Carbonate–carbonate immiscibility, neighborite and potassium iron sulphide in Oldoinyo Lengai natrocarbonatite

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Abstract

Porphyritic natrocarbonatite lavas erupted from the Oldoinyo Lengai volcano (Tanzania) on 17 October 1995 and 15–19 December 1995 differ from previously studied lavas in that they preserve textures indicative of groundmass carbonate–carbonate immiscibility. The immiscible fractions are considered to involve: a Na-K-Ca-CO_2-Cl-rich, F-bearing fluid crystallizing gregoryite, sodian sylvite, potassium neighborite as well as a complex Ba-rich carbonate; and a Na-rich, Cl-poor carbonate liquid approximating to a nyerereite-gregoryite cotectic composition. Compositional data are given for potassium neighborite, this mineral being the first recognized occurrence of a fluorine-based perovskite group mineral in a magmatic environment. New compositional data are also given for a previously recognized potassium iron sulphide which indicate that this phase is probably a solid solution between the ternary sulphides, KFe_3S_4, $K_2Fe_3S_4$, and KFe_2S_3. Textural and paragenetic data are interpreted to suggest that these recent lavas are more evolved than previously investigated Oldoinyo Lengai lavas and that natrocarbonatite is a highly evolved rather than a primitive magma.

Keywords: carbonatite, liquid immiscibility, neighborite, potassium iron sulphide, sylvite, Oldoinyo Lengai, Tanzania.

Introduction

The natrocarbonatite lavas erupted from the volcano Oldoinyo Lengai (Tanzania) are the only known examples of active carbonatite magmatism. The unusual composition and mineralogy of the lavas relative to common calcite carbonatite are well documented (Dawson *et al.*, 1995, 1996; Peterson, 1990; Church and Jones, 1995), although their origin and evolution remains controversial (Church and Jones, 1995; Gittins, 1989; LeBas, 1989; Twyman and Gittins, 1987). This paper does not attempt to discuss the problems of the genesis of natrocarbonatite but focuses on the petrology of the final stages of crystallization of the magma and demonstrates that lavas erupted in the crater of Oldoinyo Lengai on the 17th October 1995 and from 15–19th December 1995 have significant textural and mineralogical differences to previously studied lavas.

Sampling and analytical methods

The majority of the material studied was collected from a small, rapidly flowing, phenocryst-rich lava emanating from the breached north side of hornito T37 on 17 October 1995. Samples were collected from the crust of the flowing lava and from phenocryst-poor material squeezed up from the interior of the flow. All samples were immediately sealed in plastic with silica gel to prevent hydration. The temperature of the interior of the lava flow, as measured by thermocouple, was 538°C (J. Keller, pers. comm.). Polished thin sections of the lava were prepared approximately two weeks after their collection using kerosene to prevent the dissolution of water-soluble phases. Vetsch (1995) reports that this hornito was still active during December 1995 and that the temperature of the flow was 510°C.

Vetsch (1995) also recorded intermittent effusive activity at hornito T36 (vents A–D) during

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December 1995. Very fluid black lava with a temperature of 508°C issued from these vents and formed thin channelled flows identical to those described by Keller and Krafft (1990). These sites were inactive on 17th October, although the presence of altered channelled lava flows indicated that they were previously active. The magma extruded from hornito T36 cooled to form small thin pahoehoe flows composed of fine-grained, phenocryst-poor to aphyric natrocarbonatite. Samples from T36 (vent D) were not examined until November 1996. During storage some surface alteration occurred but the interior of the samples remained as dense, fresh black natrocarbonatite. Polished thin sections were also prepared using kerosene.

The texture of the lavas was studied by back-scattered electron (BSE) imagery using a Hitachi 570 scanning electron microscope equipped with a Link Tetra BSE detector. Mineral compositions were determined by X-ray energy dispersive spectrometry using the LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm Mn_K). X-ray spectra were obtained with an accelerating voltage of 20 kV and a beam current of 0.86 nA. Spectra were collected and processed with LINK ISIS-SEMQUANT software. Full ZAF corrections were applied to the raw X-ray data. Well-characterized minerals and synthetic compounds were used as analytical standards.

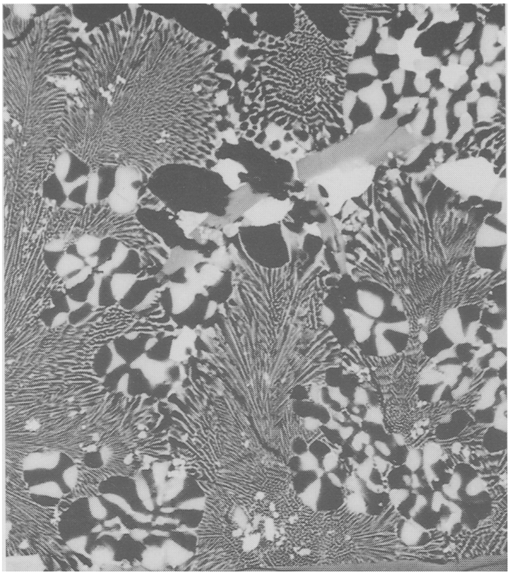

FIG. 1. Back scattered electron image of the groundmass of the 17 October 1995 T37 flow, showing discrete globules of gregoryite–sylvite (black and white) set in a quenched matrix of nyerereite–gregoryite. (400 × ; field of view is about 100 μm).

Carbonate–carbonate immiscibility

The overall petrography of the 17 October 1995 flow does not differ significantly from that of earlier flows as described by Dawson *et al.* (1995), Keller and Krafft (1990) or Peterson (1990). Thus, it consists predominantly of tightly packed, flow aligned, phenocrysts of gregoryite and nyerereite set in a fine-grained matrix. These phenocrysts were not quantitatively analysed but do not appear to be significantly different in their compositions from those occurring in previously studied lavas.

The December 1995 T36 natrocarbonatite is similar to the above lavas but poorer in phenocrysts. In places, filter pressing has resulted in the formation of patches which are essentially aphyric. These areas are petrographically similar to the fine-grained matrix of the phenocryst-rich lavas form hornito T37.

The fine-grained matrix of the October and December flows is of complex mineralogy and texture. Figure 1 demonstrates that the October flow consists of a relatively coarse-grained, subrounded fraction set in very fine-grained material which exhibits a distinctive quench texture. Figure 2 illustrates the pronounced development of this quench texture in the aphyric portions of the December T36 flows. Texturally-distinct fractions of natrocarbonatite groundmass have been recognized previously by Peterson (1990, Fig. 3a), and Dawson *et al.* (1996, Fig. 2). However, the October and December 1995 material differs in that the fractions are organized into a distinctive texture which is interpreted below to suggest that two liquids were present during the consolidation of the flows.

Figures 1–3 show that the coarse-grained fraction consists of sub-rounded-to-spherical patches 10–30 μm in diameter. Figure 3 demonstrates that these patches are cross-sections of ovoid-to-globular structures. The globules consist primarily of an intergrowth of a gregoryite-like mineral and sodian sylvite. The former cannot be analysed satisfactorily, as even with low beam current employed for analysis, it immediately decomposes. However, the X-ray spectrum is similar to that of the gregoryite phenocrysts. Previous studies of earlier-formed lavas have also concluded that a similar groundmass mineral is gregoryite (Dawson *et al.*, 1996; Peterson 1990). The sylvite occurs either as broad leaf-like crystals which radiate from the centre of the globule or form an irregular intergrowth with the gregoryite-like mineral in a texture reminiscent of the paw-print of a cat (Fig. 1.). The radial aggregates of sylvite in some instances may emanate from a

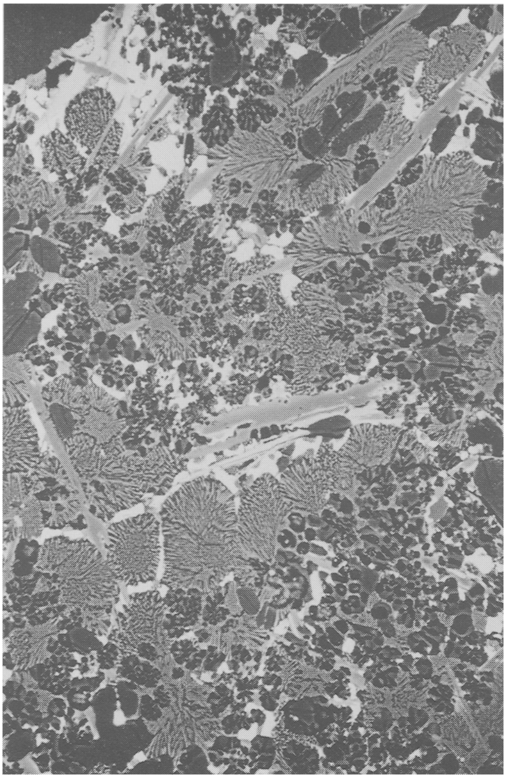

FIG. 2. Back scattered electron image of an aphyric portion of the December 1995 T36 flow showing discrete globules of gregoryite–sylvite set in a quenched matrix of nyerereite–gregoryite. Irregular regions of high average atomic number (white) are Ba-Sr-Ca-carbonate. Resorbed lath-like crystals are relict phenocrysts of nyerereite. (140 ×; field of view is about 250 μm × 1150 μm).

nucleus of an anhedral crystal of potassium iron sulphide, manganoan sphalerite, alabandite, or Ba-Ca-Sr carbonate. Many of the globules are bimineralic, although others contain at their margins irregular patches of Ba-Ca-Sr carbonate. The latter may include crystals of potassium neighborite and euhedral apatite.

The fine-grained material which encloses the globules displays a plumose-to-dactylotypic texture (Figs. 1, 2 and 4). The dendrites of relatively high average atomic number are composed of nyerereite-like material. The material of low average atomic number intergrown with these is a gregoryite-like mineral. Both phases are impossible to analyse quantitatively because of their small size and/or decomposition under the electron beam. The overall texture is suggestive of rapid crystallization and is similar to that produced by quenching of a eutectic composition.

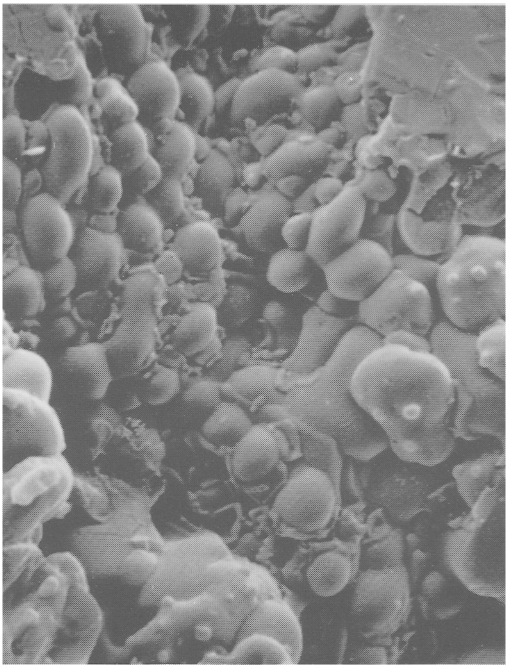

FIG. 3. Scanning electron micrograph of the groundmass of the 17 October 1995 flow illustrating the morphology of the gregoryite–sylvite globules. (1600 ×; field of view about 10 × 30 μm).

Sylvite is notably absent from this quenched material and Ba-Ca-Sr carbonate is very rarely found. Anhedral-to-subhedral crystals of alabandite, apatite, rare potassium iron sulphide and a calcium silicate considered to be tilleyite (c.f. Dawson *et al.*, 1995) are randomly dispersed throughout this material.

Globules of gregoryite–sodian sylvite dispersed throughout a quenched carbonate-rich matrix as depicted in Figures 1–4 have not been previously described from the Oldoinyo Lengai natrocarbonatite. The globules are not filled vesicles, as they co-exist with numerous vesicles which are barren of any of the minerals encountered in the rock. The globules also cannot represent pseudo-immiscible textures resulting from surface tension effects between early and late crystallization portions of a liquid undergoing filter pressing during rapid crystallization. In such a case the globules, even assuming that such structures would form, should exhibit concave margins towards the dendritic material as they

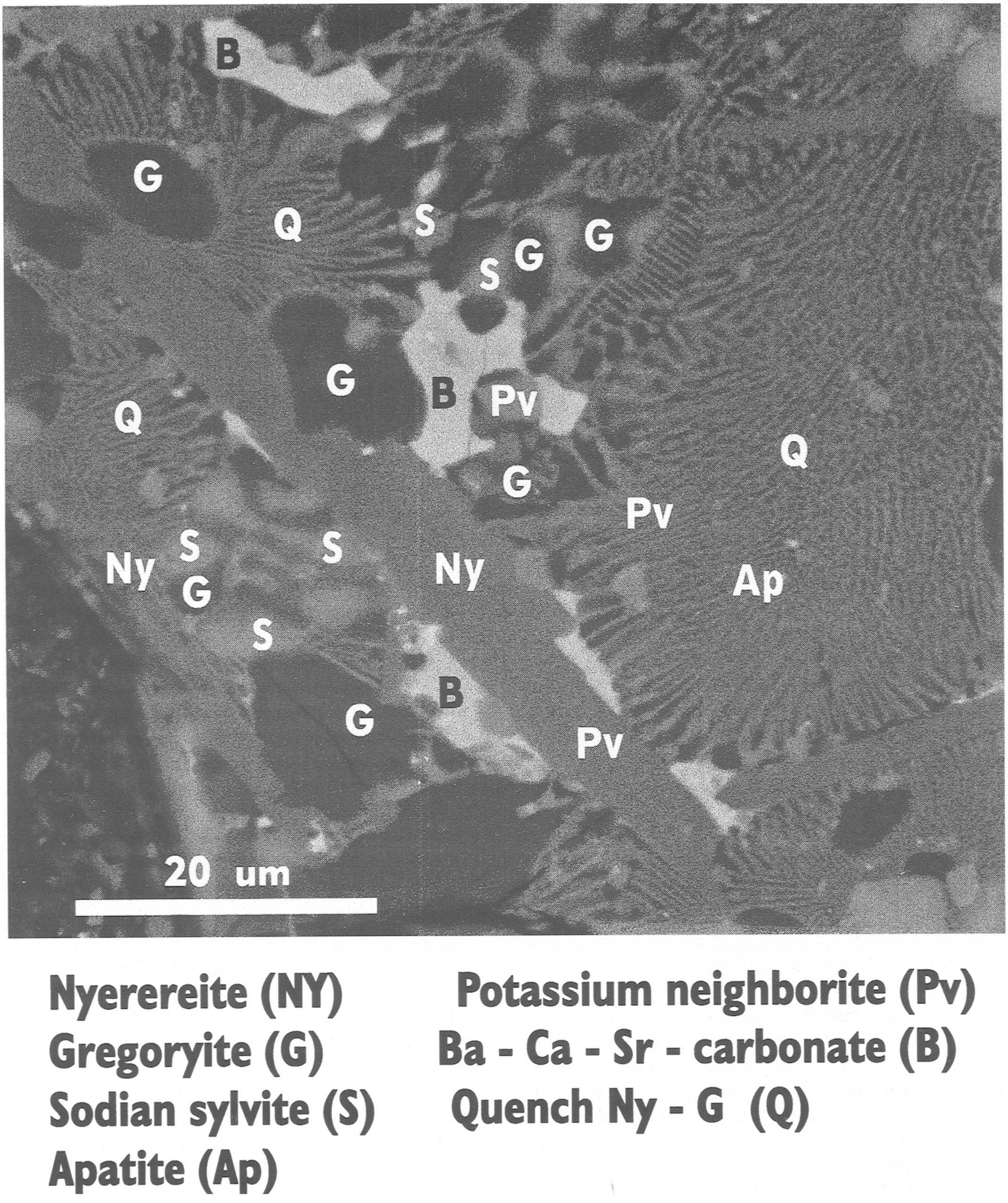

FIG. 4. Paragenesis of potassian neighborite. Back scattered electron image.

would represent liquid squeezed into the interstices between the crystallization fronts bounding areas of quenched material. In fact, the globules commonly occur as isolated objects within broad areas of dendritic material (Fig. 2). As no other process can provide a satisfactory explanation of the observed texture it is proposed that the globules at the time of eruption formed an immiscible liquid hosted by the material which now exhibits the quench texture.

The globules are interpreted as former immiscible liquids as they: have spherical morphologies indicative of surface tension differences between them and their host; contain one phase, gregoryite, which is common to the both globule and host; differ in grain size and mineralogy from their host, i.e. subsequent to their formation they followed a different crystallization trend. Globules do not exhibit plumose/dactylotypic quench textures and are coarser grained than their host suggesting that they remained liquid after quenching of the host (see below). Slower crystallization would account for the segregation and concentration of Ba-Ca-Sr complex carbonate at the periphery of the globules.

Neighborite–potassium neighborite

A fluoride mineral is common within the coarser-grained parts of the matrix of the 17 October 1995 lava. Here it occurs as small (< 10 μm) anhedral grains which are intimately intergrown with sodian sylvite [(K,Na)Cl], Ba-Ca-Sr-carbonates, gregoryrite and nyerereite. Grains may be poikilitically enclosed in Ba-Ca-Sr-carbonates and commonly decorate the margins of nyerereite laths (Fig. 4). The fluoride is not found within the fine-grained dactylotypic-textured portions of the matrix. A similar fluoride was found in lesser amounts in the December 1995 flows.

Energy dispersive spectra demonstrate that the mineral consists primarily of F, Na, K, Mg and Ba with minor amounts of Sr, Ca and Fe, and does not contain substantial amounts of oxygen or carbon (Fig. 5). The mineral is thus considered not to be a fluorocarbonate. Table 1 gives representative compositions and shows that the mineral varies significantly with respect to its Ba and Mg contents. Recalculation of the composition on the basis of 3 fluorine atoms per formula unit (apfu) suggests that the structural formula of the mineral is $A^{+}B^{2+}F_3$; where A = K or Na, and B = Mg, Ba, Sr, Ca, or Fe. Recalculation on the basis of 2 fluorine apfu results in non-integral stoichiometry for both total cations and fluorine, demonstrating that the mineral is unlikely to be a difluoride such as MgF_2.

Although X-ray diffraction data cannot be obtained on these small intergrown grains, the structural formula suggests that the mineral belongs to the perovskite group. Numerous synthetic fluorine-based perovskites, including $NaMgF_3$ and $KMgF_3$, of the type $A^{+}B^{2+}F_3$ are known (Ludekens and Welch, 1952; Portier *et al.*, 1969), with the mineral neighborite being the natural analogue of $NaMgF_3$ (Chao *et al.*, 1961). On the basis of the Goldschmidt (1928) tolerance factor (t) for perovskite stability (t = 0.7–1.0), a barium analogue, $KBaF_3$, (t = 0.77) of $KMgF_3$ perovskite is theoretically possible but does not as yet appear to have been synthesized. $NaBaF_3$ (t = 0.66) is likely to be unstable and/or may not adopt the perovskite structure. Ludekens and Welch (1952) were unable to synthesize these perovskite compounds by reactions involving mixtures of NaF–BaO and KF–BaO.

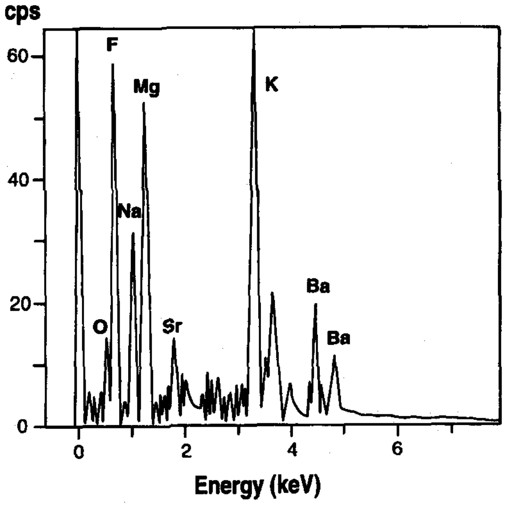

FIG. 5. Energy dispersive X-ray spectrum of potassium neighborite.

The data in Table 1 indicate that the fluoride mineral is essentially an intermediate member of a solid-solution series between neighborite and its potassium analogue, i.e. $NaMgF_3$–$KMgF_3$. The latter end-member is best referred to here as potassium neighborite, although this variety may justifiably be given a new name. The mineral contains less than 0.2 Ba apfu. This small amount of Ba is likely to be tolerated in the lattice without disruption of the perovskite structure. Neighborite is isostructural with orthorhombic $CaTiO_3$ perovskite (space group *Pbnm*; Zhao *et al.*, 1994), whereas synthetic $KMgF_3$ is cubic (space group *Pm*3*m*; Burns *et al.*, 1996). Solid solutions of $(Na,K)MgF_3$ have not yet been studied to determine the composition at which the symmetry change occurs.

Clearly, this paragenesis of neighborite differs greatly from that of the type locality, where it is found as a sodic authigenic mineral in a dolomitic oil shale of the Green River (Wyoming) Formation. Potassium neighborite has not been previously described, and its occurrence in the Oldoinyo Lengai lavas directly reflects the unusual sodi-potassic character of the residual liquids.

Previous mineralogical studies of Oldoinyo Lengai natrocarbonatites have not reported the presence of fluorine-based perovskite group minerals. Keller and Krafft (1990) report sellaite (MgF_2) and fluorite in the groundmass of the June 1988 lavas; whereas Peterson (1990) and Dawson *et al.* (1995, 1996),

TABLE 1. Composition of Na-K-Ba-fluorides from Oldoinyo Lengai

wt.%	1	2	3	4	5	6	7
Na	8.65	8.91	9.11	9.54	9.64	9.14	9.63
K	16.83	16.66	16.13	15.56	15.76	16.62	15.86
Mg	17.45	17.53	17.33	17.42	16.03	14.83	15.25
Ba	8.00	8.23	7.31	6.23	11.20	15.19	13.49
Ca	0.56	0.70	2.08	2.60	0.58	0.51	0.42
Sr	0.77	0.60	1.04	0.76	1.12	0.69	0.71
Fe	0.62	0.70	1.04	0.76	n.d.	n.d.	n.d.
F*	46.21	46.50	47.43	47.59	44.81	43.65	43.93
Total	99.26	100.02	101.20	100.28	99.43	100.42	99.29
Structural formulae on the basis of 3 fluorine atoms							
Na	0.464	0.475	0.476	0.497	0.533	0.519	0.544
K	0.531	0.522	0.496	0.477	0.513	0.555	0.526
Mg	0.885	0.884	0.856	0.858	0.838	0.796	0.814
Ba	0.072	0.073	0.064	0.054	0.104	0.144	0.127
Ca	0.017	0.021	0.062	0.078	0.018	0.017	0.014
Sr	0.011	0.008	0.014	0.010	0.016	0.010	0.011
Fe	0.014	0.015	0.011	0.011	–	–	–
Total	1.994	1.998	1.980	1.985	2.023	2.042	2.035
K+Na	0.995	0.997	0.972	0.974	1.046	1.074	1.070
M^{2+}	0.999	1.002	1.008	1.012	0.977	0.968	0.965

F* = total F calculated from cations expressed as fluorides. All samples from the 17 October 1995 flow.

recognized only fluorite in the 1963, November 1988 and June 1993 lavas, respectively. Examination of new samples of the 1993 blocky flow (Church and Jones, 1995) in this study confirmed the presence of fluorite only, this being intergrown in an unusual trellis-like (?eutectic) texture with a gregoryite-like material.

Potassium iron sulphide

Potassium iron sulphide occurs as small (1–200 μm) anhedral grains. These occur in both the coarse gregoryite–sylvite globules and the dactylotypic fractions of the quenched matrix. Commonly, sulphide grains are found at the centres of radial aggregates of sylvite. There is no regular association with any of the groundmass phases and the irregular distribution and habit suggests that the sulphides were present in the magma prior to eruption. Single crystals of alabandite (Mn,Fe)S and manganoan sphalerite (Zn,Mn)S exhibit similar parageneses. The occurrence of a K-Fe-sulphide in these lavas is remarkable given that the bulk of the S present occurs as SO_4 in gregoryite and nyerereite, suggesting that oxygen fugacity conditions prior to and during extrusion were too high to permit the formation of sulphides. On the basis of these observations the sulphides are interpreted as representing a transported cognate assemblage rather than primary groundmass phases.

The sulphides show considerable inter-grain compositional variation but apparently lack within grain zonation. Table 2 gives representative compositions and indicates that some examples may contain considerable quantities of sodium. The sodium contents do not result from the excitation of adjacent sodic minerals as the X-ray spectra of all analysed grains lacked X-ray peaks (O, C, Ca, Cl, *REE*) attributable to potential Na-bearing contaminants. Mn is the only significant minor element present and the sulphides are notable for their paucity in Ni, Co and Cu relative to other naturally occurring ternary alkali transition element sulphides such as rasvumite or djerfisherite. These differences merely reflect the paucity of the Oldoinyo Lengai magmas in these elements. Chlorine was not detected in any of the grains analysed.

Figure 6 illustrates the compositional range exhibited by the K-Fe-sulphides compared with the ideal composition of other naturally-occurring and

TABLE 2. Representative compositions of potassium iron sulphide

Wt.%	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Na	0.38	0.46	0.80	1.31	1.63	1.54	3.23	4.14	3.83	2.58	2.18	0.38	0.08	0.20
K	12.05	12.98	12.04	14.76	14.13	14.02	12.46	12.45	12.50	12.55	11.69	14.07	13.36	11.80
Mn	1.70	1.48	1.42	1.42	1.42	1.17	1.18	1.62	1.34	1.21	0.39	1.08	1.11	1.66
Fe	44.71	46.10	47.21	46.91	46.61	46.87	45.68	43.81	44.35	45.65	46.88	46.14	47.34	46.1
Cu	0.16	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.	1.72	0.19	–
S	37.96	37.17	37.30	36.80	37.36	35.90	37.33	37.41	37.55	37.46	37.59	35.95	38.06	37.6
Total	99.65	98.55	100.61	99.08	101.15	100.62	99.89	99.39	99.37	99.20	99.04	99.51	100.16	97.36

Compositions 1–11, October 1995 flow; 12-13, 1993 blocky flow; 14, November 1988 flow (Dawson *et al.*, 1995)
n.d. = not detected.

synthetic ternary sulphides and indicates that they have compositions which are totally unlike those of djerfisherite, thalfenisite, thalcusite, bartonite and murunite. The data plot within a field bounded by KX_3S_4, $K_2X_3S_4$ and KX_2S_3; where X is a transition metal. The KX_2S_3 compounds include KFe_2S_3, which occurs in nature as the mineral rasvumite (Clarke and Brown, 1980). The K content of the Oldoinyo Lengai sulphide (Table 2) is considerably less than that of ideal rasvumite (15.83 wt.%) although Fe and S contents are similar (45.22 and 38.95 wt.%, respectively). Low K contents relative to rasvumite are unlikely to reflect alkali loss during analysis at the very low beam currents employed. Compositions approach those of rasvumite only when K is relatively high, whereas K-poor compositions are similar to KFe_3S_4. Dawson *et al.* (1995) have also noted that ternary alkali sulphides in the November 1988 lava have compositions (Table 2. anal. 14) closer to $K(Fe,Mn)_3S_4$ than to rasvumite.

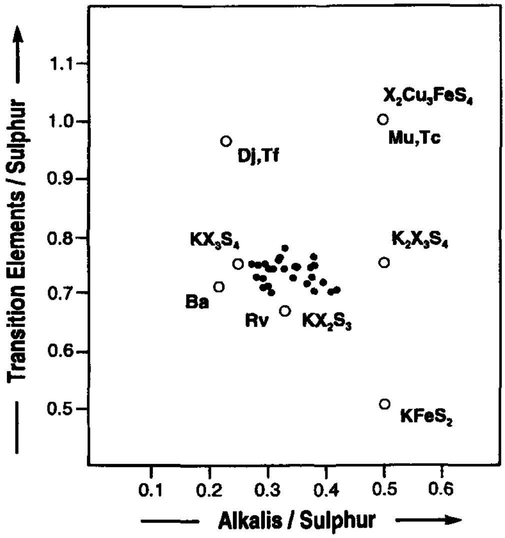

FIG. 6. Composition of Oldoinyo Lengai potassium iron sulphide plotted (atomic ratios) in terms of total transition metals/sulphur versus total alkalis/sulphur (after Clarke, D.B. *et al.* Occurrence of potassium iron sulphides in a melilitite from Polzen, Czech Republic, in prep.). Also shown are the ideal compositions of some other synthetic and naturally-occurring ternary sulphides. Dj = djerfisherite, Tf = thalfenisite, Mu = murunite, Tc = thalcusite; Ba = bartonite, Rv = rasvumite.

Attempts to extract sufficient material for XRD analysis have not been successful. Consequently, the structure of this ternary sulphide remains unknown. Recalculation of the compositions given in Table 3 on the basis of either 3 or 4 sulphur apfu in both instances does not result in near integral stoichiometry for alkalis, Fe+Mn or S. The variation in total alkalis/sulphur (atomic) illustrated in Fig. 5 suggests that the minerals are solid solutions between KFe_3S_4, $K_2Fe_3S_4$ and KFe_2S_3 (rasvumite). Neither KFe_3S_4 nor $K_2Fe_3S_4$ appear to have been synthesized, although diverse $A_2M_3S_4$ (A = K, Rb; M = Ni, Pd, Pt) compounds are well known (Eichhorn, 1994). Compounds of this type consist of edge sharing MS_4 units which are linked to form six-membered rings. Individual MS_4 planes are parallel to an orthorhombic c-axis and joined by bonds involving alkali elements, which are situated in the open tops and bottoms of the rings. If the Oldoinyo Lengai sulphide belongs to this structural group, then it would be a defect structure in which the alkali element sites are only partially filled.

TABLE 3. Representative compositions of sodian sylvite

wt.%	1	2	3	4
NaCl	21.76	25.13	29.34	30.81
KCl	77.60	74.01	70.54	69.55
Total	99.35	99.14	99.89	100.36

Cl calculated by stoichiometry.

Other minerals

Sodian sylvite. A mineral which represents solid solution between halite and sylvite occurs in the coarse-grained immiscible fractions of the groundmass (Figs. 1 and 3). Data obtained on sylvite grains in different samples from the 17 October flow Table 3 demonstrates that although considerable intergrain compositional variation (26–36 mol.% NaCl) is present the mineral may be regarded as sodian sylvite. Dawson *et al.* (1995) observed that Na was present in solid solution in the sylvite but were unable to obtain satisfactory compositional data for sylvite as the high beam current used for electron microprobe analysis caused fluorescence of adjacent minerals. However, in a subsequent study of coarser grains, Dawson *et al.* (1996) were able to demonstrate that 10.2–9.7 wt.% Na (representing 31 mol.% NaCl) was present in solid solution in sylvite.

Ba-Ca-Sr-Na carbonate. A Ba-Ca-Sr-Na-rich mineral is associated with the coarse-grained immiscible fractions of the groundmass. Dawson *et al.* (1995) have previously termed this mineral 'phase X'. The mineral forms irregular patches which are found either at the rims of sylvite-gregoryite globules or moulded onto the margins of nyerereite phenocrysts. Euhedral-to-subhedral neighborite and apatite are commonly poikilitically included by the phase. The mineral appears to be absent from the dendritic quenched areas of the groundmass.

Table 4 indicates that the mineral has a complex composition. Dawson *et al.* (1995), on the basis of low analytical totals, suggested that it is a carbonate. The presence of a significant C peak in the X-ray spectrum (Fig. 7) provides confirmation of this hypothesis and clearly demonstrates that Cl is also a significant component of the mineral. The grain size of the material analysed is sufficiently large (30–50 μm) that excitation of adjacent sylvite can be eliminated as a source of the Cl peak observed in the X-ray spectra. Further, Cl shows no correlation with Na and K, as would be expected if sylvite contamination were present. In contrast to the observations of Dawson *et al.* (1995) and Jago (1991), fluorine was not detected in any of the material analysed. Within and between grains the carbonate is of relatively uniform composition (Table 4). Compositions in this flow differ from those found by Dawson *et al.* (1995) and Jago (1991) in being poorer in calcium and richer in sodium. These differences may reflect secular changes in the composition of the magma as in these earlier lavas F is sequestered by fluorite rather than neighborite (see below).

The mineral is unquestionably a carbonate. Although the role of Cl in the structure is not clear, it is possible that it may play a role analogous to that

TABLE 4. Representative compositions of Ba-Ca-Sr-Na-carbonate

wt.%	1	2	3	4	5	6	7	8
FeO	0.13	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.a.
MnO	0.37	n.d.	0.21	0.24	n.a.	n.a.	n.a.	n.a.
MgO	2.15	1.36	1.51	2.05	0.75	3.72	3.16	2.62
CaO	6.71	6.92	7.44	8.91	30.75	11.31	10.06	10.01
SrO	6.96	6.41	6.82	6.52	5.76	7.38	9.10	8.57
BaO	38.32	39.67	38.40	37.29	18.58	44.09	44.53	44.83
Na_2O	10.54	8.27	8.52	9.08	2.79	2.83	2.36	2.54
K_2O	2.76	2.18	2.64	2.37	8.42	3.17	3.87	3.47
La_2O_3	n.a.	n.a.	n.a.	n.a.	0.26	1.11	1.05	1.11
Cl	2.96	2.36	2.98	2.48	3.63	1.01	1.30	1.25
F	n.d.	n.d.	n.d.	n.d.	1.64	1.07	3.38	3.12
Total	70.90	67.17	68.52	68.94	72.53	75.61	78.81	77.52

Compositions 1–4, 1995 flow (this work); 5–6, 1988 flow (Dawson *et al.*, 1995); 7–8, 1988 flow (Jago, 1991). n.d. = not detected, n.a. = not analysed.

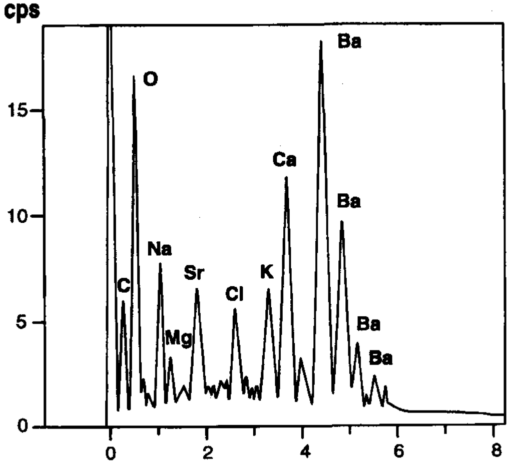

FIG. 7. Energy dispersive X-ray spectrum of Ba-Ca-Sr-Na carbonate.

of fluorine in the *REE*-fluorocarbonates. Previous studies have regarded this carbonate mineral as a calcite-witherite-strontianite-$(Na,K)_2CO_3$ solid solution (Dawson *et al.*, 1995) or witherite (Dawson *et al.*, 1996; Peterson, 1990). However, there are no crystallographic grounds for this hypothesis and lacking structural information, the mineral could even be regarded as a solid solution between olekminskite, potassian burbankite, alstonite etc. Rather than attempting to assign the composition to particular end member compounds, it is suggested here that the phase represents a quenched high temperature complex carbonate solid solution. Similar complex Ba-Sr-Ca-*REE* carbonates are found in the Little Murun potassic complex (Konyev *et al.*, 1991; Vorobyev and Piskunova, 1987). These occur as intergrowths which have been shown to represent all stages in the breakdown of a single precursor complex Sr- Ba-Ca-*REE* carbonate solid solution. Discrete identifiable minerals of relatively simple composition are found only in the samples which have undergone complete exsolution and low temperature equilibration (Vorobyev and Piskunov, 1985, 1987). On the basis of these studies, it is expected that the Oldoinyo Lengai complex carbonate would have undergone similar exsolution if it had not been rapidly quenched.

Conclusions

The data and observations presented here have a bearing on the final stages of the evolution of Oldoinyo Lengai natrocarbonatite magma. From the petrography of the October 1995 flow and earlier flows (Dawson *et al.*, 1995, 1996; Peterson, 1990) it is evident that the bulk composition of the lavas cannot represent the composition of their parental magma. The very high modal abundance of phenocrysts of gregoryite and nyerereite indicates that crystal accumulation has occurred prior to eruption. These phenocrysts may represent flotation cumulates collected in the apical regions of the magma chamber as suggested initially by Dawson *et al.* (1966).

The morphology and distribution of manganoan sphalerite, alabandite, potassium iron sulphide and rare calcium silicate suggests that these minerals did not crystallize *in situ* and also represent a fragmented transported assemblage.

The fine-grained matrix of the lavas contains a mineral assemblage with may be regarded as representing phases crystallizing along a cotectic in the system nyerereite–gregoryite–sodian sylvite–F–CO_2, and may represent the actual liquid present in the magma chamber currently underlying the crater floor. The compositions of the aphyric flows determined by Keller and Spettel (1995) may approach those of this material. Extrusion of this liquid is accompanied by the fragmentation and concentration of diverse cumulates of earlier-formed nyerereite and gregoryite. Immediately subsequent to eruption, rapid quenching and segregation of the liquid into two immiscible fractions occurred. One, represented by the gregoryite–sodian sylvite intergrowths, may be regarded as a Na-K-Ca-CO_2-Cl-rich, and containing F, P and large alkaline earth cations, whereas the other is Cl-poor and appears to have a eutectic-like composition in the system nyererite-gregoryite. The former which is F- and Cl-bearing would undoubtedly remain fluid longer than the latter on the basis of the experimental studies of Gittins and Jago (1991). This conclusion is supported by experimental studies of the NaCl–KCl solvus (Waldbaum, 1969) which show that at 1 atmosphere the critical temperature on the solvus is at ~480°C and that KCl containing from 40 to 20 mol.% NaCl can exist as a single phase down to temperatures ranging from 475 to 400°C, respectively.

The absence of fluorite in these highly evolved lavas and the presence of neighborite demonstrates that the nature of the F-bearing liquidus phases in natrocarbonatite liquids must change as crystallization proceeds. In this context, Jago and Gittins (1991) have shown that in the system Na_2CO_3-$CaCO_3$-F crystallization of NC_{ss} (a solid solution of Na-Ca carbonate analogous to gregoryite) and CaF_2 along a cotectic leads ultimately to a final eutectic at 560°C where NC_{ss}, CaF_2 and NaF crystallize together. These data suggest that NaF (villiaumite) might be the last fluoride to form in natrocarbonatites. Villiaumite was sought in the October and December lavas but not found, and its absence must be directly related to the compositional differences between the natural magma and the experimental system. Thus, it is proposed that natural natrocarbonatite liquids do indeed precipitate a Na-bearing fluoride as the ultimate F-bearing phase after a period of fluorite crystallization, but because of the presence of other components in the magmas this phase is neighborite rather than villiaumite. The absence of fluorite suggests that in complex natural systems the stability field of CaF_2 is much reduced or even eliminated at low temperatures. Clearly, further experimental studies of appropriate synthetic natrocarbonatite systems are warranted.

Thus, it is envisioned that the upper levels of the Oldoinyo Lengai magma chamber are dominated by liquids of exotic composition, as represented by the (K,Na)Cl, F-rich matrix of material erupted by the October 1995 and other flows, together with accumulations of nyerereite and gregoryite. The impetus for eruption of this material may be either influx of silicate magma, e.g. the 1993 blocky flow in which silicate–carbonate immiscibility has been documented (Church and Jones, 1995; Dawson *et al.*, 1996), or merely the accumulation of volatiles. Regardless, the material erupted undoubtedly represents the very last dregs of differentiation of the parental magma plus crystals derived from earlier stages of evolution. The liquids erupted certainly cannot represent primary natrocarbonatite magma.

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