NNL regions [22]. The carbonatite-bearing complexes of Dorowa and Shawa are associated with silica-undersaturated intrusives which occur as small plugs of olivine ijolite (Zwibe and Chikomo plugs) and a regional swarm of fine-grained nephelinitic dykes. The general geology of the complexes has been described by Johnson [23] and Lee [24].

The Dorowa Complex is essentially composed of a huge area of fenitised basement rocks approximately 3 km by 1.5 km in which a number of thin dykes and a small plug of carbonatite are found. Both calcitic and dolomitic carbonatites occur: the sample analysed in this study is a dolomite carbonatite from the plug. Fenite assemblages range from quartz syenitic through quartz-free syenitic (‘pulaskitic’) to nepheline syenitic.

Shawa is a circular plug-like intrusion some 5.5 km in diameter composed largely of serpentinised dunite surrounded by arcuate zones of ijolitic rocks on the southwestern and northeastern sides. Dolomitic carbonatite occurs as a steeply inclined ring dyke 1.6 km in diameter and 30–400 m in width in the centre of the dunite plug. The carbonatite is built of several periods of intrusion as evidenced by cross-cutting relationships between different phases of the generally well-foliated carbonatite types in the dyke. Numerous small unoriented carbonatite dykes cut the serpentinite. Three samples from the ring dyke were selected for analysis.

3.2. Nephelinites

Intrusions of general nephelinitic–ijolitic character occur in the form of a regional swarm of nephelinitic dykes and as two small circular plugs less than 100–150 m in diameter of olivine-bearing ijolite termed Zwibe and Chikomo. The Zwibe plug

occurs less than 1 km to the west of the southern edge of the Dorowa fenites whereas Chikomo lies some 4.5 km to the south-southeast. Both plugs are composed of coarse-grained ijolite in which forsteritic olivine (Fo_{70–85}) occurs with strongly zoned aegirine–augite, nepheline and biotite with minor amphibole, apatite and titanomagnetite.

Dykes of fine-grained, generally porphyritic nephelinite are commonly seen cutting the basement gneisses and Proterozoic dolerites of the Mashonaland Suite in most of the river beds between the Dorowa and Shawa complexes. Nepheline and aegirine–augite are the most common phenocryst phases while coarse apatite is commonly found as a phenocryst phase in some dykes. Samples used in this study are from the Hande and Murove rivers.

4. Geochemistry

Major and trace element analyses are tabulated in Table 1. A detailed discussion of the petrochemistry of the Buhera carbonatites and nephelinites is beyond the scope of the current communication; only a brief review of salient features will be presented.

4.1. Buhera ijolites and nephelinite dykes

Ijolites from the Chikomo plug have a very limited range in Mg# (45–50) and their high CaO, Ni and Cr contents suggest accumulation of olivine and clinopyroxene. Both the Zwibe ijolites and the nephelinitic dykes reflect substantially greater degrees of differentiation with Mg# varying from 44 to 20. Both Cr and Ni decrease by nearly two orders of magnitude with falling Mg# reflecting the fractionation of magnesian olivine. By comparison to the Mashikiri nephelinites [22], the Buhera rocks have similar Ni and Cr levels whereas TiO₂ contents are substantially depleted at equivalent Mg# relative to the volcanics. This is unlikely to reflect fractionation and is interpreted to indicate a source difference. CaO is higher and Na₂O lower in the Mashikiri volcanics.

Chondrite-normalised REE profiles (Fig. 3a) show the LREE enriched profiles typical of undersaturated alkaline rocks and lack Eu anomalies. Profiles of each sample suite are coherent and sub-parallel:

profiles remain parallel as REE levels increase systematically from La_N values of ± 20 in the Chikomo ijolites to ± 30 in the Zwibe ijolites and 35–50 in the nephelinitic dykes.

4.2. Carbonatites

The REE compositions of the carbonatites are compared to those in the nephelinites in Fig. 3b: Dorowa carbonatite ZD-13 has very similar REE contents to the nephelinitic dykes while Shawa carbonatites ZS-1 and ZS-2 differ from the silicates only in their elevated concentrations of the MREE. Sample ZS-4 (Shawa) has remarkably low concentrations of all REE: the lowest yet reported for an undoubted magmatic carbonatite. Extreme variability of P₂O₅ amongst the analysed carbonatites suggests apatite control: fractionation of apatite is consistent with the concave MREE profile in sample ZD-13 in Fig. 3b whereas accumulation of apatite in the Shawa carbonatites would explain the complementary convex MREE in ZS-1 and ZS-2.

5. Isotopic data

Isotopic data for the Buhera sample suite are presented in Table 2; analytical procedures and data assessments are provided in a footnote to the table.

5.1. $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$

The data are depicted on a conventional $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ plot in Fig. 4. The shaded field encompasses about 85% of all published data from world carbonatites less than 200 Ma in age [25,26]. The base of the field and its extension is parallel to the so-called 'East African Carbonatite Line' [27].

A profound distinction is evident between the isotopic compositions of the Shawa carbonatites and the nephelinitic intrusions. The three analysed dolomitic carbonatites from Shawa cluster at the high ϵ_{Sr} edge of the carbonatite reference field (within error of $\epsilon_{\text{Sr}} \approx +4$, $\epsilon_{\text{Nd}} \approx 0$) while the Dorowa carbonatite has similar ϵ_{Sr} but substantially more negative ϵ_{Nd} (–9). It is significant that ZS-4, the Shawa carbonatite with very low REE concentrations, is isotopically indistinguishable from the other Shawa

Table 1
Geochemical data for silicate and carbonatite rocks from the Buhera District, SE Zimbabwe

	Ijolites										Nephelinitic dykes						Carbonatites			
	Chikomo					Zwibe					Hande R.		Murwe		Dorowa		Shawa			
	ZCH-1	ZCH-2	ZCH-3	ZCH-5	ZCH-18	ZD-16	ZD-17	ZD-18	ZH-1	ZH-4	ZH-7	ZS-18	ZD-13	ZS-1	ZS-2	ZS-4				
SiO ₂	44.88	42.44	43.11	42.12	41.61	43.21	41.61	40.05	46.06	44.61	46.31	42.21	0.51	0.00	0.00	0.00				
TiO ₂	1.20	0.93	1.20	1.14	1.40	1.25	1.40	0.65	0.46	1.22	0.35	0.62	0.00	0.04	0.01	0.10				
Al ₂ O ₃	9.99	11.96	11.86	15.15	17.39	11.26	17.39	22.54	16.65	12.68	17.30	15.40	0.00	0.00	0.00	0.00				
Fe ₂ O ₃	10.30	9.34	10.16	8.35	9.10	10.98	9.10	6.56	6.86	9.68	6.43	9.23	2.76	4.30	3.92	6.82				
MnO	0.16	0.10	0.12	0.10	0.13	0.16	0.13	0.08	0.13	0.15	0.12	0.19	0.54	0.20	0.16	0.24				
MgO	11.03	10.15	9.63	8.59	9.79	9.79	4.25	2.35	3.17	5.80	2.78	3.80	14.87	18.78	17.65	16.87				
CaO	10.74	12.92	12.04	10.41	7.58	11.78	4.17	4.17	5.84	8.67	6.48	6.48	35.31	31.43	33.46	31.61				
Na ₂ O	7.08	8.07	7.69	9.54	7.32	7.32	11.59	14.85	12.81	7.83	12.24	10.97	0.07	0.04	0.05	0.01				
K ₂ O	2.00	1.83	1.93	1.97	2.86	1.90	2.86	3.43	2.26	1.81	2.17	1.20	0.00	0.00	0.00	0.00				
P ₂ O ₅	0.84	0.85	0.75	1.05	1.19	1.00	1.19	1.19	1.08	0.98	1.14	0.70	0.55	4.00	5.39	0.03				
H ₂ O	0.27	0.19	0.20	0.23	0.34	0.51	0.34	0.35	0.52	0.56	0.48	0.50	0.34	0.16	0.14	0.14				
LOI	0.63	0.66	0.65	0.71	2.24	0.67	2.24	3.20	3.74	5.46	3.91	7.96	43.81	40.43	38.55	43.30				
Total	99.12	99.44	99.34	99.36	99.68	99.83	99.68	99.42	99.58	99.45	99.71	99.26	98.76	99.38	99.33	99.12				
Ni	232	163	171	183	36	157	36	16	11	61	6	19	0	0	0	7				
Nb	33	8	10	14	26	24	26	34	62	43	53	58	6	7	6	14				
Zr	111	43	57	64	90	91	90	86	191	141	218	136	108	102	248	99				
Y	19	9	14	15	20	20	20	19	17	18	18	23	19	15	23	0				
Sr	633	365	451	406	713	607	713	734	798	822	621	636	2515	2061	1823	1966				
Rb	48	30	31	27	60	39	60	60	42	50	28	47	0	0	0	0				
U	3	4	10	7	5	7	5	0	2	10	3	8	1	2	0	3				
Th	1	3	0	0	0	7	0	3	2	6	8	8	0	0	1	4				
Pb	6	0	2	3	2	7	2	6	26	15	21	18	31	2	0	10				
Cr	560	428	527	326	40	430	40	7	3	50	1	7	0	6	5	3				
V	251	165	280	208	250	247	250	103	104	238	74	122	22	34	28	34				
Ba	1266	245	359	391	719	987	719	805	1462	1409	987	946	368	121	138	415				
La	11.6	6.4	7.0	7.7	10.8	10.0	10.8	11.6	15.3	18	13	13	41	18	15	2				
Ce	24.0	14.5	15.8	17.1	22.9	21.4	22.9	23.7	29.8	36.1	28.0	28.0	58.8	45.2	36.6	6.5				
Pr	3.0	2.0	2.2	2.2	2.9	3.0	2.9	3.0	3.9	4.6	3.6	3.6	5.9	7.2	5.0	0.9				
Nd	12.6	9.3	9.5	10.1	12.4	12.4	12.5	11.8	14.1	17.1	14.1	14.1	19.5	30.9	23.9	4.2				
Sm	2.5	1.8	1.9	2.1	2.7	2.5	2.7	2.3	2.6	3.1	2.8	2.8	3.2	7.3	6.0	0.8				
Eu	0.9	0.6	0.7	0.7	0.9	0.9	0.9	0.8	1.0	1.0	1.0	1.0	1.1	2.4	2.3	0.3				
Gd	2.7	2.1	2.1	2.3	3.0	2.8	3.0	2.6	2.9	3.2	3.0	3.0	3.2	6.6	7.1	0.9				
Dy	2.8	1.8	1.9	2.2	2.9	2.9	3.3	2.7	2.9	3.2	2.9	2.9	3.1	4.1	5.7	0.5				
Ho	0.5	0.3	0.3	0.4	0.6	0.6	0.6	0.5	0.6	0.6	0.5	0.5	0.6	0.6	0.9	0.1				
Er	1.5	0.8	0.9	1.0	1.6	1.5	1.6	1.4	1.6	1.6	1.4	1.4	1.5	1.2	1.7	0.2				
Yb	1.5	0.7	0.8	1.0	1.5	1.5	1.5	1.4	1.5	1.5	1.4	1.4	1.4	0.7	1.0	0.2				
Lu	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.0				

Major and trace elements (excluding RfF) were analysed on fused glass discs and pressed powder pellets by conventional XRF techniques by Rocklabs cc. Rare earth elements were determined by ICP-ES at Royal Holloway [41].

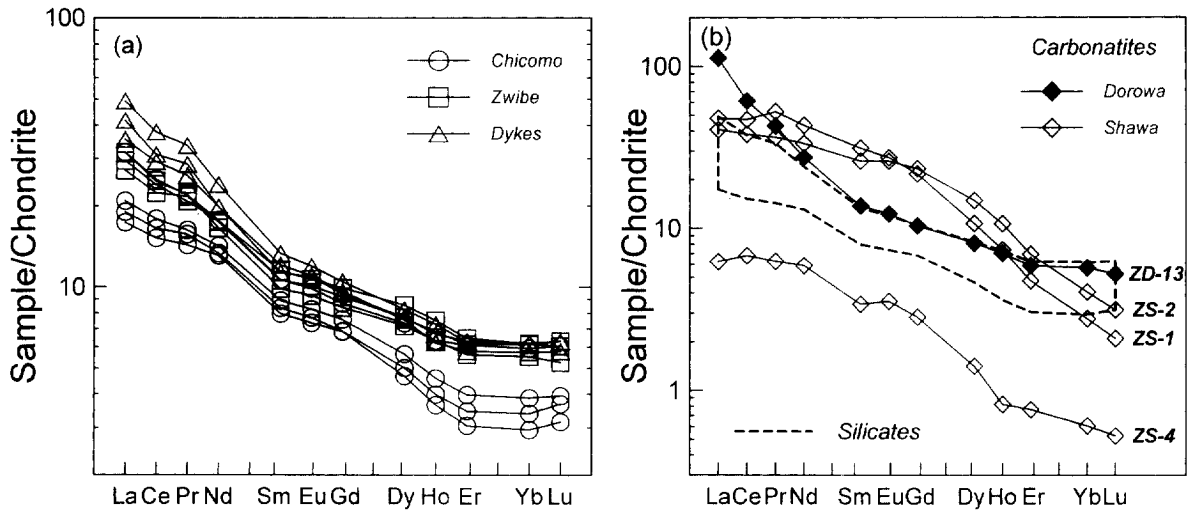


Fig. 3. Chondrite-normalised rare earth element variation diagram for data from: (a) the Chikomo and Zwibe ijolites and nephelinitic; (b) dolomitic carbonatites from the Shawa and Dorowa complexes (the dotted field bounds the REE variation in the ijolitic/nephelinitic rocks depicted in (a)).

carbonatites. The Buhera nephelinites have significantly less radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ (more negative ϵ_{Nd}) than the Nuanetsi picrites. Very little variation in $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ is evident within each of the suites of nephelinite samples; the Zwibe ijolites have the highest ϵ_{Nd} (-15), the Chikomo ijolites and the Hande

dykes have lower ϵ_{Nd} (-20), the dykes having the highest ϵ_{Sr} ($+20$).

5.2. $^{206}\text{Pb}/^{204}\text{Pb}-^{207}\text{Pb}/^{204}\text{Pb}-^{208}\text{Pb}/^{204}\text{Pb}$

Pb isotopic data for eight nephelinites and three carbonatites are shown in Fig. 5 in comparison to the established fields for rhyolitic and basic rocks from the Nuanetsi area. Present-day Pb ratios are plotted: no precise U/Pb or Th/Pb are available and it is not possible to estimate the degree to which these ratios might have been altered after emplacement. A vector is drawn on the $^{206}\text{Pb}/^{204}\text{Pb}-^{207}\text{Pb}/^{204}\text{Pb}$ plot indicating the magnitude of the 190 Ma correction for sample μ values of 0, 5 and 10.

The nephelinites have unradiogenic Pb: $^{206}\text{Pb}/^{204}\text{Pb}$ values vary from 17.2 to 17.6. While the uraniumic Pb ratios compare closely with the composition of the Nuanetsi picrites and mafic volcanics, $^{208}\text{Pb}/^{204}\text{Pb}$ is consistently lower than those noted in the picrites. Despite the marked contrast in ϵ_{Nd} between the Buhera nephelinites and carbonatites, no distinction in Pb isotopic composition is indicated: the carbonatites have slightly higher present-day $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than the nephelinites; however, adjusting these along 190 Ma sample isochrons suggests that their initial values are in-

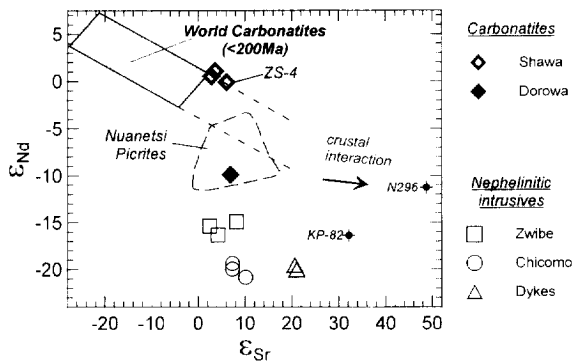


Fig. 4. $\epsilon_{\text{Sr}}-\epsilon_{\text{Nd}}$ plot of data for the carbonatites and nephelinitic/ijolitic intrusives from the Buhera District. The stippled rectangular field bounds over 85% of published analyses for carbonatites less than 200 Ma in age (see text). Shown for comparison is the field for the Nuanetsi picrites, interpreted as indicating mixtures of SCLM and sub-lithospheric plume reservoirs. Picrite sample N296 is crustally contaminated and so provides an estimate of the effect of crustal interaction [19]. All epsilon values are calculated at 190 Ma.

Table 2

Isotopic data for silicate and carbonatite rocks from the Buhera District, SE Zimbabwe

	Chikomo ijolite				Zwihe ijolite		
	ZCH-1	ZCH-2	ZCH-3	ZCH-5	ZD-16	ZD-17	ZD-18
$^{87}\text{Sr}/^{86}\text{Sr}$	0.705777	0.705631	0.705529	0.705410	0.705554	0.705430	0.705286
\pm	13	17	13	15	15	13	13
$\epsilon_{(\text{Sr})}$ 190 Ma	10.1	7.3	7.4	5.9	8.2	4.3	2.5
$^{143}\text{Nd}/^{144}\text{Nd}$	0.511475	0.511559	0.511532		0.511788	0.511726	0.511760
\pm	10	8	26		36	11	30
$\epsilon_{(\text{Nd})}$ 190 Ma	-20.8	-19.2		-19.8	-14.8	-16.2	-15.2
$^{206}\text{Pb}/^{204}\text{Pb}$	17.189		17.447	17.394	17.351		17.455
$^{207}\text{Pb}/^{204}\text{Pb}$	15.532		15.492	15.495	15.494		15.523
$^{208}\text{Pb}/^{204}\text{Pb}$	37.494		37.681	37.598	37.496		37.647

	Nephelinite dykes				Dorowa carbonatite	Shawa carbonatite		
	ZH-1	ZH-4	ZH-7	ZS-18	ZD-13	ZS-1	ZS-2	ZS-4
$^{87}\text{Sr}/^{86}\text{Sr}$	0.705253	0.706431	0.706283	0.704939	0.704851	0.704729	0.704672	0.704902
\pm	16	16	15	15	15	16	14	17
$\epsilon_{(\text{Sr})}$ 190 Ma	5.3	21.1	20.7	-1.6	6.9	3.7	2.9	6.1
$^{143}\text{Nd}/^{144}\text{Nd}$		0.511512	0.511549		0.512019	0.512636	0.512619	0.512540
\pm		10	25		14	8	9	21
$\epsilon_{(\text{Nd})}$ 190 Ma		-19.9	-19.4		-9.7	1.2	0.7	0.1
$^{206}\text{Pb}/^{204}\text{Pb}$	17.471	17.408	17.594		17.780	17.907	17.788	17.840
$^{207}\text{Pb}/^{204}\text{Pb}$	15.488	15.567	15.557		15.516	15.607	15.490	15.529
$^{208}\text{Pb}/^{204}\text{Pb}$	37.700	37.742	37.846		37.912	38.114	38.038	37.989

Analyses were performed in the laboratories of the Council for Geoscience using conventional techniques previously applied at the CSIR as described in Refs. [25,42]. After digestion in HF-HNO₃, Sr and total REE were eluted with 2.5 M and 6 M HCl from cation exchange columns packed with 6 ml of Bio-Rad AG50W-x12, 200–400# resin. Nd was purified on Teflon-supported HDEHP eluted with 0.4 M HCl. Pb was separated on micro-columns containing 40 μl AG1 \times 8 resin using 0.5 M HBr and H₂O. All isotopic analyses were determined on a Finnegan MAT261 multi-collector spectrometer operated in static mode: $^{87}\text{Sr}/^{86}\text{Sr}$ was measured on single Ta filaments; $^{143}\text{Nd}/^{144}\text{Nd}$ on double Ta-Re filament assemblages and Pb isotopes on single Re with silica gel. Instrumental fractionation of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ was corrected by normalising measured $^{86}\text{Sr}/^{88}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ values to 0.1194 and 0.7219, respectively. Pb ratios were corrected empirically by analysing the NIST standards (formerly NBS) SRM 981 and 982. Analytical errors (1σ) are better than 0.01% for $^{87}\text{Sr}/^{86}\text{Sr}$, 0.005% for $^{143}\text{Nd}/^{144}\text{Nd}$, 0.07% for $^{206}\text{Pb}/^{204}\text{Pb}$ and 0.1% for $^{207}\text{Pb}/^{204}\text{Pb}$ and 0.12% for $^{208}\text{Pb}/^{204}\text{Pb}$. Epsilon values are calculated at 190 Ma using the following values for the present-day composition of CHUR/Bulk Earth: $^{87}\text{Rb}/^{86}\text{Sr} = 0.0847$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7047$, $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.51264$. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were calculated using Rb/Sr determined by XRF ($\pm 1.5\%$ 1σ) and Sm/Nd by ICP ($\pm 1.0\%$ 1σ).

distinguishable. Also noteworthy is the fact that the Dorowa carbonatite has identical Pb isotopic composition to Shawa carbonatites ZS-2 and ZS-4.

6. Discussion

6.1. Are carbonatites the products of liquid immiscibility?

Conjugate silicate and carbonatitic liquids must be in chemical, and hence isotopic equilibrium at

the point of immiscible separation. Any difference in isotopic composition between associated carbonatite and silicate components of a complex would thus indicate either: (i) that if immiscibility occurred, contrasting trace element compositions of the carbonate and silicate fractions resulted in their isotopic compositions being modified to differing extents through interaction with country rocks; or (ii) that the carbonatite and silicate components are not related by immiscibility.

Option (i) is usually supported on the basis of the higher Sr and Nd concentrations in average car-

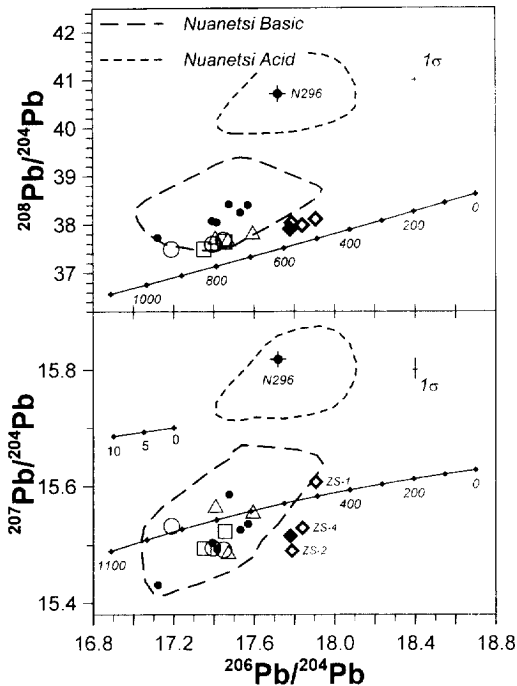


Fig. 5. $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ variation in the Buhera carbonatites and nephelinite/ijolites (symbols as in Fig. 4). Pb values are present-day values; the scale bar in the $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ plot indicates the magnitude of the correction for sample μ values of 0, 5 and 10. Fields for basaltic and rhyolitic volcanics from the NNL are shown for comparison (data from Ref. [28]) and data for the Nuanetsi picrites (present day) are shown as solid dots [19]. Note the substantial enrichments in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ in the contaminated picrite N296. Growth curves are calculated according the model of Stacey and Kramers [29]; tick marks are placed at 100 Ma intervals.

bonatites relative to average nephelinites and typical continental crust. However, as emphasized in Fig. 6, no substantial contrast in Nd composition exists between the Buhera nephelinites and the Dorowa and Shawa carbonatites. Carbonatite ZS-4 has lower Nd contents than all the nephelinites and yet has the same ϵ_{Nd} as the other Shawa carbonatites; Dorowa carbonatite ZD-13 has four times the Nd content of ZS-4 and yet has a substantially less radiogenic ϵ_{Nd} value of -10 . The Zwibe and Chikomo ijolite plugs have similar Nd contents, yet they differ in their isotopic compositions by 5 ϵ_{Nd} units.

Published experimental data which support the generation of carbonatite through liquid immiscibility were predominantly obtained at pressures of

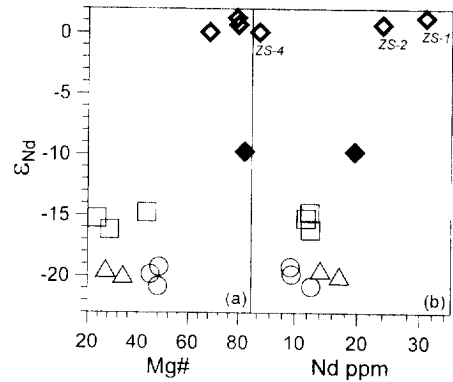


Fig. 6. Plot of (a) Nd concentration and (b) Mg# vs. ϵ_{Nd} for Buhera carbonatites and silicates. Symbols are as in Fig. 4.

below 0.5 GPa (e.g. [16,30]), equivalent to crustal depths; there is little evidence for carbonate immiscibility in realistic liquid compositions at mantle depths. A recent study has shown that the range of possible silicate liquids produced by melting carbonated mantle peridotite, and their differentiation products, do not intersect the miscibility gap at mantle pressures [31]. As a consequence, available experimental data suggest that silicate–carbonate liquid immiscibility is unlikely to occur during magmatic processes in the mantle but may be possible in the crust [31].

Data for NNL picrite sample N296 provide an indication of the influence of crustal interaction on Sr–Nd–Pb isotope patterns: this sample is plotted on the variation diagrams in Figs. 4 and 5 and shows that crustal contamination leads to significant increases in ϵ_{Sr} , $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$. The Buhera nephelinites show no evidence of such interaction. Contamination of silicate rocks is widely thought to occur through AFC type processes (e.g. [32]), heat of crystallisation providing the energy for the assimilation process. The Zwibe ijolites exhibit extensive degrees of internal differentiation with Mg# varying between 20 and 44 and yet these ijolites show a very limited range in ϵ_{Sr} – ϵ_{Nd} values. This observation suggests that differentiation essentially took place in a closed system and hence the isotopic signature of these, and by implication the other nephelinites, is a primary source feature which was not substantially modified during emplacement and crystallisation.

We therefore conclude that the marked distinc-

tion in $\varepsilon_{\text{Sr}}-\varepsilon_{\text{Nd}}$ between the Buhera nephelinites and carbonatites is a primary feature and provides unambiguous evidence against an association by liquid immiscibility: the Dorowa and Shawa carbonatites must have evolved from a primary carbonate magma not directly related to the silicate magma parental to the Buhera nephelinites.

Isotopic differences between carbonatites and their associated alkaline silicate are a feature of several other complexes as well: in the Napak (Uganda), Kerimasi (Tanzania) and Spitskop (South Africa) complexes silicate components (nephelinites, phonolites and intrusive equivalents) have $\varepsilon_{\text{Sr}}-\varepsilon_{\text{Nd}}$ values which are significantly more enriched than those of the carbonatites [26]. Unlike the Buhera complexes, however, the source of the 'enriched' end-member cannot be unambiguously constrained in these cases. We propose that the striking isotopic differences in the Buhera complexes is not unique but is simply a function of the presence of isotopically anomalous SCLM in this region: it is this isotopically anomalous mantle which exposes processes common to all carbonatites but which are masked in regions underlain by younger, less complex and isotopically uniform sub-continental lithosphere.

6.2. Source of carbonatite magmas

Combined geochemical and Sr, Nd, Pb and Os isotopic data for the Nuanetsi picrites and basalts indicate that these volcanics are derived from mixing between asthenospheric mantle ($\varepsilon_{\text{Nd}} \geq 0$) magmas and enriched SCLM-derived partial melts ($\varepsilon_{\text{Nd}} \ll 0$) [20,21]. The Buhera nephelinites have less radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ (more negative ε_{Nd}) than the picrites and thus must be predominantly derived from the enriched lithosphere. Conversely, then, the Shawa carbonatites are sourced predominantly from the sub-lithospheric material.

The consequences of these relationships are profound: clearly, the Shawa carbonatites must have existed as a *discrete carbonate magma* at depths in the mantle *below* that of the enriched zone sampled by the Buhera nephelinites and the NNL volcanics! The Dorowa carbonatite has $\varepsilon_{\text{Sr}}-\varepsilon_{\text{Nd}}$ values which are intermediate between the nephelinites and the Shawa carbonatites, equivalent to the Nuanetsi picrites. We interpret the Dorowa carbonatite data as

resulting from the incorporation of enriched lithospheric material during ascent. If the enriched reservoir producing the nephelinites is the entire SCLM then this requires that the ultimate source of the carbonatite magmas be below the lithosphere, i.e. from the asthenosphere.

The close similarity in Sr, Nd and Pb isotopic character between carbonatites and ocean island basalts (OIB) has been used as evidence that, like OIB, carbonatites were derived from sub-lithospheric plume material [33]. A carbonatite source in the convecting asthenospheric mantle would be consistent with the limited variability in $\varepsilon_{\text{Sr}}-\varepsilon_{\text{Nd}}$ observed in world carbonatites from widely divergent geographical regions having very different lithospheric ages and evolutionary histories. Less direct evidence for a plume source for carbonatites is the recent discovery of plume-like Ne isotopes in apatites precipitated in carbonatite-metasomatised mantle lherzolite xenoliths from Australia [34].

However, Sweeney et al. [35,36] argued that the sub-lithospheric component in the Karoo mafic volcanics is derived from a mantle segment more depleted than that of the source of oceanic islands: upwelling of asthenosphere during lithospheric attenuation is favoured over a deep-mantle plume.

Current experimental constraints on the $P-T$ conditions under which carbonatite melts exist in the mantle are summarised in Fig. 7. Magnesian carbonatite liquids are generated by melting carbonated peridotite at pressures of 2.1–3.2 GPa [1,2,4]; partial re-equilibration at pressures below 1.7 GPa shifts the melt to more calcic carbonatite compositions [3]. These pressures are equivalent to mantle depths of less than 100 km: most geophysical models would certainly consider the continental lithosphere to extend to greater depths than these.

The Buhera data essentially require that the $\varepsilon_{\text{Sr}}-\varepsilon_{\text{Nd}}$ signatures in the carbonatites be sourced from a reservoir which is discrete from, and deeper, than that from which the nephelinites were derived. (The enriched signature in the Dorowa sample relative to that from Shawa indicates that the enriched SCLM reservoir must have been accessible to the carbonatites during ascent.) If only the upper part of the SCLM is enriched and isotopically anomalous, then the carbonatites could conceivably be derived from lithospheric segments below the enriched zone.

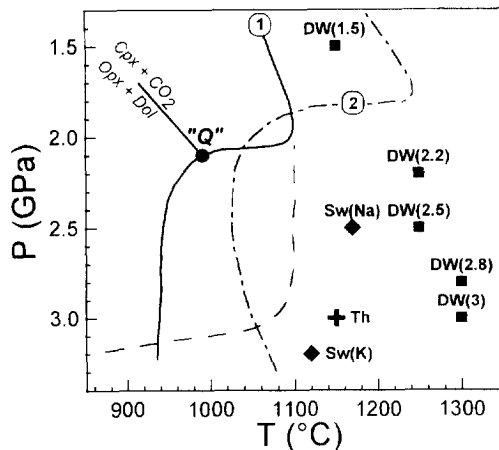


Fig. 7. Phase diagram depicting the P , T conditions under which carbonatite melts are in equilibrium with mantle peridotites of various compositions. The shaded area is the P - T region in which magnesian carbonate melt co-exists with amphibole lherzolite in the system Hawaiian pyrolite- CO_2 - H_2O ; curve (1) is the solidus for this system and Q is the invariant point marked by the intersection of the solidus with the carbonation reaction $4\text{Opx} + \text{Dol} = 2\text{Ol} + \text{Cpx} + \text{CO}_2$ [1]. Points labelled with the prefix DW (numbers in brackets indicate pressures in GPa) mark the equilibrium conditions for carbonate melts equilibrated with wehrlite (higher pressures) and harzburgite (low pressure); melts become progressively more calcic with falling pressure [3]. Sw [4] and Th [2] represent melts in equilibrium with phlogopite- ($Sw(K)$) and Th) phlogopite-pargasite-lherzolite ($Sw(Na)$). Curve (2) is the solidus for peridotite- CO_2 [40].

Experimentally determined solidi for various peridotite- CO_2 systems (see Fig. 7) all have a pronounced thermal maximum, or 'ledge', at ca. 2.0 GPa where the solidus intersects a series of carbonation reactions (e.g. [37]). Low-degree partial melts generated at pressures above 2 GPa should intersect this ledge on ascent and freeze. Those crossing the ledge at temperatures below that of the relevant invariant points, labelled 'Q' on one of the solidus curves shown in Fig. 7, will simply crystallise carbonate whereas at temperatures above Q carbonate disappears through metasomatic reaction with the release of free CO_2 . The trace of this ledge in a mantle- CO_2 system thus represents a zone in which extensive trace element fractionations and enrichments will occur: this zone has been called the 'metasome' [38]. Low-degree melts of peridotite (melilitites, nephelinites and carbonatites) at pressures above 2 GPa would be characterised by

highly fractionated LREE/HREE (very low Sm/Nd) and very slightly fractionated Rb/Sr relative to normal mantle [10,39]. Carbonatitic and melilititic to nephelinitic melts are known to be highly mobile through mantle peridotite and would thus be able to separate from the point of generation at melt proportions below 0.1% [9,10]. It is thus unlikely that the entire SCLM would be enriched by these melts: the melts are likely to rise through the lower SCLM and be preferentially retained in the vicinity of the thermal maximum in the peridotite- CO_2 solidus at 75 ± 5 km.

A mantle segment enriched by these melts will, with time, develop highly negative ϵ_{Nd} signatures at only moderately positive ϵ_{Sr} values: precisely the signature which characterises the anomalous SCLM reservoir sampled by the Karoo silicate lavas in the NNL and Buhera areas. The Buhera nephelinites have T_{CHUR} ages of up to 2600 Ma: since these old T_{CHUR} ages are not artefacts of crustal contamination, this anomalous SCLM reservoir could be produced by carbonatitic or nephelinitic melts trapped at the solidus ledge during the Palaeoproterozoic.

7. Conclusions

Geochemical and isotopic characteristics of nephelinitic intrusives in the Buhera district of SE Zimbabwe indicate that the enriched SCLM source identified in Karoo lavas of the North Lebombo-Nuanetsi region extend under the Zimbabwean Craton. Carbonatites from the Shawa Complex show no evidence of an enriched mantle reservoir and must be derived from a more depleted reservoir in the deep lithosphere or asthenosphere. Isotopic and geochemical differences between the Buhera carbonatites and nephelinites indicate that these lithologies are not related by liquid immiscibility. Rather, we propose that the carbonatites evolved from primary carbonate melts produced by melting of carbonated lithospheric peridotite at depths of 100 km or more whereas the nephelinites originated by melting of a previously enriched ± 75 km depth zone. There is no reason to suppose that the Buhera carbonatites are in any way unique: the substantial isotopic contrasts seen are a reflection of the highly anomalous nature of the sub-continental lithospheric mantle in

this region. We believe that the Buhera carbonatites evolved in the same way as other carbonatites: enhanced isotopic contrasts in the lithospheric mantle reveal processes common to all carbonatites but which remain undetected in regions where the upper mantle is more isotopically homogeneous.

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