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CALCIOCARBONATITE DYKES AT OLDOINYO LENGAI, TANZANIA: THE FATE OF NATROCARBONATITE

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ABSTRACT

Carbonatite dykes are described for the first time from the active natrocarbonatite volcano Oldoinyo Lengai, Tanzania. The dykes are fine grained, with a microporphyritic texture of polycrystalline, granular calcite microphenocrysts. The porous texture is indicative of solution and leaching processes. Groundmass phases are fluorite with 2.1–3.9 wt.% Sr, Mn-rich magnetite (up to 10.2 wt.% MnO), REE- and Si-rich fluorapatite (up to 20.6 wt.% REE_2O_3 and 9.9 wt.% SiO_2) and a Mn–Ba hydroxide. Chemically, the dykes are Ca-carbonatitic, with high concentrations of F, Sr, Fe and Mn. Total alkalis are below 2 wt.%. Compared with fresh natrocarbonatite, the REE, Y, Zr, Th, Nb and Pb are enriched, whereas Rb, Cs, Ba, Cl and S are markedly depleted. Stable isotope ratios are $\delta^{13}C$ –1.95 ‰ PDB and $\delta^{18}O$ +24.12 ‰ SMOW, well outside the compositional field of primary Lengai natrocarbonatites, indicating extensive atmospheric exchange and re-equilibration, in particular of oxygen. These dykes are interpreted as alteration products of the typical Lengai natrocarbonatite. From the evidence at Oldoinyo Lengai, we believe that calcite carbonatites may have different origins. In contrast to the widespread primary magmatic crystallization of calciocarbonatitic melts, alteration and replacement exchange of original natrocarbonatites of Oldoinyo Lengai produce secondary calcite carbonatites. Using the criteria presented here, a distinction between calcitized natrocarbonatites and primarily calciocarbonatitic extrusive rocks is possible, on the basis of textural evidence mimicking the porphyritic texture of natrocarbonatite, and on the polycrystalline nature of calcite pseudomorphs after nyerereite. Noteworthy in the secondary calcite are the high Sr contents (2.2–3.5 wt.% SrO), and variable Ba contents (0.3–2.2 wt.% BaO). A prominent primary feature in the calciocarbonatite of the dykes is the sheaf-like intergrowth texture of fluorite, which is typical of fresh natrocarbonatites from Oldoinyo Lengai. Stable isotope ratios are independent criteria indicating extensive alteration and secondary exchange.

Keywords: Oldoinyo Lengai, calcite carbonatite dykes, natrocarbonatite alteration, mineralogy, chemical balance, stable isotopes, Tanzania.

SOMMAIRE

Nous décrivons pour la première fois des filons de carbonatite découverts sur le volcan natrocarbonatitique actif de Oldoinyo Lengai, en Tanzanie. Ces filons possèdent une granulométrie fine, avec une texture microporphyritique et des microphénocristaux polycristallins et granulaires. La texture poreuse semble indiquer un processus de solution et de lessivage. La matrice contient fluorite avec entre 2.1 et 3.9% Sr (poids), magnétite riche en Mn (jusqu'à 10.2% MnO), fluorapatite riche en terres rares et Si (jusqu'à 20.6% d'oxydes de terres rares, 9.9% SiO_2) et un hydroxyde de Mn–Ba. Chimiquement, les filons ont une composition calciocarbonatitique, et montrent une forte teneur en F, Sr, Fe et Mn. Le total des alcalins est inférieur à 2%. En comparaison d'une natrocarbonatite saine, les teneurs en terres rares, Y, Zr, Th, Nb et Pb sont enrichies, tandis que celles de Rb, Cs, Ba Cl et S sont très faibles. Les rapports des isotopes stables, $\delta^{13}C$ égal à –1.95 ‰ PDB et $\delta^{18}O$ égal à +24.12 ‰ SMOW, sont nettement en dehors des valeurs typiques de la natrocarbonatite saine de Lengai, ce qui indique un échange important avec l'atmosphère et un ré-équilibrage, impliquant surtout l'oxygène. Ces filons seraient le produit d'une altération d'une natrocarbonatite typique. D'après l'évidence recueillie à Oldoinyo Lengai, nous croyons que les calciocarbonatites pourraient avoir plus d'une origine. En comparaison de la cristallisation primaire de carbonatites à partir d'un magma, l'altération et le remplacement de natrocarbonatite à Oldoinyo Lengai peuvent mener à une carbonatite calcitique secondaire. Il s'avère possible de distinguer entre une natrocarbonatite remplacée par la calcite et une calciocarbonatite extrusive primaire en utilisant les critères présentés ici, par exemple, l'évidence texturale simulant la texture porphyritique de la natrocarbonatite, et le caractère polycristallin de la calcite

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remplaçant la nyéréréite. Aussi, la calcite secondaire possède des teneurs élevées en Sr (2.2–3.5% SrO), et des teneurs variables en Ba (0.3–2.2% BaO). Une caractéristique de la calciocarbonatite de ces filons est la présence d'une texture en intercroissance de la fluorite, ce qui est typique de natrocarbonatite saine à Oldoinyo Lengai. Les rapports des isotopes stables fournissent des critères indépendants indiquant une altération avancée et un échange secondaire.

(Traduit par la Rédaction)

Mots-clés: Oldoinyo Lengai, filons de carbonatite à calcite, altération de natrocarbonatite, minéralogie, bilan chimique, isotopes stables, Tanzanie.

INTRODUCTION

Oldoinyo Lengai, in the Tanzanian rift valley, is the world's only active carbonatite volcano and is well known for the unusually alkali-rich composition of its carbonatites, not found elsewhere (Dawson 1962a). Continuous observation of the actual effusive period since 1988 (Dawson *et al.* 1990, Keller & Krafft 1990) has underlined the instability and rapid alteration of natrocarbonatite at the surface. In the light of actualism, this raises some basic questions for carbonatite petrology: where are the natrocarbonatites of the geological past? How would we recognize these possible past equivalents of the present activity? It was suggested in a number of papers (Hay 1983, 1989, Deans & Roberts 1984, Clarke & Roberts 1986, Dawson *et al.* 1987) that the present natrocarbonatite activity of Oldoinyo Lengai is the key for the interpretation of dominantly calcitic or dolomitic carbonatite magmatism elsewhere in the geological past. However, tracing the processes of conversion of alkali-rich natrocarbonatite to its calcite-dominant, alkali-free products of alteration (Dawson *et al.* 1987, Dawson 1993, Keller & Hoefs 1995) should help to clarify characteristic differences between primary magmatic crystallization of calcite carbonatites and secondary mineralogical (calcite) and chemical (Ca-carbonatitic) compositions.

Natrocarbonatites of the effusive period from 1960 to 1966 (Dawson 1962a, b, Du Bois *et al.* 1963) and of the recent period starting in 1983 (Nyamweru 1988, Keller & Krafft 1990, Dawson *et al.* 1995a, b) are practically SiO_2-free carbonate melts with >40 wt.% alkalis. The composition of the lavas has been rather constant over the observation period since 1960 (Dawson 1989, Keller & Krafft 1990, Dawson *et al.* 1995b), with the exception of the 1993 Chaos Crag flows described by Dawson *et al.* (1994), Church & Jones (1995) and Simonetti *et al.* (1997).

The dominant variety of recent natrocarbonatite at Oldoinyo Lengai is porphyritic with phenocrysts of tabular nyerereite and more oval-shaped gregoryite. Phenocrysts range from 1 to 2 mm, and make up *ca.* 50 vol.% of the rock. An average modal composition of the porphyritic lavas was given in Keller & Kraft (1990) as 26% nyerereite and 22% gregoryite phenocrysts, and 52% groundmass (vol.%). Peterson (1990), on the basis of point-count data, gave a range of phenocryst contents from 35.6 to 75.6%. The groundmass is composed of sylvite, halite and fluorite, in addition to fine-grained Na–Ca-carbonates, as among the phenocrysts.

At Lengai, no carbonatite with primary calcite or with a primary Ca-carbonatitic chemical composition has been detected, in contrast to other carbonatite volcanoes in the adjacent sector of the Gregory Rift. A calcite carbonatite clast in the recent pyroclastic series of Oldoinyo Lengai (Dawson 1989, Gittins & Harmer 1997) has the characteristics of transformed natrocarbonatite (Dawson 1993). At Kerimasi, Lengai's southern neighbor volcano, both intrusive and extrusive calcite carbonatites are reported (Mariano & Roeder 1983, Keller 1989, Church 1995). In contrast, Hay (1983) interpreted calcitic carbonatite clasts in pyroclastic material from a late stage of Kerimasi as altered natrocarbonatite. Shombole near the northern shore of Lake Natron is a nephelinite–phonolite volcano with Ca-carbonatite lavas and pyroclastic material (Peterson 1989). Another carbonatite complex about 20 km north–northwest of Lengai is the poorly known Mosonik, which appears to be dominantly calcitic according to Guest *et al.* (1961) and a reconnaissance sampling of the authors. With a K/Ar age of 3.5 Ma (Isaacs & Curtis 1974), Mosonik is much older than the Quaternary Kerimasi and Oldoinyo Lengai volcanoes.

THE ALTERATION OF NATROCARBONATITES

Freshly erupted natrocarbonatitic lavas of Oldoinyo Lengai are black to dark gray. The natrocarbonatite minerals sylvite, halite and gregoryite, and to a lesser extent nyerereite, are water-soluble and are transformed at the surface and under meteoric influences in a very short time into secondary products (Dawson 1962b, 1993, Dawson *et al.* 1987, Keller & Kraft 1990, Zaitsev & Keller 2006).

Observations during natrocarbonatite eruptions from 2000–2003 showed that just hours after solidification, the rims of carbonatite lava flows become covered by white efflorescences and coatings. X-ray-diffraction data confirm the presence of thermonatrite $Na_2CO_3 \cdot H_2O$ and nahcolite $NaHCO_3$ as the earliest secondary minerals to form on the surface of natrocarbonatite lava (Zaitsev & Keller 2006). Nahcolite and thermonatrite are also known from "efflorescences" or "salt fringes and tubes" that occur along cooling cracks in natrocarbonatite flows (Dawson 1962b, Keller & Kraft 1990, Genge *et al.* 2001). White crusts of trona

$Na_3H(CO_3)_2{\bullet}2H_2O$ also have been observed. Within one or two days, the natrocarbonatite flows turn light gray and become increasingly covered with white incrustations, and within a few weeks the material turns brownish, friable, soft and earthy.

Dawson *et al.* (1987) have described the replacement of nyerereite $Na_2Ca(CO_3)_2$ by pirssonite $Na_2Ca(CO_3)_2{\bullet}2H_2O$ in a pre-1960 carbonatite lava from Barry's Pinnacles (Keller & Krafft 1990) in the southern part of the active crater. They explained the formation of the H_2O-bearing pirssonite as an intermediate step in the calcification of natrocarbonatite.

Another secondary hydrous Na–Ca carbonate, gaylussite $Na_2Ca(CO_3)_2{\bullet}5H_2O$, has been recognized by Keller & Kraft (1990) in the altered pahoehoe crust of a natrocarbonatite lava from an early 1988 eruption. Within only a few weeks of the eruption, the texture of the lava was still recognizable as a porphyritic natrocarbonatite, identical to the texture of fresh material, nyerereite was only partly altered, the amount of gregoryite was greatly reduced, but sylvite was completely dissolved.

Secondary calcite as well as trona has been found in partly altered natrocarbonatite by Du Bois *et al.* (1963), and abundant finely crystalline calcite at Oldoinyo Lengai has been described from the so-called "Footprint Tuff" by Hay (1989). Formation of the mineral was considered to be a result of transformation of natrocarbonatite ash by leaching by meteoric water.

In 1993, B. Dawson published the results of a reinvestigation of a carbonatite sample previously termed a calcite carbonatite (Dawson 1962b, 1989). With new mineralogical, geochemical and isotopic data, Dawson (1993) proposed that the "sövite" (calcite carbonatite) was formed during complete alteration of natrocarbonatite. In a discussion paper, Gittins & Harmer (1997) discounted the natrocarbonatite alteration model and claimed it was primary calciocarbonatite.

In this paper, we present detailed mineralogical and geochemical descriptions of two calcite carbonatites from Oldoinyo Lengai that, for the first time, were found in the form of dykes.

ANALYTICAL METHODS

Cathodoluminescence studies of the carbonatite dykes were performed at Freiburg University using polished thin sections with a cold-cathode instrument of Nuclide Corporation (Luminoscope) mounted on the petrographic microscope. The presence of calcite, fluorite, magnetite and apatite was confirmed by X-ray-diffraction data.

Mineral compositions were determined by energy-dispersive spectrometry (EDS) using a JEOL 5700LV scanning electron microscope equipped with a light-element (Be to U) detector at the Natural History Museum (London). EDS spectra were acquired for 100 seconds (live-time) with an accelerating voltage of 20 kV and a beam current of 1 nA. Owing to the low stability of some minerals under the electron beam and the significant loss of Na, a defocused beam (5 × 5 to 10 × 10 μm) was used for analyses. The spectra were processed with the INCA Oxford Instruments software package. Well-characterized minerals and synthetic materials were used as standards. Additional silicate minerals were analyzed by wavelength-dispersion spectrometry (WDS) using a Cameca SX–100 electron microprobe located in the Institut für Mineralogie, Petrologie und Geochemie at Freiburg. The microprobe was operated at 15 kV and 20 nA.

Whole-rock analyses were carried out by X-ray fluorescence (XRF) with a Philips PW 2404 instrument at the Institut für Mineralogie, Petrologie und Geochemie in Freiburg. Fused Li tetraborate pellets (1 g sample to 4 g flux) were calibrated against international reference samples with a special carbonatite calibration. Concentrations of trace elements in the carbonatite dykes were determined by inductively coupled plasma – mass spectrometry (ICP–MS) at the Natural History Museum (London), and fresh natrocarbonatite OL 259 was analyzed for trace elements by ICP–MS at the CNRS Nancy.

Carbon and oxygen isotope compositions were measured by Jochen Hoefs in the Stable Isotope Laboratory of the Geochemisches Institut Göttingen (for analytical details, see Keller & Hoefs 1995).

THE CARBONATITE DYKES

Field occurrence

The two dykes described in this paper occur on the southern slope of Oldoinyo Lengai at elevations of *ca.* 2800 m and 2750 m, respectively. They cut the southward-dipping phonolitic lavas and agglomerates of the southern cone, about 20 and 70 meters below the southern rim of the inactive south crater. The exact field-locality is shown in Figure 1. Dyke I (OL 227, Fig. 2a) and dyke II (OL 327, Fig. 2b) are similar in their geological and petrographic appearance. Both are 5–10 cm wide, subvertical, and both strike northwest (120°). The dykes outcrop close to the present-day surface of the volcanic slope.

Carbonatites had not been observed in the predominantly phonolitic sequence of the southern crater and cone. The extrusion of natrocarbonatite is part of the very recent geological history of Oldoinyo Lengai's northern crater (Fig. 1a). Hence, the dykes are assumed to be related to this modern evolution, although there are no direct field-relationships linking the dykes to the northern crater. There is also little direct evidence for the age of the oldest carbonatites at Lengai. Dawson (1998) and Hay (1989) have argued, with a number of cross-correlations between Olduvai Gorge and Oldoinyo Lengai, that natrocarbonatitic eruptions have occurred during at least the last 1250 years. Keller and Klaudius (unpubl. data) identified ash-sized clasts of

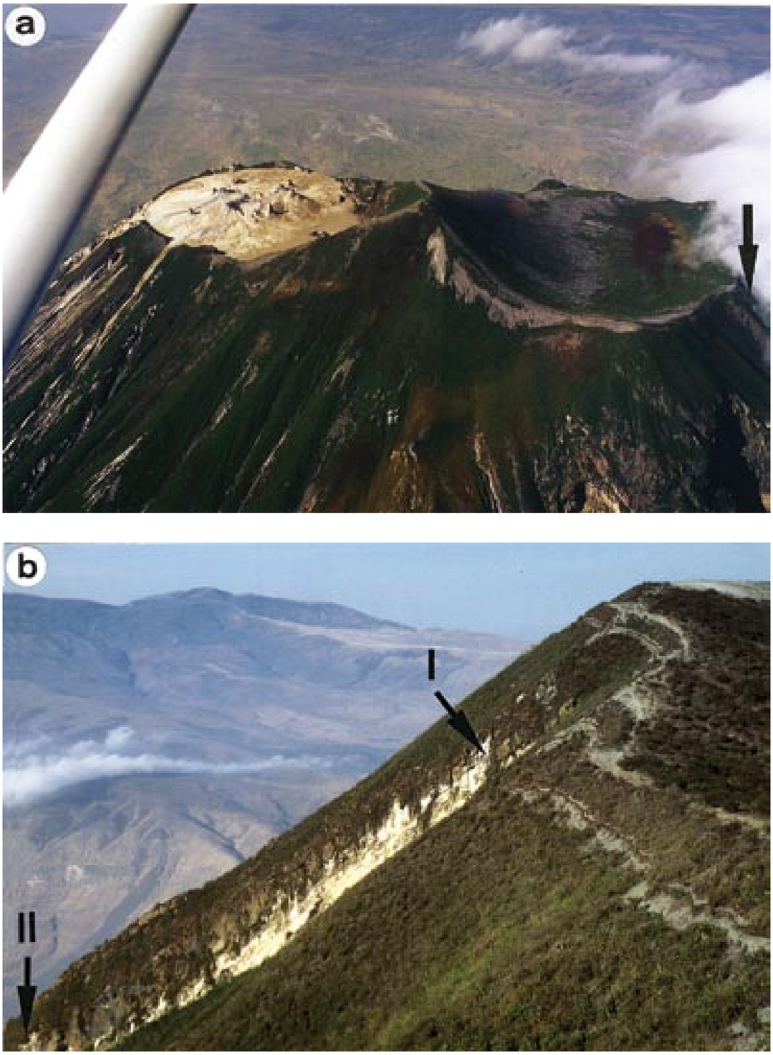


FIG. 1. Location of calcite carbonatite dykes at the southern rim of Oldoinyo Lengai crater. (a) Aerial view of Oldoinyo Lengai summit area with active North and inactive South craters (photo by Jurgis Klaudius, June 6, 2002). (b) Rim and southern flank of the South crater of Oldoinyo Lengai, with dyke localities.

natrocarbonatite within a tephra bed at the rift escarpment west of the cone, dated at 1880 ± 100 a B.P. (uncalibrated ^{14}C). These are so far the oldest confirmed natrocarbonatites at Lengai.

Composition and mineralogy of the host phonolite

The carbonatite dykes are hosted by phonolitic lavas of the southern cone of Oldoinyo Lengai (Dawson 1962b, Donaldson *et al.* 1987). The phonolite is porphyritic, with centimeter-sized phenocrysts of alkali feldspar and nepheline. Additional phases are clinopyroxene, magnetite, sodalite, titanite and apatite. According to their chemical composition (MgO <1 wt.%, Mg# <25, Ni and Cr <10 ppm, Rb 139 ppm, Sr 1680, Ba 1600, Zr 600, and Y 36 ppm), this phonolite is a highly fractionated product of differentiation, as are all silicate lavas from Oldoinyo Lengai (Donaldson *et al.* 1987). The phonolite OL 226, host for the dyke I, is moderately peralkaline,

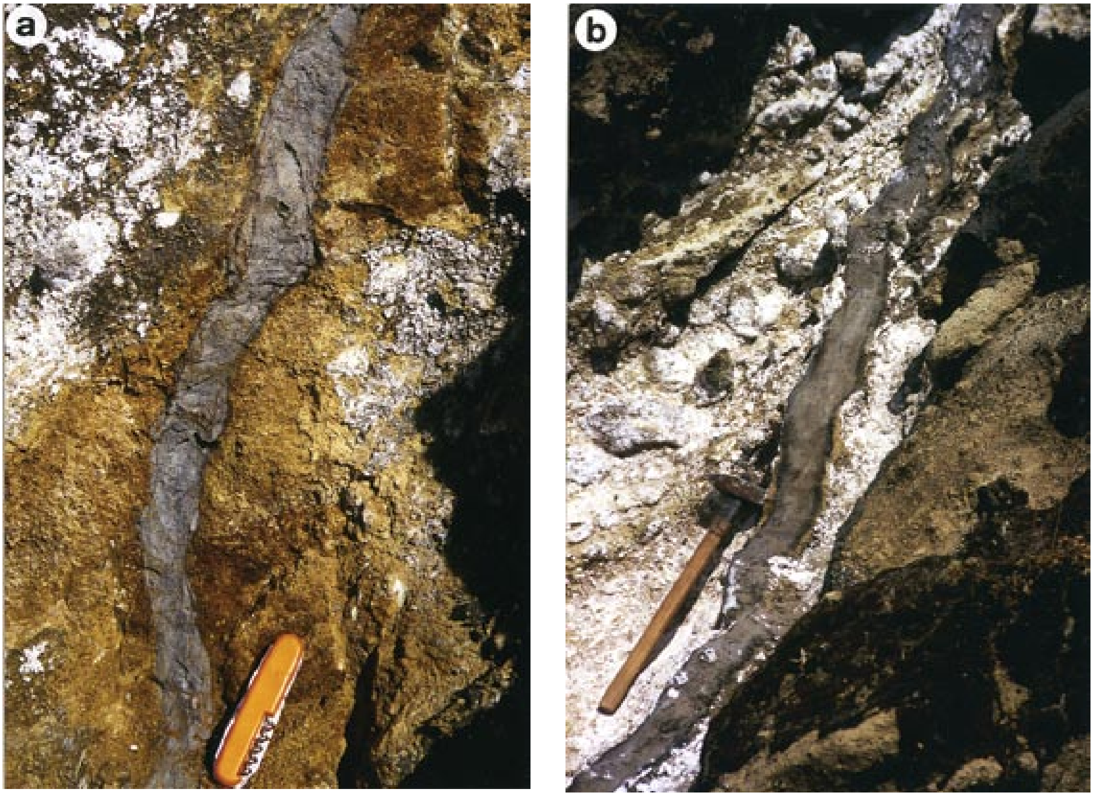


FIG. 2. Calcite carbonatite dykes. (a) Dyke I (OL 227), and (b) dyke II (OL 327).

(Na + K)/Al = 1.09, with Na_2O 9.3 wt.% and K_2O 5.0 at SiO_2 51.9 and Al_2O_3 19.1 wt.%, respectively.

Representative compositions of alkali feldspar, nepheline, clinopyroxene, sodalite and titanite in phonolite OL 226 are given in Table 1. The composition of magnetite is discussed in the section on compositions of minerals of the carbonatite dykes.

Phenocrysts of *alkali feldspar* are commonly zoned in BSE images. The electron-microprobe data show large variations in alkalis, K_2O from 5.5 to 10.7 wt.% and Na_2O between 3.9 and 7.4 wt.%. The core consists of a sodium-rich variety of alkali feldspar (anorthoclase), with up to 0.66 atoms per formula unit (*apfu*) Na, whereas the rim is potassium-rich (sanidine), with a maximum of 0.62 *apfu* K. Minor elements include Ba (0.3–2.8 wt.% BaO), Fe (0.3–1.0% FeO) and Sr (0.2–0.7% SrO).

Nepheline phenocrysts are relatively uniform in composition and show no systematic variation between core and rim. Nepheline contains 4.0–5.5 wt.% K_2O (12.6–16.9 mol.% Ks), 16.3–17.2 wt.% Na_2O (78.5–82.1 mol.% Ne), with a small amount of Fe_2O_3 (between 0.9 and 2.3%), and traces of CaO (<0.2%) and MnO (<0.1%) (Table 1). The calculated excess of SiO_2 in the nepheline ranges from 3.7 to 7.9 mol.% (average 5.3%). Nepheline of similar composition has been described from lavas and blocks of sanidine phonolite, and nepheline from phonolitic nephelinite lavas contains between 7.0 and 8.2 wt.% K_2O (Donaldson *et al.* 1987).

Clinopyroxene is typically zoned, BSE images of phenocrysts showing distinct differences between core and rim. In some cases, the core is resorbed, and the rim is commonly characterized by oscillatory zoning. Clinopyroxene compositions range from diopside to aegirine-augite in core-to-rim profiles (Table 1). Diopside is enriched in Al (up to 2.2 wt.% Al_2O_3) and Ti (up to 1.0% TiO_2) and depleted in Mn (<0.4% MnO) compared to aegirine-augite, with 0.5–1.6 wt.% Al_2O_3, 0.2–0.7% TiO_2 and 0.6–0.8% MnO. The composition of clinopyroxene microphenocrysts is similar to that of the rim on phenocrysts. Donaldson *et al.* (1987) also reported Al-rich aegirine as a rare groundmass phase in the phonolites.

Microphenocrysts of *sodalite* are chemically homogeneous and correspond to a nearly stoichiometric $Na_4(AlSiO_4)_3Cl$ (Table 1). In addition to Cl, it also

TABLE 1. CHEMICAL COMPOSITION OF MINERALS FROM PHONOLITE

Mineral	Anr	Sa	Ne		Di	Ae-aug		Sdl		Ttn
	core	rim	core	rim	core	rim	rim	core	rim	
SiO_2 wt.%	64.86	64.81	44.84	45.70	50.98	49.38	49.50	36.53	37.19	30.31
TiO_2	n.a.	n.a.	b.d.	b.d.	0.85	0.70	0.36	b.d.	0.19	36.39
Al_2O_3	19.54	18.72	32.05	31.63	2.08	1.44	0.67	30.19	29.81	0.81
Fe_2O_3*			1.43	1.61	6.02	9.47	10.87			2.43
FeO*	0.33	0.62			4.12	10.26	11.14	0.75	0.99	
MnO	n.a.	n.a.	b.d.	b.d.	0.31	0.71	0.79	b.d.	b.d.	b.d.
MgO	n.a.	n.a.	b.d.	b.d.	12.31	6.16	4.43	b.d.	b.d.	b.d.
CaO	0.10	b.d.	0.11	b.d.	22.63	18.58	16.20	0.23	0.28	28.03
N.a.$_2$O	6.07	4.26	16.95	16.86	1.37	3.00	4.08	25.71	25.45	0.13
K_2O	7.04	10.11	5.16	4.77	b.d.	b.d.	b.d.	0.34	0.22	b.d.
SrO	0.72	0.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BaO	1.33	0.82	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Nb_2O_5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.74
SO_3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.95	1.17	n.a.
Cl	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6.24	6.38	n.a.
-O=Cl								1.41	1.44	
Total	99.99	99.65	100.54	100.57	100.67	99.70	98.04	99.53	100.24	98.84
Si *apfu*	2.966	2.964	4.275	4.339	1.895	1.922	1.967	2.965	3.018	1.007
Al	1.053	1.009	3.599	3.536	0.091	0.066	0.031	2.885	2.850	0.032
Ti	-	-	-	-	0.024	0.020	0.011	-	0.012	0.909
Fe^{3+}	-	-	0.102	0.115	0.169	0.277	0.325	-	-	0.061
Fe^{2+}	0.013	0.024	-	-	0.128	0.334	0.371	0.051	0.067	-
Mn	-	-	-	-	0.010	0.023	0.027	-	-	-
Mg	-	-	-	-	0.682	0.357	0.263	-	-	-
Ca	0.005	-	0.011	-	0.902	0.775	0.690	0.020	0.024	0.998
N.a.	0.538	0.377	3.134	3.104	0.099	0.226	0.315	4.044	4.006	0.008
K	0.411	0.590	0.628	0.578	-	-	-	0.035	0.023	-
Sr	0.019	0.008	-	-	-	-	-	-	-	-
Ba	0.024	0.015	-	-	-	-	-	-	-	-
Nb	-	-	-	-	-	-	-	-	-	0.011
Total	5.029	4.987	11.749	11.672	4.000	4.000	4.000	10.000	10.000	3.026
S	-	-	-	-	-	-	-	0.058	0.071	-
Cl	-	-	-	-	-	-	-	0.858	0.878	-
Total								0.916	0.949	

All data reported pertain to sample OL 226. * All Fe expressed as Fe_2O_3 in nepheline and titanite and as FeO in anorthoclase or sanidine and sodalite, Fe^{2+}/Fe^{3+} in clinopyroxene is estimated from stoichiometry. b.d.: below detection limit, n.a.: not analyzed. The proportion of cations is calculated on the basis of 8 O for anorthoclase (Anr) or sanidine (Sa), 16 O for nepheline (Ne), 6 O for clinopyroxene (Di: diopside, Ae-aug: aegirine-augite, 5 O for titanite (Ttn) and 10 cations for sodalite (Sdl).

contains between 0.8 and 1.3 wt.% SO_3. Rare *titanite* contains Fe and Al as major trace elements (Donaldson *et al.* 1987) and detectable Nb (0.6–0.9 wt.% Nb_2O_5, Table 1).

Petrography and mineralogy of the carbonatite dykes

The dykes are fine-grained, and gray in color. The rock is porous and friable, such that it is easily cut with a knife. In hand specimen, both dykes are indistinguishable, characterized by a microporphyritic to trachytoid texture defined by tabular calcite laths. The dykes have sharp contacts with their host rock (Fig. 2), and there is no indication of fenitization of the host phonolite, even on a mm scale. Calcite microphenocrysts show a symmetrical banding parallel to the contact with the phonolite (Fig. 3). The fine-grained, dark groundmass consists of fluorite and magnetite with a subordinate amount of apatite.

Calcite occurs as polycrystalline, granular laths up to 1 mm in size (Figs. 4a, b, 5). Morphologically, the mineral is similar to the calcite grains described in carbonatite sample BD 83 by Dawson (1993). Cathodoluminescence shows a heterogeneous, spotty, internal structure of calcite microphenocrysts, with cathodoluminescence (CL) colors from yellow to dark red (Figs. 4c, d). The yellow color is commonly observed in the core of calcite grains, whereas rim and mantle parts are orange to red. Some calcite grains are characterized by corrosion relationships between core and rim. BSE imagery confirms the internal heterogeneity of the calcite laths, which are light to dark gray (Fig. 6). The observed distribution of color broadly corresponds with the CL observation. A dark gray BSE color is common for grain cores, and a gray to light gray color is characteristic of crystal rims, with orange-red CL colors.

In terms of composition, calcite from both dykes has a typical carbonatitic trace-element fingerprint, with Sr and Ba as key elements (Table 2). Both elements show noticeable variations in their contents: 2.2–3.5 wt.% SrO and 0.3–2.2 wt.% BaO. These values are among the highest recorded in carbonatitic calcite, which normally contains up to 2% SrO and 0.2% BaO (*e.g.*, Sokolov 1985, Dawson *et al.* 1996b, Zaitsev 1996). High concentration of Ba, up to 0.9% BaO, has been reported from carbonatite calcite (*e.g.*, Pouliot 1970), but these high values were obtained from analysis of carbonate concentrates. The calcite from the dykes contains variable Mn concentrations, ranging from below detection limit to 1.3 wt.%. The concentration of both MgO and FeO is very low and does not exceed 0.3 wt.%.

Noteworthy is the relatively high and rather constant Na content in calcite, from 0.4 to 0.8 wt.% Na_2O. Published data (*e.g.*, Dawson & Hinton 2003, Rosatelli *et al.* 2003) and unpublished data of the authors show that Na in carbonatitic calcite is usually very low (<0.2 wt.% Na_2O, and commonly below detection limit). This is also true for calcite from the calcite carbonatite clast from Oldoinyo Lengai, in which Na_2O is <0.02 wt.% (Dawson 1993). Only one published composition of calcite has a similar Na_2O content, 0.6 wt.% (Dawson 1993), and this is from intergranular calcite in the partly altered, pirssonite-bearing natrocarbonatite (Dawson *et al.* 1987). Such calcite also has significant contents of Sr and Ba.

Calcite with morphological and chemical similarities to the Oldoinyo Lengai calcite is known from Tinderet pyroclastic carbonatites (lapilli tuffs and agglomeratic lapilli tuffs), which have been interpreted as calcified natrocarbonatite (Deans & Roberts 1984). It also occurs as corroded tabular granular aggregates and contains up to 0.8 wt.% Na_2O, 0.3% K_2O and 0.6–1.4% SrO.

Fluorite is a typical groundmass mineral in both dykes. It forms sheaf-like aggregates (Fig. 7). These are morphologically identical to intergrowths of fluorite, sylvite and nyerereite described from fresh natrocarbon-

TABLE 2. CHEMICAL COMPOSITION OF CALCITE

	low z 1	high z 2	high z 3	high z 4	high z 5	low z 6	high z 7	low z 8	low z 9	high z 10
Na_2O wt.%	0.50	0.51	0.51	0.52	0.44	0.68	0.69	0.59	0.72	0.76
MgO	b.d.	0.17	0.25	0.14	b.d.	b.d.	0.17	0.20	0.11	0.22
K_2O	b.d.	b.d.	b.d.	b.d.	b.d.	0.12	b.d.	0.18	b.d.	b.d.
CaO	51.56	50.35	50.75	51.10	51.47	51.80	50.36	51.95	51.86	50.72
MnO	0.51	0.95	0.88	0.27	b.d.	0.25	1.24	0.34	0.25	0.33
FeO	b.d.	b.d.	0.14	0.12	0.15	b.d.	b.d.	0.16	b.d.	0.10
SrO	2.47	2.28	3.07	3.53	3.36	2.20	3.13	2.30	2.67	3.38
BaO	1.21	2.05	0.95	0.87	0.45	0.59	0.85	0.75	0.68	1.27
CO_2*	42.52	42.20	42.66	42.60	42.34	42.44	42.53	42.98	42.80	42.64
Total	98.77	98.51	99.21	99.15	98.21	98.08	98.97	99.45	99.09	99.42
Na *apfu*	0.017	0.017	0.017	0.017	0.015	0.022	0.023	0.019	0.024	0.025
Mg	-	0.004	0.006	0.004	-	-	0.004	0.005	0.003	0.006
K	-	-	-	-	-	0.003	-	0.004	-	-
Ca	0.944	0.928	0.926	0.933	0.947	0.946	0.918	0.937	0.939	0.922
Mn	0.007	0.014	0.013	0.004	-	0.004	0.018	0.005	0.004	0.005
Fe	-	-	0.002	0.002	0.002	-	-	0.002	-	0.001
Sr	0.024	0.023	0.030	0.035	0.033	0.022	0.031	0.022	0.026	0.033
Ba	0.008	0.014	0.006	0.006	0.003	0.004	0.006	0.005	0.005	0.008
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

All analyses were made of calcite in sample OL 227. All Fe expressed as FeO. * CO_2 calculated by stoichiometry, b.d.: below detection limit. The proportion of cations calculated on the basis of 1 $(CO_3)^{2-}$ group. Low z corresponds to dark areas on BSE images and yellow color on CL; high z corresponds to bright areas on BSE images and red color on CL (Figs. 4, 5 and 6).

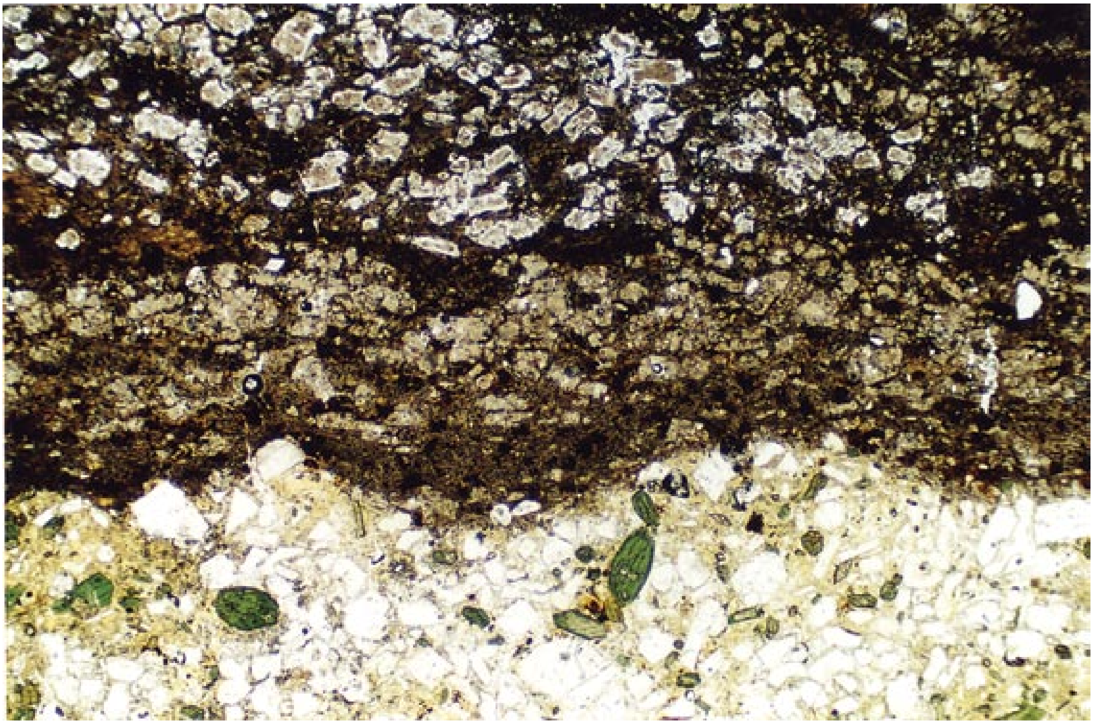


FIG. 3. Microphotograph of carbonatite–phonolite contact (dyke I, OL 227). Plane-polarized light, field of view: 5 × 3.5 mm.

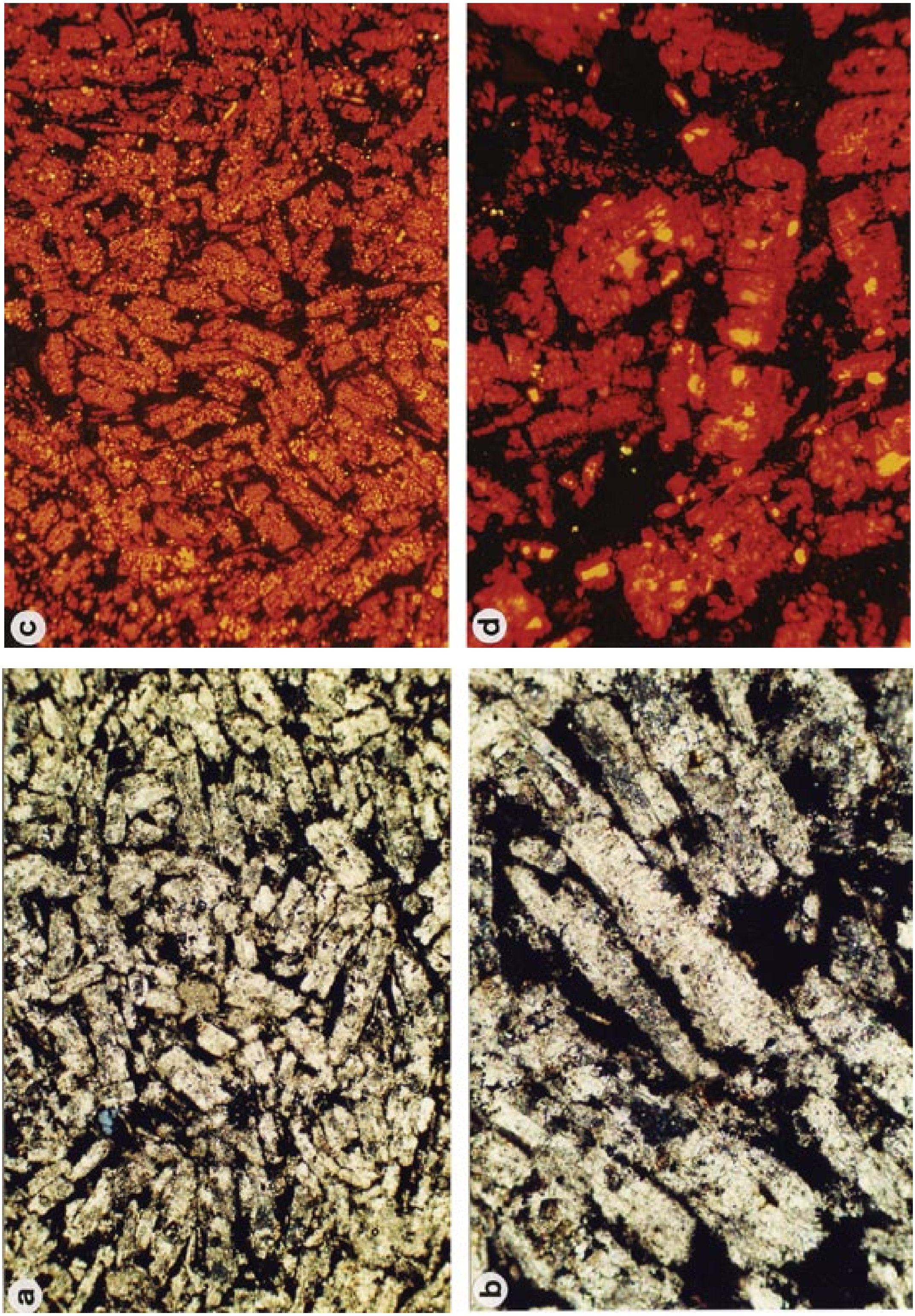
atite (Dawson *et al.* 1995b, Fig. 2, Koberski & Keller 1995, Figs. 1, 2), of fluorite and gregoryite (Church & Jones 1995, Fig. 5c) and of gregoryite, halite, sylvite and fluorite (Peterson 1990, Fig. 3). These features have also been observed by the authors as typical for all natrocarbonatites erupted since September 2000. Rarely, fluorite forms concentrically zoned aggregates that contain relics of the sheaf-like textures and also occurs as fine anhedral grains in calcite. Fluorite contains Sr up to 3.9 wt.% SrO and minor amounts of Ba (≤0.7 wt.% BaO). Its composition is similar to fluorite from fresh natrocarbonatite (Table 3).

Magnetite occurs in the groundmass as subhedral to anhedral grains up to 10 μm in size (Fig. 5b). A characteristic feature of the magnetite is its enrichment in Mn (6.9–10.6 wt.% MnO) (Table 4), and it also has appreciable amounts of Si and Ca (1.5–3.0% SiO_2 and 2.0–4.0% CaO), with minor Mg and Ti (1.1–1.9% MgO and 1.0–1.2% TiO_2). Up to 0.5 wt.% of Nb_2O_5 has also been found in the magnetite.

Magnetite with a high proportion of the jacobsite end-member, $MnFe_2O_4$, is a common accessory mineral in fresh natrocarbonatite (Shive *et al.* 1990, Dawson *et al.* 1995b, Church & Jones 1995). Higher levels of Mn (up to 20.3 wt.% MnO) have been described in magnetite from pirssonite-bearing natrocarbonatite (Dawson *et al.* 1987). Also, Dawson's (1993) calcite carbonatite sample contains magnetite of similar composition to that in the dykes. Magnetite of the host phonolite contains less Mn and more Si and Ti compared to the magnetite of the dykes (Table 4).

Apatite forms round to oval grains up to 15 μm in size in the groundmass of the dyke carbonatites (Fig. 5b). It is

FIG. 4. (a) Thin section view of the texture of dyke I (OL 227) with polycrystalline calcite microphenocrysts in a matrix of fine-grained calcite, fluorite, magnetite and fluorapatite. Plane-polarized light, field of view: 5 × 3.5 mm. (b) Detail of granular, polycrystalline calcite microphenocrysts. Crossed polars, field of view: 1 × 0.7 mm. (c) Cathodoluminescence image of calcite textures in dyke I. General view of microporphyritic texture, with granular microphenocrysts of calcite luminescing orange and yellow; field of view: 3.2 × 2.2 mm. (d) Detail of calcite microphenocrysts, with areas showing different luminescence colors; field of view: 1.4 × 0.96 mm.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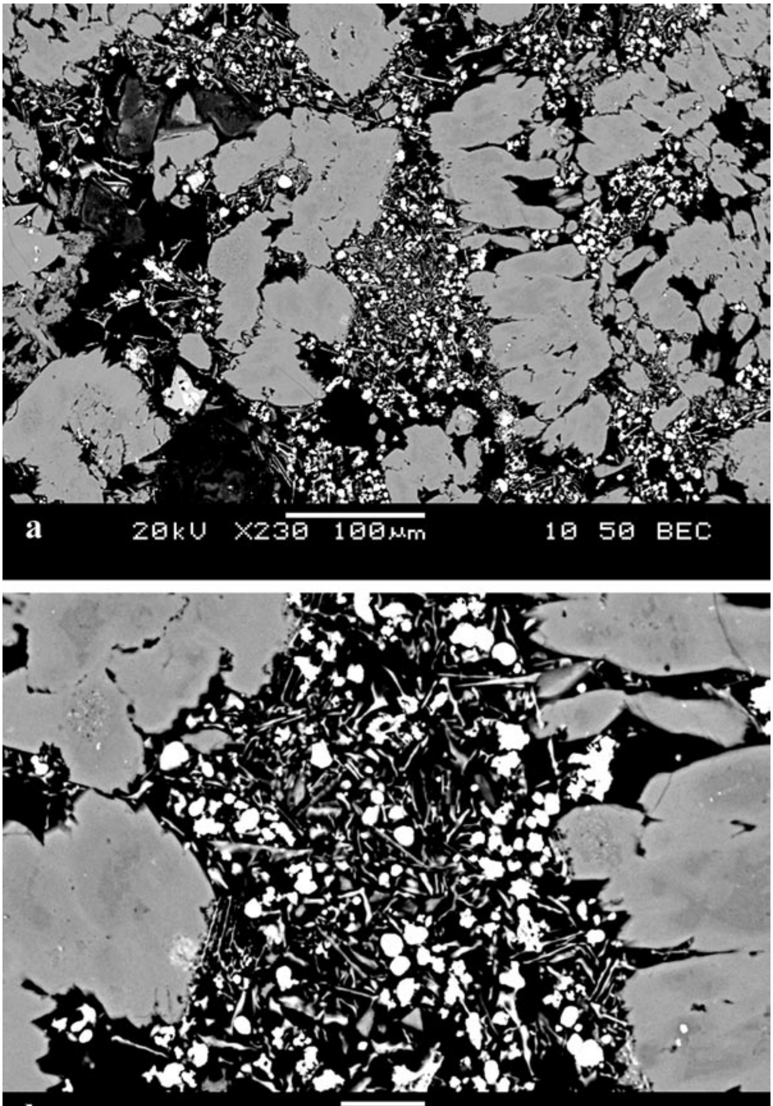

FIG. 5. Back-scattered-electron (BSE) images showing granular microphenocrysts of calcite set in a matrix of fluorite, magnetite, fluorapatite and calcite, dyke I (OL 227). (a) General view, (b) detail of groundmass (magnetite: white, subhedral and anhedral, fluorapatite: white, round and oval).

a REE- and Si-rich variety of fluorapatite (3.0–3.9 wt.% F) with 18.7–20.6 wt.% REE_2O_3 and 8.7–9.9 wt.% SiO_2 (Table 5). The fluorapatite also contains appreciable SrO (2.5–3.4%), FeO (0.5–2.7%), MnO (0.7–1.1%) and Na_2O (0.9–1.1%). In terms of end members, this gives 7.3–7.6 mol.% of $(Na_{2.5}REE_{2.5})_{\Sigma 5}(PO_4)_3F$ (substitution scheme $2Ca^{2+} \rightleftharpoons Na^+ + REE^{3+}$), 15.9–17.3 mol.% of $(Ca_2REE_3)_{\Sigma 5}(SiO_4)_3F$ (substitution scheme $Ca^{2+} + P^{5+} \rightleftharpoons REE^{3+} + Si^{4+}$), and fluorapatite $[Ca_5(PO_4)_3F]$ is the dominant end-member at 59.7–63.8 mol.%. Apatite of similar composition (high in REE and Si) has been described from lavas and lapilli of a 1992 eruption (Church & Jones 1995) and as rod-shaped crystals in a calcite carbonatite (Dawson 1993, Table 5).

REE- and Si-poor varieties of apatite have been reported from natrocarbonatites of an 1988 eruption (Dawson *et al.* 1995b) and also from Dawson's (1993) calcite carbonatite. In neither case does the published composition recalculate to an apatite formula, suggesting analytical problems. The apatite from natrocarbonatites is extremely alkali-rich, $9.7 < Na_2O + K_2O < 10.8$ wt.% (Dawson *et al.* 1995b). The lattice apatite from the calcite carbonatite contains very high F (6.6–8.1 wt.%).

An unidentified *Ba–Mn mineral* occurs in the dykes, forming fine-grained, porous aggregates of irregular

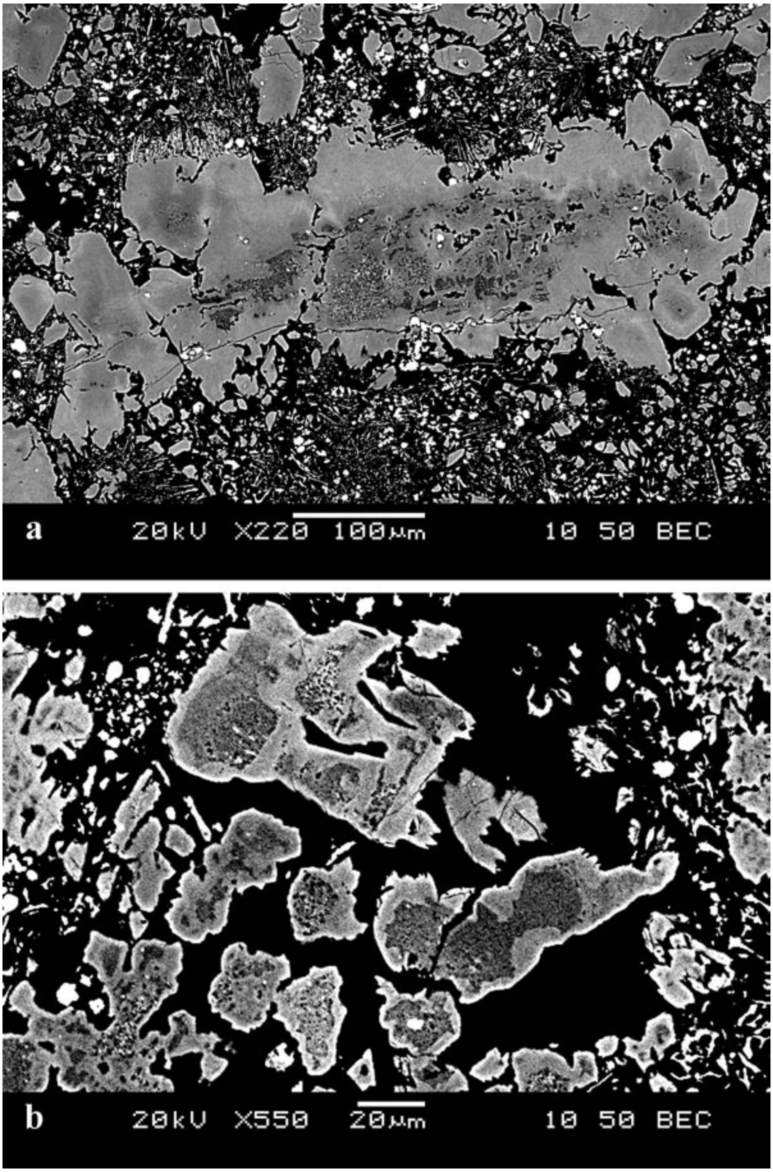

FIG. 6. Back-scattered-electron (BSE) images showing heterogeneous, spotty internal texture of (a) polycrystalline microphenocryst of calcite, and (b) anhedral calcite in the groundmass. Gray porous cores (low average atomic number) show a depletion in Sr and Ba compared to the white rim (high average atomic number) of calcite grains. Dyke I (OL 227).

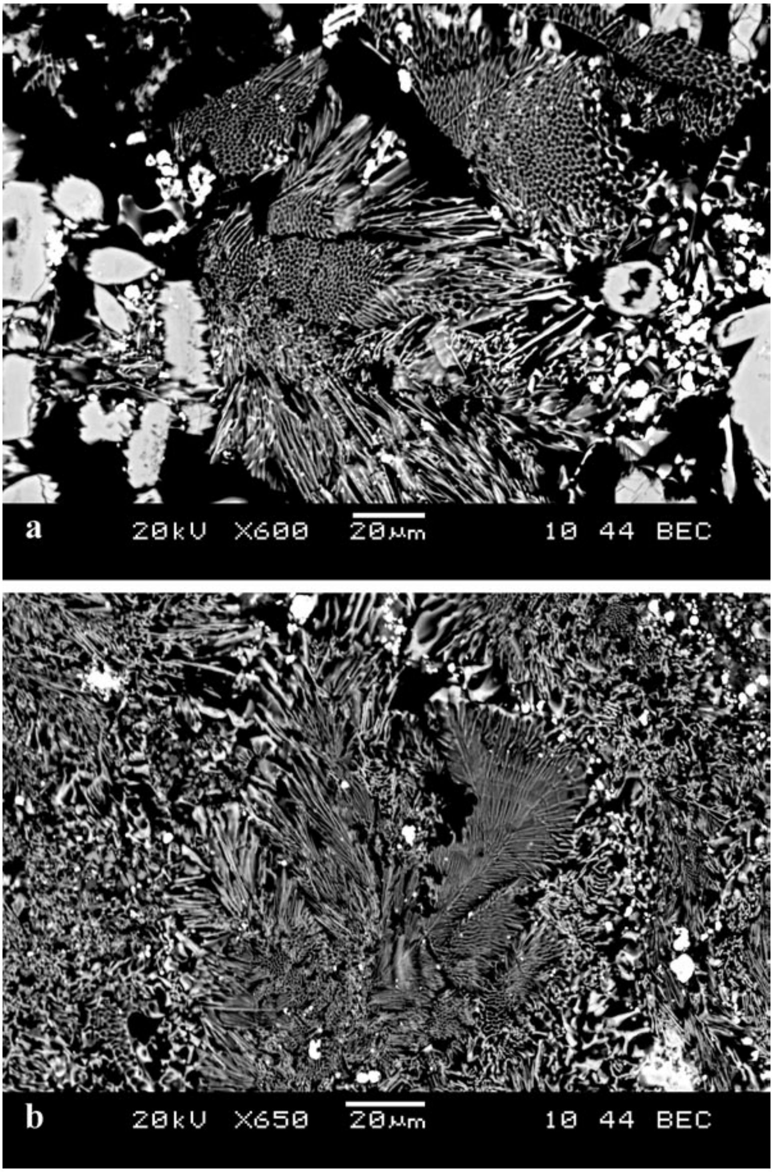

FIG. 7. Back-scattered-electron (BSE) images of the groundmass of dyke I (OL 227), showing sheaf-like fluorite, typical for primary fluorite in natrocarbonatites (Keller & Kraft 1990, Dawson *et al.* 1995b).

shape, up to 150 µm across. BSE images show a heterogeneous internal structure in the aggregates and round to oval individual grains commonly showing concentric zoning. Corroded magnetite is a common relict mineral inside these aggregates. The composition is highly variable in terms of both major and trace elements (Table 6). The main components are Mn (52–55 wt.% MnO_2) and Ba (11–12 wt.% BaO). Low analytical totals suggest the presence of volatiles (in form of H_2O or OH groups) in the mineral. It may also contain high Si (up to 21% SiO_2) and Fe (up to 9.2% Fe_2O_3), also alkalis (1.9–3.4% Na_2O and 1.2–3.3% K_2O), calcium (2.1–3.1% CaO), niobium (0.3–2.1% Nb_2O_5) and aluminum (0.3–2.1% Al_2O_3). The morphology of these aggregates and their composition suggest some similarities with "romanèchite" described from the Oldoinyo Lengai calcite carbonatite of Dawson (1993).

A few small grains (<1 μm) of *S-bearing mineral(s)* have been found in the groundmass of the dyke. EDS spectra also show the presence of Mn and Fe, suggesting that the mineral may be alabandite (*e.g.*, Keller & Kraft 1990).

Composition of the carbonatite dykes

Major- and trace-element compositions for the two dykes are given in Table 7. In accordance with the calcite-dominant mineralogy, the bulk composition is that of a calcite carbonatite. The second major element is Fe (3.4–4.0 wt.% Fe_2O_{3total}). The Mn content also is high (1.1–1.2% MnO) owing to the presence of Mn-rich magnetite and Mn-bearing calcite. Conspicuous are the high contents of fluorine (5.9–6.2% F), strontium (2.4–3.1% SrO) and barium (0.5–0.8% BaO).

Xenocrystic minerals of alkali feldspar, nepheline and clinopyroxene from the host phonolite, identified in thin sections of the carbonatite dykes, may explain the elevated contents of silica (1.3–2.4% SiO_2) and Na in the bulk rock, with 0.8–1.5% Na_2O twice as high as in the calcite (Tables 3, 7).

A completely altered natrocarbonatite lava, OL 133, occurs on the western slope of Oldoinyo Lengai along the ascent track, at about 2000 m above sea-level. It probably resulted from an eruption before the 100-year historical observation period at Lengai, therefore called "pre-modern". This lava is texturally recognized as natrocarbonatite, but is now calcitic in composition and shows similar peculiarities in its bulk-rock composition to the dykes, *e.g.*, high F, Sr and Ba (Table 7). The only published composition of a calcite carbonatite from Oldoinyo Lengai shows very low fluorine (0.2 wt.%) (Dawson 1993).

As representative of the composition of modern natrocarbonatites, we use the data for OL 259, which is a completely fresh sample of lava erupted in September, 2000 (Table 7). The porphyritic natrocarbonatites erupted between 1988 and 2004 have a fairly constant bulk-rock composition (Keller & Kraft 1990, Dawson *et al.* 1995b, Simonetti *et al.* 1997).

The calciocarbonatite dykes are strongly enriched in rare-earth elements (7100–7200 ppm REE), the highest REE content reported for either silicate or carbonatite rocks from Oldoinyo Lengai (Keller & Spettel 1995, Dawson *et al.* 1995b, Simonetti *et al.* 1997). The dykes show the typical carbonatitic enrichment in the light REE, with $(La/Sm)_{CN}$ values of 16 and $(La/Yb)_{CN}$ values between 98 and 109 (chondrite values of McDonough & Sun 1995). Compared with fresh natrocarbonatite or with silicate rocks from Oldoinyo Lengai, the dykes are distinctly enriched in heavy REE (100–200 times chondritic, Fig. 8).

The dykes are also characterized by relatively high Pb (334–341 ppm), Nb (161–282), Zr (85–117) and Th (151–173) and contain very low Rb (2.9–3.4 ppm), Hf (0.7–0.8) and Ta (0.2–0.4) (Table 7).

TABLE 3. CHEMICAL COMPOSITION OF FLUORITE

Sample Rock	OL 227 Dyke I				T 51 Lava
	1	2	3	4	5
Ca wt.%	48.57	48.13	50.41	49.67	49.48
Sr	3.10	3.91	2.09	2.53	2.57
Ba	0.68	b.d.	b.d.	b.d.	0.32
F	47.61	47.00	46.38	47.98	48.00
Total	99.96	99.04	98.88	100.18	100.37
Ca *apfu*	0.967	0.971	1.030	0.981	0.977
Sr	0.028	0.036	0.020	0.023	0.023
Ba	0.004	-	-	-	0.002
Total	0.999	1.007	1.050	1.004	1.002
F	2.000	2.000	2.000	2.000	2.000

b.d.: below detection limit. Cations calculated on the basis of two atoms of fluorine per formula unit (*apfu*). Samples: T 51: lava flow from hornito T 51, eruption of July 2000.

TABLE 4. CHEMICAL COMPOSITION OF MAGNETITE

Sample Rock	OL 227 Dyke I				OL 226 Phonolite
	1	2	3	4	5
MgO wt.%	1.11	1.94	1.55	1.41	0.24
Al_2O_3	0.31	0.69	0.72	0.52	0.64
SiO_2	1.54	2.98	2.22	2.74	4.61
CaO	3.29	4.01	2.87	2.03	1.99
TiO_2	1.15	0.99	0.99	1.18	2.81
MnO	6.95	8.45	9.89	10.59	1.91
Fe_2O_3*	67.56	68.10	67.34	66.83	61.96
FeO*	18.52	12.96	14.06	14.18	23.91
ZnO	0.11	b.d.	0.28	b.d.	0.47
Nb_2O_5	0.53	0.41	0.44	0.39	0.72
Total	101.07	100.53	100.36	99.87	99.26
Mg *apfu*	0.062	0.107	0.086	0.079	0.014
Al	0.014	0.030	0.032	0.023	0.029
Si	0.057	0.110	0.083	0.103	0.175
Ca	0.131	0.159	0.115	0.082	0.081
Ti	0.032	0.028	0.028	0.033	0.080
Mn	0.219	0.265	0.312	0.337	0.062
Fe^{3+}	1.896	1.893	1.890	1.890	1.774
Fe^{2+}	0.577	0.401	0.439	0.446	0.760
Zn	0.003	–	0.008	–	0.013
Nb	0.009	0.007	0.007	0.007	0.012
Total	3.000	3.000	3.000	3.000	3.000

* Fe^{2+}/Fe^{3+} estimated from stoichiometry. b.d.: below detection limit. Cations calculated on the basis of four atoms of oxygen per formula unit (*apfu*).

TABLE 5. CHEMICAL COMPOSITION OF FLUORAPATITE

Sample	OL 227			B.D. 83		no number
Rock	Calcite dyke			Calcite clast		Lava 1992
	1	2	3	4	5	6
Na_2O wt.%	0.97	1.04	0.99	0.24	0.14	b.d.
MgO	0.18	b.d.	b.d.	n.a.	n.a.	b.d.
SiO_2	8.75	9.32	9.86	8.90	10.10	10.43
P_2O_5	26.08	25.35	25.03	25.30	25.10	21.20
K_2O	b.d.	b.d.	b.d.	0.12	0.04	n.a.
CaO	36.54	37.28	36.89	42.50	38.50	34.32
MnO	1.06	0.82	0.75	0.04	0.09	b.d.
FeO*	2.67	0.51	0.56	n.a.	n.a.	1.23
SrO	2.50	3.36	3.08	2.43	1.25	2.71
BaO	0.27	0.16	0.23	n.a.	n.a.	n.a.
Y_2O_3	b.d.	b.d.	b.d.	0.10	0.16	n.a.
La_2O_3	5.86	6.64	6.28	6.47	7.89	8.40
Ce_2O_3	9.17	10.47	10.08	7.49	10.20	11.27
Pr_2O_3	0.89	0.61	0.75	0.69	0.60	n.a.
Nd_2O_3	2.31	2.37	2.22	1.58	2.16	2.64
Sm_2O_3	0.44	0.56	0.48	n.a.	n.a.	n.a.
F	3.01	3.89	3.09	3.46	2.97	n.a.
-O=F	1.27	1.64	1.30	1.46	1.25	
Total	99.43	100.74	98.99	97.86	97.95	92.20
Na *apfu*	0.178	0.192	0.186	0.043	0.027	-
Mg	0.025	-	-	-	-	-
K	-	-	-	0.014	0.005	-
Ca	3.708	3.794	3.826	4.249	4.117	3.868
Mn	0.085	0.066	0.061	0.003	0.008	
Fe	0.211	0.041	0.045	-	-	0.108
Sr	0.137	0.185	0.173	0.131	0.072	0.165
Ba	0.010	0.006	0.009	-	-	-
Y	-	-	-	0.005	0.009	-
La	0.205	0.233	0.224	0.223	0.290	0.326
Ce	0.318	0.364	0.357	0.256	0.373	0.434
Pr	0.031	0.021	0.026	0.023	0.022	-
Nd	0.078	0.080	0.077	0.053	0.077	0.099
Sm	0.014	0.018	0.016	-	-	-
Total	5.000	5.000	5.000	5.000	5.000	5.000
Si	0.829	0.885	0.954	0.830	1.008	1.097
P	2.091	2.039	2.051	1.998	2.121	1.888
Total	2.920	2.924	3.005	2.828	3.129	2.985
F	0.901	1.169	0.946	1.021	0.938	-

* All Fe expressed as FeO. b.d.: below detection limit, n.a.: not analyzed. The proportion of cations is calculated on the basis of five cations. Compositions 4 and 5 are taken from Dawson (1993), and composition 6 is from Church & Jones (1995).

STABLE ISOTOPES

The oxygen and carbon isotopic composition of natrocarbonatite from Oldoinyo Lengai was defined by Keller & Hoefs (1995), who included values for whole-rock lavas and for the separated phenocrysts of nyerereite and gregoryite. The effect of atmospheric weathering was also tested with altered samples. The fresh, whole-rock lavas and the phenocrysts of nyerereite and gregoryite fall in a restricted field within the primary carbonatite field (Taylor *et al.* 1967, Hoefs 1997). All available C and O isotope values from fresh lavas (Javoy *et al.* 1988, Hay 1989, Keller & Hoefs 1995, Dawson *et al.* 1995b) confirm the natrocarbonatite field of Keller & Hoefs (1995). This "Lengai Box" is considerably more restricted than the broader field of primary igneous carbonatites, the "Carbonatite Box" of Taylor *et al.* (1967) (Table 8, Fig. 9).

The composition of fresh natrocarbonatite within the "Lengai Box" averages $\delta^{13}C = -6.80 \pm 0.41$‰ PDB and $\delta^{18}O = +6.51 \pm 0.51$‰ SMOW, and this is considered to reflect the basically unchanged mantle composition of the Lengai carbonate phase.

Weathering and alteration of natrocarbonatite rapidly change this isotopic signature, mainly toward higher $\delta^{18}O$, less so toward higher $\delta^{13}C$ (Suwa *et al.* 1975, Keller & Hoefs 1995) (Fig. 9). The sample of dyke I (OL 227) shows a $\delta^{13}C = -1.95$‰ PDB and a $\delta^{18}O = +24.12$‰ SMOW, and lies at the extreme end of the alteration trend (Table 8, Fig. 9). The isotopic composition of the dyke is similar to that of sample OL 133, the "calcitized" pre-modern lava on the western slope (Table 8). Sample OL 133 shows every aspect of an altered natrocarbonatite. Its chemical composition is similar to that of the dykes (Table 7), the higher SiO_2 content resulting from small crystal aggregates and globules of ijolitic material, similar to the ones described from the 1993 natrocarbonatite flows (Church & Jones 1995, Dawson *et al.* 1994, 1996a).

The rapid effect of isotopic alteration by equilibration with atmospheric humidity is demonstrated by a lava sample from a 1996 eruption (Table 8, data from Lee *et al.* 2000). The authors stated that this sample from "...Oldoinyo Lengai represents a fresh carbonatite lava collected from the summit caldera and analyzed within a year (sample was collected black, but it turned to a gray color within several weeks after collecting it in July 1996)" (Lee *et al.* 2000). Yet, this sample shows

TABLE 6. CHEMICAL COMPOSITION OF THE Ba-Mn MINERAL

Sample	OL 227			BD83
Rock	Dyke I			calcite clast
	1	2	3	4
Na_2O wt.%	1.89	2.21	3.42	2.14
MgO	0.17	b.d.	0.40	0.03
Al_2O_3	0.31	0.38	2.14	0.19
SiO_2	6.07	5.76	20.93	1.27
K_2O	1.33	1.24	3.29	0.87
CaO	2.20	2.14	3.12	1.65
TiO_2	b.d.	b.d.	b.d.	0.31
MnO_2*	53.43	53.35	28.54	70.60
Fe_2O_3**	1.92	1.69	9.21	0.77
SrO	b.d.	b.d.	b.d.	0.16
Nb_2O_5	1.59	2.05	0.32	n.a.
BaO	11.91	11.70	7.01	12.70
PbO	1.93	2.26	0.84	n.a.
Total	82.75	82.60	79.21	90.69

* All Mn expressed as MnO_2. ** All Fe expressed as Fe_2O_3. b.d.: below detection limit, n.a. = not analyzed. Composition 4 is taken from Dawson (1993).

an increase in $\delta^{18}O$ of *ca.* 5‰ in comparison with the "Lengai Box" of fresh natrocarbonatites.

In summary, the stable isotope diagram of Figure 9 defines the narrow "Lengai Box" and shows the alteration trend of natrocarbonatite exposed to low-temperature meteoric exchange. The data place the calciocarbonatitic dyke at the far end of this alteration trend.

DISCUSSION

The key question arising from the occurrence of calcite carbonatite dykes at Oldoinyo Lengai is their origin: is calcite and the calciocarbonatitic bulk-rock composition a primary magmatic feature or a subsolidus result of secondary processes? This question is particularly important in relation to the discussion between Gittins & Harmer (1997) and Dawson (1993) on the origin of the calcite carbonatite clast BD 83, the only heretofore proposed calciocarbonatite from Oldoinyo Lengai.

The textural and mineralogical features of the calcite dykes described here bear many similarities to those of recent natrocarbonatites from Oldoinyo Lengai (*e.g.*, Keller & Kraft 1990, Dawson *et al.* 1995b). The bulk of

TABLE 7. CHEMICAL COMPOSITION OF CALCITE CARBONATITE DYKES WITH ALTERED AND FRESH NATROCARBONATITE FOR COMPARISON

Sample	OL 227 Dyke I	OL 327 Dyke II	OL 133 Pre-modern altered lava	OL 259 Fresh lava 2000
SiO_2 wt.%	1.28	2.38	7.72	0.23
TiO_2	0.09	0.23	0.23	0.02
Al_2O_3	0.18	0.27	2.42	0.00
Fe_2O_3*	3.42	4.04	4.34	0.44
MnO	1.14	1.24	0.93	0.47
MgO	0.34	0.08	0.84	0.43
CaO	49.95	45.91	42.29	15.11
SrO**	3.06	2.37	2.35	1.46
BaO**	0.79	0.51	1.67	1.54
Na_2O	0.82	1.50	2.75	32.74
K_2O	0.16	0.24	0.59	8.30
P_2O_5	0.81	0.88	1.65	0.75
CO_2	33.00	34.40	30.00	30.56
Cl	b.d.	b.d.	b.d.	4.12
SO_3	0.17	0.06	0.13	2.80
F	5.88	6.19	3.06	3.03
H_2O	1.14	2.13	1.18	0.01
-O=F,Cl	2.48	2.61	1.29	2.21
Total	99.75	99.82	100.86	99.80
Cs ppm	0.12	0.14	b.d.	4.50
Rb	2.88	3.41	b.d.	195
Pb	341	334	152	69.30
Th	151	173	33	5.62
U	8.64	9.34	16	13.60
Nb	161	282	339	30
Zr	85	117	92	1.3
Hf	0.71	0.82	n.a.	b.d.
Ta	0.18	0.42	n.a.	b.d.
Y	339	378	125	8
V	133	49	383	189
Zn	1007	580	576	80
La	2425	2606	1286	646
Ce	3217	2945	1563	790
Pr	278.8	303.1	n.a.	51.1
Nd	842	925	412	122
Sm	98.05	105.50	n.a.	7.65
Eu	28.90	31.37	n.a.	2.98
Gd	94.52	100.20	n.a.	4.86
Tb	11.78	12.50	n.a.	0.53
Dy	55.60	58.93	n.a.	2.13
Ho	10.88	11.77	n.a.	0.16
Er	28.29	30.77	n.a	0.49
Tm	3.53	4.05	n.a.	0.04
Yb	15.96	19.11	n.a.	0.21
Lu	1.83	2.40	n.a.	0.03

* all Fe expressed as Fe_2O_3, ** calculated from ppm values. b.d.: below detection limit, n.a.: not analyzed.

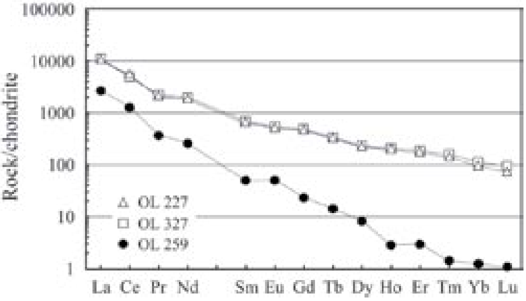

FIG. 8. Chondrite-normalized REE diagram of calciocarbonatite dykes (open symbols), compared to fresh natrocarbonatite (black symbols). Values used for normalization from McDonough & Sun (1995).

TABLE 8. STABLE ISOTOPES IN NATROCARBONATITE AND ALTERATION PRODUCTS AT OLDOINYO LENGAI

Sample	$\delta^{13}C$ PDB ‰	$\delta^{18}O$ SMOW ‰	Reference
Dyke I, OL 227	-1.95	24.12	this work
Pre-modern lava, OL 133	-3.63	23.22	this work
Lava 1988, OL 102	-6.87	6.32	Keller & Hoefs (1995)
Lava 1988, OL 105	-6.30	6.49	Keller & Hoefs (1995)
Gregoryite, GREG	-7.14	5.78	Keller & Hoefs (1995)
Nyerereite, NYERE	-6.65	6.74	Keller & Hoefs (1995)
Lava 1988	-6.93	6.96	Javoy *et al.* (1989)
Lava 1988, BD 4151	-6.7	6.2	Dawson *et al.* (1995b)
Lava 1988, BD 4159	-6.6	6.0	Dawson *et al.* (1995b)
Lava 1988, BD 4166	-6.1	5.9	Dawson *et al.* (1995b)
Lava 1985	-7.1	6.8	Hay (1989)
Lava 1985	-6.8	7.3	Hay (1989)
Lava 1960	-7.6	7.1	O'Neil & Hay (1973)
Fresh natrocarbonatite (average $n = 11$)	-6.80	6.51	
standard deviation	0.41	0.51	
Altered lava 1988, OL 115	-3.3	17.4	Keller & Hoefs (1995)
Partly altered pirssonite – nyerereite lava, OL 4	-6.2	12.4	Keller & Hoefs (1995)
Lava 1996, partly altered	-6.4	11.8	Lee *et al.* (2000)
Clast, "calcite carbonatite", BD 83	-4.16	24.53	Dawson (1993)
Clast in "Footprint Tuff"	-3.5	26.0	Hay (1989)
Clast in "Footprint Tuff"	-4.1	26.0	Hay (1989)
"Primary Magmatic Carbonatite Box"	-4 to -8	+6 to +10	Taylor *et al.* (1967) Hoefs (1997)
"Lengai Box"	-6 to -8	+5.5 to +7.5	Keller & Hoefs (1995) this work

the dykes is composed of calcite microphenocrysts. The polycrystalline nature of these subhedral, complexly zoned, lath-shaped aggregates (Figs. 4, 5) is in sharp contrast to the monocrystalline, commonly zoned calcite phenocrysts from magmatic calciocarbonatite extrusive rocks, *e.g.*, from Kaiserstuhl and Kerimasi (Keller 1981, 1989, Mariano & Roeder 1983) that otherwise possess similar tabular crystals. The morphology and internal structure of the Oldoinyo Lengai calcite revealed by both CL observations (Fig. 4) and BSE imagery (Figs. 5, 6) are also quite different from calcite found in high-temperature intrusive phoscorites and carbonatites (Demény *et al.* 2004) and silicate rocks (Zaitsev & Chakhmouradian 2002).

A high Sr content in calcite is commonly considered a distinguishing feature of primary crystallization from a carbonatitic magma. However, magmatic calcite contains only traces of Na, even where associated with Na-rich carbonate minerals like burbankite $(Na,Ca)_3(Sr,Ca,REE,Ba)_3(CO_3)_5$ or carbocernaite $(Ca,Na)(Sr,REE,Ba)(CO_3)_2$ (Zaitsev 1996, Zaitsev *et al.* 1998).

Natrocarbonatites are commonly enriched in fluorine, with contents between 1.5 and 5.2 wt.% (*e.g.*, Keller & Kraft 1990, Dawson *et al.* 1995b), which is mostly concentrated in fluorite; other hosts for F include rare fluorapatite, sellaite and neighborite (Keller & Kraft 1990, Mitchell 1997). Compared to fresh natrocarbonatite, the carbonatite dykes show an even higher fluorine content, ranging from 5.9 to 6.2 wt.%. A remarkable feature of the groundmass fluorite of the dykes is its morphological and chemical similarity to fluorite from fresh natrocarbonatite.

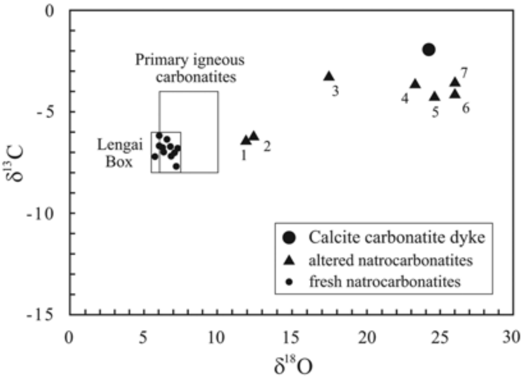

FIG. 9. Stable carbon and oxygen isotope compositions (in ‰ relative to PDB and SMOW, respectively) for the carbonatitic rocks of Oldoinyo Lengai, showing the narrow Lengai Box for unaltered recent flows, an alteration trend for altered natrocarbonatites, and the calciocarbonatite dyke I (sample OL 227) composition at the far end of this alteration trend. References: 1: Lee *et al.* (2000), 2 and 3: Keller & Hoefs (1995), 4: this work, 5: Dawson (1993), 6 and 7: Hay (1989). For other sources of data, see Table 8.

In view of the textural and compositional features of the calcite and fluorite described, and also those of the REE–Si-rich fluorapatite and Mn-rich magnetite, there is little doubt that the calciocarbonatite dykes originate from a natrocarbonatitic protolith. Textural features inherited from natrocarbonatite are the main evidence for this. However, most petrographic, mineralogical, chemical and isotopic characteristics are the result of alteration processes. Leaching of the water-soluble minerals in natrocarbonatite and subsolidus formation of new minerals resulted in the far-reaching chemical re-equilibration of the carbonatite composition.

The predominance of tabular-shaped calcite microphenocrysts in the dykes suggests that nyerereite was the major phenocryst phase, with gregoryite being subordinate in the original natrocarbonatite. Both nyerereite and gregoryite are known to be unstable under atmospheric conditions and are easily replaced by subsolidus pirssonite, gaylussite and other Na (±Ca) carbonates (*e.g.,* Dawson *et al.* 1987, Keller & Kraft 1990).

The calculation of possible reactions to describe the volume-for-volume replacement (Zaitsev *et al.* 1998) shows that replacement of nyerereite by pirssonite or gaylussite requires only the addition of water to these systems. In both cases, if we assume no change in volume during alteration, the reactions can be written as:

a) nyerereite to pirssonite

$$Na_2Ca(CO_3)_2 + 1.62H_2O \rightarrow$$
$$0.81Na_2Ca(CO_3)_2{\bullet}2H_2O + 0.38Na^+$$
$$+ 0.19Ca^{2+} + 0.38CO_3^{2-}$$

b) nyerereite to gaylussite

$$Na_2Ca(CO_3)_2 + 2.78H_2O \rightarrow$$
$$0.56Na_2Ca(CO_3)_2{\bullet}5H_2O + 0.89Na^+$$
$$+ 0.44Ca^{2+} + 0.89CO_3^{2-}$$

c) the transformation of pirssonite to gaylussite also requires only water to be added to the system:

$$Na_2Ca(CO_3)_2{\bullet}2H_2O + 1.44H_2O \rightarrow$$
$$0.69Na_2Ca(CO_3)_2{\bullet}5H_2O + 0.62Na^+$$
$$+ 0.31Ca^{2+} + 0.62CO_3^{2-}$$

All the reactions show an enrichment of a residual solution in Na, Ca and $CO_2(aq)$. The subsequent transformation of minerals can be written as:

d) pirssonite to calcite

$$Na_2Ca(CO_3)_2{\bullet}2H_2O + 1.80Ca^{2+} + 0.80CO_3^{2-} \rightarrow$$
$$2.80CaCO_3 + 2.00Na^+ + 2.00H_2O$$

e) gaylussite to calcite

$Na_2Ca(CO_3)_2{\bullet}5H_2O + 3.07Ca^{2+} + 2.07CO_3^{2-} \rightarrow$
$4.07CaCO_3 + 2.00Na^+ + 5.00H_2O$

Available low-temperature thermodynamic data for alkali carbonate systems, *e.g.*, for the system Na_2O–CaO–CO_2–H_2O (T in the range 0–50°C; Königsberger *et al.* 1999), show that the stability fields of pirssonite, gaylussite and calcite depend on temperature and Na_2CO_3 concentration in solution (or simply the Na^+ activity in water). Our measurements of air and ground temperature in the summit craters of Oldoinyo Lengai range from 8 to 45°C. These temperature fluctuations could initiate mineral transformations, *e.g.*, pirssonite $\rightleftharpoons$ gaylussite and gaylussite $\rightleftharpoons$ calcite. Removal of Na_2CO_3 from the system will lead to transformation of both pirssonite and gaylussite to calcite (Fig. 6d in Königsberger *et al.* 1999). Mineral transformation will occur at Na_2CO_3 concentrations in water of 2.7–2.8 m (molality) at T in the range 40–50°C to ~1 m at T = 10°C.

Note that natural examples of fully euhedral pseudomorphs of calcite after gaylussite have been described from the Tatarian limestone, Timan, Russia (Yushkin 1990).

The reactions (a), (b) and (c) show that for the formation of calcite according to reactions (d) and (e), the system does not require an external source of Ca. This element will be introduced during replacement of nyerereite by pirrsonite, and even more Ca will be available if replacement of pirssonite by gaylussite occurs.

Petrographic, CL and BSE observations on the morphology of the calcite phenocrysts suggest a certain volume-change between the precursor mineral and the calcite. The difference between ideal prismatic phenocrysts and observed calcite phenocrysts was roughly calculated as 20–30 vol.%. Assuming 30% volume reduction, reactions (d) and (e) can be expressed as:

f) pirssonite to calcite

$Na_2Ca(CO_3)_2{\bullet}2H_2O + 0.96Ca^{2+} \rightarrow 1.96CaCO_3$
$+ 2.00Na^+ + 2.00H_2O + 0.04CO_3^{2-}$

g) gaylussite to calcite

$Na_2Ca(CO_3)_2{\bullet}5H_2O + 1.85Ca^{2+} + 0.85CO_3^{2-} \rightarrow$
$2.85CaCO_3 + 2.00Na^+ + 5.00H_2O$

The interpretation of the calciocarbonatitic dykes as end members of natrocarbonatite alteration also finds support in the partly altered natrocarbonatites described by Dawson *et al.* (1987), Hay (1989), Keller & Krafft (1990), Dawson (1993) and Keller & Hoefs (1995).

On the basis of textural and mineralogical evidence, the original composition of the dykes should find its analogue in the recent natrocarbonatite. There is no absolute reference for this possible original composition of natrocarbonatite. For comparison with fresh natrocarbonatite, we chose one of our compositions from a September 2000 flow (OL 259, porphyritic lava of vent T49). Our major- and trace-element data for lavas from 1988, 1993, 1995, 2000 to 2004, and published compositions of natrocarbonatite (Dawson *et al.* 1987, Keller & Krafft 1990, Dawson *et al.* 1995b, Simonetti *et al.* 1997) show only slight variations. The exceptions from the rather constant composition are some 1993 lavas, which are peculiar for their high content of globular silicate inclusions (Church & Jones 1995, Dawson *et al.* 1996a, Simonetti *et al.* 1997). Therefore our composition OL 259 (Table 7) can be taken as representative of the modern activity. It is, however, not assured that former alkali carbonatite invariably had exactly the same composition as the recent flows.

Using the modern composition of natrocarbonatite as the only available reference, a chemical balance for the exchange processes can be estimated. The assumption of alteration by meteoric water is supported by the stable isotope data. Figure 10 shows enrichment–depletion factors between dyke OL 227 and modern lava OL 259. In parallel with Na and K, Rb and Cs are almost quantitatively removed by leaching, and the same is observed for Cl and S. The same trends are observed in the altered natrocarbonatite OL 133 (Table 7). Barium also is depleted, but to a lesser extent. The more immobile elements show an enrichment that is mainly passive, resulting from leaching of about 50 wt.% of the natrocarbonatite material. Strontium and fluorine are examples of this process. Calcium shows a threefold enrichment compared to natrocarbonatite. However, several elements, in particular Th, Zr, Y and HREE, show extreme enrichment-factors, which can only be explained by extensive redistribution of these elements during the process of alteration and transformation. The differential pattern of enrichment and depletion of major and trace elements is shown in Figure 10.

CONCLUSIONS

The calcite carbonatite dykes at Oldoinyo Lengai, the active natrocarbonatitic volcano, display textural, mineralogical and chemical criteria that have been inherited from the natrocarbonatite protolith; for the major part, they are the product of alteration and subsolidus recrystallization. Chemical exchange processes, leaching and passive enrichment, have substantially changed the composition of the natrocarbonatite.

The alkali carbonate nyerereite has been texturally replaced by calcite. Whether this is a direct replacement or had some intermediate steps is unknown. Comparison with recent alteration (Dawson *et al.* 1987, Zaitsev & Keller 2006) suggests pirssonite as an intermediate step. The resulting calcite microphenocryst laths are polycrystalline, granular aggregates. This secondary calcite is strontium-rich (up to 3.5 wt.% SrO) and sodium-enriched (0.4–0.8 wt.% Na_2O), reflecting the high contents of the precursor natrocarbonatite. Fluorite in the dykes is preserved in its original and typical sheaf-like texture. Accessory fluorapatite and magnetite have also not been affected by alteration processes.

Comparison between dyke calciocarbonatite and fresh natrocarbonatite shows that the chemical transformation is complete, with practically no alkalis remaining, and CaO showing a threefold increase. The chemical enrichment–depletion trend is very distinctive (REE, F, Ca, Sr, Th, Zr, Y enriched, Na, K, Rb, Cs, Ba, U depleted).

The stable isotopes define the narrow ”Lengai Box“ of a primary mantle carbonate. Starting from this composition, the alteration trend in natrocarbonatites is traced, and the stable isotope composition of the dyke sample lies at the extreme, high-δ^{18}O end of this trend.

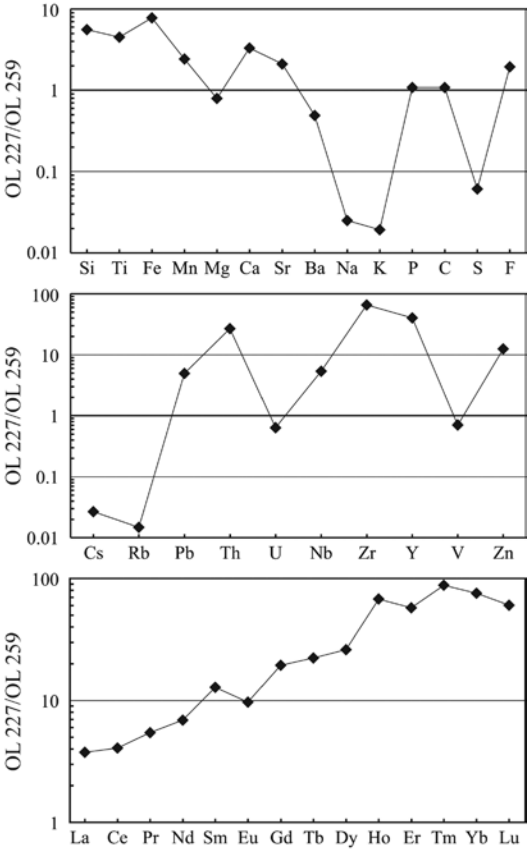

FIG. 10. Enrichment-depletion diagram for chemical alteration, and a comparison of dyke I (OL 227) with a fresh natrocarbonatite flow (OL 259). OL 227/OL 259 element ratios are calculated from data in Table 7.

In contrast to the natrocarbonatite of Oldoinyo Lengai, worldwide occurrences of carbonatite, in particular extrusive varieties, are dominantly calcitic in composition (Keller 1989). A transformed origin from original alkali carbonatites has been suggested in a number of papers (Hay 1983, 1989, Deans & Roberts 1984, Clarke & Roberts 1986, Dawson *et al.* 1987). The processes of transformation from alkali-rich natrocarbonatite to alkali-poor calcite carbonatite can be traced and quantified on the basis of the dykes at Oldoinyo Lengai. The results elucidate characteristic differences between “genuine” primary magmatic crystallization of calcite carbonatites and “calcitized”, mineralogically and chemically secondary compositions.

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