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Ankerite carbonatite from Swartbooisdrif, Namibia: the first evidence for magmatic ferrocarbonatite

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Abstract Although general accounts of carbonatites usually envisage Ca-Mg carbonate melts evolving by fractional crystallisation to Fe-rich residua, there is longstanding concern that ferrocarbonatites may actually be products of hydrothermal rather than magmatic processes. All previously published examples of ankerite- and/or siderite-carbonatites fail to show one or more of the isotopic criteria (all determined on the same sample) thought to be diagnostic of crystallised magmatic carbonate liquids. Ferrocarbonatite dykes cut Archaean-Proterozoic basement at Swartbooisdrif, adjacent to the NW Namibia-Angola border. Their age is uncertain but probably ~ 1.100 Ma and their associated fenites are rich in sodalite. Where unaffected by subsequent recrystallisation, their petrographic textures resemble those of silicate layered intrusions; ankerite, magnetite and occasionally calcite are cumulus phases, joined by trace amounts of intercumulus pyrochlore. Ankerite is zoned, from Ca(Mg, Fe^{2+})(CO₃)₂ cores towards ferroan dolomite rims. Calcite contains $\sim 1.7\%$

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SrO, plus abundant, tiny exsolved strontianite grains. Magnetite is close to pure Fe₃O₄. Pyrochlore has finescale euhedral oscillatory zoning and light-REEenriched rims. ICP-MS analysis of magnetite and pyrochlore from the carbonatite allows calculation of their modal amounts from mass-balance considerations. Sodalite from the fenite is REE poor. Geothermometry, using either the calcite-dolomite solvus or oxygen isotope fractionation between calcite and magnetite, gives temperatures in the range 420-460 °C. Initial Sr, Nd and Pb isotopic ratios of the ferrocarbonatites $({}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.7033; \epsilon \text{Nd} = 0.2-1.0; {}^{206}\text{Pb}/{}^{204}\text{Pb} = 16.37;$ 207 Pb/ 204 Pb = 15.42; 208 Pb/ 204 Pb = 36.01) are appropriate for an \sim 1,100-Ma magmatic carbonatite. Likewise, carbonate $\delta^{18}O = 8.0$ and $\delta^{13}C = -7.36$ indicate little or no subsequent shift from magmatic values. It appears that dense ankerite and magnetite dominated crystal accumulation from a melt saturated in these phases, plus calcite and pyrochlore, with prior fractionation of a silicate mineral and apatite. The resulting ferrocarbonatite lacks a silicate mineral (excluding fenite xenocrysts) and apatite. It has unusually low (basalt-like) REE abundances and (La/Lu)_n, and low concentrations of Ba, Rb, U, Th, Nb, Ta, Zr and Hf. Very high Nb/Ta and low Zr/Hf imply that the evolution of the parental magma involved immiscible separation of a carbonate from a silicate melt. The sodalite-dominated Swartbooisdrif fenites suggest that the parental melt also had a substantial Na content, in contrast with the ferrocarbonatite rock.

Introduction

The existence of natural terrestrial Ca–Mg carbonate melts containing up to a few percent Fe oxide is generally accepted, and the lavas of Oldoinyo Lengai, Tanzania, are incontrovertible evidence of Na-rich carbonatite melts (Bell and Keller 1995). An array of volcanological, mineralogical and geochemical criteria, reviewed by Barker (1989, 1993), has been proposed for deciding whether an individual carbonatite occurrence has a magmatic origin. Experimental studies of appropriate synthetic systems have also shown clearly that a "magmatic" carbonatite may not necessarily ever have been all-liquid melt because crystal accumulation processes appear to operate efficiently in carbonate melt systems (Lee and Wyllie 1998; Petibon et al. 1998; Lee et al. 2000).

Minor ankerite- and siderite-carbonate rocks occur in many complexes dominated by Ca-Mg carbonatite. Within a magmatic carbonatite framework, such ferrocarbonatites are generally seen as the low-temperature product of fractional crystallisation of Ca-Mg carbonate melts (e.g. Le Bas 1977, 1981, 1989; Gittins 1989; Cooper and Reid 1998; Le Bas 1999). This process is usually inferred to concentrate Fe, Mn, Co, Cr, V, Ba, Th, Pb and light rare-earth elements (REE) in ferrocarbonatites, whereas Ti, P, Ni, Sr, Nb, Ta, Zr, Hf, U and heavy REE behave more erratically (e.g. Le Bas 1989; Woolley and Kempe 1989; Cooper and Reid 1998; Le Bas 1999). Nevertheless, some carbonatite specialists are sceptical as to whether Fe-rich carbonate magmas exist. Thus, Barker (1993) followed von Eckermann (1948) and others in doubting the magmatic parentage of most, if not all, ankerite and siderite carbonatites, and Bailey (1993) did not discuss ferrocarbonatites at all in a detailed review of carbonate magmas. The lack of convincing erupted ferrocarbonatites and the difficulties encountered by experimentalists trying to study ironbearing carbonate melts (e.g. Lee et al. 2000) have both weakened the case for ferrocarbonatite magmas. Another recent approach (Gittins and Harmer 1997) took the IUGS classification system of carbonatites (Le Maitre 1989; Woolley and Kempe 1989) to task for permitting too many diverse carbonatites to be named

ferrocarbonatite. Their revised nomenclature (see below) reclassified all previous ferrocarbonatites except a trio of African siderite carbonatites: Buru, Chilwa and Kugwe. All three have C–O isotopic ratios indicating extensive interaction with hydrothermal systems (see below).

Here we describe intrusive ankerite-magnetite-calcite carbonatite, with a trace of pyrochlore, from Swartbooisdrif, NW Namibia, and show that this example possesses all the mineralogical and geochemical features suggested by others for carbonatites of magmatic origin. Furthermore, it classifies (marginally) as ferrocarbonatite in the Gittins and Harmer (1997) nomenclature (see below). However, we shall argue that the rock has a cumulate texture (although with local subsolidus recrystallisation) and that its mineral proportions, and hence bulk composition, are therefore not necessarily those of the melt from which it accumulated.

Swartbooisdrif

All of the well-known carbonatites in the northern half of Namibia are Cretaceous in age and lie within the E–W branch of the Neoproterozoic-Cambrian, Pan-African Damara mobile belt at 20–22°S (Verwoerd 1986, 1993; Horstmann and Verwoerd 1997; Harris and le Roex 1998; le Roex and Lanyon 1998). At least two Precambrian carbonatites occur within older Namibian basement terranes to the south (Horstmann and Verwoerd 1997). Apart from a Pan-African coastal strip ~100 km wide, northernmost Namibia is underlain by Archaean-Proterozoic basement of the Congo craton. Carbonatites and syenites are emplaced in the cratonic basement adjacent to the Angolan border, ~200 km inland from the Atlantic coast, in the Epembe-Swartbooisdrif area (Fig. 1). This is the southern end of an

Fig. 1. Sketch map of the Epembe-Swartbooisdrif area, simplified after Menge (1986) and 1:500,000 Tactical Pilotage Chart P3B (Defense Mapping Agency Aerospace Center 1991). GPS co-ordinates for the Swartbooisdrif Mine are 17°20'26.0" south and 13°46'59.5" east (using the WGS 84 datum). Geological formations are not differentiated in Angola, and the Dwyka sediments are not discussed in this report



elongate group of more than 35 alkalic complexes – 10 containing carbonatites – which extends for \sim 800 km northwards into Angola (Issa Filho et al. 1991; Alberti et al. 1999). Although the Epembe and Swartbooisdrif groups of intrusions have been previously treated as separate complexes, 30–40 km apart (e.g. Tuttle and Gittins 1966), it is apparent from Fig. 1 that their plutons approach to within 20 km. It is therefore probably appropriate to view this isolated syenite-carbonatite field as a single suite (Verwoerd 1993; Von Seckendorff et al. 2000), unless future radiometric dating separates the subgroups.

The gneiss-amphibolite basement in this part of Namibia, Kaokoland, has recently yielded radiometric dates of \sim 2,600 Ma, with evidence of an older protolith (Seth et al. 1998). In the Epembe-Swartbooisdrif region (Fig. 1), the basement is intruded by the 1,155-Ma anorthosite-leucotroctolite Kunene complex (Menge 1986; Alberti et al. 1999; Von Seckendorff et al. 2000). Radiometric ages of ca. 1,100 Ma have been obtained from biotite and zircon in Epembe alkaline rocks (quoted by Menge 1986) but published details are lacking and there has been controversy as to whether or not the intrusions might instead be part of the early-Cretaceous Etendeka magmatism (Verwoerd 1993); the northernmost Etendeka lava outliers are ~100 km SW of Epembe. Our limited fieldwork at Swartbooisdrif failed to locate any samples which can be dated but our structural observations (see below) are consistent with a Precambrian age for the emplacement of the carbonatites, during the final stabilisation of the Congo craton.

Small quarries at Swartbooisdrif expose the relationship between carbonatite dykes and the surrounding Kunene-complex anorthosites. The carbonatites form a dense plexus of planar to contorted dykes and dykelets, up to 2 m thick, together with irregular amorphous bodies of similar size. Local weak flow-banding occurs within the dykes. Swirling planar structures, some marked by small fenitised xenoliths, are also seen on a scale of 20-30 cm in some places and suggest that the carbonatite was a melt. Much of the carbonatite is pale buff and uniform in hand specimen, with only a few percent of magnetite scattered evenly throughout. Elsewhere, deep-blue sodalite is a variable additional phase; it is absent from some carbonatite dykes but chokes others with crystals up to several cm in size, which are often brecciated.

The coarse granular Kunene anorthosite host rock between carbonatite dykes has been fenitised in a zone which is typically about ten times wider than the dyke. The fenite is dark and foliated, contrasting with the anorthosite. Locally intense shear zones develop within the fenite. It appears that the carbonatite was emplaced when the region was undergoing deformation, and that recrystallisation during fenite formation allowed local shearing to take place. Menge (1986) described sodalite, albite, analcite, cancrinite, biotite and riebeckite from the fenites. Von Seckendorff et al. (2000) have recently published a detailed study of oxide and sulphide minerals in the fenites; their report includes a new map of the Swartbooisdrif area. The blue tint of the sodalite fenite, plus monomineralic pods of sodalite up to 8 m in size (Menge 1986) make this locality a source of both ornamental and semiprecious stone. Sparse < 20-cmthick hypersthene-phyric basaltic dykes cut both carbonatites and fenites.

Petrography and mineralogy

We collected the most homogeneous sodalite-free carbonatite. Nevertheless, thin sections showed abundant, disaggregated fenitised anorthosite in all but two samples, PB24 and PB29. Our petrography is based on multiple thin sections of these and PB27, a composite sample of an \sim 2-cm-wide carbonatite vein cutting fenite. PB24 and PB29 show considerable section-to-section modal and textural variation. Ankerite predominates, together with a few percent each of calcite and magnetite, traces of albite and quartz, and very rare pyrochlore. The overall carbonatite texture strongly resembles that of silicate cumulate rocks in a layered intrusion. Thus, most of the ankerite forms <4-mm subhedra with (calcite-free) intergrown margins (i.e. "adcumulus"). However, in up to $\sim 10\%$ of each thin section, smaller (<1.5 mm) ankerite subhedra are surrounded by interstitial calcite. Furthermore, calcite subhedra (<1.5 mm) occur within these "orthocumulate-textured" areas, with a frequency varying from zero to ~ 10 per section (each section 5–6 cm²). In hand specimen the < 3-mm magnetite euhedra appear to be evenly distributed through the carbonates but their abundance ($\sim 10\%$ overall) is extremely variable on a thin-section scale. Magnetites <2 mm in size are mostly octahedra, whereas larger crystals have outgrowths into interstitial areas between neighbouring ankerites.

Sparse, irregularly rounded albite and quartz grains are scattered throughout PB24 and PB29. In PB27 the "orthocumulate" texture predominates - subhedral ankerite, magnetite and calcite with interstices filled by the same phases. Where contacts between carbonatite veins and fenite cross thin sections, grains of quartz and albite may be seen at all stages of detachment from the altered basement gneisses and incorporation into the carbonatite. The other distinctive feature of PB27 is pyrochlore in < 0.5-mm, honey-brown octahedra, with abundance varying in a thin section from zero to clusters of 20–30 crystals. Modal abundances (wt%) of pyrochlore and magnetite are estimated below by chemical mass-balance calculations. Both the cumulate-like textures of these carbonatites and the lack of either any eu-subhedral silicate mineral or apatite (Wyllie 1989; Lee and Wyllie 1998; Petibon et al. 1998; Lee et al. 2000) are evidence that they are not simply frozen samples of Fe-rich carbonate liquids. Instead, they appear to be accumulations of phenocrysts (subsequently partially recrystallised) from a melt which was saturated with ankerite, calcite, magnetite and possibly pyrochlore. The site of the crystal accumulation is discussed further below.

Mineral compositions

Most mineral analyses were made using electron microprobes at Cambridge and Manchester universities (see Appendix for details). In addition, separated grains of magnetite and pyrochlore in the carbonatite, and sodalite in the fenite, were analysed by ICP-MS at Durham (Appendix). Representative microprobe analyses of carbonates and Fe-oxides are given in Table 1, and the ICP-MS results (together with microprobe data for pyrochlore) in Tables 2 and 3.

Ankerite

The ankerite subhedra are concentrically zoned (Table 1), with FeO varying outwards from about 17.4% (core) to 12.6% (rim), MgO 8.6 to 11.3%, CaO 26.8 to 28.0%, and MnO 2.2 to 3.0%. Figure 2 plots the principal elements involved in this zoning: Mg, Mn and Fe. The cation sums of individual analyses do not vary sufficiently from 6.0 to justify using stoichiometry to estimate Fe^{3+} ; all the Fe is therefore treated as Fe²⁺. Mn, like Mg, is relatively enriched in crystal rims and therefore these two cations are grouped on Fig. 2, rather than the conventional (Fe^{2+} + Mn) grouping. This diagram shows that the zoning is between ankerite crystal cores and rims which show extensive solid solution towards dolomite. We note that, if the zoning data were not available to guide our choice of how to treat Mn, the conventional (Fe^{2+}) + Mn) grouping produces ankerite crystal core analyses with 1.70 cations p.f.u. of $(Fe^{2+} + Mn)$. This equals the most "Fe-rich" ankerite solid solution known (Goldsmith 1983). SrO varies from 0.43 to 0.68%, with core values which are generally higher than rims but the zoning is not entirely progressive. Sparse tiny ($< 10 \mu m$) strontianite grains in the ankerite may be products of local exsolution (see below). SiO₂ is undetectable in crystal cores and just detectable ($\sim 0.1\%$) in outermost zones.

Calcite

Both subhedral and interstitial calcite are rich in SrO (~1.7%), despite also containing abundant <10-µm exsolved strontianite grains (cf. Dawson et al. 1996). Crystals lack clear radial zoning in general but cathodoluminescence reveals that a few of the largest grains have relatively Fe-rich cores. Microprobe analyses show trends of rising MgO (0.3 to 0.7%) and FeO (2.5 to 3.9%), correlated with falling CaO (51.9 to 50.3%). MnO ranges from 1.7 to 1.9% but independently from the other major oxides. The partitioning of Fe, Mn and Sr between Swartbooisdrif calcite and

	27 hem3	0.01		<u>99.60</u>	0.06	0.91	I	1	I	0.01	I	I	I	100.59
gnetite Hematite	27 1em2	0.00	10.0	00.36	0.04	0.91				0.07			1	01.40
	B27 tem1	0.01		00.15 1	0.02	0.91				0.01				01.10 1
	7 F agr3 h			9.11 1	0.02	0.87	0.03 -	I	0.03 -	0.16	I	I		0.22 1
	7 2 agr2 ma		I	9.26 6	0.07	0.89 3	0.03	Ι	0.04	0.21	Ι	Ι	I	0.50 10
	7 2 ıgr1 má		I	9.21 6	0.02	0.82 3	0.02	I	0.02	0.24	I	I	I	0.33 10
	7 2 1gc3 ma		I	9.43 6	0.02	1.23 3		I	0.01	0.01	Ι	Ι	I	0.70 10
	7 2' igc2 ma		I	9.28 6	0.10 (1.22 3	I	I	•	•	I	I	I	0.60 100
	27 2' gc1 ma		I	30 6	0.02 (1.18 3	- 10.0	Ι	- 40.0	Ι	Ι	Ι	I).55 100
on- Mâ	27 PB ma		I	69	U	01 31	02	02 -	U	55 -	94 –	02 -	I	56 100
Str.			I	Ι	I	6 0.0	0.0	13 0.(I	0.0	58.	0.0	I	11 59.
G	27 1 calc		I	Ι	I	0 2.6	7 1.7	6 0.4	I	7 51.2	a	I	I	0 56.0
	27 calc⁄		I	I	I	5 2.7	3 1.6	9.0	I	1 51.8	a	I	I	56.7
	27 calc3	1 1	I	I	I	3.16	1.68	0.48	I	51.34	e	I	I	56.66
	27 calc2		I	Ι	I	3.87	1.82	0.70	I	50.29	a	I	I	56.68
Calcit	PB27 calc1		I	I	Ι	2.72	1.80	0.47	Ι	51.81	1.65	Ι	I	58.45
	27 ankr6	0.01	I	I	I	12.58	3.03	11.28	Ι	27.79	0.51	Ι	I	55.20
	29 ankr5	0.01	I	Ι	Ι	12.85	2.96	10.94	I	27.74	0.54	I	I	55.04
	27 ankr4	0.01	I	I	I	12.99	2.92	10.84	Ι	27.46	0.45	Ι	I	54.67
	27 ankr3		I	Ι	Ι	13.40	2.93	10.75	Ι	27.90	0.50	I	I	55.48
	29 ankr2	0.01	1	I	I	13.57	3.08	10.45	I	27.55	0.43	I	I	55.09
	27 ankr1	0.01	1	I	I	12.86	2.72	10.96	I	27.99	0.55	I	I	55.09
	27 ankc6		1	I	I	15.47	2.78	9.37	I	27.35	0.44	I	I	55.41
Ankerite	27 ankc5		1	I	I	16.07	2.60	8.89	I	27.60	0.49	I	I	55.65
	27 ankc4		1		1	17.17	2.61	8.67	1	26.75	0.63	I	I	55.83
	27 ankc3					17.25	2.38	8.83		27.07	0.61			56.14
	9 unkc2					7.39	2.32	8.62		06.90	0.50		1	55.73
	PB27 2 ankc1 a		I	1	1	17.18 1	2.24	8.94	1	26.79 2	0.68	1	1	55.83 5
Mineral	Sample	SiO ₂ TiO	Al,0,	Fe_2O_3	Cr_2O_3	FeO	MnO	MgO	NiO	CaO	SrO	Na ₂ O	K ₂ O	Total

Representative electron microprobe analyses of minerals in Swartbooisdrif ferrocarbonatites (Fe₂O₅ calculated from stoichiometry; see Appendix for analytical techniques). c

Crystal core, r crystal rim

Fable 1.

'SrO not determined

Table 2. ICP-MS analyses of Swartbooisdrif mineral separates. *nd* Not detected (< 0.01 ppm in most cases). δ^{18} O was determined on hand-picked magnetite (see text)

Method	ICP-MS								
Mineral Sample Rock-type	Magnetite PB29 Carbonatite	Sodalite PB31 Fenite	Pyrochlore ^a PB27 Carbona- tite						
$wt\% \\ TiO_2 \\ MnO \\ Nb_2O_5 \\ Ta_2O_5 \\ \end{cases}$	0.04 0.01	0.00 0.01	1.92 0.07 65.50 0.15						
ppm Ba Cr Cu Ga Hf Nb Ni Pb Rb Sc Sr Ta Th U V Y Zn Zr La Ce Pr Nd Sm Eu Gb Dy Ho Er	6.8 111 nd 13 nd 8.5 287 0.11 nd 0.2 13.6 0.05 0.03 nd 335 0.07 85 0.05 0.13 0.29 0.04 0.13 0.29 0.04 0.13 0.02 nd nd 0.2 0.11 0.05 0.05 0.13 0.29 0.04 0.13 0.02 nd 0.02 0.01 0.05 0.05 0.11 0.05 0.02 0.01 0.02 0.02 0.04 0.02 0.01 0.01 0	31 nd 9.1 27 0.02 0.86 nd 1.3 0.08 0.3 35 0.02 1.1 nd 0.61 nd 0.93 2.6 4.5 0.49 1.7 0.27 0.08 0.18 0.03 0.10 0.02 0.07	8,080 8.4 50 3.2 11.0 As oxide 19.8 2,850 15.1 61 1,8530 As oxide 1,140 8.9 5 5 5 5 5 5 5 5 5 5 5 5 5						
Tm Yb Lu $\delta^{18}O$	nd 0.01 nd -3.12	$0.01 \\ 0.04 \\ 0.01$	ь b						

^aListed pyrochlore element/oxide abundances are suspect unless microprobe probe data are also available. Nevertheless, they give abundance data for elements not usually analysed in this mineral (see text)

^bICP-MS analysis of the 2-mg pyrochlore separate was complicated by a white precipitate which appeared to redissolve in a trace of HF. All these element abundances were extremely low and are assumed to be absorbed on traces of precipitate

ankerite is similar to that of the calcite-dolomite pairs in African carbonatites studied by Dawson et al. (1996).

Strontianite

The strontianite grains within calcite are so small that all analyses (Table 1) must be suspected of contamination by the $CaCO_3$ matrix. Light-REE peaks are visible in the EDS spectrum of this phase.

Magnetite

The magnetite is close to pure Fe_3O_4 (Table 1). Crystal cores contain no detectable SiO₂, Al₃O₃ or MgO, and TiO₂, Cr₂O₃, V₂O₅, CaO, MnO and NiO are all close to microprobe detection limits. TiO₂ remains < 0.01% near crystal margins, whereas Cr₂O₃, MnO and NiO seem to rise very slightly, to 0.02-0.04%. Only CaO appears to rise appreciably, with corresponding slight falls in FeO. We consider this to be due to secondary fluorescence from nearby ankerite, rather than CaO zoning in the magnetite, because the marginal CaO values are very variable (0.15–0.53%). A few magnetite crystals are partially replaced by small irregular areas of hematite. This is pure Fe_2O_3 (Table 1), except for trace amounts of TiO₂, Cr₂O₃ and V₂O₅. ICP-MS analysis of the magnetite (including the small hematite patches) shows low Ba and Sr contents (Tables 2 and 3) which probably relate to sparse, tiny carbonate inclusions, visible in polished sections. If the limiting assumption is made that no Ni or V entered the carbonates, the Ni and V contents of the ferrocarbonatite (Table 4) and its magnetite (+ hematite) can be used to calculate the modal amount (wt%) of the latter. The approximate mode of 10%magnetite is probably better constrained than can be obtained by volumetric analysis of this irregularly distributed phase. The light REE, Er and Yb in the magnetite define a normalised REE pattern with $(La/Yb)_n \sim 10$ (Fig. 3b). Finally, a single ~ 20 -µm interstitial crystal of rutile with detectable Nb was found.

Pyrochlore

The euhedral pyrochlore octahedra have prominent oscillatory zoning (cf. Hogarth et al. 2000). Tables 2 and 3 includes both microprobe and ICP-MS data, together giving a comprehensive analysis of this mineral. Nb abundance in the ferrocarbonatite rock is rather variable (Table 4), with an average of 18 ppm. Even if the carbonates and magnetite are assumed to be Nb free, the maximum amount of pyrochlore in the ferrocarbonatite cannot be more than ~ 0.004 wt%. The element abundances in Swartbooisdrif pyrochlore can be matched by examples from published analyses of this variable phase (e.g. Hodgson and Le Bas 1992; Williams 1996; Williams et al. 1997; Hornig-Kjarsgaard 1998; Hogarth et al. 2000; Nasraoui and Bilal 2000; Seifert et al. 2000). PB27 has notably high contents of Na₂O and F (Tables 2 and 3). Thin outer rims of crystals in PB24 are LREE rich (Tables 2 and 3).

Sodalite

This mineral dominates the fenites surrounding the ferrocarbonatite dykes and many veins are carbonatitesodalite mixtures. Trace elements were determined on hand-picked grains by ICP-MS, in order to see whether

Table 3. Electron microprobe data for pyrochlore

Label	Microprobe Pyrochlore PB27										
	Core pb27-12	Core pb27-4	Core pb27-9	Rim pb27-2	Intermediate pb27-3	Rim pb27-10	Intermediate pb27-11	Rim pb24-1			
F	4.9	5.5	5.5	5.0	5.9	5.4	6.2	3.6			
Na ₂ O	8.8	8.5	8.7	8.6	8.6	8.5	8.6	7.8			
Al_2O_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
SiO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			
CaO	13.2	13.7	13.9	14.3	14.3	13.8	13.8	13.1			
TiO ₂	1.6	2.0	1.4	1.4	2.2	1.4	2.1	1.6			
Fe ₂ O ₃	0.2	0.0	0.1	0.1	0.0	0.1	0.1	0.3			
SrO	1.5	1.5	1.4	1.3	1.3	1.4	1.5	1.6			
Y_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2			
Nb ₂ O ₅	67.4	67.2	68.4	68.4	67.9	68.6	67.0	71.1			
La_2O_3	0.6	0.5	0.4	0.3	0.3	0.4	0.5	0.8			
Ce_2O_3	1.3	1.1	0.8	0.6	0.7	0.8	0.9	1.4			
Nd_2O_3	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.6			
Ta_2O_5	0.3	0.0	0.0	0.2	0.0	0.1	0.0	0.0			
PbO	0.1	0.0	0.2	0.2	0.1	0.1	0.1	0.1			
ThO ₂	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.0			
UO_2	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0			
Total	100.5	100.7	101.3	101.1	101.7	101.0	101.2	102.2			
Recalc- $O = F$	2.1	2.3	2.3	2.1	2.5	2.3	2.6	1.5			
Corrected total	98.4	98.4	99.0	99.0	99.3	98.7	98.6	100.7			

Fig. 2. Cation proportions of Mg + Mn and Fe (O=6) in Swartbooisdrif ankerite (Table 1)



this phase acts as a major host for any unexpected elements. Most trace-element abundances are <1 ppm (Table 2 and 3).

Mineral-equilibria thermometry

We have used two approaches in attempting to derive estimates of ferrocarbonatite palaeotemperatures from mineral equilibria.

- 1. The calcite-dolomite geothermometer may be used, provided the effect of Fe on this solvus is recognised and calibrated. Experimental studies by Powell et al. (1984) and Anovitz and Essene (1987) give this calibration.
- 2. Oxygen isotopic ratios were determined for separated carbonates and magnetite from sample PB29 (Tables 2 and 3). Although we are aware of no published data for oxygen isotopic equilibria between ankerite and magnetite, the δ^{18} O fractionation between dolomite and calcite is relatively small (e.g. 0.50 at 450 °C;

Table 4. Whole-rock analyses of Swartbooisdrif carbonatites and carbonatite-fenite mixtures (total Fe as Fe_2O_3 ; see Appendix for discussion of analytical techniques used for PB24 and PB24a)

Sample	PB24	PB24a	PB27	PB28	PB29
(wt%)					
SiO ₂	3.23	2.99	10.37	18.33	3.14
TiO	0.01	0.01	0.02	0.18	0.01
A1.O.	0.60	0.67	2.78	5.42	0.01
$A_{12}O_3$	10.47	10.20	2.70	19.26	10.10
Fe_2O_3	19.47	19.29	17.55	18.30	19.19
MnO	2.16	2.23	1.97	1.72	2.24
MgO	8.05	8.11	7.50	6.15	8.43
CaO	27.36	27.58	24.04	19.33	26.96
Na ₂ O	0.42	0.47	1.68	3.19	0.24
K ₂ O	0.01	0.00	0.01	0.04	0.01
$P_2 O_5$	0.02	0.01	0.03	0.03	0.02
BaO		0.01			
SrO		0.32			
LOI ^a	37.68	37.68	33.08	26.61	38.26
Total	00.10	00.37	00.02	00.35	08 77
Total	<i>99.10</i>	99.37	99.02	99.55	90.77
(ppm)					
Ва	146		185	169	156
Cr	27		58	38	17
Cu	8		2.5	7.1	3.1
Ga	7.8		8.6	13.3	5.9
Hf	0.10		0.11	0.09	0.10
Nb	15.2		120	136	22.3
NG	27		40	27	20
Dh	16.6		+0	18.0	20.4
PU D1	10.0		19.0	18.9	20.4
Rb	0.22		0.49	0.44	0.18
Sc	12.7		11.9	16.3	12.3
Sr	5,105		6,085	4,487	5,062
Та	0.03		0.05	0.18	0.06
Th	0.65		1.99	4.39	0.51
U	0.05		0.27	0.19	0.02
V	27		37	69	25
Y	28.5		44.1	36.5	38.8
Zn	101		149	164	205
Zr	0.98		3.20	2.79	2.08
La	44.1		55.0	129	55.1
Ce	101		123	214	126
Pr	12.3		16.0	23.6	16.1
Nd	47.3		61.4	79.0	60.7
Sm	8 70		11.65	11.88	11 /3
5m Fu	2.85		4.06	2.60	2 71
Gd	2.85		4.00	0.07	0.65
Th	1.06		10.03	9.27	9.03
10	1.00		1.00	1.57	1.45
Dy	5.68		8.37	/.15	/.46
Ho	1.02		1.63	1.34	1.40
Er	2.66		4.00	3.33	3.52
Tm	0.41		0.69	0.57	0.57
Yb	2.48		4.04	3.21	3.43
Lu	0.38		0.66	0.52	0.52
Isotopic ratio ^b					
87g /86g	0.70227				0 70222
Sr/Sr_m	0./032/				0.70332
$^{\circ}Rb/^{\circ}Sr_{m}$	0.0001				0.0001
$^{143}Nd/^{144}Nd_{m}$	0.512079				0.512053
$^{147}Sm/^{144}Nd_{m}$	0.1123				0.1138
${}^{87}{ m Sr}/{}^{86}{ m Sr}_{ m i}$	0.70327				0.70332
¹⁴³ Nd/ ¹⁴⁴ Nd	0.51127				0 51123
ϵNd	1.0				0.2
206 Ph / 204 Ph	16.47				16.22
$207 \mathbf{p}_{h}/204 \mathbf{p}_{h}$	10.47				10.52
$208 \text{ p}_{h}/204 \text{ p}_{h}$	26.14				13.42
206p1 /204p1	30.14				30.11
$\frac{100}{207}$ PD/ $\frac{204}{204}$ PDi	16.44				16.31
$\frac{207}{208}$ Pb/ $\frac{204}{204}$ Pb _i	15.40				15.42
²⁰⁰ Pb/ ²⁰ Pb _i	36.01				36.02
$\partial^{10}O$	8.12				7.90
∂ ¹³ C	-7.37				-7.36

 a LOI is loss on ignition (see text for discussion). Brod (1999) showed that carbonatite LOI is about 1% less than CO₂ determination ^bRadiogenic isotopic ratios corrected to age 1,100 Ma. Stable isotopic ratios determined on carbonates

(see text)



Golyshev et al. 1981). We therefore calculated palaeotemperatures for Fe-rich calcite cores from calcite-magnetite oxygen-isotope equilibria (Chiba et al. 1989; Clayton and Keiffer 1991).

Despite our reservations about each individual calculation, all four methods (two using each approach) gave answers within the temperature range 420–460 °C. These compare with the measured liquidus temperatures of 550-600 °C for Oldoinyo Lengai natrocarbonatite magmas (Pinkerton et al. in Bell and Keller 1995), and support the view that this carbonatite has undergone relatively little low-temperature alteration.

Chemistry

We analysed four bulk-rock samples for major and trace elements. Two of these, PB27 and PB28, had high enough SiO₂ contents that they were either silicocarbonatites or mixtures of carbonatite and fenite. Once certain that the second explanation was the correct one (based on petrography), we determined both stable and radiogenic isotopic ratios in the two SiO₂-poor samples, PB24 and PB29 (Table 4). Major elements were determined by XRF and trace elements by XRF and ICP-MS (see Appendix for details).

Major elements

 SiO_2 in PB24 and PB29 is typical for a carbonatite but we showed above that none of the major minerals analysed contained enough SiO₂ to account for this concentration in the rock. At Swartbooisdrif the SiO₂ (and Al_2O_3) seems to be almost entirely accounted for by fenite feldspar and quartz xenocrysts. Total iron as Fe₂O₃, MgO, CaO and Na₂O are similar to the mean ferrocarbonatite values suggested by Woolley and

Kempe (1989) but TiO₂, K_2O and P_2O_5 are at the low end of the range in their compilation. The high MnO is characteristic of ferrocarbonatites (Woolley and Kempe 1989) and our mineral analyses show that it is hosted by both ankerite and calcite (Table 1). Swartbooisdrif classifies as a ferrocarbonatite in the IUGS system (Le Maitre 1989), and it falls on the ferrocarbonatiteferruginous calciocarbonatite boundary in the revised system proposed by Gittins and Harmer (1997), in which molecular rather than weight proportions of CaO, MgO, MnO and total Fe as FeO are used.

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When the two classification diagrams are seen together (Fig. 3b), it is apparent that Gittins and Harmer (1997) have proposed restricting the name ferrocarbonatite in such a way as to exclude almost all carbonatites previously given this name, for reasons explained in their paper. Siderite-rich carbonatites remain ferrocarbonatites in the Gittins and Harmer classification (1997) but most ankerite carbonatites do not. Detailed geochemical accounts of three suites of relatively Fe-rich carbonatites have been published since mid-1997: Grønnedal-Iká, SW Greenland (Pearce et al. 1997); Marinkas Quellen, southern Namibia (Smithies and Marsh 1998) and Barra do Itapirapuã, Brazil (Andrade et al. 1999). Siderite occurs in the Grønnedal-Iká carbonatites, and ankerite in the other two suites. Applying the Gittins and Harmer classification strictly, only one sample each from Swartbooisdrif (PB29) and Marinkas Quellen (MKC16) are ferrocarbonatites. Nevertheless, it is probably more realistic to allow for analytical error and take the view that the other Swartbooisdrif sample (PB24), 2-3 more from Marinkas Quellen and one from Barra do Itapirapuã (4/ 10.30) are marginal ferrocarbonatites (Fig. 3).

Trace elements

Woolley and Kempe (1989) showed that carbonatites typically have low Ni contents (<65 ppm) but variable Cr (frequently >100 ppm). Both Ni and Cr are low in the Swartbooisdrif ferrocarbonatite (~38 and 22 ppm respectively; Table 4). Elements which are normally incompatible in basaltic (s. l.) magmatic systems, apart from K and Rb, are usually strongly enriched in carbonatites and especially so in ferrocarbonatites. However, the only elements which show much higher concentrations in PB24 and PB29 than the basaltic range are Sr and, to a lesser extent, Pb. The PB24 and PB29 rare-earth-element (REE) and Y abundances are within the range characteristic of oceanic basanites, their Ba, Nb, U and Th contents fall in the ocean-island tholeiite range (e.g. Thompson et al. 1984), and their TiO₂ and P₂O₅, Zr, Hf and Ta values are extremely low.

Figure 4 shows that the chondrite-normalised REE patterns of the two carbonatites are very similar, although their overall slopes vary slightly. Both include small positive Eu anomalies and both are distinctly sigmoidal in shape. One of the carbonatite-fenite composite samples, PB27, has light-REE abundances similar to carbonatite PB29 but a flatter pattern overall. The other mixed sample, PB28, has similar heavy REE to PB29 but substantially more light REE. The data in Tables 2 and 3 show that sodalite is definitely not the cause of this relative REE enrichment in the fenite. The minuscule strontianites within the Swartbooisdrif calcite are probably the main REE host in this rock. The extensive data of Hornig-Kjarsgaard (1998) show that REE abundances are characteristically much higher in calcite carbonatites than in PB24 and PB29; only a Jacupiranga dolomite-carbonatite (op. cit.) shows comparable Σ REE. Another ankerite carbonatite with relatively low REE (91 ppm La) is the "marginal ferrocarbonatite" 4/10.30 from Barra do Itapirapuã (Fig. 3; Andrade et al. 1999).

Normalised data for a wide range of elements which show incompatible behaviour in basaltic systems (Fig. 5) are useful for summarising other trace-element features of the Swartbooisdrif carbonatites, and comparing these synoptically with other carbonatites and silicate rock types. Figure 5c shows how oceanic Mg-rich basanites and nephelinites have smooth, humped patterns on such diagrams, peaking at Nb and Ta, and often with a trough at K (and sometimes Rb) if the rock-type is strongly alkalic. By contrast, the PB24 and PB29 patterns (Fig. 5a) show remarkable relative enrichments and depletions of trace elements. Other carbonatites share these characteristics world-wide (Fig. 5b, c), although we can find no comparable published sets of chemical data for ferrocarbonatites. It is unfortunate that the Marinkas Quellen (Smithies and Marsh 1998) and Barra do Itapirapuã (Andrade et al. 1999) ankeritecarbonatite analyses lack elements essential to construct the type of plots shown in Fig. 5. The patterns of most

Fig. 4a, b. Chondrite-normalised rare-earth elements (Sun and McDonough 1989). a Swartbooisdrif ferrocarbonatites PB24 and PB29 (Table 4) and carbonatite-fenite composite samples PB27 and PB28. b Hand-picked magnetite from ferrocarbonatite PB29 and sodalite from fenite (Tables 2 and 3). Electron microprobe analyses (average) of pyrochlore from PB27 (Tables 2 and 3). Pm has been interpolated by averaging normalised Nd and Sm





those of Swartbooisdrif (Fig. 5b). There is great interelement variability amongst carbonatites world-wide,

Angolan carbonatites (Alberti et al. 1999) are similar to even amongst samples from individual complexes. This is particularly evident with such elements as Sr and P which concentrate in one of the major carbonatite Fig. 5a-c. Normalised trace-element abundances (Thompson et al. 1984; derivation of normalisation factors discussed therein). a Swartbooisdrif ferrocarbonatites PB24 and PB29 (Table 4). b Carbonatites from NW Russia (W122 k, Turiy Peninsula, Ivanikov et al. 1998) and SE Angola (BA 11.90, Bailundo and LU 24.45, Lupongola, Alberti et al. 1999). c Carbonatites from SE Brazil (HB011, Jacupiranga, Huang et al. 1995) and NW Russia (Kv12, Kovdor, Verhulst et al. 2000), together with Hawaii basanite RTH31 and Bermuda Rise melanephelinite BD5-4 (Thompson et al. 1984; Thompson, unpublished data)

minerals. U/Th and Pb/Ba also both vary greatly; note that the latter ratio is particularly high in PB24 and PB29. Nearly all carbonatites show large relative depletions (troughs on Fig. 5) of Rb, K and Ti. Although there are intermediate variants, the element pairs Nb-Ta and Zr-Hf tend to divide carbonatites into two chemical subgroups. One type (Fig. 5b) shows strong relative depletions in both element pairs, with relatively low (mostly below chondritic) Zr/Hf and Nb/Ta. In the other type (Fig. 5c) the relative depletions of these elements are less; Zr/Hf is similar to values in oceanic lavas (e.g. basanite RTH31 and melanephelinite BD5-4 on Fig. 5c; Thompson et al. 1984; Thompson, unpublished data), and Nb/Ta is similar or lower. We shall discuss these ratios further below, in connection with the genesis of PB24 and PB29.

Isotopes

Details of our isotope analytical methods are given in the appendix. We calculated initial Sr–Nd–Pb isotopic ratios using a tentative age of 1,100 Ma for Swartbooisdrif (Menge 1986). The age corrections (Table 4) are negligible for all ratios except ¹⁴³Nd/¹⁴⁴Nd and ²⁰⁸Pb/²⁰⁴Pb (both very small). The combination of low initial ⁸⁷Sr/⁸⁶Sr (0.7033) with ϵ Nd ~0 to +1 (Table 4) places Swartbooisdrif centrally in the main field of world-wide Mesozoic and younger carbonatites thought to have unaltered magmatic compositions (Harmer and Gittins 1998).

Initial ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios for PB24 and PB29 differ substantially from those of many well-known Mesozoic and younger carbonatites (Fig. 6). The simplest explanation is that the age of Swartbooisdrif is indeed ~ 1.100 Ma, because the PB24 and PB29 data plot within the fields of initial Pb isotope ratios for 1,000–1,150 Ma carbonatites from the Canadian Shield (Kwon et al. 1989). These authors argued that, in general, Pb isotope ratios in Archaean-Recent carbonatites varied in a manner concordant with the view that their sources were from the same convectingmantle reservoirs as modern ocean-island basalts. A complicating feature of the Swartbooisdrif carbonatites is their very high ratios of Pb to such elements as Ba, Th and U (Fig. 5a), a feature which is not characteristic of carbonatites in general (Fig. 5b, c). Perhaps some crustal Pb has contaminated this carbonatite. If the contaminant was high-grade metamorphic, Archaean-Proterozoic acid crust, it might well have had Pb isotopic ratios similar to those of the carbonate magma. Huang et al. (1995) discussed this matter in detail, with reference to the Jacupiranga carbonatite, Brazil (Fig. 5c).

Carbon and oxygen isotopic ratios are widely used to distinguish carbonatites which have been affected by solidification and post-solidification processes, such as degassing or interaction with meteoric groundwater, from those which appear still to preserve magmatic ratios. The solid-line box on Fig. 7, a plot of carbonate C-O isotopic ratios, encloses values which characterise most well-studied carbonatites which have undergone no detectable post-magmatic modification (e.g. Deines 1989; Keller and Hoefs 1995; Horstmann and Verwoerd 1997; Brod 1999). Some unaltered samples from Oldoinyo Lengai plot within the much more restricted C-O isotopic field defined by fresh oceanic basalts (dashed-line box on Fig. 7), and the Swartbooisdrif ferrocarbonatites lie adjacent to these data (Fig. 7a; Dawson 1993; Keller and Hoefs 1995; Eggenkamp and Koster van Groos 1997).

Other data on Fig. 7a are carbonatites from 18 different carbonatite localities throughout Namibia (excluding Swartbooisdrif) and South Africa (Horstmann and Verwoerd 1997). These vary in age from ~ 50 to 2,050 Ma. Data from 123-129 Ma Damaraland carbonatites, NW Namibia (le Roex and Lanyon 1998) are also plotted. It is clear from Fig. 7a that, unlike southern African calcite and dolomite carbonatites, only one of the ankerite-bearing samples falls within the magmatic field. This is Marinkas Quellen, southern Namibia (Verwoerd 1993; Smithies and Marsh 1998), dated at \sim 540 Ma by Smithies and Marsh. In Fig. 3 above we showed that only one analysed Marinkas Quellen carbonatite (MKC16 of Smithies and Marsh 1998) is a ferrocarbonatite (sensu Gittins and Harmer 1997). No elemental data are published for the Marinkas Quellen sample plotted in Fig. 7a (Horstmann and Verwoerd 1997). Swartbooisdrif falls centrally in the lower δ^{13} C part of the magmatic carbonatite C–O isotopic range. Bearing in mind the predominance of sodalite in the Swartbooisdrif fenites, it may be relevant that Oldoinyo Lengai carbonatites plot in the same part of Fig. 7a.

Data for six carbonatite localities in Angola (Alberti et al. 1999) are plotted in Fig. 7b. Some of these are dated at \sim 130 Ma; others remain undated. Only values listed in Table 4 of Alberti et al. (1999) are included, and silicocarbonatites (SiO₂ > 5%) are also omitted. One complex, Lupongola, is only ~ 25 km north of Swartbooisdrif (Verwoerd 1993). We have labelled two points from this centre which fall close to Swartbooisdrif on Fig. 7b. Calcite-ankerite carbonatite is reported from Lupongola by Alberti et al. (1999) but it is ¹⁸O enriched. Ankerite appears, from Fig. 7, to be much less common in Angolan than other southern African carbonatites, but the ferrocarbonatites which were emplaced at three of these centres have mostly been oxidised to calcite + dolomite + Fe-oxide (Issa Filho et al. 1991). Whatever the reason, the almost complete lack of ankerite-bearing samples in the magmatic C-O field is striking.

Fig. 6. Initial ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb for Swartbooisdrif ferrocarbonatites PB24 and PB29. Note that the 1,100-Ma age corrections for these data are negligible to very small (Table 4). Fields of MORB, Mesozoic and younger carbonatites and geochron from Bell (1998). Field of Canadian Shield 1,000–1,150 Ma carbonatites from Kwon et al. (1989). S-K75 is the Pb isotope evolution curve of Stacey and Kramers (1975)



Additionally, we have plotted data for three wellstudied African siderite carbonatites in Fig. 7b: Chilwa (Simonetti and Bell 1994), Buru and Kugwe (Onuonga et al. 1997). These are the only three carbonatites originally accepted as ferrocarbonatites by Gittins and Harmer (1997) in their revised carbonatite classification. All have stable isotope ratios far from the magmatic values. In Fig. 3 above we identified two more ferrocarbonatites: MKC16 (Marinkas Quellen) and PB29 (Swartbooisdrif). We also pointed out that several other samples from Marinkas Quellen, PB24 (Swartbooisdrif) and 4/10.30 (Barra do Itapirapuã) are very close to ferrocarbonatites (sensu Gittins and Harmer). The fresh Barra do Itapirapuã carbonatites plot within the magmatic C–O isotopic field of Fig. 7b (Andrade et al. 1999). It is therefore likely that future research will locate samples at Marinkas Quellen and Barra do Itapirapuã which are both ferrocarbonatites (sensu Gittins and Harmer) and magmatic in their C–O isotopic ratios. Nevertheless, this is not the case at present, and Swartbooisdrif sample PB29 is the first ferrocarbonatite (sensu Gittins and Harmer) to have both radiogenic and stable isotopic ratios, determined on the same sample, concordant with a magmatic origin.

Discussion

Magmatic ferrocarbonatite: frozen melt or cumulate?

Swartbooisdrif is the first reported ferrocarbonatite (sensu Gittins and Harmer 1997) which fulfils widely recognised criteria for a magmatic rather than hydrothermal origin. Marinkas Quellen (Smithies and Marsh 1998) and Barra do Itapirapuã (Andrade et al. 1999) will doubtless provide more examples when comprehensive elemental and isotopic data are available on other individual samples. For Swartbooisdrif, we stress the Sr-rich calcite (with further exsolved strontianite), concentrically zoned ankerite, and Sr–Nd–Pb–C–O isotopic ratios in the same ranges as fresh extrusive carbonatites and magmatic silicate rocks. Nevertheless, there is no convincing evidence that this ferrocarbonatite was ever an all-liquid, Fe-rich carbonate melt. Researchers with Fig. 7a, b. δ^{13} C versus δ^{18} O in the carbonate fraction of Swartbooisdrif ferrocarbonatites PB24 and PB29 (both plot at one point; Table 4) and carbonates from carbonatites elsewhere in southern Africa. a South Africa and Namibia (Horstmann and Verwoerd 1997; le Roex and Lanyon 1998), Oldoinyo Lengai (Dawson 1993; Keller and Hoefs 1995; Eggenkamp and Koster van Groos 1997). b Angola (Alberti et al. 1999); African ferrocarbonatites (Simonetti and Bell 1994; Onuonga et al. 1997); Barra do Itapirapuã (fresh plutonic samples only), Brazil (Andrade et al. 1999). Mantle and primary igneous carbonatite fields from Eiler et al. (1997), Keller and Hoefs (1995), and Mattey (1987). See text for detailed discussion of Marinkas Quellen and Barra do Itapirapuã data in b



both field and experimental backgrounds frequently warn that most carbonatites are products of crystal accumulation, rather than frozen liquids (e.g. Le Bas 1977, 1981; Treiman and Schedl 1983; Le Bas 1989; Treiman 1989; Petibon et al. 1998; Veksler et al. 1998a; Lee et al. 2000). We emphasised above that cumulus texture is still recognisable in parts of thin sections of PB24 and PB29, and especially in PB27 – a thin carbonatite vein which may have cooled faster than the thicker Swartbooisdrif dykes. Negative evidence for crystal accumulation during the genesis of the Swartbooisdrif ferrocarbonatites is their complete lack of non-xenocrystal silicate minerals or apatite; the relevant phase diagrams predict that both should be present (Wyllie 1989; Lee and Wyllie 1998; Petibon et al. 1998; Lee et al. 2000; Barker 2001).

These very dense ferrocarbonatites appear to be an accumulation of ankerite and magnetite from a melt which was also saturated with calcite, probably with apatite and possibly with pyrochlore. Scattered calcite phenocrysts were trapped in the cumulus mush. If the phenocrysts of apatite and pyrochlore were much smaller than those of the other phases in the parental carbonate melt, they might – despite their density – be hydraulically equivalent to the calcite, rather than the ankerite and magnetite, and hence float. During crystallisation the interstitial melt was progressively depleted in iron by magnetite crystallisation, causing ankerite zoning, from ankerite (s.s.) cores towards ferroan dolomite rims. More calcite crystallised interstitially.

Links with Lupongola carbonatite complex, Angola?

The Lupongola complex, ~ 25 km north of Epembe-Swartbooisdrif, resembles the latter, in that it comprises scattered dykes, veins and pod-shaped bodies of carbonatite, syenite and phonolite, emplaced in the 1,155-Ma Kunene anorthositic complex (Issa Filha et al. 1991; Alberti et al. 1999). The carbonatites are calcite dominated, with ankerite reported in one case (Alberti et al. 1999). Lupongola is undated and has similar initial $(^{87}\text{Sr}/^{86}\text{Sr})_{130}$ to other (~130 Ma) Angolan alkalic-carbonatite complexes (Alberti et al. 1999). However, ¹⁴³Nd/¹⁴⁴Nd at 130 Ma in the Lupongola carbonatites is much lower (~ 0.5115) than the values in all the other ~130-Ma Angolan and NW Namibian carbonatites (~0.5125; le Roex and Lanyon 1998; Alberti et al. 1999). Alberti et al. (1999) use the same alternative explanations for this situation as ours for Pb isotopic ratios in PB24 and PB29 – either Lupongola is ~1,100 Ma old or it has assimilated considerable amounts of crustal Nd. Pending future research, it is clearly a possibility that Lupongola, Epembe and Swartbooisdrif are all parts of an \sim 1,100-Ma intrusive event which featured both calcite carbonatites and the small-scale Swartbooisdrif ferrocarbonatites.

We speculate that a parental carbonatite melt, cosaturated with calcite, ankerite, magnetite and possibly pyrochlore (plus a silicate mineral and apatite; Lee and Wyllie 1998; Petibon et al. 1998; Barker 2001), began to crystallise in circumstances which permitted strong gravity-driven separation of denser from less-dense minerals, as is probable in low-viscosity carbonate melts (Treiman and Schedl 1983; Treiman 1989; Petibon et al. 1998). This process resulted in mush-like separate magmas, full of either ankerite plus magnetite or calcite plus the silicate and possibly pyrochlore and/or apatite. It is very unlikely that such crystal-liquid separation could take place in situ within the thin dykes and dykelets exposed at Swartbooisdrif. A more probable scenario is separation within larger magmatic bodies beneath a major igneous centre (Lupongola?), and emplacement of the resulting magma fractions as crystal-rich sludges. The concept that dykes comprising mostly solid ankerite and magnetite, lubricated by interstitial melt, could be injected laterally for 25 km or so within the crust is supported by evidence for similar phenomena in silicate magmatic systems. Thus, it is well established that picrite dykes, jammed with dense olivine and chromite macrocrysts, radiated for similar distances from the ~60-Ma Cuillin basic-ultrabasic intrusive complex of Skve, NW Scotland (e.g. Anderson and Dunham 1966). Smithies and Marsh (1998) described ankerite-magnetite carbonatites forming radial dykes around the Marinkas Quellen complex, southern Namibia. Menge (1986) also tentatively linked the Swartbooisdrif and Zebra Mountains dykes (Fig. 1) with Lupongola magmatism.

The Nb/Ta clue to carbonatite genesis

If Swartbooisdrif is indeed a cumulate, rather than a frozen liquid, it is necessary to be very cautious when interpreting features of its elemental geochemistry as evidence for or against hypotheses for the genesis of the

parental carbonatite melt. Thus, the low concentrations in PB24 and PB29 of REE and many other elements which are usually much more abundant in carbonatites, and especially ferrocarbonatites (Fig. 5), might be primary magmatic features or may have resulted from fractional crystallisation of REE-bearing calcite and/or apatite and/or pyrochlore. Alternatively, they may be no more than a result of the crystal-liquid separation stage during the evolution of this cumulate mush. Nevertheless, the ratios Nb/Ta and Zr/Hf are very unusual in Swartbooisdrif and other carbonatites (Fig. 5). The low (subchondritic) Zr/Hf ratios of some carbonatites are shared by rhyolites and granites which have fractionated zircon during their genesis (e.g. Thompson et al. 1984), and by the carbonate melt products of silicate-carbonate melt immiscibility experiments (Hamilton et al. 1989; Veksler et al. 1998b).

The remarkable Nb/Ta variations in carbonatites are illustrated in Fig. 8. Chondritic meteorites and a range of terrestrial-oceanic basic igneous rocks from MORB tholeiites to melanephelinites all adhere closely to an Nb/Ta ratio of 17.7. This ratio does not appear to change during fractional crystallisation of mafic alkalic magma to trachyte-phonolite residua (Thompson et al. 1984). It falls to between about 6 and 12 in the leucorhyolite-leucogranite products of extreme fractional crystallisation of tholeiites (Thompson et al. 1984), but such magmas are not thought to be connected in any way with carbonatites. The only silicate rock types with even lower Nb/Ta (\sim 3.5–5.0) are S-type, strongly peraluminous granites and similar rhyolites (Thompson et al. 1984). Thus, the Nb/Ta range of carbonatites, from ~ 2 to 1,500, is much wider than for all silicate magmas. Although there is support for the hypothesis that at least some carbonatites form by direct uppermantle melting (e.g. Dalton and Wood 1993; Dalton and Presnall 1998; Moore and Wood 1998), we are unaware of published data which show how such a process could generate the Nb/Ta range. Both fractional crystallisation (CO₂-rich silicate to carbonatite magma) and liquid immiscibility (CO2-rich silicate melt to silicate and carbonate fractions) are advocated as major factors in carbonatite genesis (e.g. Gittins 1989; Hamilton et al. 1989; Le Bas 1989; Woolley and Kempe 1989; Huang et al. 1995; Ivanikov et al. 1998; Lee and Wyllie 1998: Veksler et al. 1998a, 1998b: Kurszlaukis et al. 1999; Lee et al. 2000). During fractional crystallisation of a carbonate melt, it is the widespread carbonatite mineral pyrochlore which seems most likely to control the behaviour of Nb and Ta. A plot of Nb and Ta in high-quality microprobe analyses of fresh pyrochlores (Fig. 8, inset) shows that they have an even larger range of Nb/Ta than their carbonatite hosts. Nevertheless, Nb/Ta in PB27 pyrochlore (530; Tables 2 and 3) is similar to this ratio in PB24 and PB29 (average 440; Table 4). Therefore, although pyrochlore removal would clearly tend to reduce both Nb and Ta in a fractionating carbonatite melt, it is not certain how Nb/ Ta would be affected, if at all.



Fig. 8. Nb versus Ta in Swartbooisdrif ferrocarbonatites PB24 and PB29 (Table 4) and other carbonatites. Data sources on main plot are: Angola (Alberti et al. 1999); Blue Hills, Namibia (Kurszlaukis et al. 1999); Turiy Peninsula, Russia (Ivanikov et al. 1998); Kovdor, Russia (Verhulst et al. 2000); Jacupiranga, Brazil (Huang et al. 1995); Juquia, Brazil, and Chiriguelo, Paraguay (Castorina et al. 1996); Mt Vulture, Italy (Rosatelli et al. 2000); average calciocarbonatite, magnesiocarbonatite and ferrocarbonatite (Woolley and Kempe 1989); carbonatites from Tanzania, Australia and Germany (Nelson et al. 1988); average C1 chondrite, N-MORB, E-MORB and OIB (Sun and McDonough 1989); RTH31 (basanite, Maui, Hawaii) and BD/BF5-4 (melanephelinites, Bermuda Rise) from Thompson et al. (1984) and Thompson (unpublished data). Joined points labelled "partitioning experiment between immiscible melts" are a representative data set (CS222) from silicate-carbonate melt unmixing experiments by Veksler et al. (1998b). Inset Nb versus Ta in high-quality microprobe analyses of fresh pyrochlore. Data sources are filled triangles Tables 2 and 3 ; filled squares Hodgson and Le Bas (1992), Williams (1996), Williams et al. (1997), Hogarth et al. (2000), Nasraoui and Bilal (2000), and Seifert et al. (2000)

A more clear-cut situation exists with studies of silicate-carbonate melt immiscibility. The results of one of the partitioning experiments of Veksler et al. (1998b) are plotted on Fig. 8. This is the only published study where both Nb and Ta partitioning have been determined together. The silicate fraction is enriched in both Nb and Ta, relative to the carbonate, and Nb/Ta is much higher in the latter than in the starting material. Other published data for Ta partitioning show that this varies with both pressure and temperature (Hamilton et al. 1989), but the experimental results plotted on Fig. 8 suggest that liquid immiscibility may be responsible for high Nb/ Ta in those carbonatites, such as Swartbooisdrif, which have values of this ratio well above chondritic (Veksler et al. 1998b).

The cause of Nb/Ta below 17.7 in other carbonatites is enigmatic. Thompson et al. (1984) pointed out that

one possibility might be that, in some circumstances, Nb (but not Ta) might become trivalent. The ionic radius of Nb^{3+} is very close to that of Hf^{4+} (Shannon and Prewitt 1969), and thus Nb and Ta might substitute into different minerals in a fractionation carbonatite system.

The remaining possibility is that Nb and Ta are lost differentially from the carbonatite melt during fenite formation as it crystallises. The most prominent fenite mineral around the Swartbooisdrif ferrocarbonatite dykes is sodalite (Tables 2 and 3). Studies of fluid inclusions within carbonatite minerals have repeatedly shown evidence that the carbonatite melts were originally much richer in alkalis than their frozen products (e.g. Rankin and Le Bas 1974; Veksler et al 1998a). Recently, Veksler and Keppler (2000) have shown experimentally that Na partitions strongly into the aqueous phase in a system containing carbonatite melt and co-existing (escaping) hydrous fluid. The amounts of Nb and Ta in the sodalite are small but there is a large quantity of this mineral at Swartbooisdrif, and its Nb/ Ta ratio (43; Tables 2 and 3) is lower than in the ferrocarbonatites. If Nb and Ta in the sodalite both originated entirely from the crystallising carbonate melt, their ratio is evidence that Nb did not leak preferentially into the fenites. Therefore, the low Nb/Ta of some carbonatites probably has another cause.

Conclusions

1. The Swartbooisdrif ankerite-calcite-magnetite carbonatite dykes are ferrocarbonatites, using the definition of Gittins and Harmer (1997), and the first examples found to have "magmatic" oxygen and carbon isotopic ratios. Other recently described ankerite-carbonatite suites at Barra do Itapirapuã, Brazil (Andrade et al. 1999) and Marinkas Quellen, southern Namibia (Smithies and Marsh 1998) will doubtless eventually yield further magmatic ferrocarbonatites (sensu Gittins and Harmer) but at present this is not the case, for reasons detailed above.

- 2. Despite clear evidence for some subsolidus reequilibration, the palaeotemperatures calculated using the calcite-dolomite solvus (corrected for Fe) and oxygen isotope distribution between carbonates and magnetite are relatively high, in the range 420– 460 °C. This is only ~100 °C below measured liquidus temperatures for erupted Oldoinyo Lengai natrocarbonatites.
- 3. The compositional zoning of the minerals in this ferrocarbonatite, and the Sr–Nd–Pb isotopic ratios of the rock are all concordant with its magmatic origin.
- 4. In areas of thin sections which have escaped subsequent mild recrystallisation, the petrographic texture of the ferrocarbonatite strongly resembles that of a silicate igneous cumulate, such as those found in layered intrusions. The cumulus phases are ankerite, magnetite and occasionally calcite. The intercumulus is mainly calcite, with subordinate magnetite and traces of pyrochlore.
- 5. The crystal accumulation stage in the evolution of this ferrocarbonatite makes it difficult to reconstruct the previous history of the magma. Swartbooisdrif contrasts with almost all published Fe-rich carbonatite compositions, by having basalt-like rather than high abundances of such elements as Nb, Ta, P and REE. Previous separation of apatite and pyrochlore may have depleted the melt in these elements.
- 6. The very high Nb/Ta of the ferrocarbonatite may have been inherited from an earlier episode of silicate-carbonate melt immiscibility in the evolution of the magma.

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Appendix

Analytical techniques

Mineral electron-probe microanalyses were made at Cambridge (Cameca SX50, wavelength and energy dispersive) and Manchester universities (Cameca SX100, wavelength dispersive). The beam current was 30 nA at Cambridge and 40 nA at Manchester, except for Ca, Mg and Si in carbonates (10 nA). Count times were 100 s, except for Sr in carbonates (250 s). The analyses in Table 1 are each an average of 3 spots. An accelerating voltage of 20 kV was used for pyrochlore, with a beam current of 40 nA. The standard for Na and Nb was synthetic NaNbO₃. For La, Ce and Nd, the standards were LaB₆, CeAl₂ and NdAl₂ respectively. For other elements various mineral standards and pure elements were used. Peak counting times of 10 or 20 s were used, apart from La, Ce, Nd and Ta for which the times were 150 to 250 s, giving detection limits of approximately 0.05% for La, Ce and Nd, and 0.02% for Ta. In the case of Nd, the L β line was used to avoid interferences affecting the $L\alpha$ line. We are indebted to Dr. C.T. Williams of the Natural History Museum, London, for supplying the NaNbO₃ standard.

Descriptions of our techniques for rock sample preparation and XRF, ICP-MS and radiogenic isotopic analysis are given by Gibson et al. (1999). We focus here on specific analytical problems of these carbonatites. In our major-element analyses (Brod 1999), H_2O^+ and CO_2 were not determined separately and other oxides were analysed using glass disks made by fusing ignited rock powder with flux. In order to make these robust enough to handle, and to improve XRF correction procedures, SpecPure SiO₂ was mixed 1:1 with ignited rock powder before glass preparation. The analyses are presented in Table 4 on a "wet" basis, with added SiO₂ removed by calculation and loss-on-ignition values reincorporated, so that they are comparable with published data where CO₂ is determined. Analysis PB24a provides a check on the SiO₂-addition analytical technique. It was the only fusion disk prepared without added SiO₂ which survived long enough to analyse. The result compares well with PB24, the added-SiO₂ analysis.

The basalt-like trace-element abundances of the ferrocarbonatites presented no difficulties during their XRF analysis, using pressed powder disks. However, their high Fe contents made ICP-MS analysis complicated. Initial analyses were made on solutions prepared by fusing carbonatite with lithium tetraborate and digesting the product with $HF + HNO_3$. Fe-rich precipitates resisted digestion and the resulting analyses showed La depletion, relative to Ce and Pr. Re-analysis, using acid digestion without prior fusion, produced satisfactory La/Ce but with all other trace-element abundances lowered by a few percent. Our final results use La data from the no-fusion method,

recalculated to the yields of the fusion method. The only problem encountered during ICP-MS analyses of mineral separates was that pyrochlore did not redissolve completely after acid digestion and evaporation to dryness. An apparently stable solution was obtained by adding a trace of HF but anomalously low values for REE and Th showed that this procedure was not entirely successful (Tables 2 and 3).

Stable-isotope analyses were conducted at Royal Holloway University of London. CO_2 was liberated from powdered carbonate for carbon- and oxygen-isotope measurement by temperature-controlled dissolution in phosphoric acid (McCrea 1950), using an automated preparation system. The automated system then injected the CO_2 into a Micromass IsoPrime mass spectrometer. The ¹⁸O/¹⁶O of magnetite was determined by laser fluorination (Mattey and Macpherson 1993) and gave an oxygen yield that was >90% of the expected amount. In this case the isotopic analysis was performed on a Micromass OPTIMA spectrometer. Carbon-isotope ratios are reported relative to V-PDB and oxygen ratios relative to V-SMOW.

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