Mineralogical and chemical transformation of Oldoinyo Lengai natrocarbonatites, Tanzania

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Abstract

The minerals of Oldoinyo Lengai natrocarbonatite lavas are unstable under atmospheric conditions. Subsolidus mineral assemblages in natrocarbonatites were studied in 105 samples from contemporary eruptions ranging from present day to about 100 years old. The subsolidus minerals in natrocarbonatites were formed (i) along cracks on the lava surface from hot gases escaping during cooling, (ii) as atmospheric alteration by solution of water-soluble minerals, in particular halides and gregoryite, and by hydration of nyerereite under the influence of meteoric water and (iii) by reaction with fumarole gases. After solidification, the lavas were cut by a network of thin cracks, the edges of which are covered by polymineralic encrustations. Samples collected 2–24 h after eruption contain nahcolite, trona, sylvite, and halite with accessory kalicinite and villiaumite. Atmospheric humidity results immediately (≥ 2 h after eruption) in alteration of black lavas that is marked by the appearance of white powdery thermonatrite with nahcolite on the lava surface. Subsequent reaction (weeks, months, years) of natrocarbonatite with meteoric water and the atmosphere results in the formation of pirssonite, gaylussite, shortite, trona, thermonatrite, nahcolite and calcite. Generally, the first important step is the formation of pirssonite and the end-members are calcite carbonate rocks or loose aggregates. Fumarolic activity is common for the active northern crater of the volcano. Reaction of hot (54–141 °C) fumarolic gases with natrocarbonatite leads to the formation of sulphur, gypsum, calcite, anhydrite, monohydrocalcite, barite and celestine. Changes in mineralogy of the natrocarbonatite lead to substantial chemical transformation. The most obvious chemical changes in this process are the loss of Na, K, Cl and S, combined with an increase in H_2O, Ca, Sr, Ba, F and Mn. The oxygen and carbon isotopic composition of altered natrocarbonatites shows a significant shift from the primary "Lengai Box" to high values of $\delta^{18}O$ and $\delta^{13}C$. Calcite exhibits $\delta^{13}C$ values between -2‰ and -4‰ PDB and $\delta^{18}O$ values of $+23$‰ to $+26$‰ SMOW. The observed assemblages of secondary minerals formed by reaction with atmosphere and meteoric water, the changes in chemical composition of the natrocarbonatite and field observations suggest that alteration of natrocarbonatite is an open-system low-temperature process. It takes place at temperatures between 8 and 43 °C with the addition of H_2O to the system and the removal of Na, K, Cl and S from the carbonatites. Low-temperature thermodynamic models developed for alkali carbonate systems can be used for the interpretation of Oldoinyo Lengai subsolidus mineralization.
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Keywords: Oldoinyo Lengai; Natrocarbonatite; Alteration; Nahcolite; Pirssonite; Shortite Calcite; Thermodynamic model

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1. Introduction

The natrocarbonatite lavas of the Oldoinyo Lengai volcano, East African Rift, Tanzania, consist of the water-soluble phenocryst minerals nyerereite and gregoryite, groundmass sylvite and halite and are black to dark grey. Groundmass fluorite is another major constituent of the natrocarbonatite and apatite, magnetite, monticellite, cuspidine–niocalite, sellaite, alabandite, sphalerite and galena occur as trace minerals (e.g., Peterson, 1990; Keller and Krafft, 1990; Church and Jones, 1995; Dawson et al., 1995b; Mitchell and Belton, 2004).

Subsolidus mineralogical re-equilibration of the lava starts immediately after solidification and cooling, transforming them, under atmospheric influences (air and meteoric water), in a very short time into white secondary products (e.g., Dawson, 1962; Dawson et al., 1987; Keller and Krafft, 1990; Nyamweru, 1997).

Continuous lava effusion from Oldoinyo Lengai since 1988 has provided the opportunity for sampling and testing all of the stages of atmospheric alteration and hydration of natrocarbonatites. Identification of pre-1917 carbonatites in the former, pre-1917, crater platform and in the overflow fields of the steep north flank extended the observational base considerably. Most of these transformed older natrocarbonatites form loose, sandy masses, but may contain more solid relict cores.

The occurrences of altered natrocarbonatite examined in this study are from the following units:

(1) Fresh to highly altered recent natrocarbonatites from the crater fill of the continuous lava activity since 1983, sampled from 1988 onwards to present day.
(2) Pre-1917 crater fill preserved in the remains of the similar platform formed before and during the early visits by Jaeger, Uhlig and Reck (Uhlig, 1905, 1907; Reck, 1914) and until the explosive eruption of 1917.
(3) Fields of altered natrocarbonatite in the upper north flank and upper east flank, the "flank triangles" described previously by the early visitors (Uhlig and Jaeger, 1942). These fields formed largely from overflows before the 1917 destruction, in part because they certainly existed when the first visitors gave their descriptions of the cone at the end of the 19th and beginning of the 20th century.

2. Experimental methods

X-ray powder diffraction (XRD) spectra from 105 bulk rock samples were obtained on a Bruker AXS D8 Advance spectrometer (Cu radiation, 40 kV/40 mA) for 2θ range of $2-80°$ and processed with Diffrac Plus V 5.0 software (IMPG Freiburg).

For identification of minerals in polished thin sections, we employed confocal laser Raman spectroscopy using a LabRam microspectrometer (Jobin Yvon, formerly Dilor) with a He–Ne laser (Institute of Physical Chemistry, Karlsruhe University, Germany). Raman spectra were obtained for a set of standards from the mineral collection of the NHM, London, and the reference spectra were then compared with those for the Oldoinyo Lengai minerals. The calibration of Raman spectra was done using a Si standard and Rayleigh scattering light of the laser.

The mineral compositions were determined by energy dispersive spectrometry (EDS) using a JEOL 5700LV scanning-electron microscope equipped with a light element detector, Be to U (The Natural History Museum, London). EDS spectra were acquired for 50–100 s (live time) with an accelerating voltage of 20 kV and a beam current of 1–2 nA. Due to the low stability of some minerals under an electron beam and strong loss of Na, a defocused beam (up to 20×20 μm) was used for analyses. The spectra were processed with the INCA Oxford Instruments software package.

Whole rock analyses were carried out by X-ray fluorescence (XRF) with the Philips PW 2404 instrument at the IMPG in Freiburg. Fused Li-tetraborate pellets (1 g sample to 4 g flux) were calibrated against international reference samples with a special carbonatite calibration.

3. Assemblages of subsolidus minerals

It is well known that freshly erupted natrocarbonatites are unstable and become altered, forming grayish white powder on the lava surface within a few days (Fig. 1) (e.g., Dawson, 1962, 1966; Du Bois et al., 1963; Keller and Krafft, 1990; Nyamweru, 1997; Calder and Bowden, 2001; Genge et al., 2001). These published data and the authors' own field observations indicate three major processes that lead to the formation of subsolidus (secondary) minerals at Oldoinyo Lengai (i) by sublimation from hot gases escaping during lava cooling, (ii) by atmospheric alteration and reaction with meteoric water and (iii) by reaction with fumarole gases. The subsolidus minerals

Fig. 1. Alteration of natrocarbonatite in a 24-h sequence, hornito T 49, October 2000. Photos by D. Szczepanski.

identified from the Oldoinyo Lengai natrocarbonatites are listed in Table 1.

Our observations show that subsolidus minerals in natrocarbonatites start to form just 2–3 h after lava solidification (they can even be formed immediately in case of rain); 1 year is enough to change solid natrocarbonatite lavas to unconsolidated sand.

3.1. Minerals formed during lava degassing

Immediately after solidification, the natrocarbonatite lavas are cut by a network of thin cracks with hot gases escaping from them. The edges of the cracks become covered by white, brownish and yellowish encrustations up to several centimeters in thickness which are known as "efflorescences" (Keller and Krafft, 1990) or "salt fringes and tubes" (Genge et al., 2001).

Nahcolite, sylvite and trona were previously found to be major minerals in the efflorescences on the surface of both fresh and altered natrocarbonatites (Dawson, 1962; Keller and Krafft, 1990). Efflorescences collected 2–3 h after the 10th October 2000 eruption contain sylvite, nahcolite, trona and halite as major minerals with minor to accessory kalicinite and villiaumite. Samples from the same locality collected 20–24 h later also contain thermonatrite, whereas similar encrustations collected

from the surface of 2.5-month-old lavas contain nahcolite with traces of sylvite and trona.

"Salt fringes and tubes" have been described and studied in detail by Genge et al. (2001). In contrast to previous observations, Genge et al. (2001) found thermonatrite to be the major mineral, comprising up to 70 vol.% of the salt fringes; other minerals were aphthitalite, halite and sylvite. Petrographic observations suggested that thermonatrite was the first mineral to crystallise, followed by aphthitalite, halite and sylvite. No nahcolite was found by Genge et al. (2001).

3.2. Minerals formed during atmospheric alteration and exchange with meteoric water

The earliest field observations on natrocarbonatites from Oldoinyo Lengai indicated that "soda-mud or white soda" was the dominant phase at the summit area of the volcano (Dawson et al., 1995a, and references therein). These names were used presumably as general descriptive terms for secondary minerals and not to indicate the presence of the minerals natrite, nahcolite or natron. The secondary minerals formed during the first few weeks at the surface of natrocarbonatite lavas were identified, on the basis of X-ray analysis, as calcite and trona by Du Bois et al. (1963).

Table 1
Subsolidus minerals in Oldoinyo Lengai natrocarbonatites

Minerals	Minerals formed due to		
	Lava degassing during cooling	Atmospheric alteration and hydration by meteoric waters	Reaction with fumarole gases
Nahcolite $NaHCO_3$	+++	+++	
Trona $Na_3H(CO_3)_2 \cdot 2H_2O$	+++	+++	
Thermonatrite $Na_2CO_3 \cdot H_2O$	+++	+++	
Halite $NaCl$	+++		
Sylvite KCl	+++		
Aphthitalite $K_3Na(SO_4)_2$	++	+	
Kalicinite $KHCO_3$	+		
Villiaumite NaF	+		
Pirssonite $Na_2Ca(CO_3)_2 \cdot 2H_2O$		+++	
Gaylussite $Na_2Ca(CO_3)_2 \cdot 5H_2O$		+++	
Shortite $Na_2Ca_2(CO_3)_3$		+++	
Kogarkoite $Na_3(SO_4)F$		+	
Calcite $CaCO_3$		+++	+++
Sulphur S			+++
Gypsum $Ca(SO_4) \cdot 2H_2O$			+++
Anhydrite $CaSO_4$			++
Monohydrocalcite $Ca(CO_3) \cdot H_2O$			++
Fluorite CaF_2		+	++
Barite $BaSO_4$			++
Celestine $SrSO_4$			+

+++ major minerals, ++ minor minerals, + accessory minerals.
Data are from this work, Dawson (1962, 1993), Du Bois et al. (1963), Dawson et al. (1987), Hay (1989), Keller and Krafft (1990), Koberski and Keller (1995), Genge et al. (2001) and McFarlane et al. (2004).

The XRD patterns of a white powder collected from the surface of lava 3, 15 and 24 h after the eruption (hornito T49, October 2000) are quite similar and show the presence of thermonatrite and nahcolite as the principal secondary minerals with subordinate amounts of aphthitalite. A solid thin (5 mm) white crust collected from a lava surface exposed for approximately 2.5 months (hornito T51, erupted July 2000) contains trona and pirssonite as major secondary minerals, minor gaylussite and nahcolite, and accessory kogarkoite.

Brownish-grey sandy/dusty samples, collected approximately 1 year and 2 months after the eruption of a thick flow (1–1.5 m) of blocky lava from hornito T37 (erupted July 2000), consist of calcite, gaylussite and relict fluorite. Relatively fresh blocks of natrocarbonatite containing nyerereite, gregoryite, halite and sylvite were still preserved in gaylussite–calcite "sand" and secondary trona and nahcolite were found in the rims of these blocks.

Various subsolidus minerals have been identified in samples collected from the old, pre-1917, carbonatite platform of Oldoinyo Lengai and some of the modern eruptions (1966, 1988). The principal minerals are nahcolite, pirssonite, gaylussite, shortite and calcite (Table 1).

Nahcolite is widespread in altered natrocarbonatite, forming nests, veinlets and thin veins inside carbonatite flows. It fills cracks in carbonatites and forms monomineralic veins from 1 mm to 10 cm width. Some of the veins are characterised by a comb structure where prismatic nahcolite crystals grow from the walls to the axial zone of the vein (Fig. 2a).

Dawson et al. (1987) described the pirssonite from partly altered microporphyritic lava. For a long time, the mineral was known only from one outcrop at Oldoinyo Lengai, the so-called "Barry's Pinnacles" (Dawson et al., 1987; Keller and Krafft, 1990; Koberski and Keller, 1995), but now pirssonite has been found in many Lengai natrocarbonatite samples. Pirssonite typically occurs as replacement rims on nyerereite crystals (Fig. 2b), it also forms thin veins that cut nyerereite. Some samples of altered natrocarbonatites contain full polycrystalline pseudomorphs of pirssonite after nyerereite with preservation of the original tabular shape of nyerereite phenocrysts. The pseudomorphs do not have the perfect prismatic shape of the original nyerereite and some degree of volume change is clearly visible. Subhedral to anhedral pirssonite grains are also observed between the pseudomorphs.

Gaylussite was described first from Oldoinyo Lengai by Keller and Krafft (1990) and field observations suggested that it was formed within a few weeks after eruption. Gaylussite has been found in many samples of altered natrocarbonatite with exposure ages of ≥ 2–2.5 months. It is commonly associated with pirssonite, nahcolite and trona. Primary natrocarbonatite minerals such as nyerereite, and in places sylvite and halite are still present.

Shortite has not been previously reported from Oldoinyo Lengai. It occurs in highly altered natrocarbonatites of the pre-1917 platform, which is preserved at the eastern and western rim of the northern crater and found below the young combeite nephelinite rim-lava (Keller and Krafft, 1990). X-ray diffraction patterns show shortite, nahcolite, and fluorite with subordinate calcite, thermonatrite and trona. Except for fluorite, no other primary natrocarbonatite minerals are preserved. Shortite occurs as euhedral square-shaped or prismatic crystals up to 1.2×0.5 mm. Morphologically it looks like "phenocrysts" in a calcite–thermonatrite–trona–fluorite groundmass (Fig. 2c). Associated nahcolite appears to be a late-formed mineral—it fills cavities and encloses shortite and fragments of groundmass.

Calcite has been known at Oldoinyo Lengai for a long time (Dawson, 1962, 1993; Du Bois et al., 1963). As a secondary mineral, calcite associated with trona has been reported from partly altered natrocarbonatites 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).

Recently, two calcite carbonatite dykes have been described by Keller and Zaitsev (in press) from the southern crater of Oldoinyo Lengai. Calcite occurs as polycrystalline, granular laths with crystals up to 1 mm in size. From textural, mineralogical and geochemical features, Keller and Zaitsev (in press) concluded that the calcite carbonatite dykes at Oldoinyo Lengai are definitely transformed natrocarbonatites. Calcite, associated with fluorite, was also found to be a major mineral in sandy/dusty altered natrocarbonatites which occur in the recent northern crater, and in the western, eastern and northern flanks of the Oldoinyo Lengai cone. It appears that calcitic, fine-grained, often loose alteration products are the end members of natrocarbonatite alteration.

3.3. Minerals formed by reaction with fumarole gases

Surprisingly, fumarolic activity at Oldoinyo Lengai has not received much attention. Measurements of fumarolic gas temperatures vary from 49 to a maximum
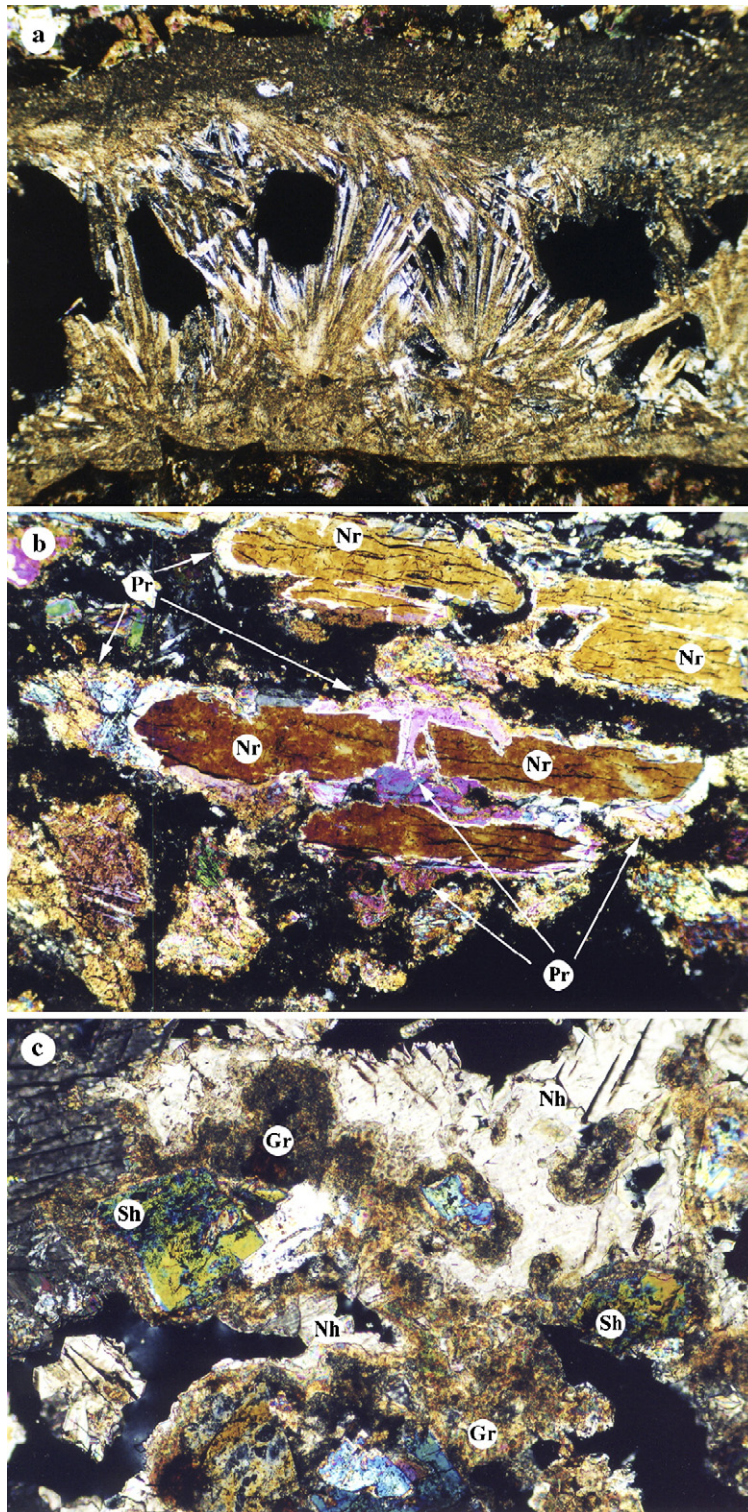
Fig. 2. (a) Nahcolite vein with comb structure. Eruption time–July 2000, hornito T 51, sample collection–October 2000. Field of view is 3.45 mm; (b) nyerereite (Nr) replaced by pirssonite (Pr). Eruption time–July 2000, hornito T 51, sample collection–October 2000. Field of view is 1.37 mm; (c) shortite (Sh), nahcolite (Nh) and calcite–thermonatrite–trona–fluorite groundmass (Gr). Eruption time–pre-1917, west crater rim. Field of view is 1.37 mm. All photomicrographs were taken under crossed polarized light.
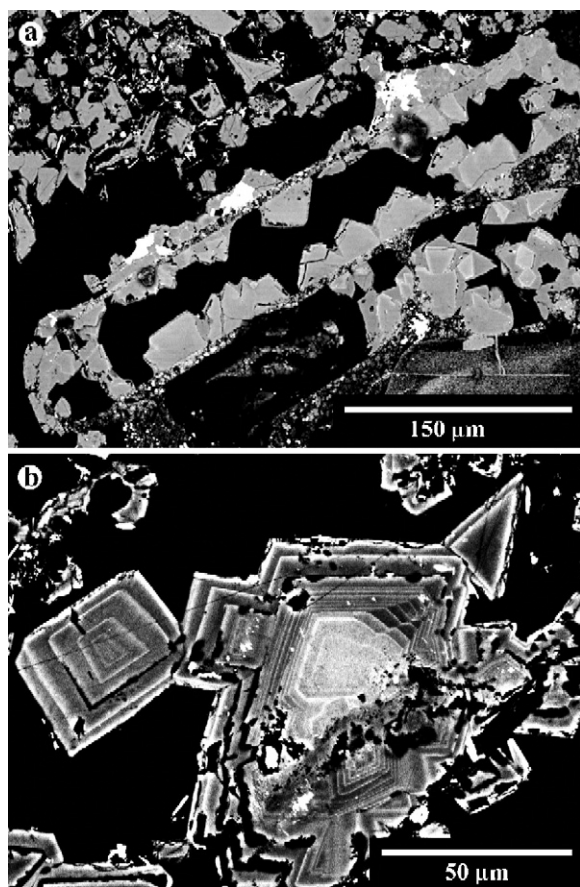
Fig. 3. BSE images of (a) euhedral calcite crystals (grey) outlining the morphology of a former nyerereite crystal, white–Sr-rich barite; (b) zoned euhedral calcite crystal. Eruption time–July 2000, hornito T 46, sample collection–October 2000.

of 312 °C (Dawson, 1962; Keller and Krafft, 1990; Koepenick et al., 1996). The composition of gas from fumaroles at Oldoinyo Lengai has been studied by Javoy et al. (1989) and Koepenick et al. (1996) who reported CO_2–H_2O gases containing 64–74 mol% CO_2, 24–34% H_2O (48.7% and 49.2%, respectively, in Javoy et al., 1989) with traces of H_2, CO, H_2S, HCl, HF and CH_4. Field spectroscopic measurements (open-path Fourier transform spectroscopy) of fumarolic gases by Oppenheimer et al. (2002) revealed a much higher water content of about 75 mol%; however, the observed high water content was attributed to a mixing of magmatic and meteoric water or contamination by old hydrated natrocarbonatites. Sulphur is the only mineral previously reported from fumaroles (Keller and Krafft, 1990; Koepenick et al., 1996).

Three active fumarolic fields were studied in detail: the first in the north-western part of the crater near hornito T49, the second in the central part of the crater,

hornito T46 (both were sampled in October 2000 with an estimated lava eruption age of 2–2.5 months) and the third in the northern area of the crater near the same hornito T49 (September 2001). For the third locality, measurements of *T*, pH and Eh were made using a NEO-LABs thermocouple GMH 2000 and GPHR 1400 pH-Meter (calibration steps 7+4+9).

The temperature of the gases was measured as 54.5 °C (at the surface), 73.8–74.7 °C (25 cm down the crack) and 141.1 °C (1 m down the crack). The measured pH and Eh of natrocarbonatite were pH=6.0–6.2 and Eh=87 mV for a sample from a 1-cm surface layer and pH=8.6 and Eh=240 mV for a sample 20 cm down from the surface (for pH and Eh measurement both samples were put in a plastic box and cooled to a temperature of 20 °C).

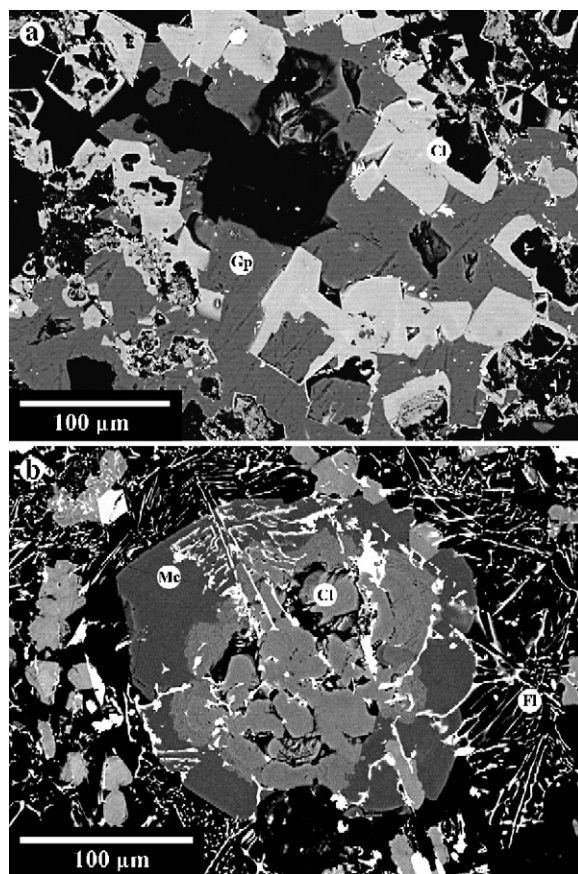The surface of natrocarbonatite in contact with fumarolic gases is typically covered by numerous

Fig. 4. BSE images of (a) subhedral calcite crystals (Cl) enclosed and partly replaced by gypsum (Gp); (b) aggregate of subhedral to anhedral calcite crystals (Cl) with rim of monohydrocalcite (Mc), Fl–sheaf-like aggregates of relict fluorite. Eruption time–July 2000, hornito T 46, sample collection–October 2000.

crystals of native sulphur 1–3 mm in size. The natro-carbonatites are soft (they can be easily kneaded by hand), water-saturated and are characterised by various shades of white, grey, fawn, black or even red. XRD patterns of samples taken from the surface and various inner parts of the natrocarbonatites indicate that sulphur, calcite, gypsum, anhydrite and fluorite, in various proportions, are the major minerals.

Calcite has been found in all studied samples and several morphological varieties of the mineral were observed: (i) euhedral crystals, 20–50 μm in size, which grow inward from the outlines of former prismatic nyerereite or rounded gregoryite pheno-crysts (Fig. 3), (ii) subhedral to anhedral grains from 5 to 70 μm irregularly disseminated though the rock (Fig. 4) and (iii) polycrystalline porous masses containing <5–10-μm anhedral grains. SEM/EDS analyses show variable contents of minor elements

in calcite–MnO from 0 to 9 wt.%, SrO, from 1.0 to 4.3 wt.%, BaO from 0 to 4.0 wt.%, MgO from 0.1 to 2.3 wt.% and Na_2O from 0 to 2.0 wt.%. Each morphological variety of the mineral is characterized by a specific set of minor elements (Table 2). Some grains of calcite contain detectable phosphorous (up to 1.0 wt.% P_2O_5), sulphur (up to 1.0 wt.% SO_3) and potassium (up to 0.4 wt.% K_2O) (Table 2).

Gypsum, like calcite, is also characterized by variable morphology; it fills interstices between the calcite, encloses and partly replaces calcite grains (Fig. 4a) or forms single euhedral to anhedral grains from 1 to 700 μm diameter irregularly distributed throughout the rock (Fig. 5b). In some samples anhydrite was observed in association with gypsum. Back-scattered electron (BSE) observations suggest that gypsum was the first mineral to crystallise and anhydrite overgrows and replaces gypsum. The minerals contain Sr as the

Table 2
Electron microprobe analyses of calcite

Sample	OL 231-24										
Analysis	1	2	3	4	5	6	7	8	9	10	11
Na_2O	1.64	1.72	1.92	2.03	1.31	1.54	1.99	1.80	1.09	1.45	1.00
MgO	0.13	0.22	0.17	0.38	0.47	0.37	0.35	0.41	0.67	1.55	2.27
P_2O_5	0.37	0.42	0.49	0.60	0.48	0.97	1.03	0.89	0.79	1.02	0.93
SO_3	0.12	0.15	<0.10	<0.10	0.17	<0.10	<0.10	<0.10	0.13	0.14	0.11
K_2O	0.32	0.20	0.30	0.39	<0.10	0.17	0.32	0.31	0.17	<0.10	<0.10
CaO	48.70	48.58	48.69	47.57	48.27	45.75	45.59	46.12	45.41	40.97	39.82
MnO	0.25	0.21	0.28	0.32	0.24	0.55	0.21	1.36	2.58	7.04	9.04
FeO[a]	<0.10	<0.10	<0.10	<0.10	0.14	<0.10	0.13	0.15	0.10	0.14	0.18
SrO	3.51	3.66	3.60	3.97	3.29	3.71	4.30	3.52	2.92	1.69	1.08
BaO	2.16	1.61	1.65	2.02	3.23	4.00	3.25	3.14	3.36	2.89	2.29
CO_2[b]	42.64	42.63	42.83	42.76	42.81	42.04	42.28	42.77	42.45	42.60	42.83
Total	99.84	99.40	99.93	100.04	100.41	99.10	99.45	100.47	99.67	99.49	99.55

Sample	OL 231-24						OL 231-23				
Analysis	12	13	14	15	16	17	18	19	20	21	22
Na_2O	<0.10	0.20	0.21	0.54	0.58	0.39	0.93	1.05	1.11	1.64	1.06
MgO	0.12	0.16	0.64	0.18	1.26	1.27	0.42	0.47	0.14	0.11	0.46
P_2O_5	0.22	<0.10	0.24	0.17	0.36	0.48	0.52	0.44	0.69	0.11	<0.10
SO_3	0.58	0.63	0.20	0.39	1.08	0.65	<0.10	0.13	0.11	<0.10	<0.10
K_2O	<0.10	<0.10	<0.10	<0.10	0.22	<0.10	<0.10	<0.10	0.13	0.18	0.11
CaO	53.55	54.05	53.57	53.11	50.42	50.54	49.79	49.54	49.37	49.40	50.74
MnO	<0.10	0.20	<0.10	<0.10	0.18	0.18	0.28	0.19	0.37	0.17	0.72
FeO[a]	0.12	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.23	0.18	0.16	0.23
SrO	1.10	0.97	1.20	1.09	1.56	1.74	3.57	3.47	3.24	3.83	2.83
BaO	<0.10	0.31	0.12	0.12	<0.10	0.20	1.22	1.65	1.47	1.53	0.94
CO_2[b]	43.67	44.04	44.01	43.44	43.97	43.68	43.03	43.16	43.06	42.57	43.18
Total	99.36	100.56	100.19	99.04	99.63	99.13	99.76	100.33	99.87	99.70	100.27

Samples are from the fumarole near hornito T46, 2.5 months old lava, erupted July 2000.
Analyses 1–4 and 18–22–euhedral calcite crystals outlining the morphology of former nyerereite crystals (Fig. 3a); analyses 5–11–subhedral grains in Fig. 4a and from inner part of calcite aggregate in Fig. 4b; analyses 12–17–anhedral grains from inner part of calcite aggregate in Fig. 4b.
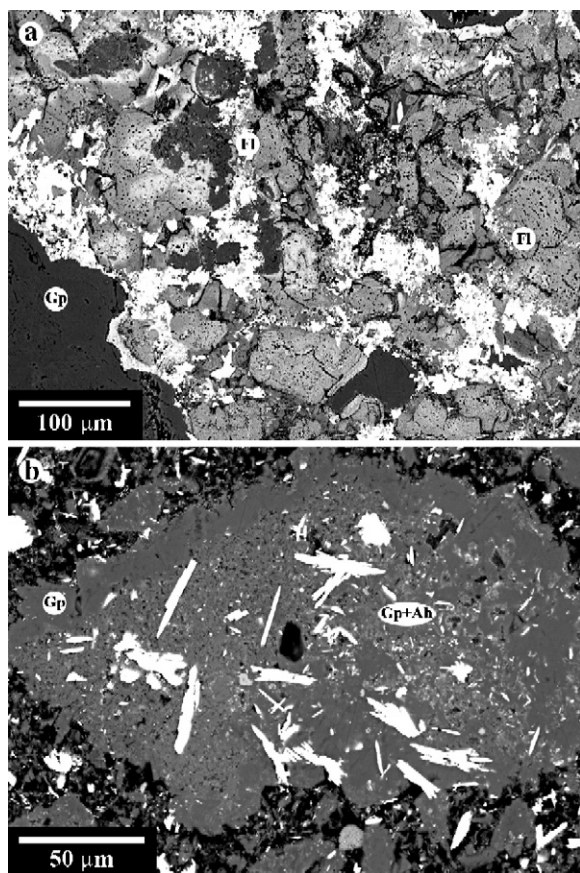[a] Total Fe as FeO.
[b] Calculated for 1 (CO_3).

Fig. 5. BSE images of (a) aggregate of porous subhedral fluorite crystals (Fl) and anhedral barite and celestine crystals (white), Gp–gypsum; (b) prismatic barite with minor celestine (white) in porous gypsum partly altered to anhydrite (Gp+Ah). Eruption time–July 2000, hornito T 46, sample collection–October 2000.

principal trace element with subordinate amounts of Fe, Mg and Na (Table 3).

A number of unidentified minerals are associated with gypsum and anhydrite, but their small size (≤ 2 µm) did not permit a detailed study. Energy-dispersive spectra (EDS) suggest that they are sulphates, sulphate–phosphates and phosphates of Ca, Na and K. One mineral, occurring in anhydrite as 10–50-µm sub-parallel laths, is a Ca phosphate containing appreciable amounts of Na_2O (3.9–5.0 wt.%) and K_2O (3.4–3.5 wt.%) (Table 3).

Monohydrocalcite was found in one sample of altered natrocarbonatite, where it occurs as a reaction rim, 5–50 µm thick, on calcite aggregates consisting of subhedral and anhedral crystals (Fig. 4b). Only Sr (0.3–0.7 wt.% SrO) was detected as trace element.

Two morphological populations of fluorite have been recognized from SEM/EDS observations: (i) relict sheaf-like aggregates, which are typical for the fresh

Table 3
Electron microprobe analyses of gypsum, anhydrite and K–Na–Ca sulphate

Sample	OL 231-22						
Mineral	Gypsum			Anhydrite		K–Na–Ca sulphate	
Na_2O	0.12	<0.10	<0.10	0.10	<0.10	5.05	3.89
MgO	<0.10	0.18	<0.10	<0.10	<0.10	<0.10	<0.10
K_2O	<0.10	<0.10	<0.10	<0.10	<0.10	3.45	3.55
CaO	32.01	32.69	32.93	39.45	40.56	29.63	31.61
FeO^a	0.28	0.28	<0.10	<0.10	<0.10	<0.10	<0.10
SrO	0.21	0.46	<0.10	0.70	0.49	1.57	1.25
BaO	<0.10	<0.10	<0.10	<0.10	0.16	0.48	<0.10
SO_3	46.51	46.86	44.90	59.88	59.97	60.38	59.94
Total	79.13	80.47	77.83	100.13	101.18	100.56	100.24

[a] Total Fe as FeO.

natrocarbonatites (Fig. 4b), and (ii) 1–2-mm aggregates of subhedral to anhedral porous fluorite crystals, up to 100 µm in size (Fig. 5a).

Abundant barite and celestine have been found in many natrocarbonatite samples affected by fumarolic gases (Fig. 5). They occur as polycrystalline masses of <10 µm anhedral grains or prismatic crystals up to 50–75 µm in length. Barite contains high levels of Sr (2.6–6.2 wt.% SrO) and celestine is rich in Ba (2.5–5.0 wt.% BaO); other trace elements are Ca, Na, Fe, Mg and K (Table 4).

4. Chemical transformation of natrocarbonatites

The natrocarbonatites undergo substantial chemical as well as mineralogical transformation. Twenty-two new whole rock samples of natrocarbonatite of various degrees of alteration and eruptive ages were analysed for major and trace elements, together with samples of fresh rock for comparison. The chemical compositions of representative samples of the altered natrocarbonatite

Table 4
Electron microprobe analyses of barite and celestine

Sample	OL 231-22						
Mineral	Barite			Celestine			
Na_2O	0.47	0.55	0.11	0.42	0.15	0.13	0.48
MgO	0.25	<0.10	0.10	<0.10	<0.10	0.20	<0.10
K_2O	0.16	0.14	0.10	<0.10	<0.10	<0.10	<0.10
CaO	1.80	1.09	0.62	0.75	0.70	<0.10	0.10
FeO^a	<0.10	0.52	0.11	0.19	0.26	<0.10	0.12
SrO	2.64	4.70	5.68	6.17	50.13	54.53	52.44
BaO	59.21	56.94	58.23	57.11	4.97	2.54	2.50
SO_3	35.89	36.15	34.93	35.62	43.71	43.21	43.91
Total	100.42	100.09	99.88	100.26	99.92	100.61	99.45

[a] Total Fe as FeO.

are given in Table 5. Fig. 6 shows variations in Na_2O, K_2O and CaO for all analysed samples. For comparison, Fig. 6 includes also data for fresh unaltered natrocarbonatites, the major primary minerals nyerereite and gregoryite and some subsolidus minerals.

The geochemistry of natrocarbonatites has been studied and discussed by Keller and Krafft (1990), Keller and Spettel (1995), Dawson et al. (1995b), Simonetti et al. (1997) and Gittins and Jago (1998). Available published data and new data from the 2000, 2001 and 2003 eruptions show some variations in composition of natrocarbonatites, e.g., Na_2O ranges from 30.2 to 33.7 wt.%, $CaO = 11.6–18.3$ wt.%, $K_2O = 6.2–9.6$ wt.%, $F = 1.1–5.3$ wt.%, $Cl = 1.6–6.2$ wt.%. This is related to textural varieties of lavas (porphyritic or aphanitic) and variations in the proportion of phenocrysts (nyerereite and gregoryite) and

groundmass minerals (sylvite, halite, fluorite and a gregoryite-like mineral). Recently, a natrocarbonatite variety with sylvite and fluorite "microcrysts" in addition to nyerereite and gregoryite phenocrysts was erupted by one of the hornitos (Mitchell, 2006).

Altered natrocarbonatites form two distinct fields on element variation diagrams (Fig. 6). The first field is related to pirssonite natrocarbonatites with relict fluorite (±gaylussite, nahcolite, thermonatrite and trona) and is close to the ideal composition of pirssonite and gaylussite. The natrocarbonatites still show high sodium contents between 19.4 and 23.2 wt.% Na_2O. Compared to fresh natrocarbonatites they are strongly depleted in K (0.3–1.2 wt.% K_2O), S (≤ 1.0 wt.% SO_3) and Cl (<0.1 wt.% Cl) and show enrichment in Ca (25.0–31.0 wt.% CaO) and H_2O (5.4–10.0 wt.% H_2O). Some samples of altered natrocarbonatites still contain

Table 5
Chemical composition of fresh and altered Oldoinyo Lengai natrocarbonatites

Sample	OL 234	OL 321-4	OL 232.10	OL 260	OL 239 A	OL 332	OL 239	OL 329	OL 328.2	OL 239 F	OL 328
Analysis	Relict fresh natrocarbonatite		Pirssonite natrocarbonatite					Calcite carbonatite			
SiO_2 (wt.%)	0.34	0.26	1.59	0.17	0.10	0.64	0.11	0.69	0.40	1.67	0.97
TiO_2	0.01	0.01	0.06	0.01	0.01	0.03	0.01	0.04	0.03	0.04	0.03
Al_2O_3	0.04	0.05	0.25	0.01	0.01	0.03	<0.01	0.05	0.02	0.04	0.02
Fe_2O_3 [a]	0.65	0.58	1.84	0.47	0.16	2.38	0.20	1.88	1.20	0.19	0.95
MnO	0.46	0.44	0.88	0.79	0.54	0.63	0.56	1.25	1.11	0.80	1.34
MgO	0.42	0.44	0.55	0.66	0.56	<0.10	0.59	0.83	0.52	1.20	1.10
CaO	16.40	15.83	27.57	26.50	27.79	24.99	27.69	46.07	45.91	46.81	45.62
SrO	1.33	1.39	1.53	1.60	1.91	1.73	1.91	3.39	3.54	3.89	3.96
BaO	0.96	1.17	1.04	1.05	1.62	1.20	1.61	2.45	2.99	4.29	3.55
Na_2O	33.68	33.08	23.21	24.13	21.67	22.69	21.89	1.73	2.91	2.36	2.44
K_2O	7.04	7.43	0.78	2.29	0.32	0.34	0.75	0.19	0.20	0.16	0.25
P_2O_5	1.13	0.90	1.21	1.09	0.77	1.06	0.74	2.68	1.51	0.66	1.71
CO_2	32.49	32.80	33.55	34.30	31.40	31.94	30.65	33.18	33.80	29.20	29.40
Cl	2.64	2.87	0.04	0.08	<0.01	0.02	0.01	<0.01	0.08	0.13	<0.01
SO_3	2.32	2.25	0.28	0.40	0.25	0.02	0.30	0.24	0.05	0.34	0.02
F	1.20	1.10	1.63	1.32	2.13	1.40	2.88	3.64	6.62	9.15	11.04
H_2O	0.14	0.17	5.37	7.29	10.00	11.70	12.00	0.84	0.86	1.32	0.69
$-O \equiv F,Cl$	1.10	1.11	0.70	0.57	0.90	0.59	1.22	1.53	2.81	3.88	4.65
Total	100.15	99.66	100.68	101.59	98.34	100.21	100.68	97.62	98.94	98.37	98.44
V (ppm)	130	155	168	193	181	150	101	246	218	174	294
Cr	6	6	10	9	9	6	2	4	3	6	6
Ni	6	6	7	41	6	7	7	9	8	13	10
Cu	7	6	7	10	5	7	6	8	6	8	7
Zn	137	126	403	142	104	934	84	373	318	117	295
Zr	<10	12	<10	<10	<10	<10	<10	80	43	86	91
Nb	64	64	193	64	49	126	33	122	58	104	59
Pb	91	101	126	97	89	72	80	476	170	119	371
Th	10	8	14	19	13	9	8	<5	<5	<5	<5
U	14	13	13	18	13	10	10	<5	<5	8	<5
La	571	623	1083	1767	700	679	761	1651	1604	1382	1647
Ce	768	770	1419	1033	778	900	950	2012	1874	1449	1924
Nd	153	135	378	241	155	184	164	424	341	170	311

[a] Total Fe as Fe_2O_3.
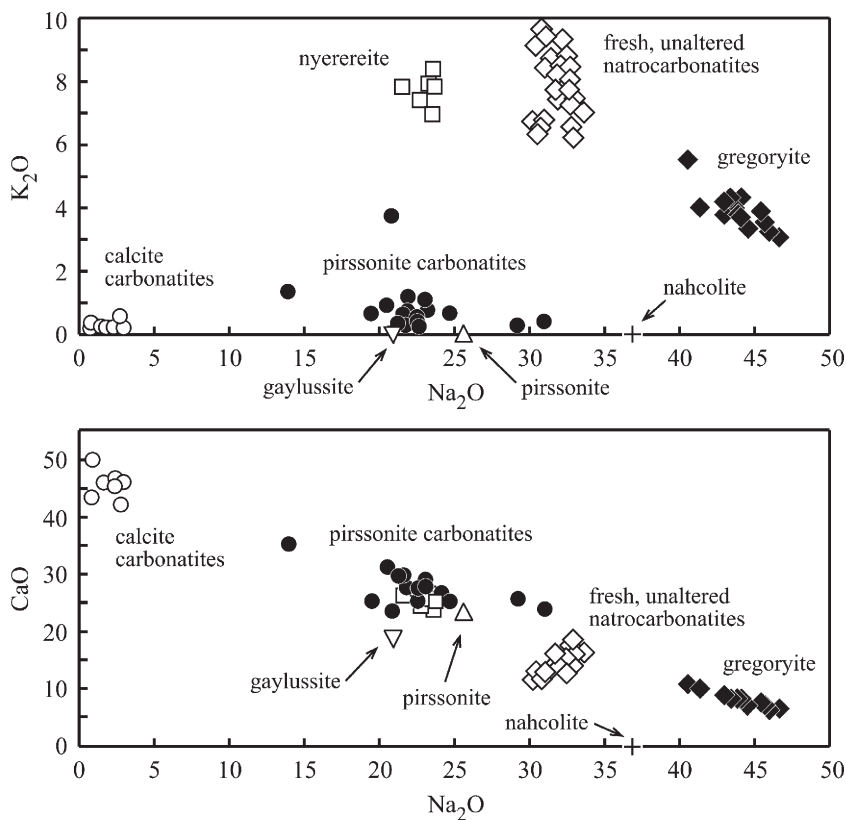
Fig. 6. Plots of Na$_2$O vs. K$_2$O and Na$_2$O vs. CaO (wt.%) for Oldoinyo Lengai carbonatites and minerals. Data for fresh natrocarbonatites, pirssonite and calcite carbonatites are from this work, Keller and Krafft (1990), Dawson et al. (1987, 1995b), Dawson (1993), Simonetti et al. (1997) and Keller and Zaitsev (in press). Data for nyerereite and gregoryite are from Peterson (1990), Keller and Krafft (1990) and Church and Jones (1995). Pirssonite, gaylussite and nahcolite–ideal composition.

abundant relics of gregoryite and nyerereite which explains the high potassium content in some of the rocks (Fig. 6). Two samples are enriched in nahcolite and therefore show higher sodium with Na$_2$O between 29.2 and 31.0 wt.%.

The second field in Fig. 6 is formed by altered natrocarbonatites that contain only small amounts of alkalis (Na$_2$O=0.8–2.9 wt.% and K$_2$O=0.2–0.6 wt.%), Cl (<0.1 wt.% Cl) and S (<0.3 wt.% SO$_3$), but are extraordinarily rich in calcium with CaO contents of 42.3–50.0 wt.%, and occasionally in fluorine (up to 11.0 wt.%). In terms of mineralogy they are fluorite–calcite carbonatites. Compared to fresh natrocarbonatites and pirssonite carbonatites these rocks show clear enrichment in Ba (up to 4.3 wt.% BaO), Sr (up to 4.0 wt.% SrO), Fe (up to 4.0 wt.% Fe$_2$O$_3$) and to a lesser extent in Mn and Mg (up to 1.3 and 1.2 wt.% of the respective oxides). Water content is low and varies from 0.7 to 2.1 wt.% H$_2$O.

The trace-element compositions of altered natrocarbonatites are not as well studied as those of fresh rocks

(Keller and Spettel, 1995; Dawson et al., 1995b; Simonetti et al., 1997). From the limited published data on Oldoinyo Lengai pirssonite natrocarbonatite (Dawson et al., 1987), gaylussite natrocarbonatite (Keller and Krafft, 1990) and calcite carbonatites (Dawson, 1993; Keller and Zaitsev, in press) and new data from this work, some preliminary conclusions can be drawn:

(1) among trace elements, rare-earth elements (REE) show the highest contents in natrocarbonatites. REE concentrations show a tendency to increase in the sequence of fresh natrocarbonatite→pirssonite carbonatite→calcite carbonatite;

(2) concentrations of Pb, V, Zr, Th and U in fresh and pirssonite carbonatites are similar; calcite carbonatites show an enrichment in Pb, V and Zr and are depleted in Th and U;

(3) concentrations of Cr, Ni and Cu are comparable in the various carbonatite types and do not change during alteration;

(4) Nb and Zn did not show any particular trend between various carbonatite varieties, but some of the pirssonite natrocarbonatites and calcite carbonatites are strongly enriched in these elements compared to fresh natrocarbonatites.

The observed enrichment of calcite carbonatites in some elements is attributed to leaching and complete dissolution of primary nyerereite, gregoryite, sylvite and halite and relative enhancement of the residual in fluorite (potential host for REE), Mn-rich magnetite (potential host for Nb and V) and REE–Si-rich fluorapatite (host for REE) (Church and Jones, 1995; Keller and Zaitsev, in press). Irregular variations in Zn and Nb contents can be explained by original heterogeneity of fresh natrocarbonatites, which have variable contents of accessory sphalerite (host for Zn) and niocalite (host for Nb) (Mitchell and Belton, 2004).

Unfortunately, the actual mass transfer of elements during alteration of the natrocarbonatites cannot be calculated, as we do not know the precise porosity and density of the studied rock samples.

5. Stable isotope variations through alteration of natrocarbonatites

The oxygen and carbon isotopic composition of natrocarbonatites and their minerals from Oldoinyo Lengai was determined by Keller and Hoefs (1995). Additional data, including a critical literature screening, are presented by Keller and Zaitsev (in press) and we refer to their Fig. 9. The average composition of fresh natrocarbonatites falls in the "Lengai Box" of Keller and Hoefs (1995) at $\delta^{13}C = -6.8 \pm 0.4‰$ PDB and $\delta^{18}O = +6.5 \pm 0.5‰$ SMOW. This is considered to reflect the basically unchanged mantle composition for the Lengai carbonate phase. Keller and Zaitsev (in press) also show that weathering and alteration of natrocarbonatites rapidly change this isotopic signature, mainly towards higher $\delta^{18}O$, less so towards higher $\delta^{13}C$. The typical calcitic end product of alteration shows $\delta^{13}C$ values between −2‰ and −4‰ PDB and $\delta^{18}O$ values of +23‰ to +26‰ SMOW. The intermediate products of the natrocarbonatite alteration (pirssonite-bearing carbonatites) exhibit stable isotope values between these two end members (Keller and Hoefs, 1995; Keller and Zaitsev, in press).

6. Discussion

Field observations show that the dominant process, which leads to the formation of various subsolidus minerals at Oldoinyo Lengai, is the alteration of natrocarbonatites under atmospheric influences. Three external factors are important: (i) water, (ii) temperature and (iii) time.

The natrocarbonatite minerals sylvite, halite, gregoryite and to a lesser extent nyerereite, are soluble minerals in water-bearing environments. The solubility of these minerals is quite high (e.g., Monnin and Schott, 1984; Königsberger et al., 1999; Marion, 2001) and during dissolution they will supply Na, K, Cl, C and S to meteoric water that can then be described as a brine.

The major sources of water at Oldoinyo Lengai are the atmosphere, nightly fog, rain (short rainy season in November–December and long rainy season in February–May) and gas emission from the northern active crater and volcano flanks (fumaroles and lava emissions). Some water is stored in altered natrocarbonatites (Table 5) and can be released by heating from erupted hot lavas and involved in the formation of subsolidus minerals (Genge et al., 2001). Observed replacement reactions in natrocarbonatites (Fig. 2b) and formation of nahcolite veins (Fig. 2a) suggest intensive meteoric water circulation at Oldoinyo Lengai on a micro- and macro-scale. Presumably, alteration during rainy seasons is dominant compared to other transformations of natrocarbonatites (M. Genge, personal communication), but precise estimation is not possible due to lack of detailed field observations of alteration of natrocarbonatite lavas during the wet seasons.

Temperature controls solubility of minerals and their stability fields in pure water and concentrated brines (e.g., Monnin and Schott, 1984; Königsberger et al., 1999; Marion, 2001). Our measurements of the air and ground temperatures in the northern Oldoinyo Lengai crater show large variations from 8 to almost 43 °C (Table 6).

Table 6
Air temperature near lava surface, inside blocks of lava and ground temperature (°C)

Time	12:00 a.m.	1:00 p.m.	7:00 a.m.
Air temperature at surface			
Under sun, no wind	35.2	42.8	
Under sun and wind	25.5		
Shadow, no wind		24.9	
Inside blocks	19.8		
No sun or wind			8.0
Ground temperature			
−6 cm	30.2	41.8	12.1
−12 cm	24.4	28.3	17.7
−25 cm	18.3	19.6	20.5
−40 cm			19.8

Near the surface of solidified lava fields the afternoon air temperature ranges from 19.8 to 42.8 °C and Table 6 shows that these variations depend on the measurement conditions. The upper part of the lavas is relatively hot ($T=30.2-41.8$ °C) and the temperature falls with increasing depth. At 25 cm from surface, the temperature does not show significant variations and ranges from 18.3 to 19.6 °C. During the early morning, much lower temperatures were measured; however, at 25–40 cm depth the temperature is very similar to mid-day observation (Table 6).

The subsolidus mineralogy at Oldoinyo Lengai suggests close a similarity to that from saline lakes, e.g., modern Lake Magadi, Lake Natron or the 1.9–1.7 Ma Lake Olduvai (e.g., Monnin and Schott, 1984; Vincens and Casanova, 1987; Hay and Kyser, 2001). The XRD pattern of a salt crust collected from the southern shore of Lake Natron shows the presence of trona, halite, anhydrite, natron and gaylussite.

Several low-temperature thermodynamic models based on the ion-interaction model developed by K.S. Pitzer have been evaluated to explain the occurrence of alkali carbonate, chloride and sulphate minerals in saline lakes, brines and evaporates (Monnin and Schott, 1984; Harvie et al., 1984; Königsberger et al., 1999; Marion, 2001) and some of these models are relevant for the formation of subsolidus minerals during the alteration of natrocarbonatites.

The low-temperature ($T=0-50$ °C) thermodynamic model for the alkali carbonate system, $CaO-Na_2O-CO_2-H_2O$, (Königsberger et al., 1999) has direct application to the subsolidus mineralogy of Oldoinyo Lengai. Königsberger et al. (1999) calculated the temperature dependence of the solubility of the calcite, pirssonite, gaylussite and natron. The stability fields of the minerals show strong relationships with temperature and Na_2CO_3 concentration in solution. Pirssonite occurs at temperatures >35 °C and a Na_2CO_3 molality (m) >2.7 (metastable equilibrium calcite–pirssonite–solution may occur at T up to 20 °C and $m>2.5$) and gaylussite is stable in a wide range of T from 12 to 40 °C and $m>2.7$. Calcite has a large stability field from $T=40-50$ °C at $m=2.8$ to $T=10$ °C at $m=1$.

According to Fig. 6d in Königsberger et al. (1999), the observed variations of temperature at the Oldoinyo Lengai summit at constant Na_2CO_3 molality can initiate mineral transformations like pirssonite $\leftrightarrow$ gaylussite and gaylussite $\leftrightarrow$ calcite. Removal of Na_2CO_3 from the system will lead to transformation of both pirssonite and gaylussite to calcite.

Thermodynamic calculations of mineral solubilities in the system $NaHCO_3-Na_2CO_3-H_2O$ (Monnin and Schott, 1984; Harvie et al., 1984; Marion, 2001) show that crystallisation of nahcolite, thermonatrite and trona takes place at low temperatures (0–50 °C) in highly concentrated solutions with molalities up to several moles per kilogram H_2O and under alkaline conditions with a pH of 8–10. The stability fields of alkali carbonates are also dependent on p_{CO_2}, which in turn controls pH and HCO_3^-/CO_3^{2-} balance in solution (Marion, 2001).

Data from Table 6 suggest that dissolution and precipitation of subsolidus minerals in the Oldoinyo Lengai natrocarbonatites will be commonly observed near the lava surface and slightly below it. Observed significant temperature variations are evidence for this. Also, during the hot day-time meteoric water is expected to evaporate resulting in the saturation of the residual solution in some phases. At a depth of 25 cm and more, the temperature does not show significant changes and will not play an important role in mineral transformation. More likely, the composition of the meteoric water is the major factor that controls subsolidus crystallization.

The duration of natrocarbonatite exposure to the atmosphere is another important factor for natrocarbonatite alteration and field observations show changes in colour of freshly erupted natrocarbonatites from black through white to grey within a short period of time (Fig. 1). Mineralogical changes on the lava surface (2, 5 and 8 days and 1, 2 and 7 months after exposure to atmosphere) were studied by Calder and Bowden (2001). Their altered samples were not collected directly in the Oldoinyo Lengai summit crater; instead, they used fresh natrocarbonatite from the 1995 eruption which was transported to the UK, crushed and subsequently exposed to the atmosphere inside a building at room temperature and average humidity for various lengths of time (A. Calder, personal communication). X-ray analyses showed formation of only two secondary minerals (trona and halite) independently of exposure time, a result quite different from ours.

Important field observations are the radical changes in mineralogy of the blocky lava flow (hornito T37, erupted July 2000), during 1 year and 2 months—about one third of the solid natrocarbonatite was transformed to a dusty sand of fluorite, gaylussite and calcite. From this fact, we can expect that without any natrocarbonatite activity the northern crater of Oldoinyo Lengai may be covered by fluorite–calcite "carbonatite" within several (two or three?) years.

In addition, it is quite likely that physical weathering (e.g., thermal expansion and contraction, wind erosion)

may also play an important role in transformation of natrocarbonatites. Unfortunately, there are no data for thermal expansion coefficients (TEC) of the major natrocarbonatite minerals nyerereite and gregoryite. Available data for other carbonate minerals (e.g., calcite, aragonite and dolomite) show highly anisotropic TEC (Fei, 1995, and references therein) and therefore, physical weathering of carbonate rocks due to these extremely anisotropic properties of carbonate minerals is considered essential (Siegesmund et al., 2000).

Field and petrographic observations show that alteration of the natrocarbonatite by hydration combined with physical weathering destroys the primary magmatic textures of the lavas exposed at the surface of the Oldoinyo Lengai volcano and transforms solid lavas to unconsolidated soil-like deposits. The original texture of the natrocarbonatites is still visible in rock samples from the internal parts of the lava flows (>15 cm from the lava surface) or in lavas exposed for a relatively short time only.

Formation of calcite carbonatites at Oldoinyo Lengai as a result of natrocarbonatite alteration was proposed by Dawson et al. (1987) and the presence of H_2O-bearing pirssonite was identified as an important intermediate step in the calcification of natrocarbonatites. This idea was criticised by Gittins and Jago (1991) and Gittins and Harmer (1997). Gittins and co-authors emphasized that (i) replacement of nyerereite involves a significant volume reduction ($\approx 55\%$); (ii) nyerereite and pirssonite have different crystal unit cells and the formation of perfect pseudomorphs is quite unlikely and (iii) an external source of Ca for calcite formation is needed.

We note, however, that replacement reactions between various minerals with different molar volumes (calcite and dolomite, dolomite and magnesite, phlogopite and calcite, forsterite and serpentine, pyrrhotite and pyrite, etc.) are quite common in carbonatites (e.g., Kapustin, 1980, 1987; Barker, 1989, Zaitsev, 1996; Zaitsev et al., 1998b; Chakhmouradian and Williams, 2004; Wall and Zaitsev, 2004). Full pseudomorphs are common in both early- and late-stage carbonatites (e.g., Kapustin, 1980; Wall and Mariano, 1996; Zaitsev et al., 1998a). Pseudomorphs are porous, polycrystalline and often contain several minerals.

Replacement relationships between minerals have been extensively studied in low-temperature salt systems (chlorides, sulphates, chromates, etc.) by Glikin and Sinai (1991) and Glikin (1996, 2001). Their experimental data show that formation of

polycrystalline pseudomorphs is observed for binary salt systems where minerals do not form solid solutions and do not show substitution in either cationic or anionic sites.

Possible reactions for the formation of calcite at Oldoinyo Lengai have been suggested by Keller and Zaitsev (in press). The reactions show that for the formation of calcite an external source of Ca is not needed, it is introduced during replacement of nyerereite by pirssonite or gaylussite and even more Ca will be available if replacement of pirssonite by gaylussite occurs. Natural examples of fully euhedral pseudomorphs of calcite after gaylussite have been described from the Tatarian limestone, Timan, Russia (Plotnikov and Yanulov, 1973; Yushkin, 1990).

7. Conclusions

From a review of published information on subsolidus mineralization in Oldoinyo Lengai natrocarbonatites (e.g., Dawson, 1962, 1966, 1993; Dawson et al., 1987; Keller and Krafft, 1990; Genge et al., 2001; Keller and Zaitsev, in press), new field observations, and mineralogical and geochemical data presented here we can conclude that

(1) At Oldoinyo Lengai subsolidus minerals are formed (i) from hot gases escaping from solidified lavas (lava degassing), (ii) due to atmospheric alteration and reaction with meteoric water and (iii) by reaction with fumarolic gases.

(2) 20 minerals, identified by XRD, Raman spectroscopy and SEM/EDS, are known as subsolidus minerals—they are hydrous and anhydrous alkali carbonates, calcium, barium and strontium sulphates and alkali chlorides (Table 1). Kalicinite, villiaumite, shortite, gypsum, anhydrite, monohydrocalcite and celestine were found for the first time at Oldoinyo Lengai. Undoubtedly, future studies of altered natrocarbonatites will reveal more subsolidus minerals.

(3) Chemically, alteration of natrocarbonatites shows a rapid decrease in K, followed by a general loss of Na, K, Cl and S, combined with an increase in H_2O, Ca, Sr, Ba, F and Mn. Two chemical and mineralogical groups or stages in the alteration of natrocarbonatites are recognized. The first stage results in relatively Na-rich, Ca-enriched and K-poor carbonatites (pirssonite natrocarbonatites) and the second in Ca-rich and Na–K-poor carbonatites (calcite carbonatites).

(4) The C and O stable isotopes in altered natrocarbonatites show an intensive exchange of isotopes with atmosphere and meteoric water. The subsolidus calcite is characterized by $\delta^{13}C$ values between $-2‰$ and $-4‰$ PDB and $\delta^{18}O$ values of $+23‰$ to $+26‰$ SMOW.

(5) The formation of subsolidus minerals is an open-system low-temperature ($T=8–43\ °C$) process; it requires an external source of water (atmosphere vapour, meteoric water, fumarolic gases) and a certain period of time. Low-temperature thermo-dynamical models which were developed to explain the occurrence of alkali carbonate, chloride and sulphate minerals in saline lakes, brines and evaporates (e.g., Harvie et al., 1984; Monnin and Schott, 1984; Königsberger et al., 1999; Marion, 2001) can be applied to explain subsolidus mineral formation during the alteration of natrocarbonatites.

(6) At Oldoinyo Lengai calcite carbonatites are produced by alteration of modern natrocarbonatite lavas and pre-modern carbonatite blocks and dykes (Dawson, 1993; Keller and Zaitsev, in press).

Alteration of original alkali-rich carbonatite to calcite carbonatite has previously been suggested for a number of extrusive carbonatites, e.g., Kerimasi and Tinderet, where calcite pseudomorphs, presumably after nyerereite, were recognised (e.g., Hay, 1983; Deans and Roberts, 1984). The alteration hypothesis has been evaluated by Gittins (1989) and Bailey (1993) who emphasised that considerable caution must be exercised in application of this model to carbonatitic rocks. Replacement of nyerereite by calcite at Kerimasi was also criticised by Church (1995) and dolomite, instead of nyerereite, was suggested to be a precursor mineral. Therefore, the results of natrocarbonatite alteration at Oldoinyo Lengai should be carefully evaluated before applying this as a general model for other localities.

Acknowledgements

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