Mineralogical Magazine, April 2006, Vol. 70(2), pp. 211–218

An ephemeral pentasodium phosphate carbonate from natrocarbonatite lapilli, Oldoinyo Lengai, Tanzania

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ABSTRACT

Lapilli formed by a Strombolian eruption are associated with the formation of a large lava flow of natrocarbonatite on or about 21–22 July, 2000 at Oldoinyo Lengai volcano, Tanzania. Fresh lapilli consist of vesicular natrocarbonatite similar to that occurring in rapidly quenched lavas. The lapilli were altered at low temperature (<50ºC) by degassing to aggregates of sodian sylvite, potassian halite, trona, thermonatrite and a novel F-bearing sodium phosphate-carbonate. The latter is considered to be a new mineral as it has a composition ($Na_{5-4.5}PO_4(CO_3,F,Cl)$ that is not similar to that of nahpoite (Na_2HPO_4), dorfmanite [$Na_2(PO_3OH).2H_2O$] or natrophosphate [$Na_7(PO_4)_2F.19H_2O$]. However, in common with these minerals, it is ephemeral and undergoes rapid decomposition under normal atmospheric conditions. The sodium phosphate-carbonate and associated halide-sodium carbonate assemblages are considered to be a part of a previously unrecognized hyperagpaitic assemblage forming as sublimates at Oldoinyo Lengai.

KEYWORDS: sodium phosphate-carbonate, natrocarbonatite, sublimate, trona, thermonatrite, sylvite, Oldoinyo Lengai, Tanzania.

Introduction

THE volcano Oldoinyo Lengai (Tanzania) is unique with respect to the eruption of natrocarbonatite lavas (Dawson, 1989). Various aspects of the geology, petrology and mineralogy of these lavas have been described by Peterson (1990), Keller and Kraft (1990), Dawson *et al.* (1995, 1996), Church and Jones (1995), Mitchell (1997) and Mitchell and Belton (2004). In contrast, very little is known regarding the mineralogy of lapilli formed contemporaneously with the lavas. The only study to date is that of Church and Jones (1994) who described hollow natrocarbonatite lapilli from a 1992 eruption. At Oldoinyo Lengai, lapilli are typically formed by Strombolian-style activity associated with hornito collapse and rapid degassing of the underlying magma chamber.

This work briefly describes natrocarbonatite lapilli formed during July 2000 with emphasis on the occurrence of a novel F-bearing sodium phosphate-carbonate. Previously, Dawson *et al.* (1993) noted the presence of a Na,K,Ca-phosphate in lapilli from the 1996 ash eruption, and considered this material to represent a mixture of alkali carbonate and alkali-bearing apatite. With respect to the latter, Dawson *et al.* (1993) also reported Na-bearing (~8 wt.% Na_2O) apatite in natrocarbonatite lava. None of this material corresponds to the F-bearing, Ca-free phosphate-carbonate described here.

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DOI: 10.1180/0026461067020326

Volcanic activity at hornito T37C/D (21–22?) July, 2000

Figure 1 illustrates the locations of active and dormant vents (hornitos) in the north crater of Oldoinyo Lengai during 23–28 July, 2000. Note that the southern third of the crater is covered by an extremely large complex natrocarbonatite flow that apparently originated from the small hornitos T37C and/or T37D. Eruption of the flow was not observed but is estimated to have occurred on or about 21–22 July, 2005, as on July 23 it was still warm, and cracking sounds could be heard from

within the flow. The flow initially formed a lava lake between a lapilli field (Fig. 1) and the extinct hornito T24. Strand lines preserved on the sides of T24 indicated that this lake was at least 2 m deep before overflowing to the south. Upon breaching of the lava lake, lava flowed to the southeast forming a lava-fall adjacent to T24 before pouring as a wide flow onto the topographically lower southern part of the crater. As the lava flowed there was a change in its rheology. From T37C/D to T30 the flow formed pahoehoe lava, whereas from T30 to the flow front the lava occurred as jagged sheets of aa.

Associated with this large flow was a bedded lapilli field (Fig. 1) which extended ~100 m from the T37C/D to the eastern and southeastern margins of the crater. The maximum thickness of the lapilli deposit was ~12 cm. On 23rd July the lapilli were black, fresh and warm with white sublimates forming only around the margins of the deposit. Fresh lapilli within the lapilli bed in some instances became cemented by the white sublimate over the course of 1 day. These initial stages of alteration are considered to result from degassing of the lapilli and not from sub-aerial weathering as none of the sublimate-bearing lapilli investigated exhibited the uniform grey alteration characteristic of such weathering (Genge *et al*., 2001). By 28 July, many of the near-surface or thinly-bedded areas of lapilli had succumbed to subaerial alteration, although those in the interior of the deposit remained fresh.

The lapilli formed spheres and oval-shaped droplets ranging from ~3 mm down to ~100 μm in diameter. The larger lapilli were highly vesicular whereas the smaller ones were vesicle-free. The lapilli are similar to the hollow and vesicular lapilli described by Church and Jones (1994) and composed of rapidly quenched natrocarbonatite.

Analytical methods

Samples of lapilli and white sublimate were collected on 24 July 2000, and heat-sealed in plastic. The material was investigated during August 2000, using thin sections prepared in kerosene, by secondary and back-scattered electron imaging using a JEOL-JSM5900 scanning electron microscope. Although, the samples and thin sections were stored in a desiccator it was found that the sodium phosphate-carbonate decomposed within 6 months.

The most strongly altered lapilli and the white sublimates were investigated by standard X-ray diffraction methods. These showed that the sodium carbonates forming during the alteration are trona [$Na_3(CO_3)(HCO_3).2H_2O$] and/or thermonatrite ($Na_2CO_3.H_2O$), and that minor amounts of aphthitalite [$(K,Na)_3Na(SO_4)_2$] are also present in the sublimates. X-ray diffraction peaks attributable to the sodium phosphate-carbonate could not be recognized. This assemblage is similar to that formed by degassing on cooling lava as reported by Zaitsev and Keller (2006).

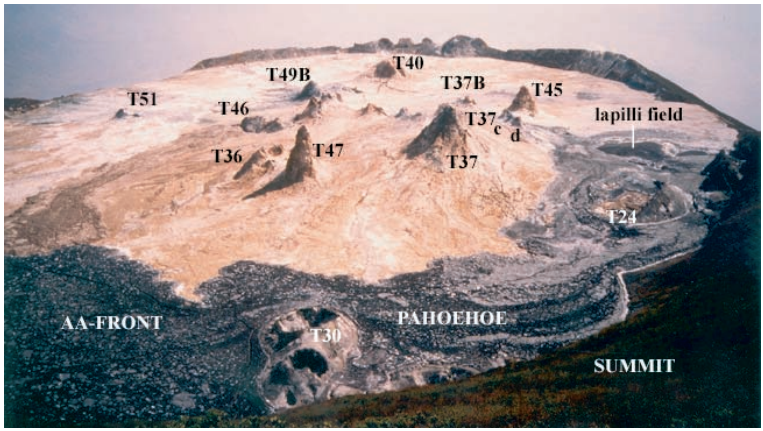

FIG. 1. The northern crater on July 26th, 2000 as viewed from the summit of Oldoinyo Lengai, showing the locations of active (T37B,C,D; T51; T46; T49B) and dormant hornitos (T24; T30; T36; T37; T40; T45), the 21−22 (?) July large lava flow, and associated lapilli field. The view is towards the north. For information on the numbering system of hornitos used at Oldoinyo Lengai see the Smithsonian Global Volcanism (www.volcano.si.edu) or the Oldoinyo Lengai (www.mtsu.edu/~fbelton/lengai.html) internet web-sites.

All mineral compositions were determined by quantitative energy dispersive X-ray spectrometry (QEDS) using a JEOL-JSM5900 scanning electron microscope equipped with a LINK ISIS 300 analytical system incorporating a Super ATW light element detector (133 eV FwHm) Mn*K*). Raw EDS spectra were acquired for 150 s (live time) with an accelerating voltage of 20 kV and beam current of 0.475 nA on a Ni standard. The raw X-ray spectra were processed with the LINK ISIS SEMQUANT quantitative software package with full ZAF corrections applied. The following well-characterized mineral and synthetic standards were used for the analyses: apatite BM 1926-665 (F, Ca, P); fluorite (Ca,F; benitoite (Ba); jadeite BM 1913-451 (Na); wollastonite (Ca). KCl (K,Cl). Attempts to analyse sodian sylvite and the sodium phosphate-carbonate with a fixed beam, even with these low beam currents, typically resulted in decomposition of the material. Compositions considered as reliable were only obtained using rastered scanning of an approximately 5 μm × 5 μm areas. Because of the small grain-size it was not possible to analyse trona/thermonatrite.

Petrography and alteration of the lapilli

Figure 2 illustrates the texture of a typical unaltered lapillus consisting of small microphenocrysts of gregoryite [$(Na,Ca,K)_2CO_3$] and abundant skeletal microphenocrysts of nyerereite [$Na_2Ca(CO_3)_2$] set in a quenched matrix of nyerereite and gregoryite-like material. The matrix also contains small, irregular (<20 μm) crystals of ferroan alabandite [(Mn,Fe)S], Mn-magnetite, and potassium iron sulphide (? rasvumite, KFe_2S_3). Vesicles in the lapilli are either completely devoid of material or filled with granulated natrocarbonatite. Alteration-free gregoryite and nyerereite have compositions similar to those given by Peterson (1990).

Alteration of the lapilli is initiated by the replacement of gregoryite crystals by trona and/or thermonatrite. Such crystals exhibit a porous appearance (Fig. 3). Concurrently, the groundmass is also replaced by trona/thermonatrite and euhedral crystals of sodian sylvite (2.5–8 wt.% NaCl) with lesser halite containing 3–3.5 wt.% KCl (Figs 3, 4). The compositions of the halides do not correspond to an equilibrium solvus temperature (Waldbaum, 1969). Typically, the alteration commences at the margins of the larger lapilli but can be pervasive in the smaller varieties. In the most advanced stages of alteration, lapilli are completely replaced by trona/thermonatrite and minor sodian sylvite with individual lapilli cemented together by a mixture of trona/thermonatrite and minor aphthitalite. Nyerereite is less susceptible to alteration than gregoryite but is also replaced by trona/thermonatrite. During the initial stage of altera-

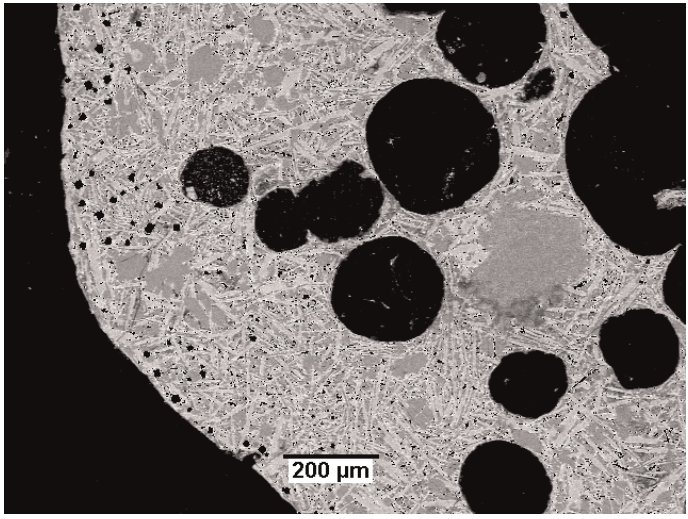

FIG. 2. Back scattered electron image of a fragment of a relatively fresh natrocarbonatite lapillus showing the presence of large empty vesicles, large phenocrysts of gregoryite (grey), and skeletal nyerereite phenocrysts. Note the formation of small euhedral crystals of sodian sylvite (white) at the left-hand margin of the lapillus.

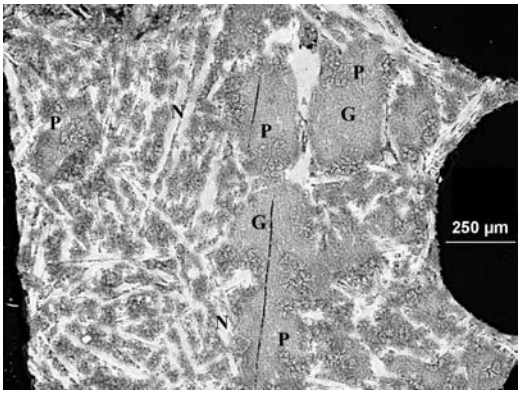

FIG. 3. Back scattered electron image of a fragment of a strongly altered natrocarbonatite lapillus illustrating the breakdown of gregoryite phenocrysts to a fine-grained/cryptocrystalline mixture of trona/thermonatrite (grey) with aggregates of sodium phosphate-carbonate (P). Skeletal nyerereite phenocrysts (white) are strongly corroded at their margins and also replaced by trona/thermonatrite.

tion, crystals develop corroded margins and take on a 'blotchy' appearance.

The formation of trona/thermonatrite is accompanied in many instances by that of small (<20 µm) subhedral crystals of sodium phosphate-carbonate (Figs 3, 5). The majority of these are associated with the alteration of pre-existing gregoryite (Fig. 3), although they can also be found randomly distributed throughout the altered natrocarbonatite matrix, where the phosphate-carbonate forms aggregates of subhedral crystals in a trona/thermonatrite matrix (Fig. 5). Typically, the crystals exhibit a well-developed fracture (Fig. 5).

Sodium phosphate-carbonate composition

Figure 6 illustrates a typical energy dispersive X-ray spectrum of the phosphate-carbonate demonstrating that Na and P are the only major cations present. The significant peaks for C and O indicate that this F-bearing mineral undoubtedly contains a significant carbonate component.

Representative compositions of sodium phosphate-carbonate are given in Table 1. Apart from their instability in the electron beam, analysis proved challenging because of the small size of the crystals. Matrix excitation was recognizable by Na contents decreasing below 50 wt.% Na_2O reflecting the presence of trona (41.1 wt.% Na_2O)

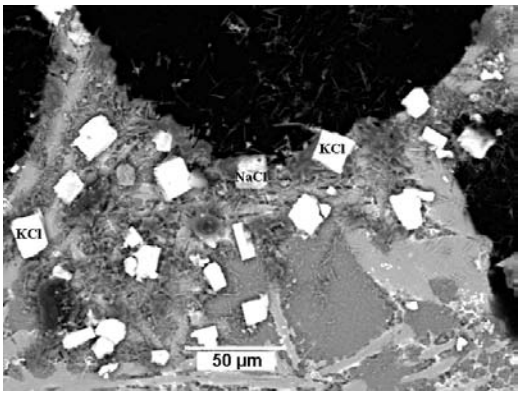

FIG. 4. Back scattered electron image of alteration at the margin of a natrocarbonatite lapillus showing euhedra of sodian sylvite (KCl) and lesser potassian halite (NaCl) set in a fine-grained aggregate of trona/thermonatrite.

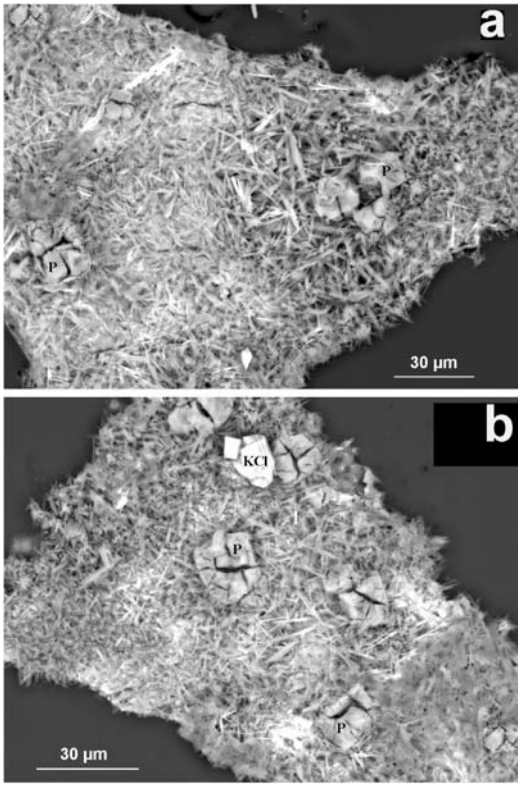

FIG. 5. Back scattered electron images of strongly altered natrocarbonatite lapilli illustrating subhedral crystals of sodium phosphate-carbonate (P) set in fine-grained aggregates of prismatic crystals of trona/thermonatrite.

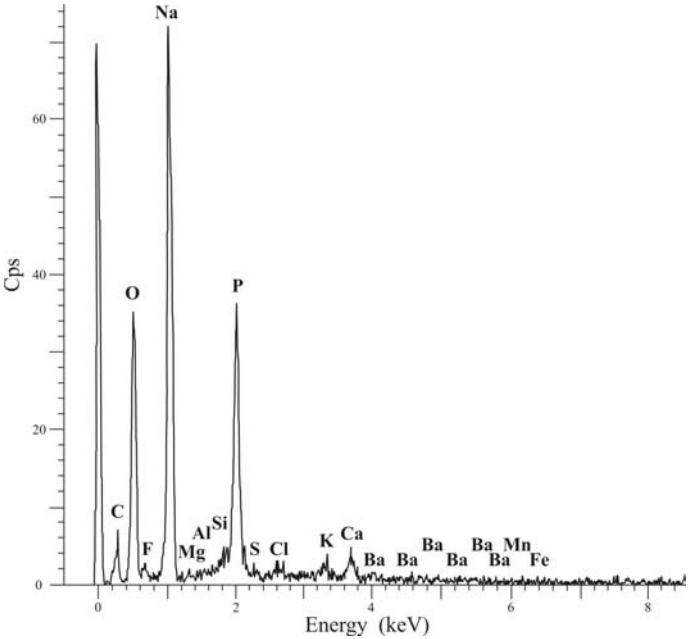

FIG. 6. Energy dispersive X-ray spectrum of sodium phosphate-carbonate.

or from increased K and Ca contents originating from nyerereite. All compositions of sodium phosphate regarded as satisfactory were obtained with raster scanning of 3 μm × 3 μm areas and contained >50 wt.% Na_2O and <5 wt.% CaO.

Assuming that the mineral is anhydrous, recalculation of the composition on the basis of 7 atoms of oxygen to give a site occupancy for P of approximately unity suggests that the stoichiometry of the compound is ~$Na_{5-4.5}PO_4.(CO_3,F)$. Thus, this sodium phosphate has a composition that is not similar to that of nahpoite (Na_2HPO_4; 43.6 wt.% Na_2O; 50.0 wt.% P_2O_5), dorfmanite ($[Na_2(PO_3OH).2H_2O]$; 34.8 wt. % Na_2O; 39.9 wt.% P_2O_5) or natrophosphate ($[Na_7(PO_4)_2F.19H_2O]$; 21.4 wt.% Na_2O; 13.8 wt.% P_2O_5), with respect to its Na or P content. It is uncertain whether or not this sodium phosphate-carbonate contains any molecular water. The association with trona/thermonatrite suggests that this is possible, although the reasonable structural formula calculated on an anhydrous basis suggests that this probability is low.

The sodium phosphate-carbonate contains F and Cl in significant quantities. If the halogen-free ideal composition of this phosphate is considered to be $Na_5PO_4.CO_3$ replacement of $(CO_3)^{2-}$ groups by F^- or Cl^- would result in a charge imbalance which can be alleviated by a reduction in the Na content to give a composition of $Na_4\square PO_4F$ for the replacement of one carbonate anion by one atom of F, where $\square$ represents a cation site vacancy. Thus, the compositions given in Table 1 are considered to represent a range approximately from an ideal pentasodium phosphate-carbonate end-member $Na_5PO_4(CO_3)$ to $Na_{4.5}\square_{0.5}PO_4(CO_3,F)$.

This sodium phosphate-carbonate is an apparently new mineral. A name cannot be assigned as the decomposition of the phase and the minor quantities of material precluded characterization of the XRD-diffraction pattern and/or any crystal structure data. Hence, discussion of the structure and relationships to other phosphates must be at best speculative. Interestingly, anhydrous phosphate-carbonates of similar stoichiometry but with differing composition are members of the bradleyite group $[Na_3M^{2+}(PO_4)(CO_3)$ where M^{2+} is Mg, Sr, Mn or Fe in bradleyite, crawfordite, sidorenkite and bonshtedite, respectively (Fahey and Mrose, 1962; Sokolova and Khomyakov, 1992; Khomyakov, 1995). In these minerals chains of Na atoms, separate PO_4 tetrahedra with the divalent cations occupy distorted 8-fold polyhedra between these tetrahedra. Conceivably, replacement of the divalent cation by two monovalent Na cations could result in the

TABLE 1. Representative compositions (wt.%) of pentasodium phosphate-carbonate.

	1	2	3	4	5
P_2O_5	27.77	23.84	24.50	26.29	26.69
MgO	1.20	1.16	1.19		
CaO	1.04	0.64	3.01		
SrO	1.00	n.d.	0.54		
Na_2O	51.31	55.82	52.81	57.40	46.61
K_2O	1.39	0.85	1.85		
F	5.11	4.93	5.12		7.14
Cl	1.03	1.11	1.00		
Total	89.85	88.35	90.02	83.69	80.44
F=O	2.15	2.08	2.15		3.01
Cl=O	0.23	0.25	0.23		
CO_2*	13.91	15.16	13.72	16.31	23.69
3 volatiles	16.29	17.49	16.10	16.31	26.70
Structural formulae based on 7 oxygens					
P	1.091	0.949	0.988	1	0.951
Na-site cations					
Mg	0.083	0.081	0.085		
Ca	0.051	0.032	0.151		
Sr	0.027	–	0.015		
Na	4.618	5.037	4.875		3.802
K	0.076	0.051	0.112		
Total	4.855	5.251	5.238	5	3.802
3 cations	5.946	6.200	6.226	6	4.753

1–3: fluoro-sodium phosphate-carbonate, Oldoinyo Lengai; 4: ideal $Na_5PO_4.CO_3$; 5: ideal $Na_4PO_4.(F)CO_3$).
* calculated CO_2 content
n.d. = not detected

composition of $Na_5PO_4(CO_3)$. However, this would also require creation of an extra site for Na in the 'crawfordite structure'.

Discussion

The presence of a novel pentasodium phosphate-carbonate and trona/thermonatrite as alteration products of lapilli indicates that significant volatile transfer of Na, Cl, F and P occurred during the cooling of this lapilli tuff. The phosphate-carbonate is not present in slightly altered lapilli in which gregoryite is present. Gregoryite typically contains 1.8–2.5 wt.% P_2O_5 (Peterson, 1990) which should be liberated when it is replaced by trona/thermonatrite. This, and the typical paragenetic association with altered gregoryite, indicates that the P is undoubtedly derived from the decomposition of gregoryite, this combining with Na, CO_2 and F-bearing gas to form the phosphate-carbonate mineral. The process is considered to occur at a low temperature (<50ºC). Speculation as to the character of the transporting gases is not warranted as there are no experimental phase equilibria for the system P-K-Na-Cl-CO_2-H-F. It is suggested above that meteoric water was not involved in the initial stage of alteration of the lapilli. If this hypothesis is correct, the phosphate-carbonate should be regarded as a sublimate. Note that Genge *et al.* (2001) claimed that alteration of natrocarbonatite lavas to assemblages of thermonatrite, halite and aphthitalite occurs only during the 'wet season' at Oldoinyo Lengai. White encrustations forming along cooling fractures on warm freshly erupted lava similar to those reported by Genge *et al.* (2001) have been described by Zaitsev and Keller (2006), and were also found at T51 (Fig. 1) during the 'dry season' in 24–26 July, 2005 (this work). Neither Zaitsev and Keller (2006) nor

Genge *et al*. (2001) reported finding any phosphate-carbonate in these assemblages. The white encrustations are interpreted in this work to be sublimates rather than efflorescence deposits. Regardless, the presence of hydrated sodium carbonates, and the observations of Koepenick *et al.* (1996) imply that some water must be present in the Oldoinyo Lengai magmatic system. This might be juvenile or recycled meteoric water. In the latter case, the water could be derived by the assimilation of hydrous altered natrocarbonatite during thermal erosion of the wall rocks of the vents.

The occurrence of an ephemeral phosphate-carbonate-halide-sodium carbonate assemblage at Oldoinyo Lengai bears a strong resemblance to the presence of similar but not identical sodium phosphates (nahpoite, dorfmanite, etc.) in the hyerpagpaitic alkaline rocks of the Khibina and Lovozero complexes (Khomyakov, 1995). The distinguishing characteristic of these rocks is that they contain sodic minerals which are readily soluble in water or altered under atmospheric conditions. Consequently, hyperagpaitic mineral assemblages are not typically preserved during subaerial weathering. Clearly, the phosphate-carbonate described here is not stable under normal atmospheric conditions and its recognition was due to the fortuitous circumstances of collection and examination immediately after formation.

Finally, it is suggested that, as an extension of the study of Zaitsev and Keller (2006), sublimates forming either in fractures in freshly erupted lavas or from fumaroles be studied in more detail to determine the exact character of Oldoinyo Lengai sublimate hyperagpaitic mineral assemblages. The application of the methods employed by Le Guern and Bernard (1982) for the collection of sublimates forming in fumaroles would be especially useful.

Acknowledgements

This research is supported by the Natural Sciences and Engineering Research Council of Canada and Lakehead University. Anne Hammond and Allan MacKenzie are thanked for assistance with sample preparation and the electron microprobe study, respectively. Othman Swalehe and Paul Mongi of Arusha are thanked for culinary and logistical assistance on Oldoinyo Lengai, together with the villagers of N'Gare Sero who act as porters; without their help, extended visits to the active crater would not be possible. Barry Dawson and Andrew Christy are thanked for their constructive reviews of the manuscript.

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[*Manuscript received 11 August 2005: revised 19 April 2006*]