

Fenitizing Processes Induced by Ferrocarbonatite Magmatism at Swartbooisdrif, NW Namibia

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The southeastern margin of the anorthositic Kunene Intrusive Complex, NW Namibia, has been subsequently invaded by Mesoproterozoic syenite, nepheline syenite and ferrocarbonatite dykes along NE- and SE-trending faults. The first generation of carbonatite intrusions frequently contains fenitized anorthositic wall-rock fragments set in a ferrocarbonatite matrix; later, subordinate veins of massive ferrocarbonatite are almost xenolith-free and cut through the main carbonatite dykes. A mantle source for both carbonatite generations is constrained by their respective oxygen and carbon isotope compositions of ankerite ($\delta^{18}\text{O}_{\text{SMOW}} 8.91\text{--}9.73\text{‰}$; $\delta^{13}\text{C}_{\text{PDB}} -6.98$ to -6.76‰). Na-rich fluids, released from the melt parental to the ferrocarbonatites, caused the fenitization of both the incorporated anorthosite xenoliths and the bordering anorthosite, syenite and nepheline syenite. This process is mainly characterized by the progressive transformation of Ca-rich plagioclase, K-feldspar and nepheline into albite and/or sodalite. The changing mineral modes indicate that the fenitizing fluids were sodium-rich and strongly Si-deficient solutions, which also contained significant amounts of Sr, Ba, Nb and the light rare earth elements. On the basis of mineral equilibria studies, it is possible to reconstruct the temperature conditions for carbonatite emplacement (c. $830 \pm 200^\circ\text{C}$) and recrystallization (c. $480 \pm 130^\circ\text{C}$), and for the metasomatic formation of sodalite (c. $700 \pm 70^\circ\text{C}$).

KEY WORDS: anorthosite; fenitization; ferrocarbonatite; sodalite; stable isotopes

INTRODUCTION

The majority of the carbonatite complexes known from world-wide localities are predominantly composed of

calcium- and magnesium-rich carbonatites. In these carbonatite centres late-stage ferrocarbonatite dykes may occur, which are characterized by strong enrichments of Fe, Mg, Ba, Sr, rare earth elements (REE), Th and U. Such ferrocarbonatites are commonly interpreted as the end-products of fractional crystallization and associated differentiation processes of the main Ca–Mg carbonatite body (Le Bas, 1977, 1981, 1989, 1999; Gittins, 1989; Woolley & Kempe, 1989; Cooper & Reid, 1998). Magmatic natrocarbonatite is known only as the effusive product of the Oldoinyo Lengai volcano, Tanzania, which is also the only known active carbonatite volcano [see Bell & Keller (1995) for a review]. However, the close spatial association of Na- and/or K-rich fenites and carbonatites (Andersen, 1989; Platt & Woolley, 1990; Morogan, 1994; Hagni & Shivdasan, 2001; Williams-Jones & Palmer, 2002) suggests that carbonatites, which are now Ca–Mg–Fe carbonatites, were alkali-rich magmas when they intruded and subsequently expelled alkali-metals and volatiles during their differentiation and crystallization. This model has been confirmed by experimental studies (Watkinson & Wyllie, 1971; Freestone & Hamilton, 1980; Koster van Groos, 1990; Lee & Wyllie, 1994, 1997, 1998; Veksler & Keppler, 2000).

Where carbonatitic centres are surrounded by metasomatic aureoles, the composition of the solidified carbonatite will differ significantly from that of the pristine carbonatite magma as a result of material losses and gains during differentiation, crystallization or post-magmatic re-equilibration. In this case, the carbonatites preserve only an incomplete memory of their magmatic

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history. The investigation of metasomatic mineral reactions at the magma to wall-rock interface and of fluid inclusions containing the fenitizing agents can thus provide important information about the geochemical nature and evolution of the fluids responsible.

The carbonatite dykes of Swartbooisdrif, NW Namibia, are an ideal study object as they are well exposed and have undergone only minor subsolidus alteration and weathering. Only few studies have been concerned with this carbonatite occurrence so far (e.g. Menge, 1986, 1996; Thompson *et al.*, 2002), including our own work (von Seckendorff & Drüppel, 1999; von Seckendorff *et al.*, 2000; this study), although it is host to a conspicuous sodalite deposit, which is confined to an area of *c.* 100 km². The Swartbooisdrif carbonatites differ from other known carbonatite occurrences in (1) their exotic fenite mineral assemblage, (2) the uncommon anorthositic mineralogy of the wall rocks that are involved in the metasomatic processes and (3) the general lack of associated Ca–Mg carbonatites and subordinate, genetically related, felsic intrusives. The aim of this study is to characterize the magmatic evolution of the carbonatite intrusions and to elucidate the interrelated metasomatic processes, which led to the formation of the sodalite occurrences.

GEOLOGICAL FRAMEWORK

The Swartbooisdrif ferrocarnatites were emplaced near the southwestern margin of the anorthositic Kunene Intrusive Complex (KIC). The KIC, a massif-type anorthosite complex, is exposed in SW Angola and NW Namibia as a north–south elongated body of about 350 km in length and 30–80 km in width. It was emplaced at the southern margin of the Congo craton. An internal biotite–plagioclase whole-rock Rb–Sr isochron age of 1347 ± 13 Ma has been determined for one anorthosite sample from the Angolan part of the complex (Mayer *et al.*, 2000). This age has been constrained by Mayer *et al.* (2004) by a concordant U–Pb age of 1371 ± 2.5 Ma using zircons from a late-stage mangerite vein, inferred to be cogenetic with the KIC. These ages are in accordance with an almost concordant U–Pb zircon age of 1385 ± 25 Ma for an anorthosite sample of the Namibian part of the KIC (Drüppel *et al.*, 2000). The anorthosite massif intruded the Palaeo- to Mesoproterozoic Epupa Complex (EC), which, in its main parts, consists of ortho- and paragneisses, metamorphosed under upper amphibolite-facies and subordinately under ultrahigh-*T*, granulite-facies conditions (Brandt *et al.*, 2003).

Close to the southernmost margin of the KIC, *c.* 7 km NW of the settlement of Swartbooisdrif, the anorthosite massif is transected by numerous SE- and ENE-trending shear zones, which were subsequently intruded by syenite, quartz syenite and younger ferrocarnatite

dykes (Fig. 1). With U–Pb zircon ages of 1385 ± 5 Ma and 1335 ± 2 Ma (Littmann *et al.*, in preparation) the syenite dykes of the Swartbooisdrif area appear to be genetically linked to the KIC. The ferrocarnatites at Swartbooisdrif, however, are distinctly younger than both the anorthosites and the syenites as is evidenced by pyrochlore U–Pb ages of *c.* 1140–1120 Ma (Littmann *et al.*, in preparation). The carbonatite dykes are host to significant amounts of sodalite, which are mined in an area of *c.* 100 km².

Another alkaline suite is exposed within the basement gneisses of the EC in the Epembe area, about 30 km SW of Swartbooisdrif. This suite mainly comprises small plugs of nepheline syenite (Ferguson *et al.*, 1975; Menge, 1986), which yielded radiometric U–Pb zircon ages of 1216 ± 2.4 and 1213 ± 2.5 Ma (Littmann *et al.*, 2000). Also assigned to the same magmatic event are east–west-striking calciocarnatite, lamprophyre and subordinate ferrocarnatite dykes (Ferguson *et al.*, 1975).

In much of the earlier literature, the Swartbooisdrif and Epembe suites are grouped together (e.g. Ferguson *et al.*, 1975; Menge, 1986; von Seckendorff *et al.*, 2000), forming the Epembe–Swartbooisdrif Alkaline Province (ESAP; Menge, 1986). In addition, intrusive bodies and dykes of syenite and calciocarnatite of the Lupongola Complex of Angola, *~*20 km NW of Swartbooisdrif, have been considered part of the ESAP (Menge, 1996; Alberti *et al.*, 1999; Thompson *et al.*, 2002). With respect to their radiometric ages, however, at least the Swartbooisdrif and the Epembe carbonatite centres appear to represent independent rock suites.

GEOLOGY OF THE SODALITE MINING AREA

The sodalite mining area near Swartbooisdrif (Fig. 1) is dominated by whitish, heavily altered anorthosites and leucogabbros of the KIC, the ‘white anorthosite’, which were subsequently intruded by small bodies of weakly altered, dark anorthosites, leucotroctolites, leucogabbros and leuconorites, the ‘dark anorthosite’ (Drüppel *et al.*, 2001). Numerous SE- and ENE-trending syenite and younger nepheline syenite and ferrocarnatite dykes were subsequently emplaced along fractures in the anorthositic rocks of the KIC. Individual dykes may be interrupted over short distances and frequently change their strike and dip direction on a local scale.

Felsic intrusives are mainly represented by brownish, strongly altered syenites, which form dykes 3–5 m wide. Where the syenite dykes are intruded by the younger carbonatites, the syenite is heavily strained and exhibits a pink colour. Exposed contacts between syenite and the younger carbonatites are curvilinear but tectonic, as syenitic fragments in all stages of detachment can be observed in the bordering carbonatite. At one locality a

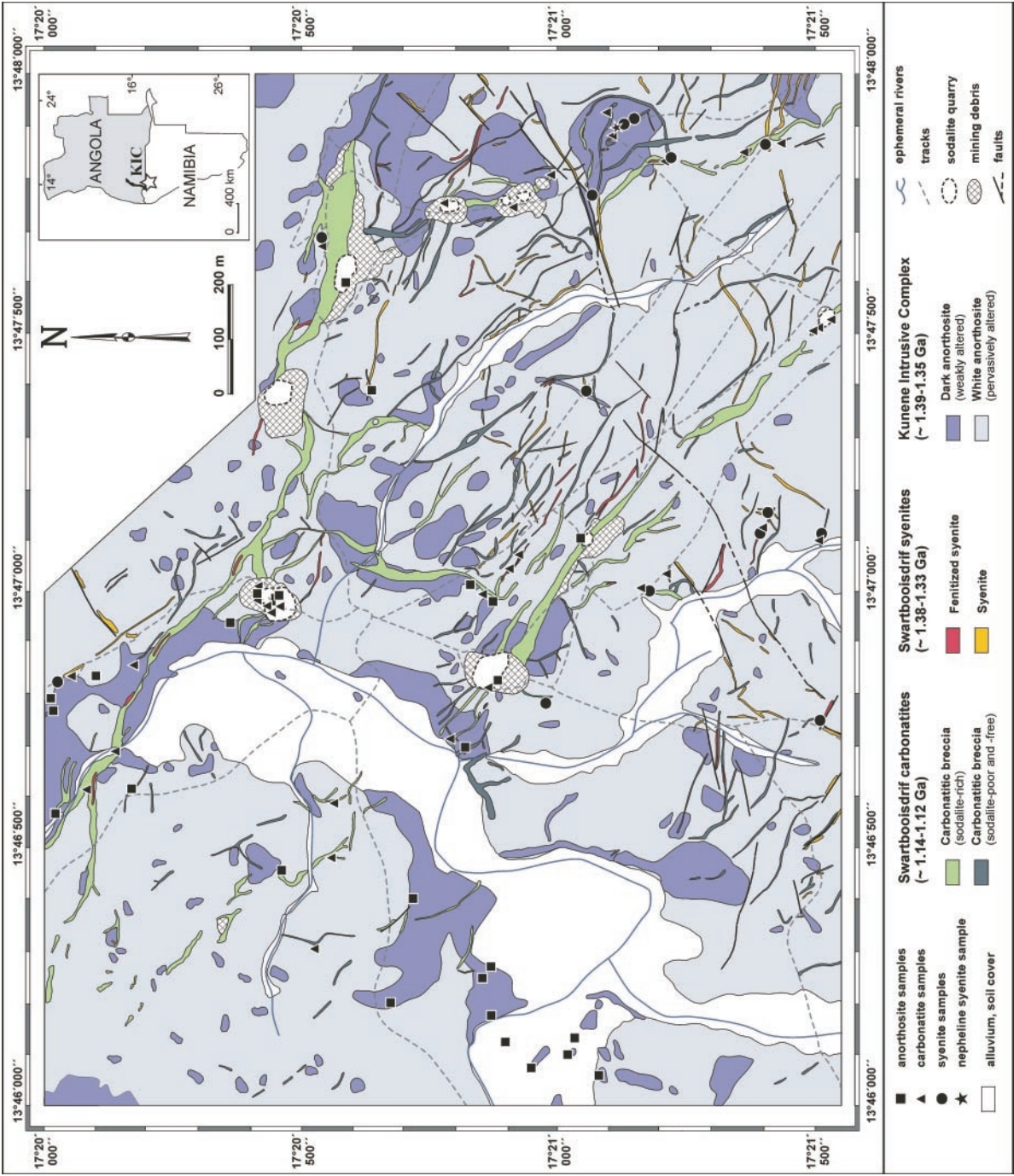


Fig. 1. Geological map of the sodalite mining area near Swartbooisdrif. The anorthositic rocks of the Kunene Intrusive Complex are crosscut by syenite, nepheline syenite and carbonatite dykes along NE- and SE-trending fault systems. Sample locations are marked.

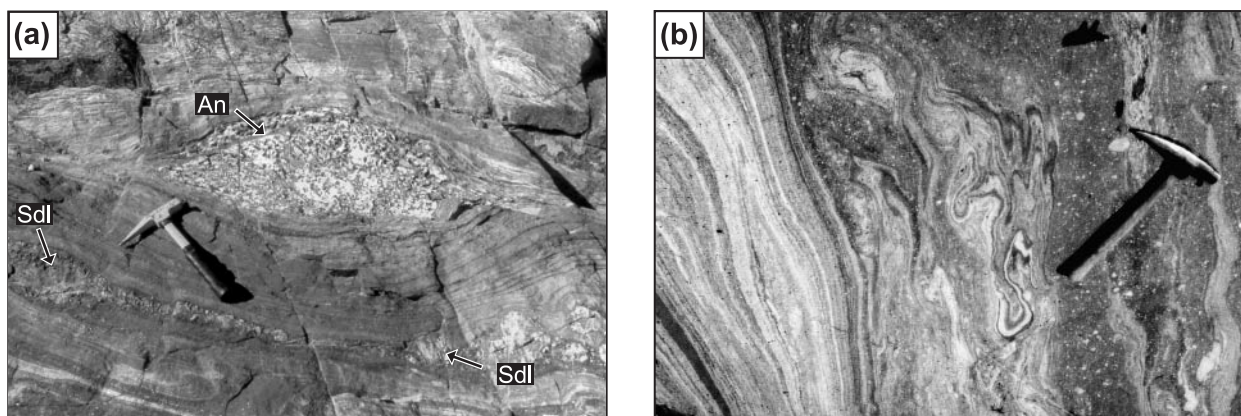


Fig. 2. Photographs of the two main carbonatite generations of the Swartbooisdrif area. (a) Carbonatitic breccia, containing fragmented xenoliths of anorthosite (An; upper middle) and sodalite (Sdl; lower part), wrapped by a laminated and ankerite-rich carbonatite matrix (locality 17°20.019', 13°46.529'). (b) Common structures in the carbonatitic breccia include compositional banding and impersistent magmatic folding (locality 17°20.417', 13°47.000').

nepheline syenite dyke was observed in direct contact with a large carbonatite dyke. The nepheline syenite is exposed over just a short distance of about 6.5 m, has a width of 30 cm to 3 m and crosscuts an older syenite. At a distance from the carbonatite, the nepheline syenite is characterized by a homogeneous texture, with medium-grained nepheline and K-feldspar being the major constituents. When approaching the carbonatite dyke, the texture of the nepheline syenite becomes progressively inhomogeneous, with fine-grained K-feldspar-rich zones alternating with irregular pegmatoidal zones, mainly composed of nepheline crystals of up to 15 cm in length. At the direct contact with the carbonatite, nepheline exhibits a pale blue tint resulting from its partial replacement by sodalite.

A major swarm of carbonatite dykes and veins occurs in the area, dissecting the syenite dykes and the anorthosite body. Two main periods of carbonatite emplacement have been recognized.

(1) The predominant carbonatite bodies, the 'carbonatitic breccia', are up to 80 m in width and frequently contain variable amounts of angular to subrounded fragments of fenitized wall-rock anorthosite and syenite, ranging continuously from 8 m down to several millimetres, set in an ankerite-rich carbonatite matrix (Fig. 2a). Most of the xenoliths are pervasively fenitized and partially broken into small particles, creating an interfragmental groundmass. A common feature of the carbonatitic breccia is a banded or streaky appearance caused by an alternation of ankerite-, magnetite- and silicate-rich layers oriented sub-parallel to the dyke walls. Flow-banding and impersistent magmatic folding on a millimetre to metre scale are common structures of this rock type (Fig. 2b), implying that the carbonatite was emplaced as a melt. Locally, the carbonatitic breccia may also contain massive carbonatite zones, almost entirely

composed of medium- to coarse-grained ankerite and minor magnetite. The occurrence of fragmented rafts of the layered carbonatitic breccia, surrounded by younger massive ferrocarbonatite, supports evidence for repeated injections of carbonatite melt. Major phases in the inhomogeneous carbonatitic breccia are ankerite (35–85 vol. %), albite (10–65 vol. %) and magnetite (15–25 vol. %), although biotite and sodalite are locally observed in significant concentrations of >25 vol. %. Cancrinite, muscovite, apatite, calcite, ilmenite, pyrochlore and sulphides are minor constituents, which rarely exceed 5 vol. %. The occurrence of sodalite is confined to regions where several larger carbonatite dykes intersect at acute angles and the modal abundance of anorthositic xenoliths increases. Variable amounts of sodalite (10–90 vol. %) occur as conspicuous deep blue lenses, layers and breccias in several of the large carbonatite dykes, but are also present in narrow metasomatic aureoles of up to 1 m in width within the bordering dark anorthosite.

(2) The main carbonatite body is transected by small veins and stringers of a second generation of almost silicate-free ferrocarbonatite, which are up to 1.5 m in width. These late-stage ferrocarbonatite veins have been recently investigated in some detail by Thompson *et al.* (2002).

ANALYTICAL METHODS

Electron microprobe analyses were performed on a CAMECA SX50 with three wavelength-dispersive spectrometers at the Institute of Mineralogy, University of Würzburg. For silicate, apatite and pyrochlore analyses the excitation voltage and beam current were set at 15 kV and 15 nA, with 1, 8 and 5 µm spot diameter, respectively. The bulk compositions of feldspars were determined with a defocused electron beam of 20 µm size. Carbonates were analysed at 12 kV, 15 nA with

8 μm spot sizes. For the calibration of Nb in pyrochlore pure Nb metal was used as a standard, whereas LaPO_4 and CePO_4 were chosen as calibration standards for La and Ce in pyrochlore and carbonates. Where possible, profiles of 10–60 points were analysed for each phase.

Major and trace elements were determined on fused glass discs using a Philips PW 1480 X-ray fluorescence (XRF) spectrometer at the Institute of Mineralogy, Würzburg. Matrix effects were corrected for automatically by the Philips X40 software. The relative analytical error for major and trace elements is 1% and 1–8%, respectively. The loss on ignition (LOI) was determined by heating 1 g of dried sample powder for 4 h at 1100°C and reweighing the sample after cooling. CO_2 was determined volumetrically by reacting 1–3 g of the sample powder with 10 ml HCl (16–18%). The FeO contents were analysed using a ZEISS PMD 2 spectral photometer. FeO contents of carbonatite samples with elevated CO_2 contents of >13 wt % were not detectable by this method, because of a strong chemical reaction of the sample powders with the $\text{HF-H}_2\text{SO}_4$ (SEROLAB) mixture.

Concentrations of the REE and Y in the anorthosites, nepheline syenite and REE-poor samples of the carbonatites were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) at the GeoForschungsZentrum Potsdam, Germany. Sample preparation followed the method of Zuleger & Erzinger (1988). Details on ICP equipment, operating conditions, background wavelength corrections and background equivalent concentrations, as well as the precision of the method, have been given by Zuleger & Erzinger (1988). The concentrations of the REE and Y in two REE-rich carbonatite samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin-Elmer/SCIEX Elan 5000 quadrupole ICP mass spectrometer at the GFZ Potsdam. The samples were dissolved in PTFE digestion vessels with 1:1 HF-HClO_4 for 16 h at 180°C. After cooling, samples were evaporated at 180°C for *c.* 4 h, dissolved with 5 ml HCl (10 mol/l) and heated again at 180°C to incipient dryness. The residues were taken up in 5 ml HCl (10 mol/l) and were heated in the closed vessels at 130°C for 12 h. After this procedure the samples were dried again and the sample cakes redissolved in 2 ml HCl (10 mol/l) and 10 ml Milli-Q water. The solutions were filled up to 50 ml with Milli-Q water. Before analysis, Ru and Re were added to aliquots of the solutions as internal standards to compensate for drift correction (Doherty, 1989), and the mixtures were diluted. A dilution factor of 50 000 was used for the measurements. Interference corrections consider the interference of MO^+ , MOH^+ and MCl^+ (Dulski, 1994). Calibration was carried out using multi-element solutions containing 10 mg/ml Rb, Sr, Y, Zr, Cs, Ba, all REE, Hf, Pb, Th and U. The precision ranged between 1 and 5% relative.

Trace element and REE analyses of sodalite in thin sections were performed with a 266 nm Nd:YAG laser (New Wave Research Inc., Merchantek Products) connected to a quadrupole ICP-MS system [Agilent 7500i; plasma power 1320 W; carrier gas flow 1.11 l/min (Ar); plasma gas flow 14.91 l/min (Ar); auxiliary gas flow 0.91 l/min (Ar)] at the Institute of Mineralogy, Würzburg. Laser parameters used were a frequency of 10 Hz and an energy setting of 50% (0.9 mJ). Ablation patterns were 600 μm long lines, ablated with a scan speed of 10 $\mu\text{m/s}$. The diameter of the sample pit created by the laser is 50 μm . Data acquisition was done in Time Resolved Analysis mode with measurements of the instrument background (20 s) and of sodalite (60 s). The certified reference material NIST 612 with the values of Pearce *et al.* (1997) was used as an external standard, whereas Si in sodalite (derived from the electron microprobe analyses) was used as internal standard. Raw counts for each element were solely corrected by subtracting the background counts and processed using the software GLITTER (Version 3.0; On-line Interactive Data Reduction for the LA-ICPMS, Macquarie Research Ltd., 2000).

Stable isotope ratios are reported for hand-picked mineral separates of feldspar, nepheline, magnetite and ankerite. Silicates and oxides were treated with ClF_3 according to the method described by Borthwick & Harmon (1982). Carbonate samples were treated with 100% phosphoric acid. CO_2 was measured mass spectrometrically with a Finnigan MAT 251 at the Geochemical Institute, University of Göttingen. All $\delta^{18}\text{O}$ values are given relative to SMOW, $\delta^{13}\text{C}$ values relative to PDB. The reproducibility of both δ values is better than $\pm 0.2\%$.

PETROGRAPHY

Fenitized anorthosite

The petrography and mineral chemistry of the anorthositic rocks of the KIC has been discussed in detail by Drüppel *et al.* (2001) and Drüppel (2003). In summary, both the white and the dark anorthosite suite display a primary magmatic assemblage of plagioclase (An_{37-53} and An_{43-75} , respectively) $\pm$ olivine (X_{Mg} 0.54–0.65) $\pm$ orthopyroxene (X_{Mg} 0.53–0.71) $\pm$ clinopyroxene (X_{Mg} 0.66–0.76) + ilmenite + magnetite $\pm$ biotite (X_{Mg} 0.39–0.67) $\pm$ amphibole (X_{Mg} 0.46–0.73; Fig. 3a).

As the contact with the carbonatitic breccia dykes is approached the magmatic plagioclase of the dark anorthosite suite becomes progressively altered to sodium-rich plagioclase (An_{1-17} ; Fig. 3b) with or without sericite. In the same direction, the modal abundance of carbonate, pyrite and chalcopyrite increases; clinopyroxene and orthopyroxene are replaced, to an increasing extent, by biotite–epidote–calcite assemblages and/or fine-grained intergrowths of bluish magnesio-riebeckite

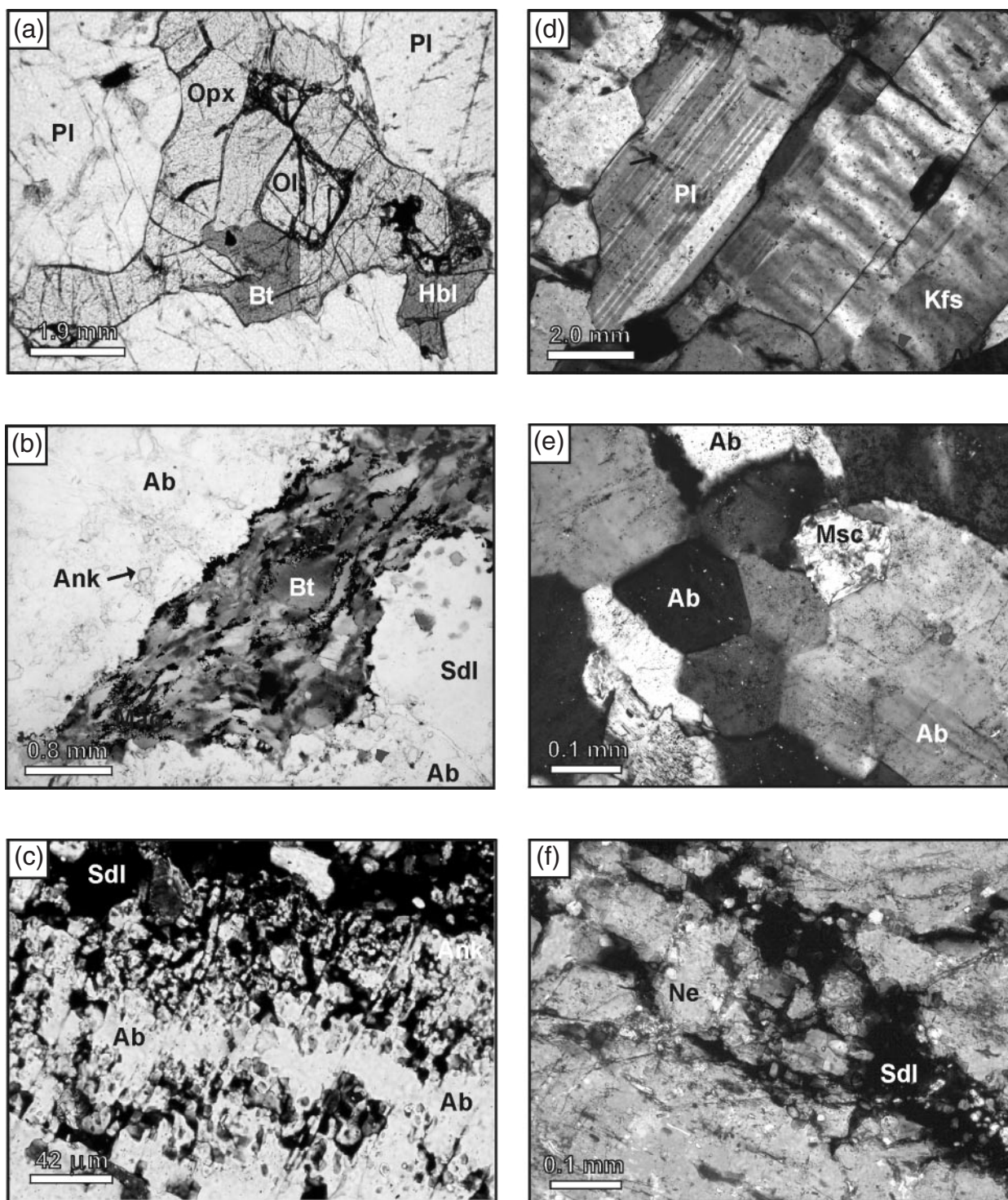


Fig. 3. Photomicrographs illustrating the mineralogical changes in anorthosites (a–c) and syenites (d–f) during fenitization. (a,b) Plane-polarized light; (c–f) cross-polarized light. Ab, albite; Ank, ankerite; Bt, biotite; Hbl, hornblende; Kfs, K-feldspar; Msc, muscovite; Ne, nepheline; Ol, olivine; Opx, orthopyroxene; Pl, plagioclase; Ne, nepheline; Sdl, sodalite. (a) Anorthosites unaffected by fenitization contain interstitial olivine. Olivine is surrounded by broad, irregular rims of orthopyroxene, biotite and hornblende. (b) At the contacts with the carbonatitic breccia, the fenitized anorthosites exhibit a banded appearance as a result of an alternation of albite–sodalite-, ankerite- and biotite-rich layers. (c) Metasomatic sodalite replaces plagioclase in the fenitized anorthosites along both its grain margins and albite-twin lamellae. (d) The main constituents of the syenites are orthomagmatic K-feldspar and plagioclase. (e) Fenitized syenites are mainly composed of granular albite associated with minor muscovite. (f) Metasomatic sodalite in the fenitized nepheline syenite replaces magmatic nepheline along cracks.

(X_{Mg} 0.75–0.82) and calcite. Fluorite and calcite may fill cracks in the rock. At the direct contact with the carbonatite dykes, the anorthosites exhibit a banded appearance as a result of alternation of layers rich in albite (An_{0-3}), ankerite and biotite (X_{Mg} 0.26–0.39) (Fig. 3b). The replacement of albite by sodalite and/or sodalite–ankerite intergrowths along both its margins and the albite twin lamellae (Fig. 3c) is responsible for the colour change of the fenitized rocks from grey to purplish blue. The absence of anhydrous Fe–Mg silicates and the progressive transformation of intermediate plagioclase into pure albite and sodalite provide evidence for the hydrous and alkali-rich nature of the fenitizing fluid. The most likely source of the fenitizing solutions is the Swartbooisdrif carbonatites, because fenitization occurs only at the contacts of large carbonatite dykes and along fractures and joints within a few metres of the carbonatites, whereas anorthosites bordering syenites are not altered.

Fenitized syenite

Unaltered syenite is characterized by a massive appearance. The main minerals present are coarse- to medium-grained K-feldspar (Or_{91-98}) containing albite exsolution lamellae (An_{1-4}) and plagioclase (An_{0-14} ; Fig. 3d). Late magmatic clinopyroxene (X_{Mg} 0.45–0.51) and/or hastingsite (X_{Mg} 0.01–0.06) form discrete grains in the interstices between feldspar crystals, whereas subordinate and texturally late quartz has been observed in only one of 28 samples investigated. Common accessories are titanite, epidote, clinozoisite, Fe–Ti oxides and zircon.

The main constituent of the syenites intruded by carbonatite is mostly twinned and subordinately untwinned granular albite (An_{0-5}) associated with muscovite (Fig. 3e), both presumably formed at the expense of former K-feldspar. Fragmented relics of chessboard albite are preserved locally. Fine-grained and granular ankerite forms part of the matrix. Heavily strained and partially recrystallized biotite (X_{Mg} 0.26–0.39) as well as anhedral ilmenite and magnetite grains occur as patches or irregular streaks. Biotite has presumably formed at the expense of magmatic hastingsite and/or clinopyroxene. Sodalite as well as minor analcite, both replacing secondary albite, have been observed in only one sample. Fissures in the rock are invaded by ankerite. In the vicinity of carbonatite, hastingsite, clinopyroxene or K-feldspar relics have never been observed in syenites, suggesting that they were pervasively altered by Na-rich hydrous fluids.

Fenitized nepheline syenite

This rock type is characterized by a streaky appearance caused by changes in the grain sizes of the nepheline and K-feldspar from medium to coarse grained. Rare unaffected parts of the nepheline syenite show euhedral nepheline and subhedral tabular perthitic orthoclase as

the cumulus phases of the nepheline syenite. Minor post-cumulus biotite (X_{Mg} 0.50–0.56) is the dominant mineral among the mafic silicates. It occurs as fine-grained anhedral intercumulus grains intimately associated with late-magmatic ilmenite.

When reaching the ferrocarbonatite contacts, the grain size of the nepheline increases, suggesting that carbonatite emplacement may have triggered the nepheline growth. Muscovite and cancrinite are localized in patches, marginally replacing individual nepheline grains. Granular ankerite fills cracks in the rock. Both at its grain margins and along cracks nepheline is altered to sodalite (Fig. 3f), suggesting an interaction of the nepheline syenite with NaCl-rich, Si-undersaturated fluids. The fact that the conversion of nepheline into sodalite is restricted to the contacts between nepheline syenite and carbonatite makes the carbonatite magma the most likely source of fenitization.

Carbonatitic breccia

Because the composition and internal structure of the carbonatitic breccia change on a millimetre scale, only a simplified description of this rock type can be given. A detailed description of the sulphide and oxide mineralogy and textures of this rock-type has been presented by von Seckendorff & Drüppel (1999), von Seckendorff *et al.* (2000) and Drüppel (2003).

Subhedral to anhedral and partially recrystallized granular ankerite (5–40 vol. %) is the main constituent of the cementing ferrocarbonatite matrix (Fig. 4a), whereas subordinate anhedral calcite fills the interstices between ankerite grains. Optically zoned apatite has been observed in two sodalite-bearing and two sodalite-free rock samples. The euhedral to subhedral apatite prisms frequently contain inclusions of albite, magnetite and rare biotite. Apatite is commonly intimately associated with subhedral biotite (X_{Mg} 0.37–0.57) and a first, mostly euhedral and inclusion-free generation of magnetite grains of up to 0.5 mm in diameter (Fig. 4b), but may also occur as isolated grains, dispersed in the carbonatite matrix. Apatite, biotite and magnetite appear to have co-crystallized early in the magmatic history of the carbonatite, although biotite and magnetite have overgrown apatite locally. At their margins, both biotite and apatite are partially recrystallized to granular mosaics, supporting evidence that shearing outlasted the carbonatite emplacement and crystallization. Common accessories are fine-grained, unzoned pyrochlore crystals up to 100 μm in diameter, pyrite and chalcopyrite. Rare albite xenocrysts are dispersed in the carbonate matrix. In clear contrast to the anhedral and fragmented albite in silicate-rich zones, these albites are oval or subrounded in shape, suggesting that they underwent a marginal solution by the carbonatite magma.

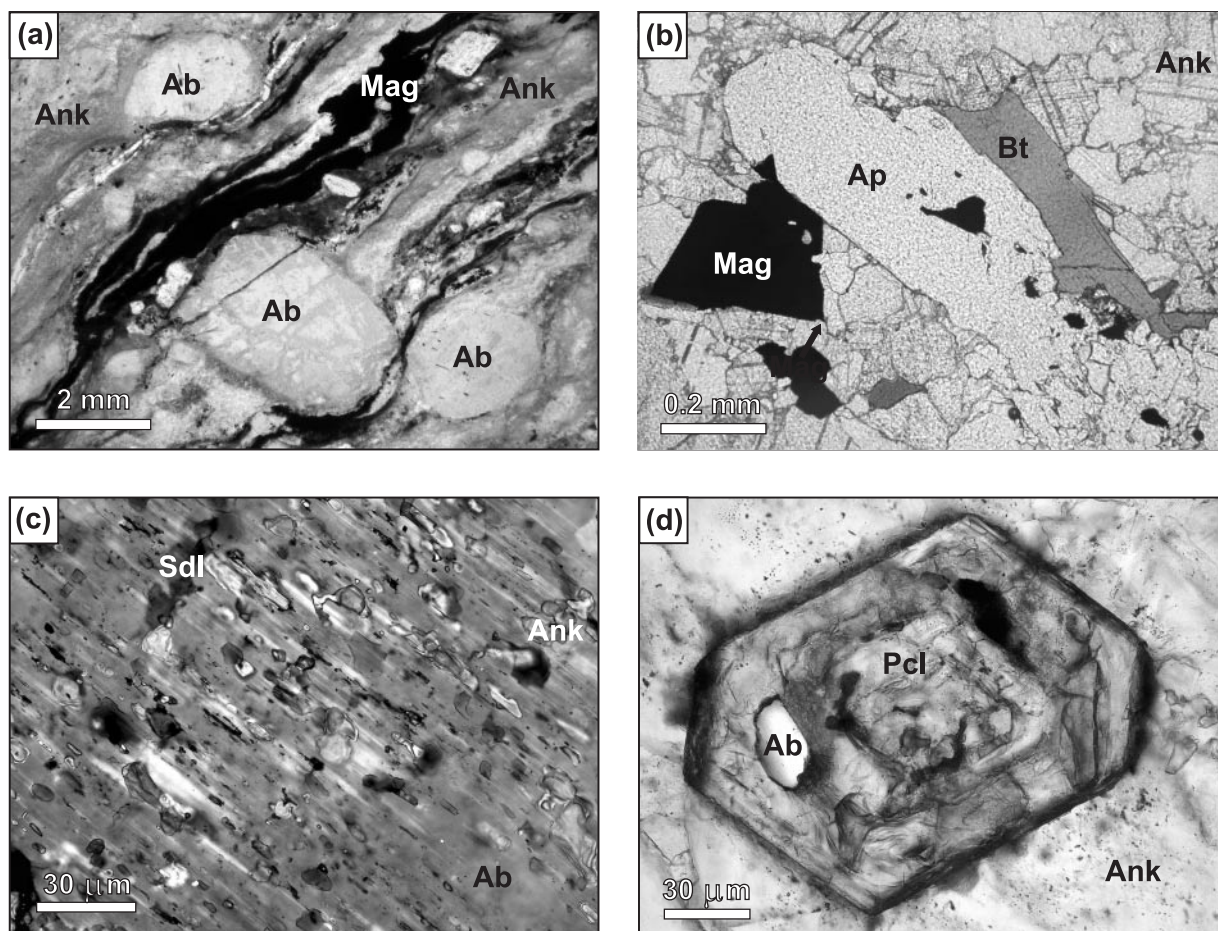


Fig. 4. Photomicrographs of both the carbonatitic breccia (a–c) and the late-stage ferrocarbonatite veins (d) of the Swartbooisdrif area. (a, b, d) Plane-polarized light; (c) cross-polarized light. Ab, albite; Ank, ankerite; Ap, apatite; Bt, biotite; Mag, magnetite; Pcl, pyrochlore; Sdl, sodalite. (a) Most samples of the carbonatitic breccia are characterized by a laminated appearance, because of an alternation of ankerite- and magnetite-rich layers that wrap fragmented albite xenocrysts. (b) Early formed euhedral prisms of apatite with frequent magnetite and biotite inclusions are intimately associated with subhedral biotite and magnetite. Anhedronal ankerite grains of the carbonate matrix border the apatite and biotite. (c) In zones predominantly composed of fragmented wall-rock xenoliths, pure albite is replaced by sodalite (isotropic) and ankerite (high relief) along both, cracks and twin lamellae. (d) Optically zoned pyrochlore, containing an albite inclusion, is surrounded by massive ankerite.

Relic fenitized wall-rock material may be enriched in layers dominated by fragmented and very fine-grained pure albite with undulose extinction. In addition, wall-rock fragments form irregular bounded zones mainly composed of twinned to untwinned granular albite pseudomorphing the former xenolith boundaries and are wrapped by carbonate-rich layers. Sodalite occurs in different textural positions: (1) as monomineralic layers where sodalite replaces very fine-grained fragmented albite; (2) as a replacement product of brecciated and albite-rich wall-rock xenoliths, surrounded by narrow reaction rims of subhedral biotite or small euhedral magnetite grains. Sodalite of both textures may be accompanied by ankerite (Fig. 4c). As evidenced by biotite–sodalite inclusion relationships, the replacement of albite by sodalite started during the end-stages of biotite formation. Along cracks sodalite is altered to an

as yet unknown, fibrous, Si-free Na–Al phase (Drüppel, 2003). A second generation of anhedronal, poikilitic magnetite grains up to 2 cm in diameter, which frequently contain inclusions of albite, sodalite, apatite, biotite and ankerite, occurs as matrix-overgrowths. Subordinate muscovite and cancrinite replace albite, whereby previously formed sodalite is preserved. Cancrinite may also be present as reaction rims around albite- and sodalite-rich patches, separating carbonate-rich from silicate-rich zones. Late-stage calcite occurs in most of the samples, where it overgrows all previously mentioned minerals. Dolomite, haematite, ilmenite, rutile, epidote, chlorite and various sulphides are common accessories.

In two REE-rich samples of the carbonatitic breccia, carbocernaite [general formula $(\text{Ca}, \text{Na})(\text{Sr}, \text{Ce}, \text{Ba})(\text{CO}_3)_2$; up to 15 vol. %] is concentrated in large brown carbonate aggregates, most probably pseudomorphing the shape of

a suspected subhedral precursor carbonate (presumably calcite or ankerite). In these samples, the Ca–Sr–REE carbonate is associated with subordinate subhedral barite and anhedral strontianite grains up to 40 µm in width, both localized between ankerite, carbocernaite and calcite grains; chalcopyrite–pyrite assemblages are replaced by late millerite and violarite. The extreme REE enrichment in the two samples may result from a strong fractionation of the carbonatite melt; however, the mineralization style, i.e. the co-crystallization of carbocernaite, strontianite and barite, rather suggests a secondary REE enrichment of these rocks by the late injection of highly fractionated, Sr-, Ba- and REE-enriched fluids.

Ferrocarbonatite

Major phases of the massive ferrocarbonatites are subhedral to anhedral ankerite grains with curved grain boundaries and subordinate subhedral magnetite grains that frequently display albite inclusions. Minor calcite fills the interstices between ankerite grains whereas rutile occurs as rims around magnetite. In one sample optically zoned pyrochlore euhedra, containing inclusions of pure albite (An_0), have been observed in the vicinity of magnetite grains (Fig. 4d). The contacts between the ferrocarbonatite veins and the older carbonatitic breccia are locally marked by trails of magnetite grains within the ferrocarbonatite. In two samples, cancrinite rims up to 2 mm are developed between the Si-poor ferrocarbonatite and the carbonatitic breccia, pointing to a minor degree of metasomatic exchange between the two rock units. Rounded fragments of sodalite and mostly untwinned albite (An_{0-1}) with undulose extinction, both presumably derived from the fenitized wall-rock anorthosite or the carbonatitic breccia, may form subordinate constituents of this rock type. Thompson *et al.* (2002) additionally described the presence of quartz within the ferrocarbonatite veins, incorporated from the fenitized wall-rock anorthosite. In clear contrast to those workers, we never observed quartz in a total of 112 samples investigated, comprising both the carbonatitic breccia and the younger ferrocarbonatite veins. The lack of quartz in our rock samples agrees well with the general absence of quartz in the anorthosites of the KIC (Drüppel *et al.*, 2001) and their fenitization products.

MINERAL CHEMISTRY OF SELECTED MINERALS

Carbonate minerals

Ankerite

Carbonates with X_{Mg} at or near the ankerite–dolomite transition were observed in two samples of the

carbonatitic breccia, where they occur (1) as euhedral, early crystallized carbonates (X_{Mg} 0.61–0.77) and (2) as inclusions (X_{Mg} 0.79–0.84) in early crystallized magnetite (Table 1). Anhedral matrix carbonates of the main carbonatite body display distinctly lower Mg contents, which slightly decrease in the sequence of sodalite-poor carbonatitic breccia (X_{Mg} 0.56–0.74) to sodalite-rich carbonatitic breccia (X_{Mg} 0.43–0.64) to REE-rich carbonatitic breccia (X_{Mg} 0.25–0.61). All analysed ankerites show minor oscillatory to patchy zoning with the Mg contents commonly decreasing from core towards the rim, probably reflecting the extensive, synchronous biotite formation. In the same direction both MnO and SrO increase from values of 0.6 to 2.5 wt % and 0.1 to 0.8 wt %, respectively. The Ce, La and Na contents of ankerite are near or below the detection limit.

Ankerite (X_{Mg} 0.43–0.64) from the ferrocarbonatite veins has Mg amounts comparable with those of matrix ankerite of the carbonatitic breccia (Table 1), but, at the same time, distinctly higher MnO contents of 2.3–3.4 wt %, suggesting its crystallization from a more fractionated melt. Most of the ankerites preserve nearly unzoned Fe-rich cores (X_{Mg} 0.43–0.49) and display strongly reversed rims (X_{Mg} 0.55–0.64) where the Mg content increases abruptly. This increase is most probably related to the onset of magnetite crystallization.

Carbonates in the fenitized anorthosites and syenites are ankerites with a patchy zonation and Mg/Fe ratios (X_{Mg} 0.48–0.64) in the range of the main carbonatite body, indicating that these rocks were invaded by the ferrocarbonatite melt.

Calcite

Calcite filling the interstices between ankerite grains of the carbonatitic breccia has high Sr/Mn ratios (0.2–0.3 wt % MnO; 0.7–0.8 wt % SrO), whereas secondary calcite that overgrows the granulated matrix displays comparably high MnO contents of 0.7–1.6 wt % and corresponding SrO contents of 0.3–1.3 wt % (Table 1). With MnO contents of 1.2–1.8 wt % and SrO contents of 0.5–0.6 wt %, calcite in the fenitized syenite has the lowest Sr/Mn of all calcites analysed.

Carbocernaite and calcian strontianite

Carbocernaite $(Ca,Na)(Sr,Ce,La)(CO_3)_2$ has been analysed in two REE-rich samples of the carbonatitic breccia (Table 1). It has been distinguished from the chemically similar mineral burbankite by X-ray diffraction and its stoichiometry. The analysed carbocernaite grains have a rather variable composition with the CaO and SrO contents in the range of 14.3–18.1 wt % and 13.6–18.6 wt %, respectively. Decreases of Ca and Sr are accompanied by increases of Na, Ce and La. The composition of the

Table 1: Representative electron microprobe analyses of carbonate minerals in the carbonatitic breccia and the ferrocarbonatite veins

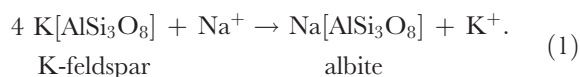
Sample:	Ku-98-59b	Ku-98-25	Ku-99-SA8		Ku-98-14		Ku-01-04		Ku-98-130a		Ku-98-130b	Ku-98-130a
Rock type:	Sdl-free CB		Sdl-rich CB		Sdl-free CB		FV		REE-rich CB		REE-rich CB	REE-rich CB
Mineral:	calcite		ankerite		ankerite		ankerite		ankerite		carbocernaite	strontianite
Position:	1-CA1 overgrowth	1-CA1 interstitial	3-CA1 core	3-CA1 rim	2-CA1 core	2-CA1 rim	C-CA7B core	C-CA7B rim	2-CA1 core	2-CA1 rim	E-REE1 core	D-REE14 core
wt %												
MgO	0.00	0.00	12.28	11.66	12.23	11.81	8.92	11.36	10.11	7.58	0.02	0.00
CaO	53.14	54.64	26.44	26.76	27.54	27.06	28.53	29.18	28.25	28.41	16.82	18.25
MnO	1.36	0.00	2.41	2.44	2.67	2.45	2.67	3.07	1.73	1.66	0.00	0.09
FeO	1.74	0.06	13.77	14.15	11.61	12.65	17.11	12.58	15.89	19.09	0.00	0.02
SrO	0.79	1.87	0.62	0.77	0.85	0.86	0.45	0.75	0.73	0.28	17.79	46.77
BaO	0.01	0.04	0.00	0.00	0.04	0.04	0.00	0.11	0.10	0.00	2.49	0.01
Na ₂ O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.35	0.11
La ₂ O ₃	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	11.66	0.10
Ce ₂ O ₃	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	16.40	0.64
CO ₂	43.95	43.73	44.35	44.24	44.11	43.77	41.72	42.45	44.36	43.41	31.71	32.51
Total	100.99	100.33	99.87	100.03	99.06	98.64	99.48	99.51	101.17	100.42	98.25	98.50

CB, carbonatitic breccia; FV, ferrocarbonatite vein; n.a., not analysed; Sdl, sodalite.

analysed carbocernaite ranges between $(\text{Ca}_{1.01}\text{Na}_{0.09}\text{Sr}_{0.58}\text{Ba}_{0.06}\text{Ce}_{0.15}\text{La}_{0.11})(\text{CO}_3)_2$ and $(\text{Ca}_{0.97}\text{Na}_{0.10}\text{Sr}_{0.50}\text{Ba}_{0.03}\text{Ce}_{0.23}\text{La}_{0.17})(\text{CO}_3)_2$. The chemistry of the carbocernaite is similar to that obtained by Wall *et al.* (1993) for carbocernaite exsolution lamellae in calcite in a REE-rich carbonatite dyke from Rajasthan, India. The analysed strontianite crystals are characterized by high CaO contents of up to 18.3 wt %.

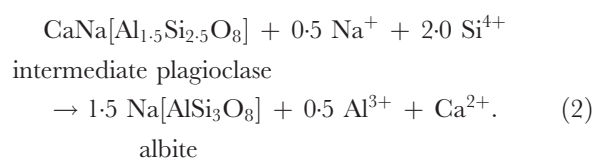
Feldspars

Representative analyses of feldspars are given in Table 2. In the unaltered syenite, alkali-feldspar (reintegrated composition $\text{Ab}_{43.3}\text{An}_{1.9}\text{Or}_{54.8}-\text{Ab}_{88.3}\text{An}_{3.1}\text{Or}_{8.6}$) exhibits a strong perthitic exsolution, with a potassium feldspar host (Or_{91-98}) containing albite (Ab_{95-99}) exsolution lamellae. Plagioclase in the syenite may be subdivided into two types, one displaying an inverse zonation with An contents increasing slightly from the core (An_{9-11}) towards the rim (An_{11-14}) and a second type of unzoned plagioclase crystals (An_{13-18}). The alkali-feldspar of the syenite is transformed into almost pure albite (An_{0-1}) via the reaction



Magmatic plagioclase (An_{37-75}) in the anorthosite neighbouring large carbonatite dykes is replaced, to an

increasing extent, by sodium-rich plagioclase (An_{1-17}) and transformed into pure albite at the direct anorthosite–carbonatite contacts, according to the reaction



In both cases, appreciable amounts of K or Ca must have been released, which presumably account for the close spatial association of albite and carbonate in the fenitized anorthosite and of albite and muscovite in the fenitized syenite. Feldspar constituting the fenitized wall-rock xenoliths incorporated by the carbonatitic breccia, as well as feldspar fragments in the late ferrocarbonatite veins, are always pure albite (An_{0-1}). Plagioclase inclusions in magnetite, apatite, biotite and pyrochlore of the carbonatites exhibit a similar compositional range.

Nepheline

The analysed compositions of magmatic nepheline are in the range of $\text{Ne}_{68.4}\text{Ks}_{19.1}\text{Qtz}_{12.5}$ to $\text{Ne}_{73.6}\text{Ks}_{18.6}\text{Qtz}_{7.8}$ (Table 3). In most cases the grains display a continuous growth zonation, with SiO_2 decreasing towards the rim. When approaching the outermost margins or cracks nepheline is significantly richer in the Ne component

Table 2: Representative electron microprobe analyses of feldspar in the fenitized anorthosite, fenitized syenite and the carbonatitic breccia

Sample:	Ku-99-11		Ku-99-12		Ku-98-07		Ku-98-40		Ku-99-11		Ku-98-56		Ku-98-71		Ku-98-131		Ku-01-04
Rock type:	Syenite		Syenite		Quartz syenite		Quartz syenite		Syenite		Fenitized syenite		Fenitized anorthosite		Carbonatitic breccia		FV
	C-FS3	C-FS3	B-FS2	B-FS2	6-FS5	6-FS5	2-FS1	A-FS1	A-FS1	9-FS1	9-FS2	1-FS1	3-FS2	1-FS1	B-FS5	B-FS5	B-FSES3
	<i>n</i> = 37	SD	<i>n</i> = 49	SD	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 107	SD	<i>n</i> = 1
Mineral:	Kfs	Kfs	Kfs	Kfs	Kfs	Ab	Pl	Pl	Pl	Pl	Pl	Pl	Pl	Pl	Pl	Pl	Pl
Origin:	magma	magma	magma	magma	magma	magma	magma	magma	magma	metas	metas	magma	metas	metas	metas	metas	metas
Position:					host	lamella	core	core	rim	core	core	core	core	core			incl. in Pcl
<i>wt %</i>																	
SiO ₂	65.46	0.58	64.28	0.36	63.47	67.84	63.81	66.07	65.53	67.57	69.01	54.42	63.73	68.29	69.52	0.59	68.27
Al ₂ O ₃	19.51	0.31	19.43	0.19	18.47	19.75	23.12	21.18	21.28	19.87	19.93	29.00	22.32	20.33	20.46	0.35	19.62
MgO	0.02	0.03	0.03	0.08	0.00	0.00	0.00	0.02	0.03	0.01	0.03	0.00	0.02	0.01	0.01	0.02	0.00
CaO	0.64	0.12	0.77	0.05	0.00	0.13	3.64	1.86	2.23	0.02	0.08	10.87	3.37	0.32	0.03	0.03	0.08
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	0.12	0.18	0.07	0.08	0.00	0.00	0.62	0.24	0.31	0.01	0.04	0.48	0.10	0.09	0.13	0.19	0.05
BaO	0.02	0.02	0.02	0.03	0.07	0.00	0.00	0.00	0.00	0.07	0.06	0.10	0.00	0.14	0.02	0.03	0.04
Na ₂ O	7.25	1.23	6.62	0.49	0.34	11.75	9.26	10.66	10.22	11.56	11.67	5.27	8.84	11.46	11.50	0.18	11.59
K ₂ O	5.75	1.90	6.60	0.72	16.18	0.11	0.49	0.12	0.14	0.04	0.12	0.17	0.10	0.03	0.07	0.02	0.04
Total	98.77	0.49	97.82	0.33	98.52	99.56	100.95	100.16	99.74	99.13	100.94	100.31	98.49	100.68	101.73	0.83	99.68
AN(Na/Ca)	3.08	0.56	3.73	0.25	0.00	0.58	17.36	8.74	10.69	0.10	0.38	52.62	17.29	1.52	0.13	0.13	0.36
AB(Na/Ca)	63.66	10.51	58.11	4.10	3.09	98.82	79.84	90.57	88.49	99.58	98.87	46.21	82.08	98.06	99.42	0.19	99.35
OR	33.22	11.00	38.12	4.26	96.79	0.60	2.79	0.69	0.82	0.20	0.65	0.99	0.63	0.18	0.41	0.13	0.23
CE	0.03	0.03	0.04	0.05	0.12	0.00	0.00	0.00	0.01	0.12	0.10	0.18	0.00	0.25	0.04	0.04	0.00

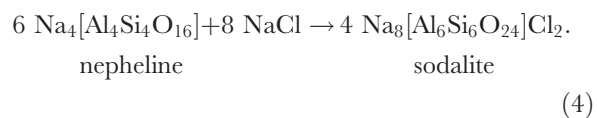
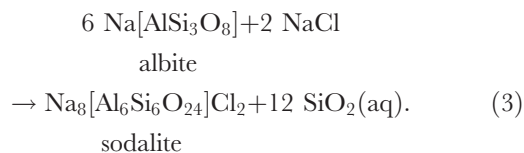
FV, ferrocarbonatite vein; *n*, number of analyses; magma, magmatic; metas, metasomatic; incl. in Pcl, inclusion in pyrochlore; SD, standard deviation.

(Ne_{73.1}Ks_{21.4}Qtz_{5.5}–Ne_{80.3}Ks_{11.2}Qtz_{8.5}). These chemical variations may result from an interaction of the nepheline syenite with sodium-rich fluids, which presumably caused the subsolidus alteration of nepheline into sodalite. A similar subsolidus origin of sodalite has been proposed by Finch (1991) for sodalite in nepheline syenites of the Igaliko complex, South Greenland. The stability of sodalite under hydrothermal conditions has been investigated experimentally by Kostel'nikov & Zhornyak (1995), who found that the stability of sodalite with respect to nepheline increases with increasing NaCl concentrations of the fluid.

Sodalite

The metasomatic sodalite, formed (1) in the fenitized wall-rock anorthosite, (2) in fenitized wall-rock xenoliths incorporated by the carbonatites and (3) as a replacement product of nepheline in the nepheline syenite, is the almost pure sodalite end-member with SO₃ contents below the detection limit (Table 4). The transformation

of plagioclase in the anorthosites and nepheline in the nepheline syenite into sodalite necessitates the introduction of large amounts of NaCl, whereas Si will be released, as is evidenced by the end-member reactions



The additional release of K during the sodalitization of nepheline may account for the close spatial association of sodalite and muscovite in the nepheline syenite, whereas it remains unclear what happened to the SiO₂, released during the sodalitization of albite in all other rock types, as free quartz has never been observed in the

Table 3: Representative electron microprobe analyses of magmatic and metasomatic nepheline in the fenitized nepheline syenite

Sample:	Ku-99-15a 15A-6-NE1	Ku-99-15a 15A-6-NE1	Ku-99-15a 15A-2-NE1	Ku-99-15a 15A-2-NE1	Ku-99-15a 15A-2-NE1
Origin:	magmatic	magmatic	magmatic	metasomatic	metasomatic
Position:	core	rim	rim	crack	crack
wt %					
SiO ₂	43.46	43.44	42.76	41.58	42.04
Al ₂ O ₃	33.40	34.03	34.23	35.01	34.33
MgO	0.00	0.02	0.00	0.00	0.01
CaO	0.01	0.00	0.00	3.05	0.07
MnO	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	0.00	0.00	0.01	0.01	0.04
BaO	0.04	0.00	0.03	0.00	0.02
Na ₂ O	15.64	16.08	15.97	17.22	15.84
K ₂ O	6.15	6.06	6.83	3.66	7.05
Total	98.71	99.65	99.84	100.52	99.39
Ne	69.77	71.75	72.43	80.30	73.08
Ks	18.04	17.80	20.38	11.22	21.39
Q	12.19	10.45	7.19	8.49	5.53

investigated samples of the carbonatitic breccia, the late ferrocarbonatite veins or the fenitized wall rocks. Two explanations may account for this observation: (1) SiO₂ is incorporated into silicate phases crystallized from the formerly silicate-poor carbonatite magma, or (2) SiO₂ was removed into higher, no longer exposed crustal levels.

For the analysis of the trace element contents of sodalite, *in situ* LA-ICP-MS analyses were performed, as measurements of hand-picked sodalite separates gave mostly unreasonable and highly variable values of the respective elements, resulting from a variable but generally high amount of mineral and fluid inclusions contained in the sodalite. Trace element contents of sodalite are generally low, but unexpectedly high values of As (422–657 ppm) have been recorded (Table 4). Remarkably, the REE patterns of sodalite are similar to those obtained for the anorthosite samples (Fig. 5), even though sodalite contains lower absolute values of the respective elements. All REE patterns are characterized by an enrichment of the light REE (LREE) and a weak positive Eu anomaly, although the Ca contents of sodalite are below the detection limit. This fact is taken as evidence that the sodalite, which is abundant in the carbonatitic breccia, was formed at the expense of plagioclase in the incorporated anorthosite xenoliths.

Apatite

Apatites in both the sodalite-free and the sodalite-rich carbonatitic breccia are strontian fluorapatites with F contents increasing from an average value of 2.80 wt % (1.3–4.8 wt %) in sodalite-rich samples to 3.64 wt % (2.2–5.1 wt %) in sodalite-free samples, with the values partly even exceeding two atoms per formula unit (Table 5). In the same sequence of samples the concentrations of Na₂O (0.33–1.09 wt %) and BaO (0–0.14 wt %) increase. The SrO contents of the apatites are in the range of 1.06–2.46 wt %, with the highest SrO concentrations obtained for an apatite of a sodalite-free carbonatitic breccia (Fig. 6). Most of the investigated apatites exhibit only minor amounts of Cl, which, however, may reach values of up to 0.31 wt % in some apatites. Even though the fluorapatites are optically zoned no chemical zonation has been detected with respect to the elements analysed by electron microprobe. High-resolution synchrotron micro-XRF analyses of apatite, however, revealed oscillatory zoning patterns with respect to the REE, whereas Fe and Y increase towards the outer margins (Drüppel, 2003; K. Drüppel & K. Rickers, unpublished data, 2003). The $\sum$ REE of apatite ranges between 0.9 and 3.1 wt %. The fluorapatites have relatively high La contents of 0.2–0.7 wt % and high, positively correlated (La/Nd)_{cn} and (La/Yb)_{cn} ratios increasing from 1.5 to 6.4 and from 33 to 240, respectively. All fluorapatites display straight REE patterns and weakly positive to distinctly negative (Eu/Eu*)_{cn} anomalies of 0.3–1.3 (Drüppel *et al.*, 2002; Drüppel, 2003). Most apatites involve a substitution mechanism of the ‘belovite scheme’ (Rønsbo, 1989): Ca²⁺ + Ca²⁺ = Na⁺ + REE³⁺. The high $\sum$ REE, (La/Nd)_{cn} and (La/Yb)_{cn} ratios of the analysed apatites as well as their straight REE patterns agree well with the findings of Bühn *et al.* (2001) for fluorapatites that crystallized from carbonatite melts.

Biotite

Representative analyses of biotite in the anorthosite and the carbonatitic breccia are given in Table 6. End-member calculations define the analysed biotites as meroxenes and lepidomelanes. All biotites are characterized by minor oscillatory to concentric zoning, involving a core preference for Al and Fe, whereas the rim trends to higher Si and Mg. Biotite displays a considerable variation of X_{Mg} between both rock types and individual samples. Based on major mineralogical differences between the respective samples, biotite in the carbonatitic breccias can be subdivided into the following three groups: (1) metasomatically formed biotite in assemblage with albite and/or sodalite in fenitized wall-rock xenoliths (Bt1); (2) magmatic biotite

Table 4: Representative electron microprobe (EMP) and LA-ICP-MS analyses of sodalite in the carbonatitic breccia

Sample:	Ku-99-OD3		Ku-98-47		Ku-98-57a		
Rock type:	Carbonatitic breccia		Carbonatitic breccia		Carbonatitic breccia		
	Min.	Max.	Min.	Max.	6-Sdl1		
<i>ppm (LA-ICPMS)</i>					<i>wt % (EMP)</i>		
As	422.000	611.000	547.000	657.000	SiO ₂	37.50	37.52
Rb	9.200	13.000	12.000	14.000	Al ₂ O ₃	31.90	31.88
Sr	9.800	14.000	13.000	14.000	Fe ₂ O ₃	0.01	0.04
Ba	57.000	92.000	80.000	89.000	CaO	0.04	0.04
Nb	0.112	0.172	0.131	0.163	Na ₂ O	23.40	23.94
Ta	0.010	0.013	0.012	0.014	K ₂ O	0.01	0.01
La	0.592	0.755	0.683	0.858	Cl	7.37	7.53
Ce	1.000	1.300	1.200	1.400	F	0.13	0.00
Pr	0.105	0.131	0.129	0.164	S	0.00	0.00
Nd	0.345	0.515	0.443	0.510	Total	100.36	100.97
Sm	0.065	0.118	0.000	0.084	O—Cl, F, S	1.72	1.70
Eu	0.044	0.065	0.051	0.073	Total	98.64	99.27
Gd	0.050	0.071	0.068	0.101			
Tb	0.009	0.021	0.007	0.012			
Dy	0.068	0.194	0.065	0.094			
Ho	0.013	0.028	0.017	0.020			
Er	0.021	0.094	0.053	0.064			
Tm	0.006	0.016	0.010	0.090			
Yb	0.042	0.081	0.058	0.100			
Lu	0.007	0.020	0.014	0.020			

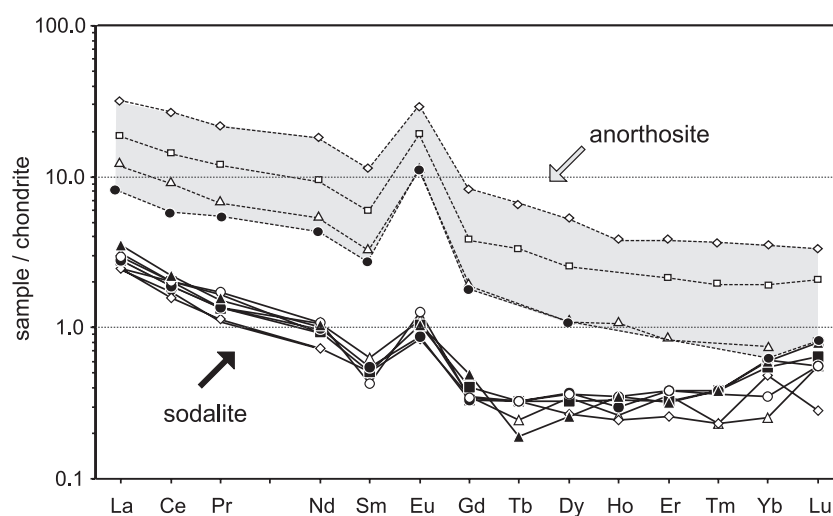


Fig. 5. Chondrite-normalized REE patterns of sodalite from the Swartbooisdrif carbonatitic breccia and anorthosites of the Kunene Intrusive Complex (analysed by LA-ICP-MS and ICP-AES, respectively) normalized using the chondrite values of Evenson *et al.* (1978).

Table 5: Representative electron microprobe analyses of apatite in the carbonatitic breccia

Sample:	Ku-98-131			Ku-99-SA8		Ku-98-14			Ku-98-48		
Rock type:	Sdl-rich carbonatitic breccia			Sdl-rich carbonatitic breccia		Sdl-free carbonatitic breccia			Sdl-free carbonatitic breccia		
	6,2AP3	6,2-AP4	6,2-AP4	2-AP2	4-AP1	2-AP2	2-AP3	2-AP3	A-AP1	A-AP2	A-AP3
wt %											
P ₂ O ₅	42.91	43.06	43.15	41.17	42.23	41.28	41.46	41.82	42.68	42.56	41.58
SiO ₂	0.01	0.02	0.00	0.02	0.03	0.02	0.03	0.01	0.04	0.03	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	53.55	52.94	53.27	53.04	52.49	51.67	51.64	51.97	53.14	52.73	52.35
MnO	0.02	0.04	0.05	0.04	0.06	0.06	0.05	0.09	0.03	0.03	0.03
FeO	0.12	0.19	0.25	0.02	0.30	0.04	0.06	0.20	0.05	0.04	0.00
SrO	1.33	1.47	1.50	1.95	1.92	1.97	1.80	1.73	1.24	1.23	1.20
BaO	0.04	0.03	0.06	0.03	0.02	0.02	0.03	0.01	0.02	0.03	0.00
Na ₂ O	0.55	0.66	0.62	0.51	0.54	0.59	0.58	0.55	0.67	0.71	0.72
H ₂ O	0.31	0.48	0.98	0.45	0.58	0.04	0.04	0.00	0.17	0.17	0.00
F	3.17	2.67	1.67	2.63	2.41	3.72	3.74	4.42	3.28	3.23	4.30
Cl	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.03	0.04	0.01
Total	102.02	101.59	101.53	99.88	100.59	99.40	99.44	100.82	101.34	100.79	100.19
O—F	1.34	1.13	0.70	1.11	1.01	1.56	1.58	1.86	1.38	1.36	1.81
O—Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Total	100.68	100.46	100.83	98.77	99.57	97.83	97.86	98.96	99.96	99.42	98.37

Sdl, sodalite.

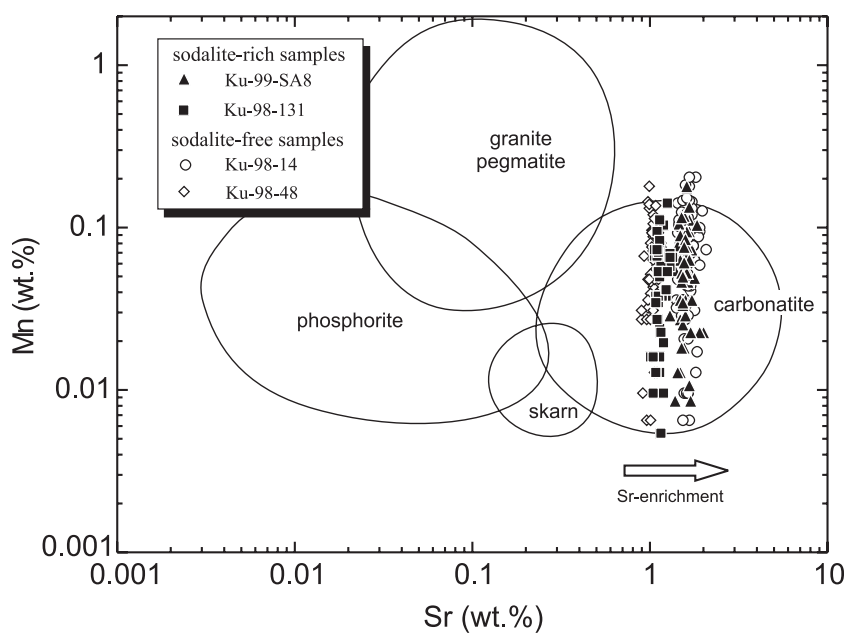


Fig. 6. Variation in Mn and Sr contents (wt %) of the Swartbooisdrif carbonatite apatites compared with apatites in skarns, phosphorites, granite pegmatites and carbonatites from world-wide localities (compiled by Hogarth, 1989). All apatites from the Swartbooisdrif carbonatites plot in the carbonatite field.

Table 6: Representative electron microprobe analyses of biotite in the anorthosite and the carbonatitic breccia

Biotite group:		Bt1		Bt2		Bt2		Bt3		Bt3		
Sample:	Ku-98-52	Ku-98-59b		Ku-98-131		Ku-99-SA8		Ku-98-14		Ku-98-48		
Rock type:	anorthosite	fenitized xenolith		carbonatitic breccia		carbonatitic breccia		carbonatitic breccia		carbonatitic breccia		
Assemblage:	Bt–Ilm assemblage	Sdl–Bt assemblage		Ap–Sdl–Bt assemblage		Ap–Sdl–Bt assemblage		Ap–Bt assemblage		Ap–Bt assemblage		
	1-BT1	2BT1	1-BT2	3-BT1	BT-L1	BT-L1	2-BT1	2-BT1	2-BT2	2-BT2	A-BT1	A-BT1
<i>wt %</i>												
SiO ₂	35.73	34.39	34.64	34.00	36.04	36.07	35.81	35.79	35.37	35.26	34.88	35.24
TiO ₂	2.19	2.24	1.91	1.60	2.83	2.73	2.75	2.68	2.44	2.53	3.40	3.44
Al ₂ O ₃	16.25	16.35	16.52	17.12	13.09	12.76	14.30	14.20	13.88	13.73	13.66	13.47
Cr ₂ O ₃	0.02	0.00	0.00	0.04	0.17	0.18	0.03	0.00	0.03	0.00	0.00	0.01
FeO	23.15	23.73	25.49	25.60	20.30	20.53	20.88	21.19	21.81	21.33	24.03	23.78
NiO	0.01	0.00	0.03	0.07	0.07	0.14	0.03	0.00	0.07	0.07	0.00	0.00
MnO	0.01	0.02	0.05	0.10	0.02	0.04	0.17	0.17	0.13	0.12	0.12	0.18
MgO	9.35	8.62	6.47	5.92	11.89	12.17	11.11	11.27	11.32	11.18	9.03	8.89
CaO	0.00	0.03	0.05	0.00	0.00	0.00	0.03	0.07	0.01	0.04	0.01	0.00
Na ₂ O	0.96	0.18	0.04	0.22	0.14	0.10	0.18	0.14	0.16	0.15	0.15	0.10
K ₂ O	8.50	8.82	9.45	9.41	9.84	9.63	9.54	9.49	9.26	9.27	9.64	9.57
BaO	0.25	0.26	0.12	0.02	0.00	0.10	0.07	0.10	0.10	0.15	0.00	0.00
F	n.a.	n.a.	0.70	0.75	2.40	2.11	1.61	1.54	2.59	2.17	0.92	1.06
Cl	n.a.	n.a.	0.02	0.08	0.00	0.01	0.04	0.00	0.03	0.02	0.06	0.01
Total	96.42	94.64	95.49	94.93	96.80	96.57	96.54	96.62	97.20	96.01	95.91	95.74
O–F	—	—	–0.29	–0.31	–1.01	–0.89	–0.68	–0.65	–1.09	–0.91	–0.39	–0.44
O–Cl	—	—	0.00	–0.02	0.00	0.00	–0.01	0.00	–0.01	0.00	–0.01	0.00
Total	96.42	94.64	95.20	94.60	95.79	95.68	95.86	95.98	96.10	95.09	95.51	95.29
X _{Mg}	0.42	0.39	0.31	0.29	0.51	0.51	0.49	0.49	0.48	0.48	0.40	0.40

Ap, apatite; Bt, biotite; CB, carbonatitic breccia; Ilm, ilmenite; n.a., not analysed; Sdl, sodalite.

in assemblage with apatite in sodalite-bearing samples (Bt2); (3) magmatic biotite in assemblage with apatite in sodalite-free samples (Bt3). The X_{Mg} of secondary Bt1 is highly variable but clusters around 0.35 (0.26–0.60), whereas magmatic biotite in assemblages (2) and (3) exhibits higher and more restricted average values of 0.49 (0.44–0.57) and 0.44 (0.37–0.52), respectively.

The highest but most variable Cl contents of up to 0.24 wt % occur in Bt1 of the fenitized wall-rock xenoliths. In contrast, magmatic Bt2 and Bt3 in assemblage with apatite contain Cl amounts at or below the detection limit (up to 0.11 wt %) corresponding to the higher X_{Mg} values (Table 6). The results are in agreement with experimental studies of Munoz & Swenson (1981) and Volfinger *et al.* (1985), who suggested a preferential incorporation of Cl into Fe-rich biotites, although the predicted trend of ‘Mg–Cl avoidance’ is not very pronounced in the rock samples investigated. In particular, Bt1 in sample Ku-98-59b has Cl contents that are much more variable than the corresponding X_{Mg} .

Therefore, it appears that Cl incorporation in the metasomatically formed Bt1 is not solely governed by Mg–Cl avoidance, but additionally results from the interaction of Bt1 with metasomatic fluids. The generally low chlorine contents in the analysed micas, especially in Bt2 and Bt3 of presumed magmatic origin, as well as those of the analysed apatites, are consistent with those found in biotite and apatite of carbonatite complexes elsewhere. According to Gittins (1989), chlorine preferentially goes into Cl- and alkali-rich fenitizing fluids, which are separated when a carbonatite magma reaches water saturation.

Distinct trends are also displayed by the Si/Al ratios of the biotite subgroups (Fig. 7). The majority of Bt1 exhibits a scattered distribution but plots within the respective compositional fields of biotite of the bordering anorthosite and syenite. In clear contrast, Bt2 and Bt3, which both crystallized from the carbonatite melt, display a distinct trend extending from high Al values towards Al-deficient compositions compared with ideal Si + Al = 4 behaviour, suggesting that the carbonatite

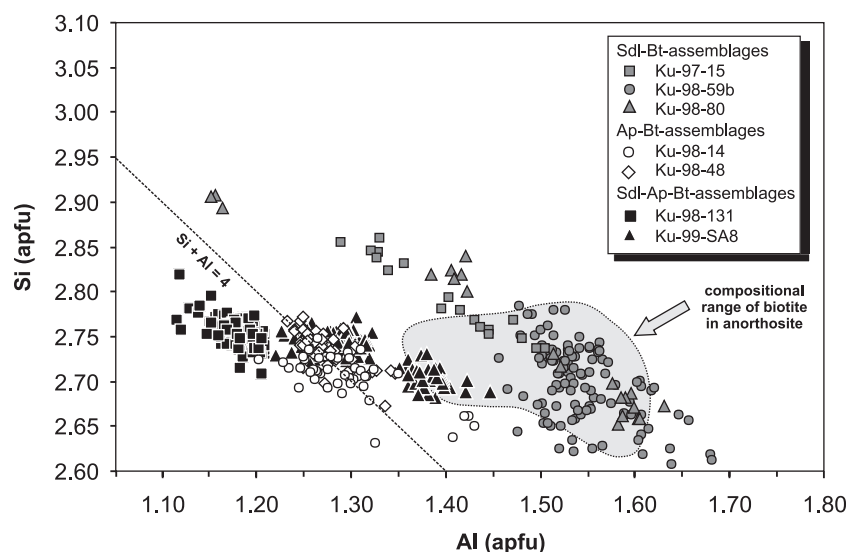


Fig. 7. Si–Al diagram (a.p.f.u.) for trioctahedral biotite from samples of the carbonatitic breccia of the Swartbooisdrif alkaline province. The shaded field marks the compositional range of magmatic biotite in anorthosite (data from Drüppel, 2003). Ideal $\text{Si} + \text{Al} = 4$ behaviour of biotite is marked as a dashed line.

melt contained only minor amounts of Al that were consumed during biotite formation.

Pyrochlore

Medium-grained and optically zoned pyrochlore is restricted to the late ferrocarbonatite veins; the grain sizes of unzoned pyrochlore crystals in the carbonatitic breccia range from fine grained to very fine grained. Electron microprobe analyses reveal high SrO and Na_2O contents of 0.96–2.24 wt % and 6.54–7.98 wt %, respectively (Table 7). The fine-scale oscillatory zonation of pyrochlore, observed microscopically, is also displayed in its mineral chemistry. All analysed grains show a concentric zonation pattern with a core preference for Ca and Ti, whereas Fe, Ba, Ce and Sr are concentrated in the rim.

GEOCHEMISTRY

Major and trace element compositions of anorthosites, syenites and carbonatites are presented in Table 8.

Anorthosite

Major and trace element data for the anorthositic rock suites display a consistent correlation pattern, involving an increase of MnO, MgO, FeO^t and TiO_2 and decreasing SiO_2 , Al_2O_3 and CaO from anorthosite to troctolite and leucogabbonorite. Because of the strong variability of the chemical composition of the anorthositic rocks, fenitized anorthosite samples mostly plot within the compositional range of unaltered anorthosites in selected Harker diagrams (Fig. 8).

Table 7: Representative electron microprobe analyses of pyrochlore in the ferrocarbonatite veins

Sample:	Ku-01-04	Ku-01-04	Ku-01-04	Ku-01-04
	04-a-PCL-A	04-a-PCL-A	04-C-PCL-4	04-C-PCL-4
Position:	rim	core	rim	core
wt %				
Nb ₂ O ₅	70.73	71.45	68.77	70.15
SiO ₂	0.21	0.00	0.49	0.00
TiO ₂	1.76	2.06	1.83	1.53
Fe ₂ O ₃	0.30	0.14	0.38	0.00
Ce ₂ O ₃	2.07	1.50	1.83	1.31
CaO	12.22	13.73	11.49	13.76
SrO	1.66	1.22	1.93	1.38
BaO	0.00	0.02	1.03	0.00
Na ₂ O	7.34	7.41	6.82	7.70
F	3.69	2.49	5.37	4.32
Total	99.98	100.02	99.95	100.14

Syenite

The data for samples of unaltered syenites form coherent arrays in major and trace element variation diagrams (Fig. 8), involving a negative correlation of SiO_2 with TiO_2 , Al_2O_3 , MnO, MgO, CaO, Na_2O and Sr, whereas K_2O , Rb and Y correlate positively with SiO_2 . Samples of weakly fenitized syenite trend to higher Na_2O , Zn, Sr, Nb, CO_2 and H_2O and lower SiO_2 , K_2O and Ba, but do not display a clear correlation for the respective elements.

Table 8: Major and trace element analyses of representative samples of the anorthosite, fenitized anorthosite, syenite, fenitized syenite, nepheline syenite, carbonatitic breccia and ferrocarbonatite from the Swartbooisdrif area

Rock type:	A	FA	A	FA	S		FS		NS	CB			CB		FV	
Sample:	98-231	98-77	97-3C	98-71	98-40	99-13	98-70s	98-103s	99-15a	98-70c	98-118	99-05	98-130a	98-130b	01-04	01-05
Comments:										Sdl-free	Sdl-poor	Sdl-rich	REE-rich	REE-rich		
wt %																
SiO ₂	49.54	45.48	47.00	42.61	65.80	59.78	52.62	59.37	49.54	38.80	22.10	41.76	4.00	11.00	1.43	b.d.l.
TiO ₂	0.09	1.69	1.88	1.46	0.25	0.32	1.62	0.23	0.01	2.05	1.47	0.13	0.18	0.31	0.04	0.01
Al ₂ O ₃	26.29	21.65	22.37	20.38	16.44	17.25	16.38	18.83	28.93	17.59	7.59	20.67	1.60	6.20	0.42	0.16
Fe ₂ O ₃	1.09	2.52	2.10	2.72	1.87	4.65	3.99	1.93	0.17	1.84	14.88	2.27	3.90	11.40	21.54	21.51
FeO	2.64	6.57	6.09	5.36	1.02	3.80	4.36	1.64	0.20	8.30	n.a.	3.31	n.a.	n.a.	n.a.	n.a.
MnO	0.05	0.09	0.16	0.09	0.05	0.16	0.22	0.04	0.02	0.39	1.44	0.57	0.02	0.45	2.43	2.33
MgO	4.85	4.22	3.14	3.46	0.30	0.14	1.06	0.49	b.d.l.	3.03	4.53	1.78	2.50	4.10	7.98	7.10
CaO	11.70	7.63	7.19	7.66	2.00	1.93	5.25	2.86	0.60	10.39	16.50	6.49	15.60	15.10	27.06	27.31
Na ₂ O	3.25	4.23	4.34	7.72	6.07	5.91	8.48	10.48	12.92	4.84	4.77	12.09	5.90	7.90	0.25	b.d.l.
K ₂ O	0.19	0.52	1.63	0.42	4.33	5.67	0.19	0.16	5.82	1.11	0.01	0.45	0.03	0.05	b.d.l.	b.d.l.
P ₂ O ₅	0.01	0.02	0.06	0.06	0.05	0.06	0.48	0.05	b.d.l.	0.22	0.45	0.05	0.07	0.58	0.01	b.d.l.
S	0.02	0.02	0.09	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.06	b.d.l.	b.d.l.	0.30	0.11	b.d.l.	b.d.l.
LOI	0.65	4.07	2.90	7.96	0.95	0.26	4.47	3.18	1.87	11.04	24.45	10.96	30.63	26.56	36.73	39.60
CO ₂	n.a.	n.a.	n.a.	n.a.	0.65	0.08	3.90	2.41	1.03	8.60	22.74	8.96	29.49	24.90	35.38	38.14
H ₂ O	n.a.	n.a.	n.a.	n.a.	0.30	0.19	0.57	0.77	0.84	2.44	1.71	2.01	1.14	1.66	1.39	1.68
Total	100.37	98.71	98.94	99.92	99.12	99.93	99.13	99.26	100.09	99.66	98.19	100.54	64.73	83.76	97.89	98.02
ppm																
Sc	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	19	b.d.l.	b.d.l.	21	19	10	26	24	13	15
V	17	154	193	178	b.d.l.	11	101	45	b.d.l.	148	40	16	b.d.l.	73	77	22
Cr	17	54	32	37	b.d.l.	b.d.l.	24	b.d.l.	b.d.l.	57	b.d.l.	12	b.d.l.	b.d.l.	13	25
Co	45	50	59	43	138	34	36	61	32	47	27	22	15	11	44	30
Ni	139	92	84	75	b.d.l.	b.d.l.	12	8	b.d.l.	52	19	11	287	86	40	27
Zn	16	77	91	65	62	201	68	53	7	207	97	53	40	115	163	120
Ga	17	17	b.d.l.	21	31	30	23	27	52	30	b.d.l.	28	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Rb	b.d.l.	5	34	0	116	120	6	b.d.l.	178	24	5	9	112	62	9	9
Sr	472	634	740	600	201	52	740	597	128	1341	4171	1801	89000	38000	5200	4893
Y	b.d.l.	b.d.l.	8	b.d.l.	79	41	44	55	19	b.d.l.	b.d.l.	b.d.l.	36	35	30	b.d.l.
Zr	b.d.l.	17	46	34	694	390	3326	2120	19	156	38	44	b.d.l.	b.d.l.	31	32
Nb	b.d.l.	b.d.l.	5	b.d.l.	55	155	57	64	7	64	374	87	b.d.l.	b.d.l.	652	b.d.l.
Mo	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	12	b.d.l.	b.d.l.	b.d.l.	b.d.l.	43	b.d.l.	b.d.l.	b.d.l.	5
Sn	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	54	38	b.d.l.	b.d.l.
Ba	112	385	829	434	1448	139	476	1171	59	665	215	443	22000	8600	234	47
Pb	b.d.l.	b.d.l.	b.d.l.	b.d.l.	29	20	28	21	16	24	9	29	700	274	22	9
Th	b.d.l.	b.d.l.	b.d.l.	b.d.l.	13	b.d.l.	b.d.l.	30	b.d.l.	b.d.l.	7	b.d.l.	556	193	6	b.d.l.
U	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	7	b.d.l.	13	b.d.l.	b.d.l.	b.d.l.	7	12	17	b.d.l.	b.d.l.
La	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	734	b.d.l.	54000	22000	140	b.d.l.
Ce	b.d.l.	b.d.l.	b.d.l.	b.d.l.	150	168	160	380	33	240	1116	195	79000	33000	290	100
Pr	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4272	1538	b.d.l.	b.d.l.
Nd	b.d.l.	b.d.l.	b.d.l.	b.d.l.	70	82	65	130	b.d.l.	70	228	65	30000	11000	100	22

A, anorthosite; CB, carbonatitic breccia; FA, fenitized anorthosite; FS, fenitized syenite; FV, ferrocarbonatite vein; NS, nepheline syenite; S, syenite; Sdl, sodalite; b.d.l., below detection limit; n.a., not analysed.

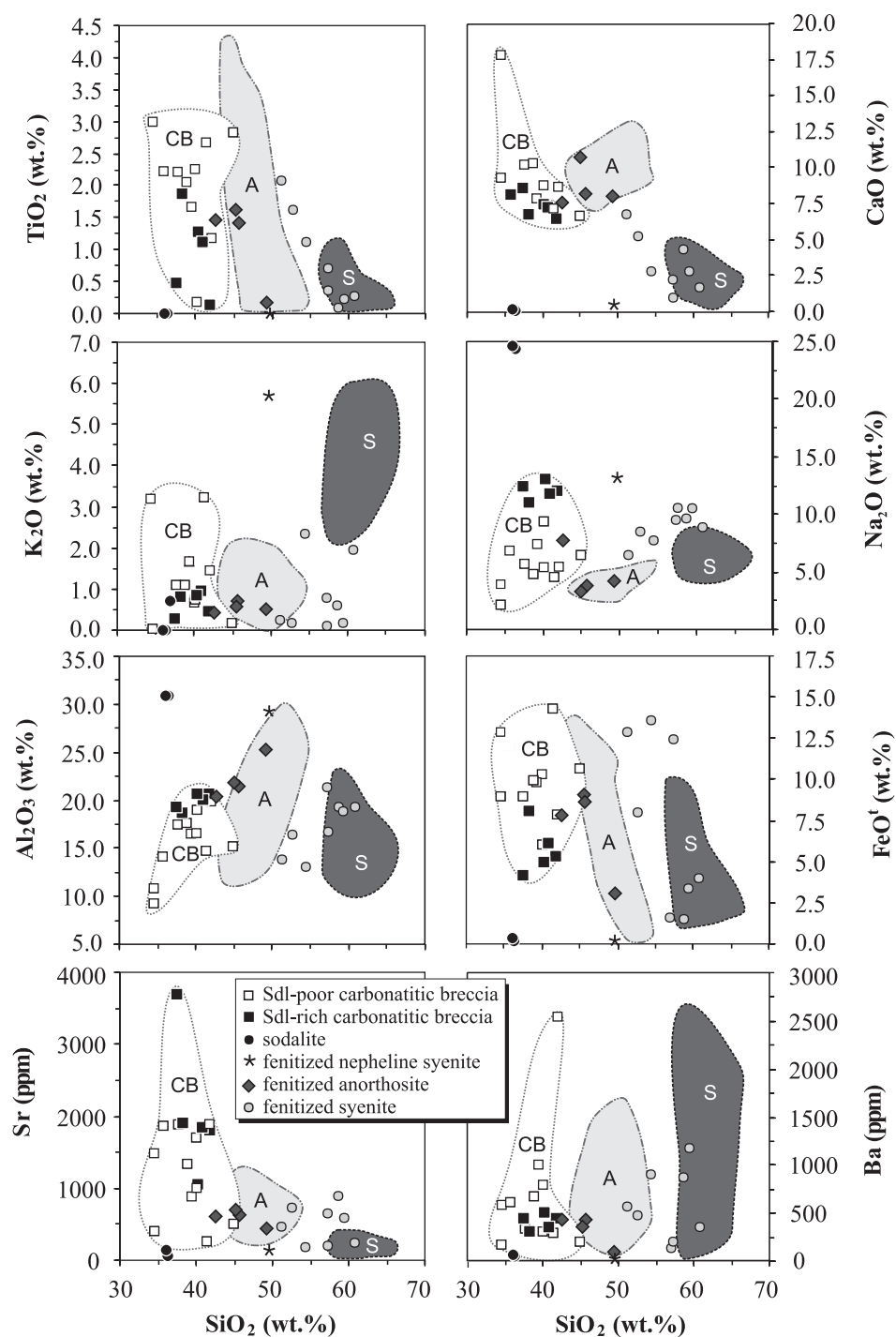


Fig. 8. Selected Harker diagrams for the fenitized anorthosite, fenitized syenite, fenitized nepheline syenite and the carbonatitic breccia from the Swartbooisdrif area. A (light grey), compositional range of anorthositic rocks of the KIC; S (dark grey), compositional range of the Swartbooisdrif syenites; CB, compositional range of the carbonatitic breccia; data for the anorthositic and syenitic protoliths from Drüppel (2003).

Nepheline syenite

The weakly fenitized nepheline syenite analysed has an alkali-rich, peraluminous and silica-undersaturated composition, thus differing significantly from the older

syenites. The Al_2O_3 , Na_2O , K_2O and Rb contents are higher than those of the fenitized syenites, whereas SiO_2 , CaO , FeO^t , Sr, Ba, CO_2 and H_2O are considerably lower (Fig. 8). With a value of 43 ppm, the ΣREE of the fenitized nepheline syenite is extremely low. The sample is

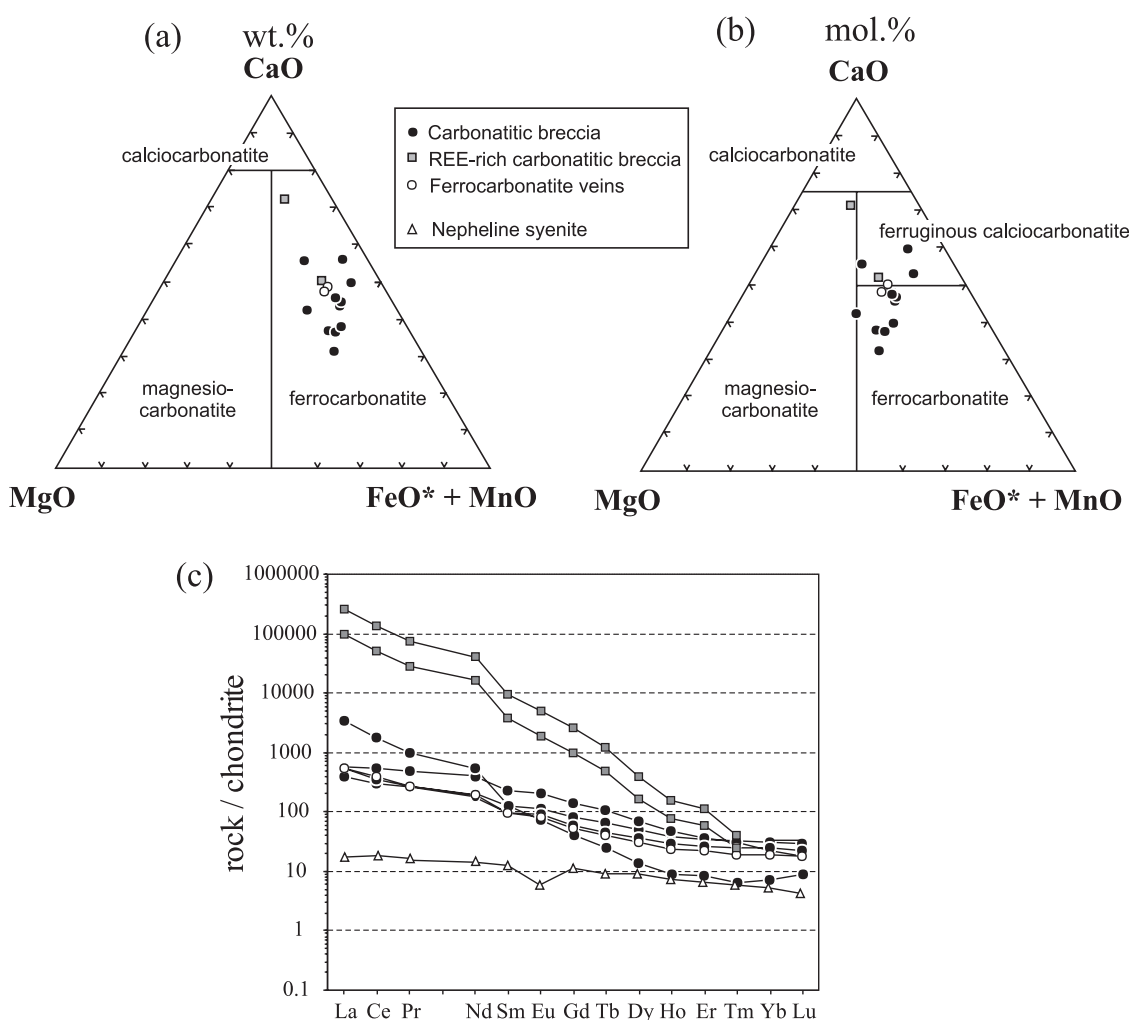


Fig. 9. Classification diagrams for carbonatites based on their major element composition, (a) IUGS classification (Le Maitre, 1989); (b) classification after Gittins & Harmer (1997). (c) Diagram showing the variations in chondrite-normalized REE abundances for REE-poor and REE-rich samples of the carbonatitic breccia, the ferrocarbonatite veins and the fenitized nepheline syenite of the Swartbooisdrif area, normalized using the chondrite values of Evenson *et al.* (1978).

characterized by a straight REE pattern and comparably low $(\text{La}/\text{Nd})_{\text{cn}}$ and $(\text{La}/\text{Yb})_{\text{cn}}$ ratios of 1.2 and 3.4, respectively (Fig. 9c). A distinctly negative $(\text{Eu}/\text{Eu}^*)_{\text{cn}}$ anomaly of 0.5 suggests plagioclase fractionation of the magma parental to the nepheline syenite.

Carbonatitic breccia and ferrocarbonatite veins

Compared with the anorthosites, the 18 samples of the carbonatitic breccia (excluding the REE-rich samples) generally contain significantly lower absolute amounts of SiO_2 (22–45 wt %) but, nevertheless, mostly display similar correlation patterns when plotted in selected Harker diagrams (Fig. 8). Hence anorthosite is assumed to be the dominant component of the wall-rock xenoliths.

Increasing carbonatite/xenolith ratios are mirrored by increases of FeO^t , CaO , P_2O_5 , S, Sr, Nb, Zn, Ba, Th, U, the LREE and CO_2 , suggesting that the above-mentioned elements represent primary constituents of the carbonatite magma. Sodalite-rich samples of the carbonatitic breccia trend to high Al_2O_3 and Na_2O , whereas the sodalite-poor and sodalite-free samples are generally higher in TiO_2 , CaO , MgO , FeO^t and V, reflected by higher contents of biotite, magnetite and ankerite.

Because most of the wall-rock fragments incorporated and subsequently fenitized by the carbonatite are almost entirely composed of albite and/or sodalite (95–100 vol. %), the totals of Na_2O were subtracted from the analyses, together with corresponding amounts of SiO_2 and Al_2O_3 (calculated for the petrographically observed albite:sodalite ratios of each single sample, i.e. 0.7–1.0 in Sdl-poor

Table 9: Recalculated composition of the carbonatite matrix of the carbonatitic breccia (see text for details)

Rock type: carbonatite matrix of the carbonatitic breccia												
Sample:	98-28	98-70c	99-04	98-08	98-73c	98-103c	98-27	98-80	98-83	99-05	99-07	99-08
<i>wt %</i>												
SiO ₂	7.82	9.84	4.32	7.45	9.52	7.44	3.64	7.19	1.82	3.42	4.82	4.04
TiO ₂	4.75	4.31	0.55	5.16	2.94	4.04	5.55	4.61	1.58	0.47	3.86	4.87
Al ₂ O ₃	8.10	9.32	4.95	7.26	10.73	5.02	2.82	3.77	1.61	3.17	3.13	2.27
Fe ₂ O ₃	8.48	3.88	5.82	7.41	6.62	6.99	6.39	7.44	3.89	8.15	10.16	5.64
FeO	11.59	17.45	12.29	16.89	13.81	17.67	18.02	18.27	9.94	11.90	11.90	13.66
MnO	1.05	0.82	1.01	0.55	1.54	0.68	1.06	0.85	1.42	2.05	0.96	0.53
MgO	5.82	6.37	10.61	10.18	5.89	9.15	8.00	10.69	7.54	6.39	3.59	2.91
CaO	21.98	21.86	21.62	20.12	21.84	19.32	20.09	16.72	27.98	23.30	25.30	28.52
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	2.39	2.34	2.14	1.53	3.58	4.04	2.39	4.53	0.93	1.62	3.28	3.29
P ₂ O ₅	0.13	0.46	0.20	0.55	0.07	1.24	0.18	1.74	3.00	0.18	0.62	0.60
S	0.00	0.13	0.00	0.09	0.00	0.00	0.12	0.00	0.10	0.00	0.00	0.60
LOI	27.89	23.22	36.49	22.82	23.46	24.42	31.75	24.20	40.20	39.36	32.39	33.07
CO ₂	23.67	18.10	28.52	17.82	18.26	21.22	27.09	21.82	35.14	32.16	26.70	26.85
H ₂ O	4.22	5.13	7.97	5.00	5.20	3.20	4.66	2.38	5.05	7.21	5.69	6.21
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

and 0.45–0.55 in Sdl-rich samples), to obtain an approximation of the composition of the carbonatite matrix (Table 9). Samples containing metasomatically formed biotite and/or muscovite were excluded from the calculation. Recalculated SiO₂ and Al₂O₃ contents display ranges of 2–10 wt % and 0.5–6 wt %, respectively, with the highest values being obtained for samples that also contain significant amounts of K₂O (1–5 wt %), mirrored by the abundance of orthomagmatic biotite. Values for FeO^t, CaO, MgO, MnO, TiO₂ and P₂O₅ are similar to those of ferrocarbonatites world-wide [compiled by Woolley & Kempe (1989)]. Following the IUGS classification (Le Maitre, 1989), which is adopted for this study, the carbonatite matrix of the carbonatitic breccia is ferrocarbonatitic in nature (Fig. 9a and b).

REE-rich samples of the carbonatitic breccia exhibit similar low SiO₂ (4–11 wt %) and Al₂O₃ contents (2–6 wt %), both positively correlated with the Na₂O content (6–8 wt %), pointing to a minor degree of wall-rock contamination. The amounts of FeO^t and MgO are too low to classify the investigated samples as ferrocarbonatites, whereas extremely high values were obtained for CaO (15–16 wt %), Sr (3.8–8.9 wt %), Ba (0.8–2.2 wt %), La (2.2–5.4 wt %), Ce (3.3–7.9 wt %) and Nd (1.1–3.0 wt %), reflected in the high modal amounts of secondary Ca–Sr–REE carbonates, strontianite and barite.

Compared with the carbonatitic breccia, the late ferrocarbonatite veins are characterized by low SiO₂ contents

(0–1.4 wt %), because of the low potential of these small-scale veins to incorporate wall-rock material. Values of FeO^t, MgO and CaO are similar to the mean values of ferrocarbonatites world-wide, as summarized by Woolley & Kempe (1989). The MnO contents are high (2.33–2.43 wt %), whereas the amounts of K₂O, TiO₂, P₂O₅ and S are near the detection limit. The late ferrocarbonatite veins exhibit Sr, La, Ce and Nd contents in the ppm range, although Sr contents may be as high as 0.5 wt %. According to the classification of both Le Maitre (1989) and Gittins & Harmer (1997) the rocks are ferrocarbonatites (Fig. 9a and b). The chemical composition of the ferrocarbonatite veins resembles the recalculated composition of the carbonatite matrix of the carbonatitic breccia, although samples of the younger ferrocarbonatite veins contain lower amounts of FeO^t, MgO, K₂O, TiO₂, P₂O₅ and S, which were presumably incorporated by previously crystallized biotite, ankerite, Fe–Ti oxides, apatite and sulphides. Consequently, the ferrocarbonatite veins are interpreted as late-stage fractionation products of the carbonatite magma that also formed the carbonatitic breccia.

The $\sum$ REE of the carbonatitic breccia and the ferrocarbonatite veins range between 9 ppm and 17.7 wt %, with the highest values obtained for the REE-rich carbonatitic breccia and the lowest for the ferrocarbonatite veins (Fig. 9c). All investigated samples have high and positively correlated (La/Nd)_{cn} and (La/Yb)_{cn} ratios and

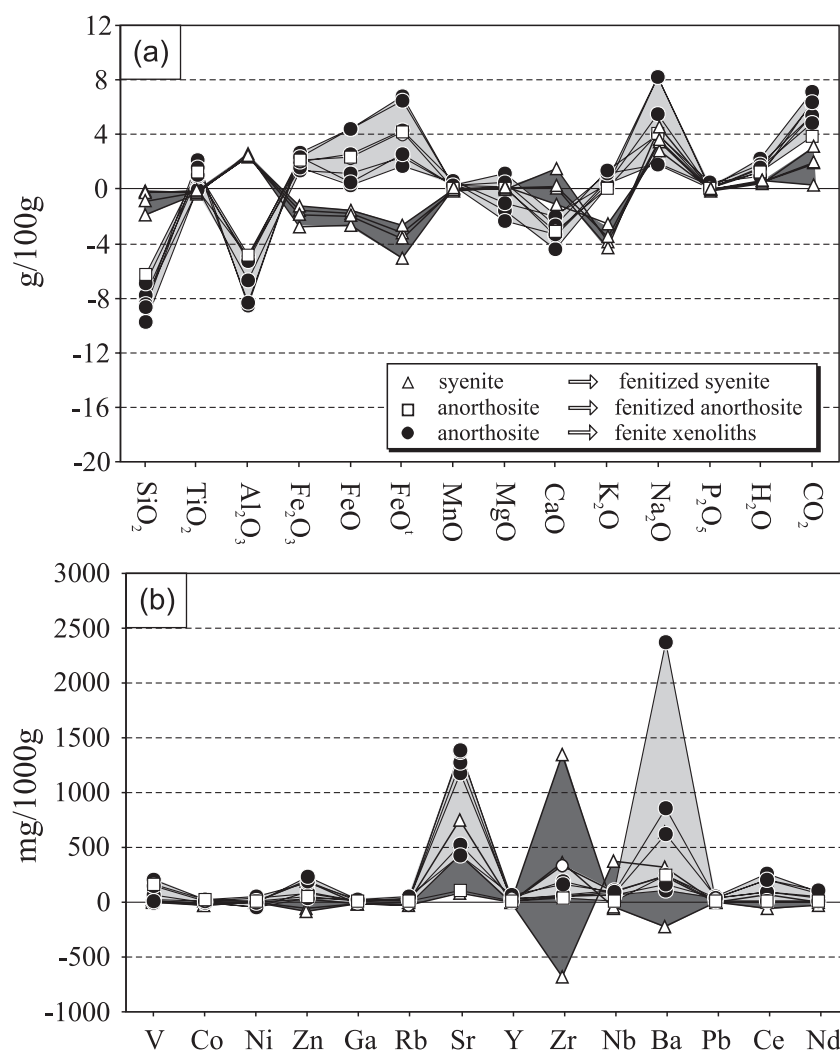


Fig. 10. Diagrams illustrating the main chemical changes of the anorthositic and syenitic protoliths caused by equilibration with fenitizing fluids. y-axis shows results of the mass balance calculations (see also Table 10); light grey, fenitization of the anorthosites; dark grey, fenitization of the syenites. (a) Major element data and (b) trace element data.

display straight REE patterns and weak positive $(\text{Nd}/\text{Nd}^*)_{\text{cn}}$ anomalies of 1.1–1.6. REE-rich samples of the carbonatitic breccia have Tm contents similar to those of the REE-poor samples of the carbonatitic breccia, but substantially more LREE, reflected by the high modal abundance of carbocernaite. Samples of the ferrocarbonatite veins and the REE-poor carbonatitic breccia have similar REE abundances, which, however, are conspicuously low when compared with other carbonatites world-wide (e.g. Woolley & Kempe, 1989; Horning-Kjarsgaard, 1998).

MASS BALANCE CALCULATIONS

To constrain the nature of the source of the fenitizing fluids, mass change calculations have been performed for

four samples of weakly fenitized syenite, one sample of a strongly fenitized wall-rock anorthosite and six samples of fenitized anorthositic xenoliths in the carbonatitic breccia using the approach of Gresens (1967). As composition–volume diagrams show no preferential clustering of intersection points of the element lines with the zero mass change axis, values of minimum total mass change have been used to determine the volume factor F_V , as was proposed by Kresten (1988). Results of the mass change calculations are illustrated in Fig. 10 and compiled in Table 10.

As is shown in Fig. 10, the fenitization of the wall-rock anorthosite was less severe than that of the anorthositic xenoliths forming part of the carbonatitic breccia. The two fenite types display similar chemical trends, suggesting that their alteration was caused by fluids of a similar composition. The main components subtracted during

the fenitization of the anorthosites are SiO_2 , Al_2O_3 and CaO , whereas FeO , Na_2O , H_2O , CO_2 , Zn , Sr and Ba and, to a lesser extent, MnO , K_2O , P_2O_5 , Y , Zr , Nb , Ce and Nd , are the main components added. MgO may be added or, more commonly, subtracted. A number of the major elements (SiO_2 , Na_2O , H_2O , CO_2) and trace elements (Sr , Ba , Nb , Ce , Nd) in the fenitized syenites show similar mobilization behaviour (Fig. 10). On the other hand, FeO^{I} and K_2O were strongly depleted during fenitization of the syenites, whereas minor Al_2O_3 was added; TiO_2 , MnO , MgO and P_2O_5 seem to have remained almost constant during metasomatism; CaO displays no clear mobilization trend.

The observed differences between the element mobilization behaviour of the syenites and the anorthosites during metasomatism does not, however, necessarily require compositional differences between the fluids responsible, but may be explained by the strongly contrasting bulk-rock compositions of the anorthositic and syenitic protoliths. Consequently, the nature of the source of fenitization may be well constrained, if the fenitization patterns of both the syenites and the anorthosites are taken into consideration: (1) metasomatism of both rock units caused increases in Na_2O , CO_2 , H_2O , Sr , Ba , Nb and the LREE, suggesting that these elements form major constituents of the fenitizing fluid; (2) both syenites and anorthosites suffered a variably severe desilication, pointing to a low silica activity in the fenitizing fluid; (3) elements that, depending on the protolith composition, may be added or subtracted are Ti , Al , Fe , Mg , Ca and K ; these elements are thought to be minor constituents of the fenitizing fluids, creating strongly differing activity gradients between the fluid and the anorthositic and syenitic protoliths.

STABLE ISOTOPES

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic compositions of carbonatites and syenites are listed in Table 11.

Carbonatites

Separated ankerite grains from four samples of the carbonatitic breccia cover a narrow range in $\delta^{13}\text{C}$ (-6.86 to -6.98‰) and exhibit a stronger variation in $\delta^{18}\text{O}$ (8.95 – 9.73‰). Similar but slightly lower values are displayed by ankerite from a late ferrocarnatite vein ($\delta^{13}\text{C}$ -6.73‰ ; $\delta^{18}\text{O}$ 8.91‰), which agree well with the values obtained by Thompson *et al.* (2002) for similar samples. The ^{13}C contents of both carbonatite generations are in good agreement with the $\delta^{13}\text{C}$ values of the fresh Oldoinyo Lengai natrocarbonatite lava and its carbonate phenocrysts (-6.3 to -7.1‰ $\delta^{13}\text{C}$) given by Keller & Hoefs (1995), who constrained a narrow restricted field for isotopically primary igneous carbonatites (Fig. 11). In

contrast, the $\delta^{18}\text{O}$ values of the Swartbooisdrif dykes are distinctly higher than those reported for unmodified mantle-derived partial melts from Oldoinyo Lengai (5.5 – 7.0‰ $\delta^{18}\text{O}$; Keller & Hoefs, 1995) and thus imply that both the carbonatitic breccia and the ferrocarnatite veins were affected by a certain degree of post-emplacement alteration.

Syenites

The $\delta^{18}\text{O}$ values of feldspar separates (K-feldspar and plagioclase) of seven samples of both the non-altered syenite and the fenitized syenite are in the range of 7.20 – 7.92‰ (average $7.45 \pm 0.24\text{‰}$) and 7.53 – 7.77‰ (average $7.65 \pm 0.12\text{‰}$), respectively. Only nepheline in the fenitized nepheline syenite exhibits a slightly lower $\delta^{18}\text{O}$ of 6.93‰ , whereas the K-feldspar from the same sample has a $\delta^{18}\text{O}$ of 7.62‰ , similar to those of the syenite feldspars. The homogeneity of the values is striking, as two samples of the fenitized syenite and the nepheline syenite display clear textural and chemical evidence for the interaction with fenitizing fluids. Two explanations may account for the obtained results: (1) the carbonatitic fluids had no influence on the $\delta^{18}\text{O}$ of the feldspars and nepheline, or (2) the metasomatic fluid had magmatic temperatures and $^{18}\text{O}/^{16}\text{O}$ ratios similar to those of the syenites. We favour model (2), as albite in the syenites and Ne-rich rims of nepheline in the nepheline syenite are not magmatic in nature but were formed during the metasomatic event.

The fact that anorthosite samples from both the Swartbooisdrif mining area and distinct parts of the anorthosite complex display similar and magmatic $\delta^{18}\text{O}$ ranges for plagioclase ($5.94 \pm 0.21\text{‰}$ and $5.82 \pm 0.15\text{‰}$, respectively; Drüppel, 2003) is taken as evidence that the circulation of carbonatite-derived metasomatic fluids was confined to shear zones and reached no large areal extent.

GEOOTHERMOMETRY AND GEOBAROMETRY

On the basis of geobarometry studies on various mineral assemblages of the anorthosites of the KIC pressures of 8 ± 1 kbar have been calculated for both their emplacement and subsolidus re-equilibration in the lower crust (Drüppel *et al.*, 2000). Consequently, the emplacement depth of the nepheline syenite and the *c.* 150 Myr younger ferrocarnatites is confined to pressures below 8 kbar.

Nepheline syenite

Nepheline liquidus thermometry after Hamilton (1964) reveals a large spread in the calculated temperatures, reaching from above the 1068°C isotherm for the

Table 10: Calculated values of absolute compositional changes of anorthosites and syenites during fenitization

Rock type:	A/FA	A/FAX (<i>n</i> = 6)		S/FS (<i>n</i> = 4)	
		Min.	Max.	Min.	Max.
<i>F_V</i> :	0.989	0.957	1.085	1.010	1.047
<i>g/100 g</i>					
Si	−2.95	−4.61	−3.30	−0.89	−0.05
Ti	0.76	−0.04	1.35	−0.19	−0.07
Al	−2.61	−4.57	−2.69	1.30	1.38
Fe ³⁺	1.45	0.92	1.63	−1.91	−0.86
Fe ²⁺	1.82	0.17	3.46	−2.02	−1.22
Fe [†]	3.27	1.29	5.29	−3.93	−2.07
Mn	0.02	0.14	0.44	−0.07	0.09
Mg	0.03	−1.43	0.66	0.01	0.17
Ca	−2.25	−3.19	−1.37	−0.77	1.10
Na	3.04	1.31	6.13	2.09	3.44
K	0.04	0.06	1.11	−3.56	−2.08
P	0.01	0.00	0.22	−0.04	0.02
C	1.04	1.33	1.96	0.10	0.88
H	0.13	0.09	0.25	0.05	0.08
O	0.00	0.00	0.00	−1.76	2.13
Gains	14.88	14.30	20.58	5.67	8.88
Losses	−14.39	−20.15	−15.50	−11.48	−6.69
G + L	0.48	−2.02	0.61	−3.79	0.40
<i>mg/1000 g</i>					
V	151.95	−11.26	200.06	12.39	27.48
Co	8.23	−15.93	18.72	−34.08	7.32
Ni	5.40	−59.18	26.11	−0.02	2.17
Zn	36.35	23.13	222.15	−77.25	199.40
Ga	5.11	−0.31	13.73	−14.12	−9.61
Rb	—	8.85	42.03	−27.26	−26.68
Sr	102.20	417.51	1368.57	86.04	750.51
Y	—	15.69	55.36	−5.85	−5.41
Zr	34.18	43.28	181.44	−679.34	1352.17
Nb	—	53.94	94.33	−53.41	379.92
Ba	241.31	98.22	2363.99	−219.24	635.39
Pb	−6.00	6.04	35.56	−0.14	0.48
Ce	—	78.45	243.28	−56.10	192.64
Nd	—	25.25	102.51	−30.03	38.02

A/FA, anorthosite/fenitized anorthosite; A/FAX, anorthosite/anorthositic xenoliths in the carbonatitic breccia; *F_V*, volume factor; G + L, sum of gains and losses; S/FS, syenite/fenitized syenite.

SiO₂-rich core compositions to temperatures as low as ~770°C at the SiO₂-poor rims of the nepheline grains. The outermost, metasomatically formed, Ne-rich margins of the pegmatoidal nepheline crystals indicate lower temperatures of 775–700°C and may thus give a first idea of the temperature range of fenitization. As both the nepheline mineral chemistry and the *T* estimates point to continuous nepheline growth, it is possible that

Na was introduced into the system before nepheline was fully crystallized.

The temperatures of the sodalitization of nepheline can be estimated from the stability field of sodalite formed by reaction (4), in relation to the NaCl concentration of the interacting fluids and temperature, based on the experimental investigations of Kostel'nikov & Zhornyak (1995). Applying ranges of 19–30 wt % NaCl eq. for the primary

Table 11: Carbon and oxygen isotopic composition of separated ankerite in samples of the carbonatitic breccia and the ferrocarbonatite veins

Rock type and sample	Mineral	$\delta^{18}\text{O}_{\text{SMOW}}$ (mineral) (‰)	$\delta^{13}\text{C}_{\text{PDB}}$ (mineral) (‰)
<i>Syenite</i>			
Ku-98-40	plagioclase	7.20	n.a.
Ku-98-40	orthoclase	7.22	n.a.
Ku-99-13	orthoclase	7.50	n.a.
Ku-99-20	orthoclase	7.92	n.a.
<i>Fenitized syenite</i>			
Ku-98-70	albite	7.77	n.a.
Ku-99-19	albite	7.53	n.a.
Ku-99-21	albite	7.52	n.a.
Ku-99-21	orthoclase	7.36	n.a.
<i>Nepheline syenite</i>			
Ku-99-15a	orthoclase	7.62	n.a.
Ku-99-15a	nepheline	6.93	n.a.
<i>Carbonatitic breccia</i>			
Ku-97-26	magnetite	-1.82	n.a.
Ku-99-02	magnetite	-4.21	n.a.
Ku-99-SA11	magnetite	-1.46	n.a.
Ku-97-26	ankerite	8.95	-6.90
Ku-99-02	ankerite	9.07	-6.97
Ku-99-SA8-2	ankerite	9.34	-6.86
Ku-99-SA11	ankerite	9.73	-6.98
<i>Ferrocarbonatite vein</i>			
Ku-01-03	magnetite	-2.63	n.a.
Ku-01-03	ankerite	8.91	-6.76

n.a., not analysed.

salt concentrations of the fenitizing fluids (Drüppel, 2003), corresponding temperatures of *c.* 730–630°C are obtained for the transformation of nepheline into sodalite.

Carbonatite

The following magmatic crystallization sequence can be established for the Swartbooisdrif ferrocarbonatites. (1) If present, apatite, pyrochlore and biotite crystallized first accompanied and followed by (2) ankerite and magnetite and followed by interstitial calcite and late rutile. (3) Dispersed grains of chalcopyrite and pyrite are most probably synchronous with a second magnetite generation. During the end-stages of the carbonatite crystallization and, more frequently, at the subsolidus stage (4) various sulphides and haematite as well as (5) late chlorite, carbocernaite, barite, strontianite and calcite of the

second generation were formed. (6) Ankerite and calcite and, subordinately, biotite and apatite were partly recrystallized. To establish the *P–T* conditions of the ferrocarbonatite emplacement and recrystallization the following approaches have been used: (1) biotite–apatite thermometry (Stormer & Carmichael, 1971; revised by Zhu & Sverjensky, 1992); (2) calcite–dolomite Fe–Mg–Ca thermometry (Anovitz & Essene, 1987); (3) equilibrium fractionation of oxygen isotopes in ankerite–magnetite pairs using the mineral–water curves of Zheng (1991, 1999).

Biotite–apatite thermometry

Temperatures have been calculated for individual biotite–apatite pairs in direct grain contact within two sodalite-bearing and two sodalite-free samples of the carbonatitic breccia. The mean error (1σ) of the geothermometer is $\pm 50^\circ\text{C}$; its pressure dependence is negligible. It should be noted, however, that the geothermometer is highly sensitive to analytical errors in fluorine. To minimize the latter error, average compositions of unzoned biotite and apatite have been calculated, using at least 20–70 single point analyses per individual grain. The results obtained for temperatures and HF fugacity data are demonstrated in a $\log(f_{\text{HF}}/f_{\text{H}_2\text{O}})$ vs $10^4/T$ diagram (Fig. 12), with the relative hydrogen fluoride fugacity $[\log(f_{\text{HF}}/f_{\text{H}_2\text{O}})]$ calculated after Andersen & Austrheim (1991). The uncertainty of the relative HF fugacity is *c.* ± 0.15 log units.

For biotite–apatite pairs from samples Ku-99-SA8 and Ku-98-131 of the sodalite-rich carbonatitic breccia average temperatures of 1100°C (1200–940°C) and 870°C (1070–740°C), respectively, have been constrained at high corresponding relative HF fugacities $[\log(f_{\text{HF}}/f_{\text{H}_2\text{O}}) - 3.9$ to $-4.6]$. Magmatic biotite–apatite pairs from the sodalite-free samples Ku-98-48 and Ku-98-14 indicate lower average temperatures of 820°C (1030–630°C) and 800°C (1010–630°C), respectively, at lower relative HF fugacities $[\log(f_{\text{HF}}/f_{\text{H}_2\text{O}}) - 3.9$ to $-5.3]$. The lowest temperatures (610–450°C) and HF fugacities $[\log(f_{\text{HF}}/f_{\text{H}_2\text{O}}) - 5.2$ to $-6.4]$ are obtained for recrystallized biotite and apatite of samples Ku-98-48 and Ku-98-14. In general, the data estimated for the Swartbooisdrif carbonatites agree well with the cooling trends of the alnöite of the Fen complex, Norway (Andersen & Austrheim, 1991) and of berforsite of the Delitzsch complex, Germany (Seifert *et al.*, 2000); the calculated temperatures are significantly higher than those measured for the fresh natrocarbonatite lava of Oldoinyo Lengai (593–540°C; Pinkerton *et al.* 1995). The temperatures of 1200–940°C, calculated for sample Ku-99-SA8, are exceptionally high, lying close to the maximum thermal stability limit of 1350°C of the pure phlogopite end-member (Trønnes, 2002). Sample Ku-99-SA8 differs

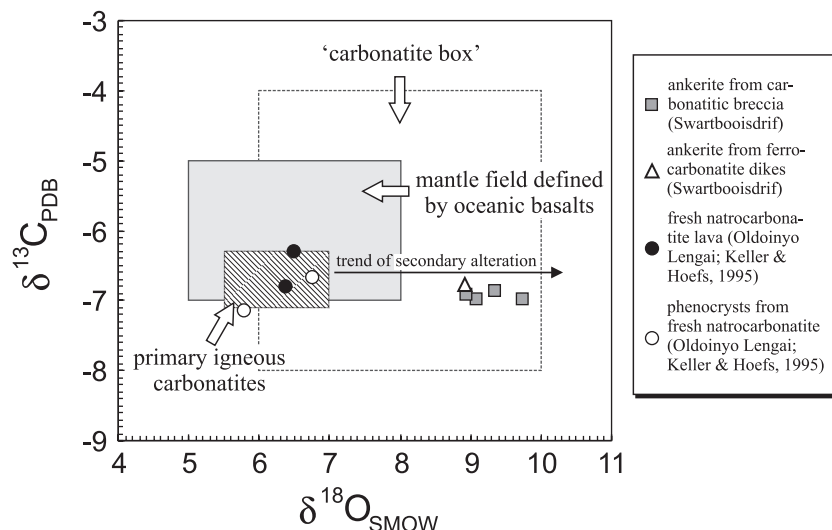


Fig. 11. $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ compositions of hand-picked ankerite mineral separates from both the carbonatitic breccia and the ferrocarbonatite veins of the Swartbooisdrif alkaline province. Diagonally striped, box shows C–O composition of primary igneous carbonatites after Keller & Hoefs (1995) based on C/O isotopes of fresh natrocarbonatite lava and phenocrysts; grey box shows mantle C–O isotopic composition based on C/O isotopes in basalts (Kyser, 1986; Nelson *et al.*, 1988; Deines, 1989); open, dashed-line box shows C–O composition of primary igneous carbonatites after Taylor *et al.* (1967), the so-called ‘carbonatite box’.

from the other three samples investigated because it is strongly affected by hydrothermal alteration. As has been shown by Coulson *et al.* (2001), biotite and, less frequently, apatite may suffer significant exchange with subsolidus fluids, making the data obtained for sample Ku-99-SA8 unreliable. The temperatures calculated for samples Ku-98-131, -14 and -48, however, largely overlap with temperatures estimated for the sodalitization of nepheline of a bordering nepheline syenite (775–630°C; see above), and those calculated for carbonates and silicates from three well-known carbonatite localities by oxygen isotope thermometry (750–550°C; Haynes *et al.*, 2003). On this basis, the estimated data give at least an approximation of the temperatures of ferrocarbonatite emplacement (*c.* 830 ± 200°C) and recrystallization (*c.* 530 ± 80°C).

Calcite–dolomite thermometry and ankerite–magnetite oxygen isotope equilibria

Calcite–dolomite Ca–Fe–Mg thermometry yielded temperatures in the range of 530–410°C for the carbonatitic breccia, the highest average values of 470°C being obtained for the REE-rich sample Ku-98-130a. These temperatures are extremely low even when compared with the effusive natrocarbonatite melt of Oldoinyo Lengai, suggesting extensive recrystallization and/or re-equilibration of the carbonates. An even lower temperature range is calculated from ankerite–magnetite oxygen-isotope equilibria for separated ankerite and magnetite grains from the carbonatitic breccia

(480–350°C) and the late ferrocarbonatite (410°C). The lower temperatures calculated from oxygen isotopic ratios are interpreted in terms of a weak subsolidus alteration of the different carbonatites, which is also supported by the oxygen isotope values of the ankerites (see above).

DISCUSSION

Origin and evolution of the Swartbooisdrif carbonatites

There is striking field evidence that both the ankerite carbonatite matrix of the carbonatitic breccia and the late-stage ferrocarbonatite veins are magmatic in origin. The carbonatitic breccias occur as dykes and veins with cross-cutting relationships and fenitized margins, and contain abundant flow-oriented xenoliths from the surrounding anorthosite and syenite. In addition, the mineral assemblage of both ferrocarbonatite generations (ankerite + magnetite + haematite + pyrochlore ± calcite ± apatite ± biotite ± rutile ± sulphides), their geochemical characteristics [high contents of incompatible elements such as Sr, Ba and REE; straight REE patterns, high (La/Yb)_{cn} ratios] and O and C isotope compositions (8.91–9.73‰ and –6.73 to –6.98‰, respectively) again indicate igneous derivation, with the $\delta^{18}\text{O}$ values suggesting only minor subsolidus alteration.

Both the carbonatite matrix of the carbonatitic breccia and the ferrocarbonatite veins can be classified as ferrocarbonatites after Le Maitre (1989), containing appreciable amounts of FeO^t, MgO, MnO and CaO, which are in the compositional range of ferrocarbonatites

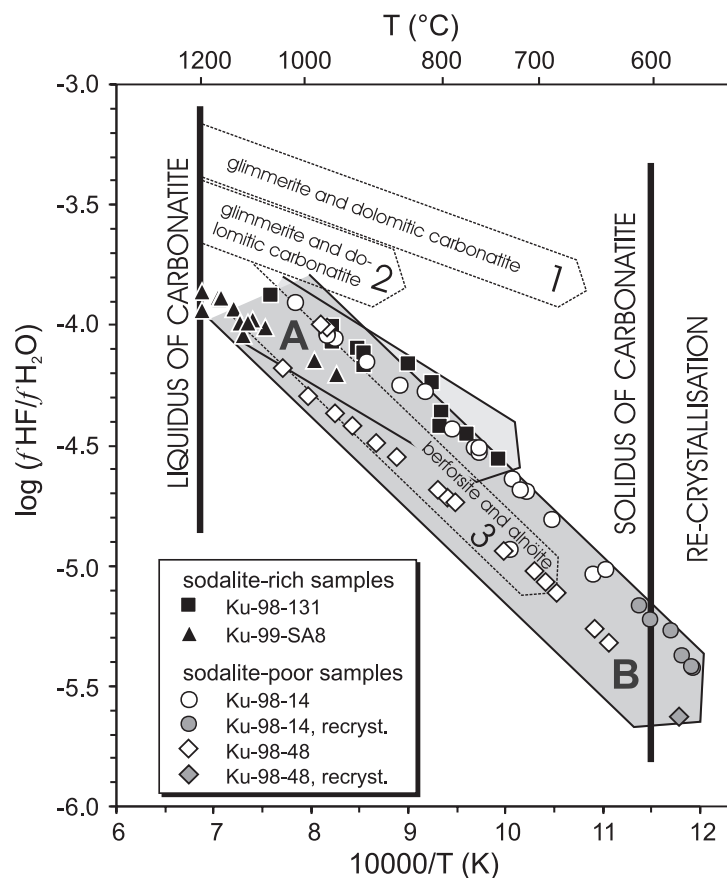


Fig. 12. $\log(f_{\text{HF}}/f_{\text{H}_2\text{O}})$ vs $10^4/T$ diagram for magmatic and recrystallized apatite from the carbonatitic breccia of the Swartbooisdrif alkaline suite. Arrow A, cooling trend derived from apatite–biotite pairs of sodalite-bearing samples of the carbonatitic breccia; arrow B, cooling trend derived from apatite–biotite pairs of sodalite-free samples of the carbonatitic breccia; arrows 1 and 2, cooling trends of glimmerite and dolomite carbonatite of the Delitzsch complex, Germany (Seifert *et al.*, 2000); arrow 3, cooling trend of alnöite of the Fen complex, Norway (Andersen & Austrheim, 1991) and of berforsite of the Delitzsch complex, Germany (Seifert *et al.*, 2000). The carbonatite liquidus $T = 1200^\circ\text{C}$ is derived from the maximum thermal stability of phlogopite (Yoder & Kushiro, 1969), whereas the carbonatite solidus of $625\text{--}650^\circ\text{C}$ is suggested by the experimental data of Wyllie (1966).

world-wide (Woolley & Kempe, 1989). Similarities in both the O and C isotopic ratios and the REE patterns of the carbonatitic breccia and the ferrocarbonatite veins provide evidence that the two rock units are genetically linked. However, when compared with the carbonatite matrix of the carbonatitic breccia, the younger ferrocarbonatite veins contain lower absolute amounts of SiO_2 , Al_2O_3 , K_2O , TiO_2 , P_2O_5 and S, implying that their formation post-dates the extensive crystallization of biotite, ankerite, Fe–Ti oxides, apatite and sulphides of the carbonatite magma. On the other hand, the geochemical characteristics of the carbonatite matrix of the carbonatitic breccia itself [high $(\text{Fe} + \text{Mg})/\text{Ca}$ ratios, low K_2O , P_2O_5 and TiO_2], as well as the trace element composition of early crystallized apatite [high LREE, high $(\text{La}/\text{Yb})_{\text{cn}}$ and $(\text{La}/\text{Nd})_{\text{cn}}$ ratios], suggest that this carbonatite unit is also the crystallization product of a highly fractionated carbonatite magma.

The modal amounts of metasomatically formed albite and sodalite in the carbonatitic breccia are high when compared with the generally small volume of the surrounding ferrocarbonatite matrix, hence suggesting that the carbonatite magma parental to the Swartbooisdrif carbonatites contained appreciable amounts of sodium before it was lost from the carbonatite magma during the fenitization. This model is confirmed by mass balance calculations of the compositional changes of anorthosites and syenites during fenitization, which suggest that the fenitizing solutions carried large amounts of Na_2O , H_2O and CO_2 as well as minor Sr, Ba, Nb and LREE. In addition, the model is generally consistent with fluid inclusion data on carbonatite fluids (e.g. Bühn & Rankin, 1999) and results from partitioning experiments (e.g. Veksler & Keppler, 2000). On the basis of experimental studies Lee & Wyllie (1994, 1997, 1998) concluded that at least two processes may account

for the enrichment of alkalis in a carbonatite magma; that is, (1) liquid immiscibility, with the immiscible carbonatite magmas tending to display calcicarbonatite compositions with variable but low (Mg + Fe) and high Na and K; and (2) after its physical separation from the silicate melt, the immiscible carbonatite magma precipitates cumulate carbonatites, leading to an enrichment of the residual melts in alkalis. With respect to these models it is noteworthy that the Swartbooisdrif ferrocarbonatites are closely associated with a nepheline syenite, which compositionally differs from the older syenites and appears to be genetically linked to the ferrocarbonatites. A process of liquid immiscibility would account for the notably low level of Ca, Mg and Fe in the nepheline syenite, as these elements show a strong preference for the carbonatite liquid (Hamilton *et al.*, 1989). Moreover, the Swartbooisdrif ferrocarbonatites are rich in Ba and Sr, but generally contain comparably low contents of Ti and the REE, which are known to partition into the silicate fraction during immiscible separation (Veksler *et al.*, 1998). Thompson *et al.* (2002) also suggested that high Nb/Ta ratios of the Swartbooisdrif ferrocarbonatites were inherited from an early episode of silicate–carbonate melt immiscibility.

Secondary REE enrichment of the carbonatitic breccia

The strong REE enrichment of two samples of the carbonatitic breccia appears to be of secondary origin, as carbocernaite occurs as a replacement product of matrix ankerite–calcite and is intimately associated with texturally late barite and strontianite, which are commonly found in carbonatites exposed to subsolidus alteration. A supergene origin for the REE enrichment can be ruled out, as ankerite from these rock types lacks fractionation to heavier $\delta^{18}\text{O}$, but has ^{18}O values in the range of ankerite from the REE-poor carbonatitic breccia. An *in situ* mechanism of hydrothermal solution of REE and their reprecipitation is not likely, as a concentration factor of over 100 times is required to achieve the REE content of the two REE-rich samples. Hence, a local injection of late-stage, fractionated carbonatite fluids is considered to be responsible for the Sr, Ba and REE enrichment.

Source and composition of the fenitizing solutions

In general terms, fenitizing reactions may be promoted by alkali-rich fluids emanating from both intrusive bodies of alkaline silicate magma (e.g. Rae & Chambers, 1988; Coulson & Chambers, 1996; Rae *et al.*, 1996; Sindern & Kramm, 2000) and carbonatite melts (e.g. McLemore & Modreski, 1990; Platt & Woolley, 1990; Bühn & Rankin, 1999; Williams-Jones & Palmer, 2002). Regarding the

field occurrence of the anorthositic and syenitic fenites at Swartbooisdrif, their metasomatic alteration appears to be directly linked to the emplacement of the ferrocarbonatites; the fenites are restricted to the contacts to large dykes of the carbonatitic breccia and fractures and joints within 5 m of the carbonatite centres, whereas anorthosites bordering syenites and nepheline syenites display no effects of a metasomatic alteration.

The petrochemical changes involved in the fenitization of the Swartbooisdrif rocks indicate that: (1) the fenitizing solutions are Si deficient with respect to the syenites and even to the comparably Si-poor anorthosites, indicating that silicate magmas such as ijolite or nephelinite are unlikely sources of fenitization; (2) the solution exceeds both anorthosites and syenites in the degree of Na, V, Zn, Sr, Ba Nb and LREE enrichment; (3) the X_{CO_2} of the solution is low (abundance of hydrous mafic silicates and of albite even in the highest-grade fenites). With respect to the hydrous nature of the fenitizing solutions, metasomatism at Swartbooisdrif differs from the commonly observed CO_2 -dominated style of carbonatite-related fenitization (Morgan & Martin, 1985; Kresten & Morgan, 1986; Kresten, 1988; Morgan & Woolley, 1988; Andersen, 1989; Morgan, 1989, 1994). As has been demonstrated by several workers, however, carbonatite-derived fluids may have quite variable $\text{CO}_2/\text{H}_2\text{O}$ ratios, indicating that CO_2 is neither the sole nor necessarily the dominant component of the fluids (e.g. Currie & Ferguson, 1971; Andersen, 1986; Morgan & Lindblom, 1995; Samson *et al.*, 1995a, 1995b; Bühn & Rankin, 1999; Williams-Jones & Palmer, 2002). Following this, the qualitative retention series of the fenitizing fluids, as estimated from the mineralogical changes and the calculated compositional changes of the Swartbooisdrif fenites [i.e. $(\text{H}_2\text{O}, \text{Na}, \text{Cl}) > (\text{CO}_2, \text{Sr}, \text{Ba}, \text{Nb}, \text{Ce}, \text{Nd}) > (\text{Ti}, \text{Fe}, \text{Mg}, \text{Ca}, \text{K}, \text{Al})$], supports the interpretation that fenitization was caused by fluids that emanated from a carbonatite magma parental to the Swartbooisdrif ferrocarbonatites.

The breakdown of igneous mineral assemblages during fenitization

From textural evidence the following sequence of fenitization reactions has been constrained for the Swartbooisdrif fenite rocks.

(1) During the initial stages of fenitization pure albite was formed at the expense of former plagioclase and K-feldspar in anorthosite and syenite, respectively. A similar pervasive albitization of magmatic alkali-feldspar has been observed in a number of fenite aureoles surrounding either carbonatite centres (e.g. McLemore & Modreski, 1990; Platt & Woolley, 1990) or intrusive bodies of alkaline silicate magma (e.g. Rae & Chambers, 1988; Coulson & Chambers, 1996; Rae *et al.*, 1996; Sindern &

Kramm, 2000) and is commonly interpreted to be caused by the introduction of alkali-rich fluids. In the case of the Swartbooisdrif fenites this process occurred simultaneously with the transformation of anhydrous Fe–Mg-silicates and Ca-amphiboles into magnesio-riebeckite and biotite, with the mineralogical changes being restricted to the contacts of large carbonatite dykes. The observed metasomatic reactions require that H₂O was the dominant component of this fluid, which additionally must have contained significant amounts of Na and minor Fe, Cl and K. The chemical trends of this early albitization are remarkably similar to those of the subsequent sodalitization, suggesting that both stages of fenitization were caused by fluids of a similar composition, i.e. carbonatite-related fluids. As is evident from inclusion relationships, the transformation of plagioclase and K-feldspar into pure albite pre-dated the early crystallization of apatite, biotite, pyrochlore and magnetite in the carbonatitic breccia and hence presumably occurred prior to or synchronously with carbonatite emplacement. From this it can be concluded that the carbonatite magma had already expelled Na-rich hydrous fluids during its early evolution. These fluids might have migrated along pre-existing structural heterogeneities and altered the brecciated anorthosite and syenite.

(2) After its emplacement the carbonatite magma reached water saturation following cooling to <800°C and fractionation of anhydrous minerals such as apatite, ankerite, magnetite and pyrochlore. In the temperature range of *c.* 700 ± 70°C the circulation of NaCl-rich solutions caused the partial transformation of albite in the fenitized anorthosite and of nepheline in the bordering nepheline syenite into sodalite. Following Gittins (1989), water saturation of carbonatites may occur at various stages of the carbonatite evolution, with the solubility of water in the carbonatite magma increasing with increasing alkali contents and thus with increasing fractionation.

(3) The fenitic mineral assemblage of cancrinite, muscovite and rare analcite, replacing albite and post-dating sodalite, implies that the evolved fluids were still aqueous brines but no longer contained sufficient Na to form sodalite. The K and Ca, required by the metasomatic reactions, may be a primary constituent of these fluids or derived as a result of K- and Ca-releasing reactions. In the case of the nepheline syenite, the close association of sodalite and muscovite, both formed at the expense of nepheline, favours the latter model.

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